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SYNTHETIC APPROACHES TO PENTAPRISMANE

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To my mama, papa and tai-tai

ACKNOWLEDGEMENT

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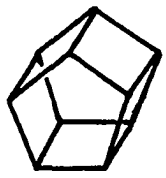
SYNTHETIC APPROACHES TO PENTAPRISMANE AND RELATED SYSTEMS

INTRODUCTION

Hexacyclo[5.3.0.$0^{2,6}$.$0^{3,10}$.$0^{4,9}$.$0^{5,8}$]decane (1), which has the trival name "pentaprismane", was first discussed in the literature in 1965, where it was presented as an interesting topological problem.[1] Computation by



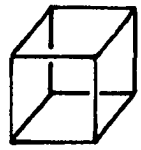
1

summing the six individual angle strains--deviation from 109°28' for normal sp^3 hybridization--about each carbon atom gives a total angular strain per carbon atom of 73°21' for 1. This value is considerably smaller than those of 105°48' and 152°42' for pentacyclo[4.2.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]octane (tetraprismane, cubane, 2) and tetracyclo[2.2.0.$0^{2,6}$.$0^{3,5}$]-hexane (prismane, 3), respectively, (Table I). Empirical force field calculations[2] (Table I) predict that 1 has a heat of formation (ΔH_f) of 114.12 (or 123.51) kcal/mole;

TABLE I. Calculated Angular Strain, Enthalpies and Strain Energies for Pentaprismane, Cubane and Prismane.

	Penta-prismane (1)	Tetra-prismane (Cubane) (2)	Prismane (3)
Angular strain per carbon atom[a]	73°21'	105°48'	152°42'
Heat of formation (ΔH_f), Kcal/mole	114.12[b] 123.51[c]	148.59[b] 149.66[c] 139.8[d] expt. 148.7[e]	128.9[d]
Strain energy Kcal/mole	135.72[b] 145.06[c]	165.87[b] 166.90[c]	

(a) Data from ref. 1. (b) Data from ref. 2. (c) Data from ref. 2, calculated based on force field described in N. L. Allinger, M. T. Tribble, M. A. Miller, and D. W. Wertz, J. Amer.Chem.Soc., 93, 1637(1971). (d) Calculated by MINDO/3 semiempirical SCF-MO method; R. C. Bingham, M. J. S. Dewar, and D. H. Ho, J.Amer.Chem.Soc., 97, 1294(1975). (e) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N.Y., 1970.



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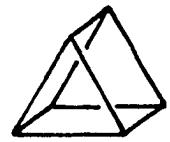
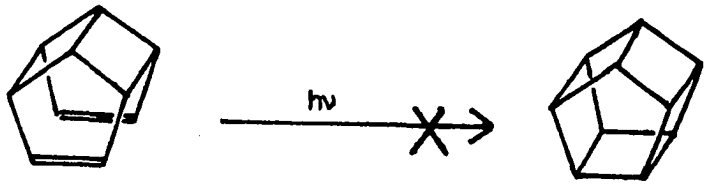


3

about 30 kcal/mole less than that of cubane (2). The expected thermodynamic stability of pentaprismane compared with its homolog cubane is also revealed by a difference of about 30 kcal/mole in the calculated strain energies (Table I). Both cubane[3-6] and prismane[7] have been successfully synthesized, but thus far the thermodynamically more stable pentaprismane has defied all attempts at rational synthesis.

In 1971, there appeared two significant attempts at the synthesis of pentaprismane in the literature.[8,9] Pettit and coworkers[8] have synthesized tetracyclo[5.3.0.$0^{2,6}$.$0^{3,10}$]deca-4,8-diene ("hypostrophene", 4) which has two nonconjugated double bonds bearing a close face-to-face relationship. However, attempted photocyclization of 4 to pentaprismane has not been successful (equation 1).[10,11]

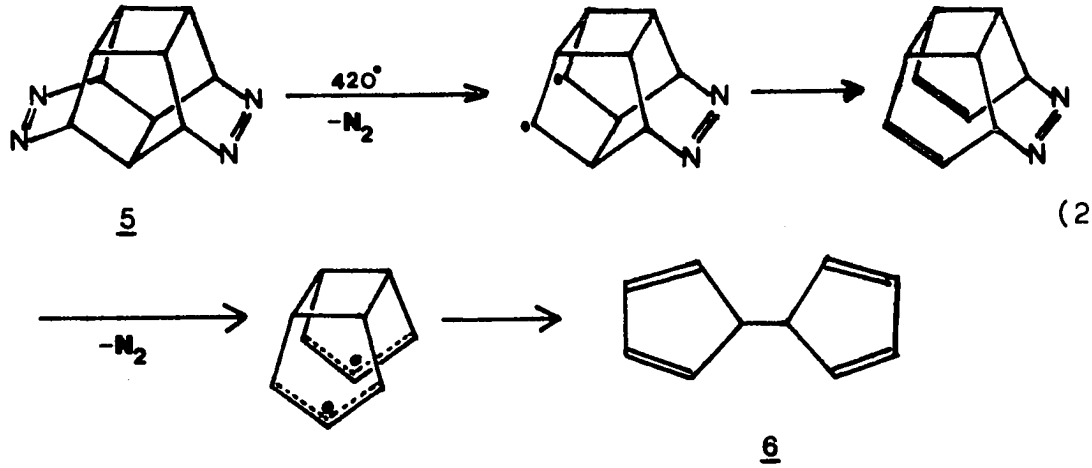


(1)

4

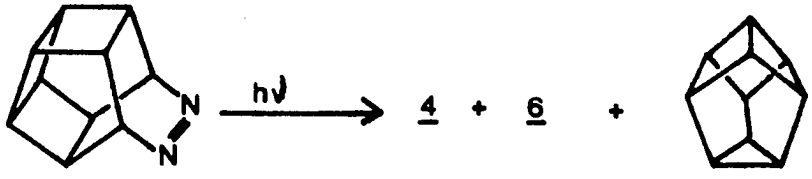
The inability of 4 to close photochemically to the saturated analog has been traced, based on photoelectron spectroscopic evidence,[10] to the presence of an exceptionally high-lying sigma level which is ideally oriented for an effective through-bond coupling of the two pi orbitals. This through-bond coupling overrides the direct through-space interaction, placing the in-phase combination of the two pi orbitals above the out-of-phase combination, and thus converting the [$_{\pi}2_{s}$+ $_{\pi}2_{s}$] photocycloaddition from a symmetry-allowed to a symmetry-disallowed reaction.

Later, Shen[9] tried without success to construct two new sigma bonds simulataneously via thermal decomposition (420°) of 2,3,7,8-tetraazahexacyclo[7.4.1.$0^{4,12}$.$0^{5,11}$.$0^{6,12}$.$0^{10,13}$]tetradeca-2,7-diene (5). At this high temperature, an allylic diradical was produced and a fragmentation process occurred, resulting in the formation of 6 as the only detectable product (equation 2).



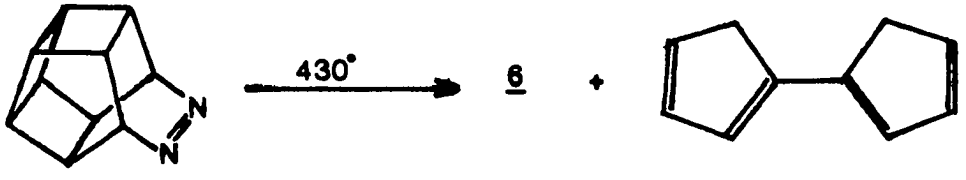
5 (2) 6

More recently, Allred and Beck[12] also failed to produce pentaprismane when they attempted to construct a sigma bond by either thermal or photochemical extrusion of nitrogen from 11,11-diazahexacyclo[6.4.0.$0^{2,7}$.$0^{3,6}$.$0^{4,12}$.$0^{5,9}$]dodeca-10-ene (7). Irradiation of 7 in n-pentane produced 4 (10%), 6 (trace), 8 (12%) and nonvolatile material (equation 3). Flash vacuum pyrolysis of 7 at 430°



7 8 (3)

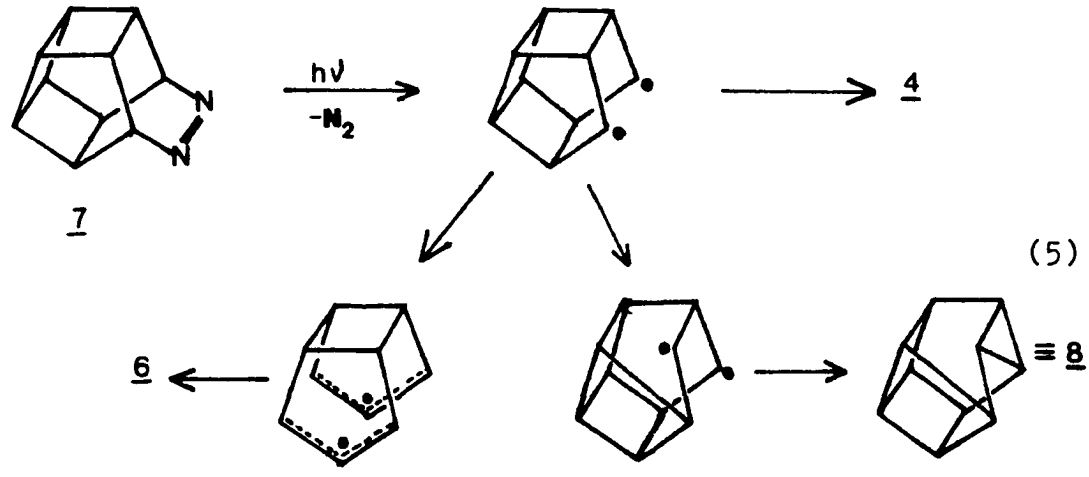
resulted in the formation of two isomeric fulvalenes, 6 and 9, as the only detectable products (equation 4). They



7 9 (4)

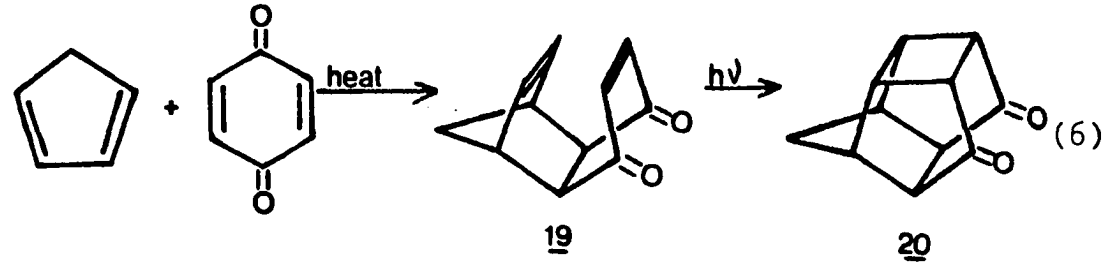
described the formation of 4 and 6, and 8 as a result of a diradical process, shown in equation 5.

In the present study, an alternative approach to the synthesis of pentaprismane was projected as outlined in Scheme I. The key intermediate in this synthetic scheme is the cage compound 12 which could be prepared via a three-



(5)

step reaction sequence from readily available hexachloropentadiene and p-benzoquinone.[13-15] The sequence parallels that adopted by Cookson and coworkers[15] in their synthesis of an analogous unsubstituted cage diketone (equation 6).

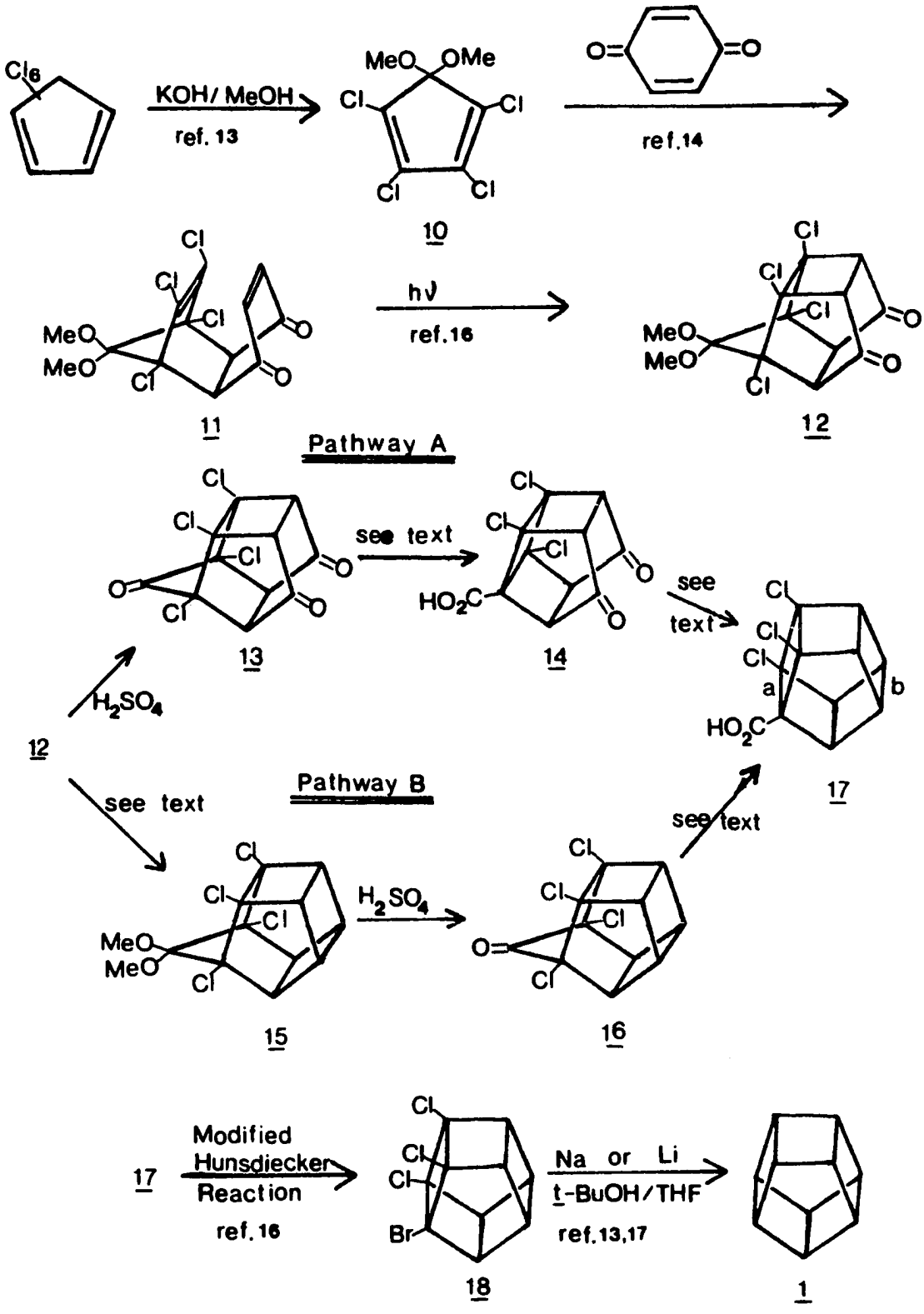


(6)

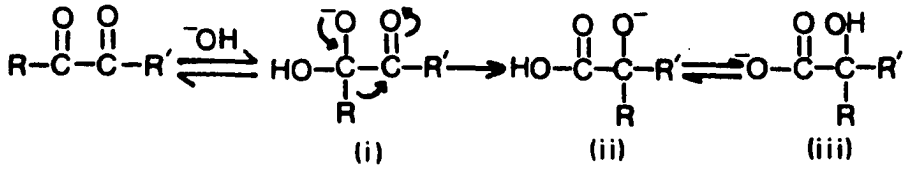
Successful construction of the final two sigma bonds (labeled "a" and "b") needed to produce pentaprismane derivative 17 would then be the key to our synthesis of pentaprismane. These two sigma bonds could be formed sequentially following either pathway A or B illustrated in Scheme I.

The formation of the sigma bond labeled "a" in 17 is keyed upon a semibenzilic acid rearrangement to effect

SCHEME I

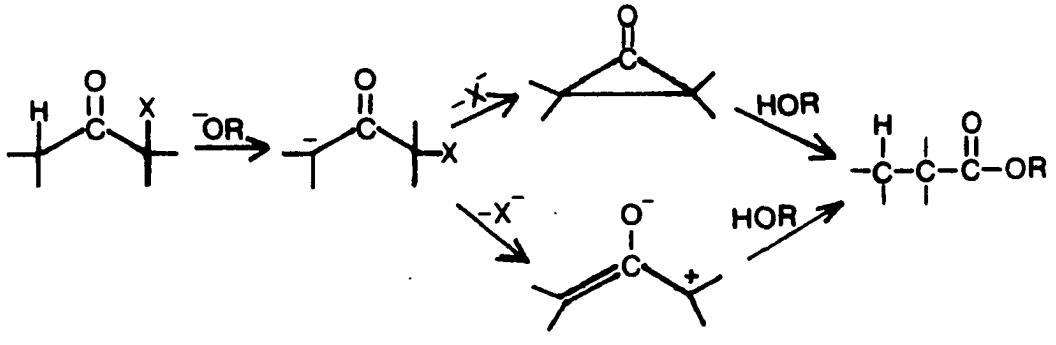

KOH/ MeOH
ref. 13
ref.14
10
hν
ref.16
11
12
Pathway A
see text
13
14
see text
17
H_2SO_4
12
see text
Pathway B
see text
H_2SO_4
15
16
17
Modified Hunsdiecker Reaction
ref. 16
Na or Li
t-BuOH/THF
ref.13,17
18
1

contraction of a five to four-membered ring. The semi-benzilic acid rearrangement could be regarded as a molecular rearrangement which arises from the action of nucleophiles on an α-haloketone via a mechanism similar to a benzilic acid rearrangement. The generally accepted mechanism for benzilic acid rearrangement[18] involves a reversible addition to an α-diketone by a nucleophile (e.g, hydroxide ion) to give intermediate (i) which then rearranges to (ii) and undergoes proton transfer to give (iii) as shown in equation 7. Skeletal rearrangement of α-haloketones in the



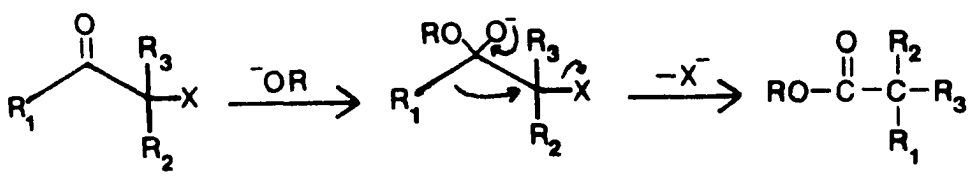
(7)

presence of certain nucleophiles to yield carboxylic acids or derivatives thereof (Favorskii rearrangement) appears to involve a symmetrical intermediate (cyclopropanone[19] or zwitterion[20]) as shown in equation 8. In cases where undue



(8)

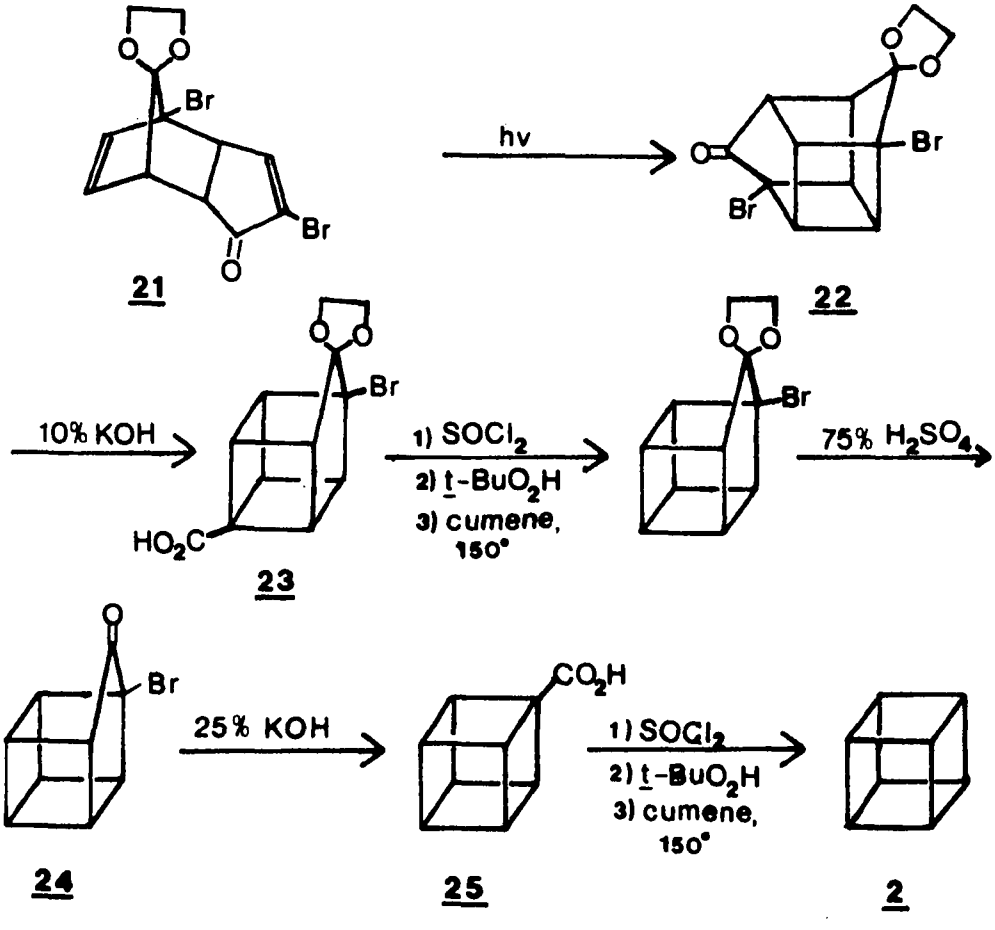
strain would be imposed by the formation of a cyclopropanone and/or where the α-hydrogen has low acidity (e.g., non-enolizable α-haloketones) or where α-haloketones lack α-hydrogen, the Favorskii rearrangement would then follow the mechanism similar to that of benzilic acid rearrangement, and may be represented by equation 9 (semibenzilic acid rearrangement).



(9)

Semibenzilic acid rearrangement of α-haloketones has been commonly utilized for the synthesis of strained ring systems.[3-6,21-31] The most noteworthy application of this rearrangement is illustrated by the key step in the synthesis of cubane (2).[3-6] The synthesis of this highly strained cage hydrocarbon developed by Eaton and Cole[3,4] is shown in Scheme II. The monoethylene ketal of the bromocyclopentadienone dimer 21 was irradiated to yield the cage compound 22, the semibenzilic acid rearrangement of 22 in aqueous potassium hydroxide afforded the ring-contracted acid 23 in 95% yield. After decarboxylation and regeneration of the carbonyl function, the resulting bromo-ketone 24 afforded cubane carboxylic acid 25 upon treatment

SCHEME II



with 25% aqueous potassium hydroxide. Alternative cubane syntheses[5,6] are also keyed upon a semibenzilic acid rearrangement to effect ring contraction of an α-haloketone to cubane derivative. The application of this rearrangement to the synthesis of polycyclic compounds is further illustrated in Table II. Successful conversion of tetrachloroketone 46 to trichloro carboxylic acid 47[31] (Table II) further encourages the present attempt at the construction

TABLE II. Examples of Semibenzilic Acid Rearrangement of α-Haloketones.

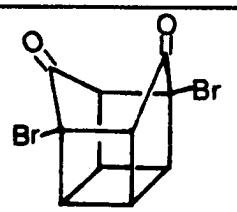
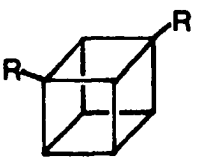
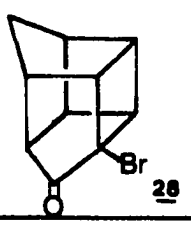
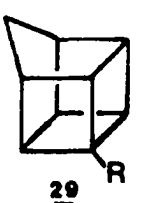
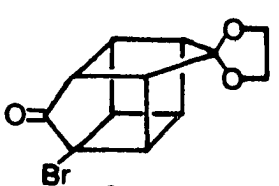
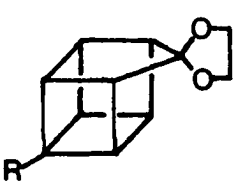
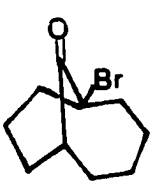
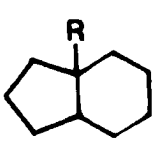
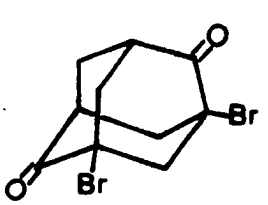
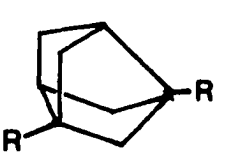
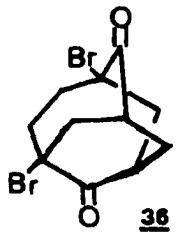
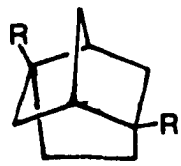
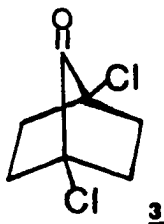
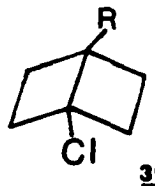
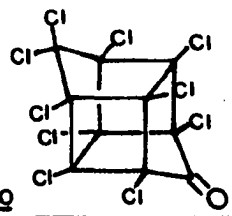
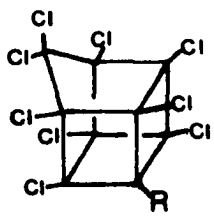
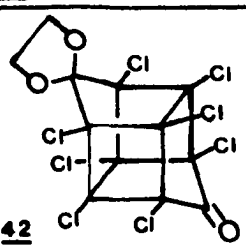
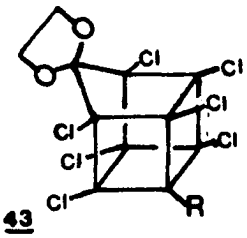
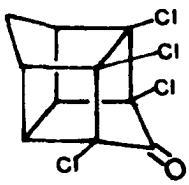
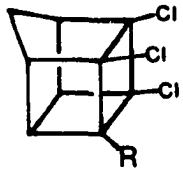
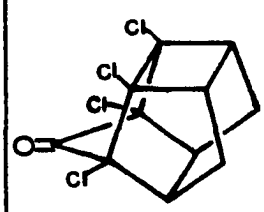
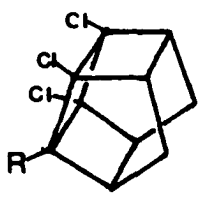
α-Haloketone	Conditions	Product (R = CO_2H)	Yield %	Ref
 **26**	aq. KOH 100°	 **27**	80	5
 **28**	30% aq.KOH reflux,4 hr	 **29**	99	21
 **30**	10% aq.KOH	 **31**	62	22
 **32**	NaOD-EtOD-D_2O	 **33**	95	23
 **34**	KOH-H_2O-EtOH,heat	 **35**		24

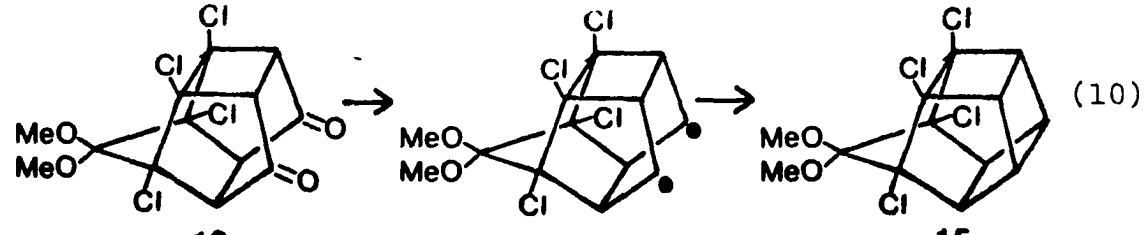
TABLE II. (Continued)

 36	KOH-EtOH-H_2O	 37	98	25 26
 38	NaOH-THF 0°-25°	 39	92.6	27 28
 40	KOH-Xylene reflux	 41	80-90	29
 42	KOH-Xylene or 10% aq. KOH	 43	95	30
 44	NaOH-PhH reflux	 45	55	21
 46	NaOH-PhH	 47	68	31

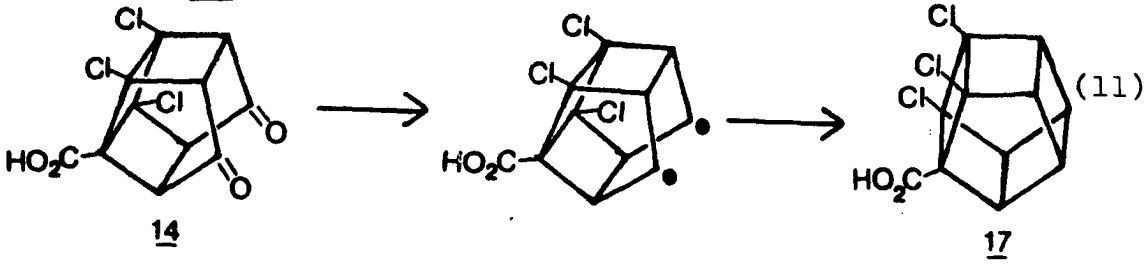
of a sigma bond via a semibenzilic acid rearrangement.

The synthesis of pentaprismane, then, would require the preparation of a cage ketone bearing at least one α-halogen atom. Treatment of this cage haloketone with base would effect a semibenzilic acid rearrangement, thereby creating the needed sigma-bond via ring contraction. Compound 12 bearing a chlorine atom alpha to a protected ketone function should provide the requisite α-haloketone by acidic hydrolysis prior to the stage of constructing a sigma-bond via the semibenzilic acid rearrangement.

The construction of the second sigma-bond ("b") (12⟶15 or 14⟶17, Scheme I) does not have precedent. At first glance, the geometry of the carbonyl carbon atoms in 12 or 14 would appear conducive to sigma-bond formation, perhaps by intramolecular collapse of the diradical derived from 12 (equation 10) or 14 (equation 11). However, prior syn-



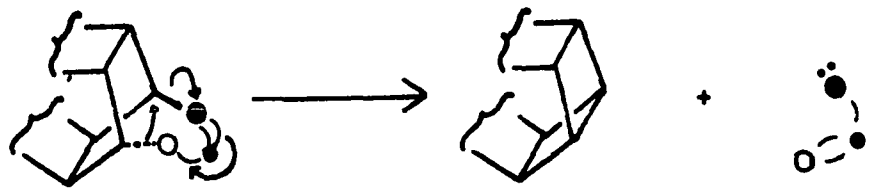
(10)



(11)

thetic approaches to pentaprismane have characteristically involved either the simultaneous formation of two new sigma bonds (equation 2) or the formation of one sigma bond (equation 3 and 4) by the expulsion of nitrogen from an azo compound via a diradical pathway. Although this type of reaction has enjoyed popularity for the synthesis of polycyclic compounds[32] (including a hydrocarbon as highly strained as prismane[7]), it fails to form any detectable amount of pentaprismane from either 5 or 7.

In view of the failure of these earlier attempts at the synthesis of pentaprismane, it would thus appear prudent to avoid diradical processes and to instead try symmetry-allowed, concerted pathways[33] for the formation of sigma bond "b". This might be accomplished through a cycloreversion process of the general type shown in equation 12.



(12)

Here, the symbol "  " represents a generalized conjugated system.

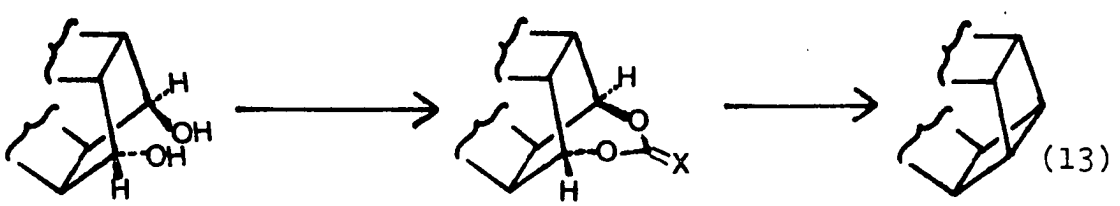
Cycloreversion processes of this kind have been commonly used for the stereospecific and stereoslective introduction of double bonds in carbon skeletons.[34] Among

them, fragmentations of heterocyclic olefin precursors derived from vicinal diols, such as 2-phenyl-1,3-dioxolanes (48a) (developed by Whitham[35]) and 2-thiono-1,3-dioxolanes (48b) (developed by Corey[36,37]) are of particular interest



48a: X = Ph,H
b: X = S

to the present study, since they could conceptually provide the novel formation of the abovementioned sigma bond from the analogous heterocyclic intermediates 49a and 49b derived from the corresponding diol which has the two hydroxyl groups ideally positioned for the formation of such intermediates (equation 13).

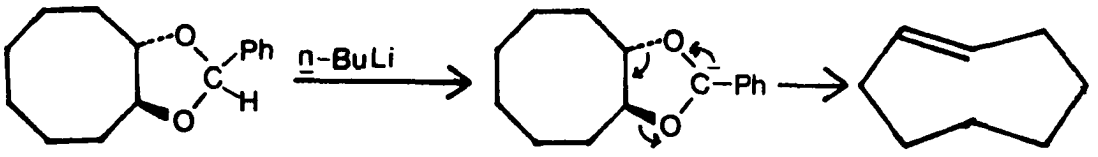


(13)

49a: X=Ph,H
b: X=S

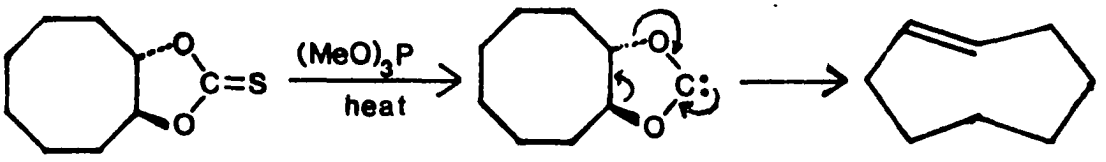
Phenyldioxolanes react with base to form olefins with the elimination of benzoate anion via a symmetry-allowed, 1,3-dipolar cycloreversion reaction.[38] A representative example is the preparation of trans-cyclooctene from the reaction of benzylidene acetal 50 with n-butyl

lithium:[35,39]



50

This trans-olefin can also be produced by treating cyclooctane-1,2-trans-thionocarbonate 51 with trivalent phosphorus[40] and, in this case, the reaction proceeds via a carbene intermediate[41] followed by elimination of carbon dioxide in a concerted manner:



51

In addition, Corey's method of elimination of 1,2-thionocarbonates has been employed to synthesize trans-cycloheptene,[42] cyclobutene,[43] and unsaturated propellanes.[44]

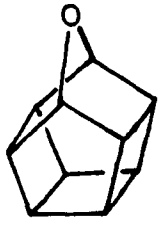
There is, however, no precedent for the formation of sigma bond by this procedure. Nevertheless, the heterocyclic compounds (49a and 49b) in our study are uniquely suited to explore the potential synthetic utility of such reactions. Foremost among the advantages of our systems is the rigidity of the carbon skeleton and the consequent proximity of the carbon atoms which eventually must become

mutually sigma-bonded, (i.e., the carbon termini comprising bond "b" in structure 17). Thermodynamically, one must balance the gain in sigma-bond formation against its cost: the extra strain energy introduced into new system relative to its precursor. However, the established existence of so highly strained compounds as cubane and prismane suggests that strain energy consideration alone in a reaction leading to a homopentaprismane (15) or pentaprismane (17) derivative should not be of overriding importance.

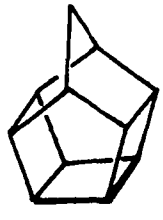
Once the cage compound 17 is obtained, we assumed that decarboxylative halogenation (17⟶18) using modified Hunsdiecker reaction[16] followed by dehalogenation (18⟶1) using sodium[13] or lithium[17] reduction should lead to pentaprismane (1). The success of the present synthetic approach to pentaprismane (Scheme I) clearly hinges upon our ability to effect the conversion 13⟶14 or 16⟶17 via a semibenzilic acid rearrangement and the conversion 14⟶17 or 12⟶15 via the above discussed cycloreversion processes.

This thesis is concerned with synthetic approaches to pentaprismane following the proposed reaction sequences shown in Scheme I. Efforts in this direction were soon jeopardized when it become apparent that semibenzilic acid rearrangement on triketone 13 and attempts at conversion of 12 to 15 all failed to produce the desired compounds. Other

methods of approach had to be developed during the course of this synthetic investigation. In this thesis, the results of synthetic approaches to pentaprismane (1) and oxahomopentaprismane (52) are presented. Successful synthesis of homopentaprismane (53) and the re-examination of Underwood and Ramamoorthy's results[45] concerning the synthesis of this hydrocarbon 53 are also presented.



52



53

RESULTS AND DISCUSSIONS

The synthesis of pentaprismane was first attempted by following the pathway A (12⟶13⟶14⟶17) as illustrated in Scheme I. Compound 12 was synthesized by photocyclization of the Diels-Alder adduct 11[14] (itself formed from tetrachlorocyclopentadiene dimethyl acetal (10)[13] and para-benzoquinone) in an overall yield of 68%. This reaction sequence parallelled earlier syntheses of some 8,11-diketones of the same cage system (equation 5).[15,46] The ready photochemical cyclization of 11 to the corresponding cage compound 12 establishes the endo stereochemistry of the Diels-Alder adduct 11. Compound 12 shows carbonyl absorption in the infrared at 1770 and 1780(sh) cm^{-1} (Figure 1a), but no pmr absorption in the olefinic proton region (Figure 1b).

Acid-catalyzed hydrolysis of polychlorinated cage ketals generally requires quite vigorous conditions, usually concentrated or fuming sulfuric acid.[47,48] This phenomenon probably could be traced to the destabilization of a potential carbonium ion at the methylene bridge by the cumulative electron withdrawing inductive effects of the

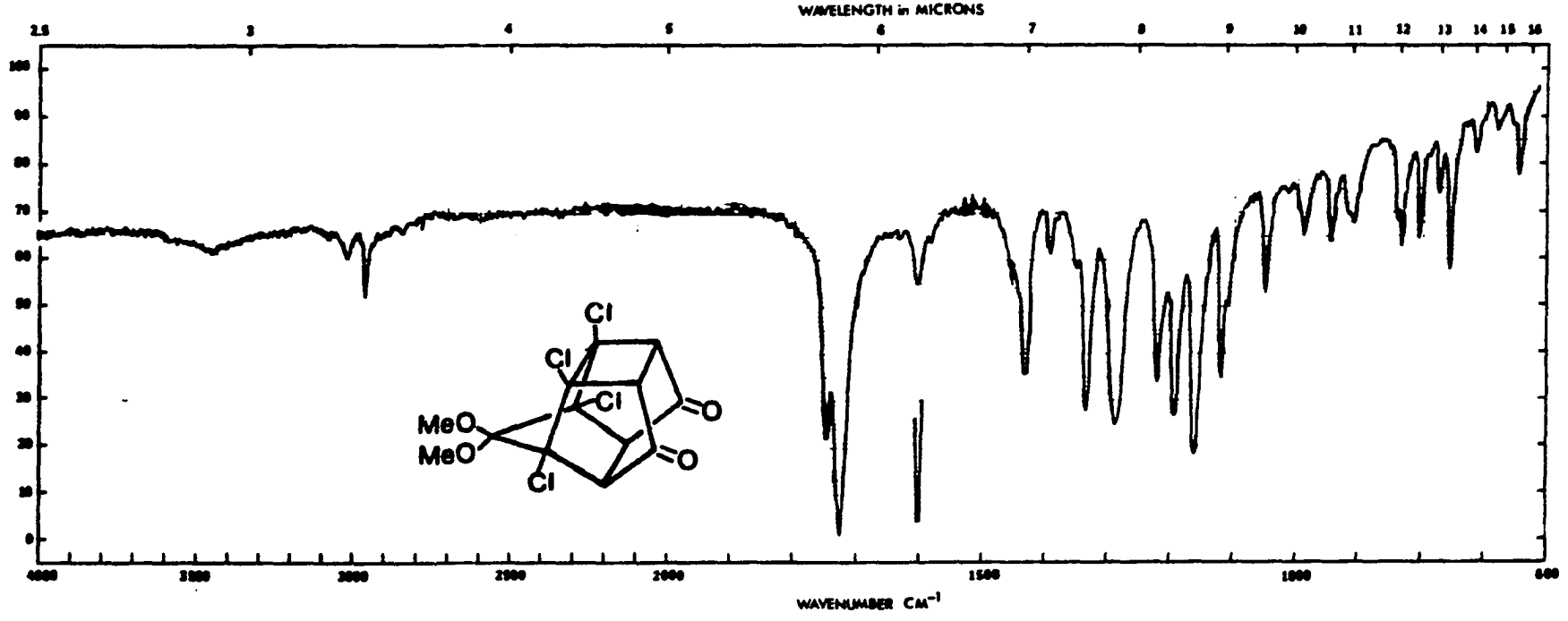


Figure 1a. Infrared spectrum (KBr) of 12.

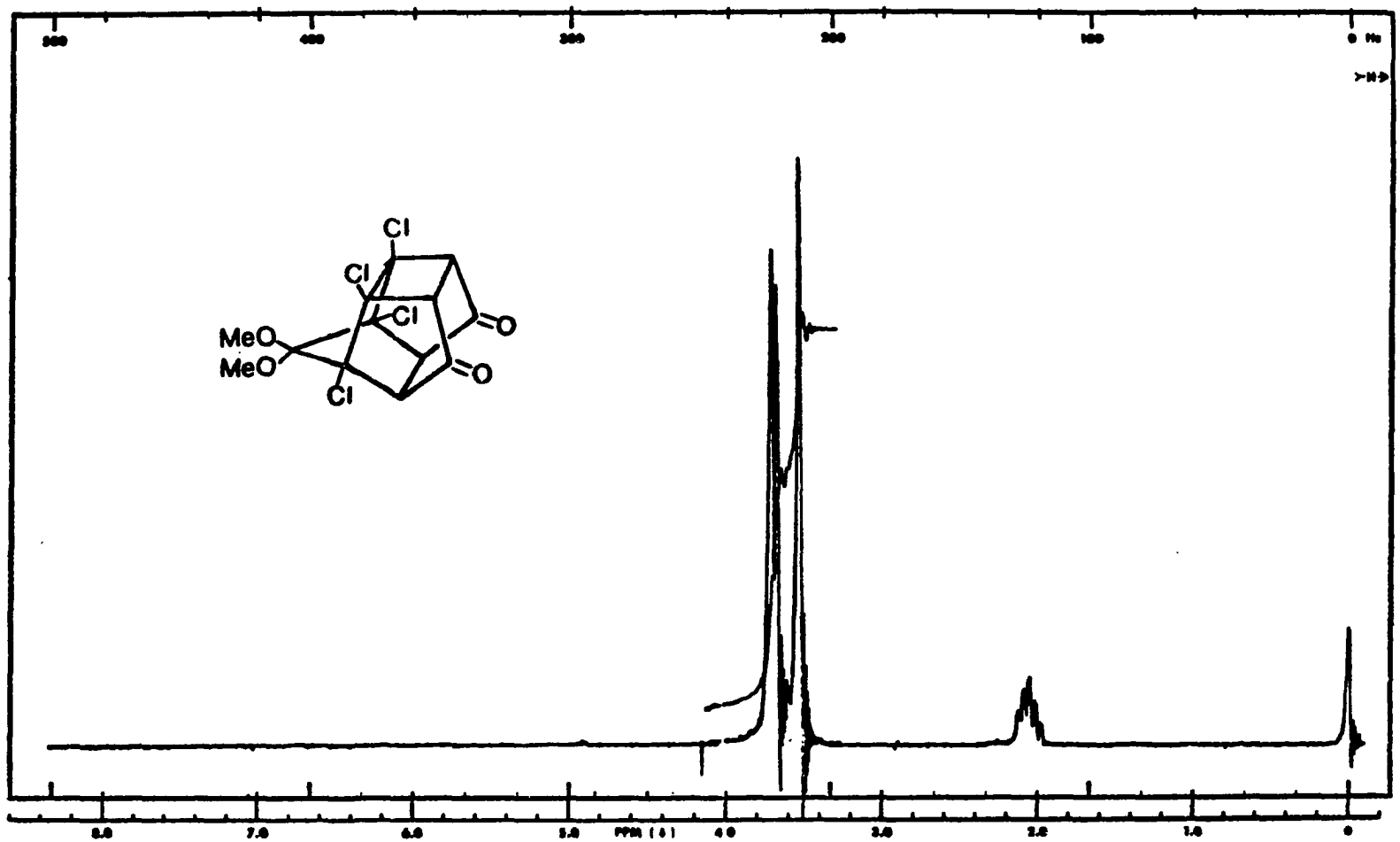


Figure 1b. Proton nmr spectrum (60MHz, acetone-d_6 solvent, TMS internal standard) of 12.

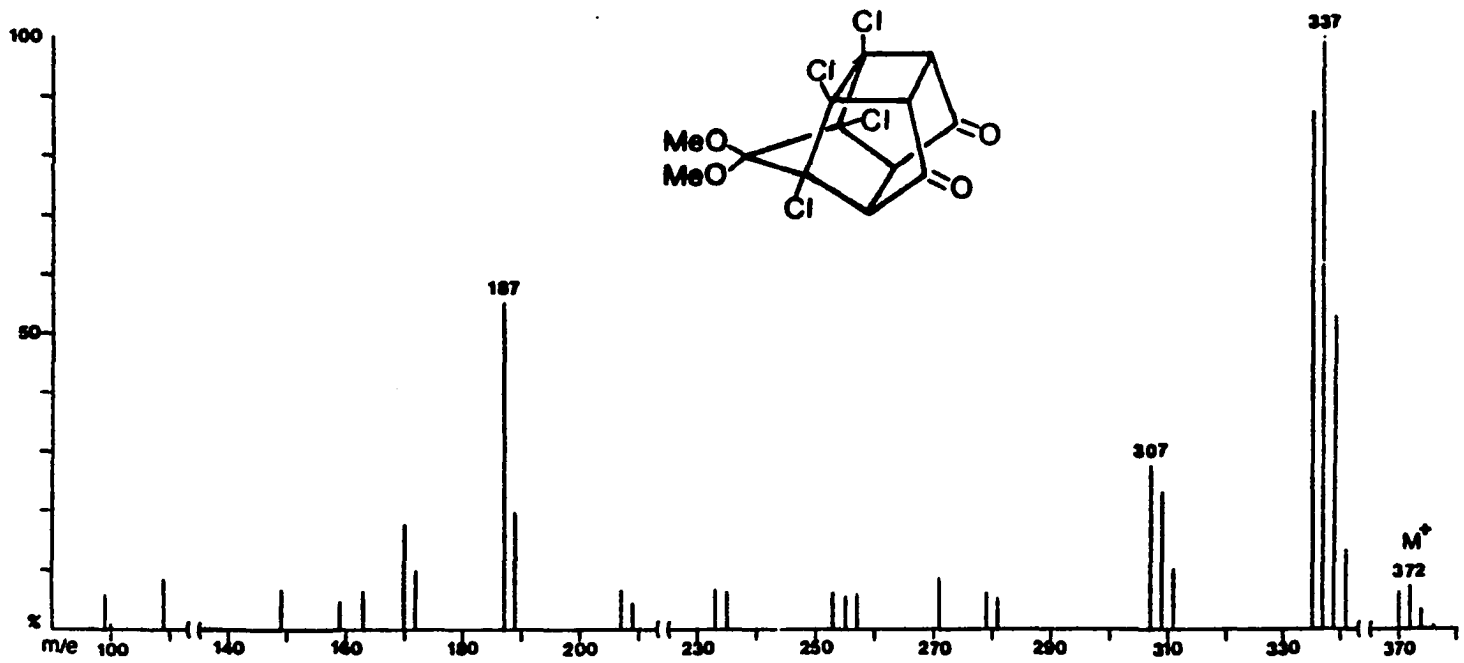


Figure 1c. Mass spectrum of 12.

chlorine atoms. Hydrolysis of 12 to the corresponding triketone 13 was achieved *via* treatment of 12 with concentrated sulfuric acid in methylene chloride.[28] In this manner, compound 13 could be obtained in a yield of 80%. On some occassions, the reactions afforded very dark brown solution and the yields were considerably lower, presumably due to contamination of the starting materials with diene 11. The structure of 13 is recognized by its characteristically complex absorption bands at 1775, 1785, 1809, and 1824 cm^{-1} in the infrared spectrum (Figure 2a) which are due to the interacting carbonyl groups[15] and the strained perchlorinated norbornanone-type ketone.[49] However, its pmr spectrum (Figure 2b) is very simple; a broad singlet at δ3.18 (acetone solution) or two broad singlets at δ3.87 and δ3.58 (pyridine solution). This triketone is very hygroscopic; it forms a hydrate (gem-diol), and even a polyhydrate on longer exposure to air, as evidenced by the corresponding pmr and infrared spectra.

In an attempt to promote semibenzilic acid rearrangement of triketone 13, a solution of 13 in toluene was refluxed over an excess of sodium hydroxide (the same conditions used by Stedman and coworkers to effect ring contraction of tetrachloro ketone 46 to trichloro acid 47[31] (Table II)). The reaction afforded a brown oil which was chromatographed on silica gel (diethyl ether eluant) and

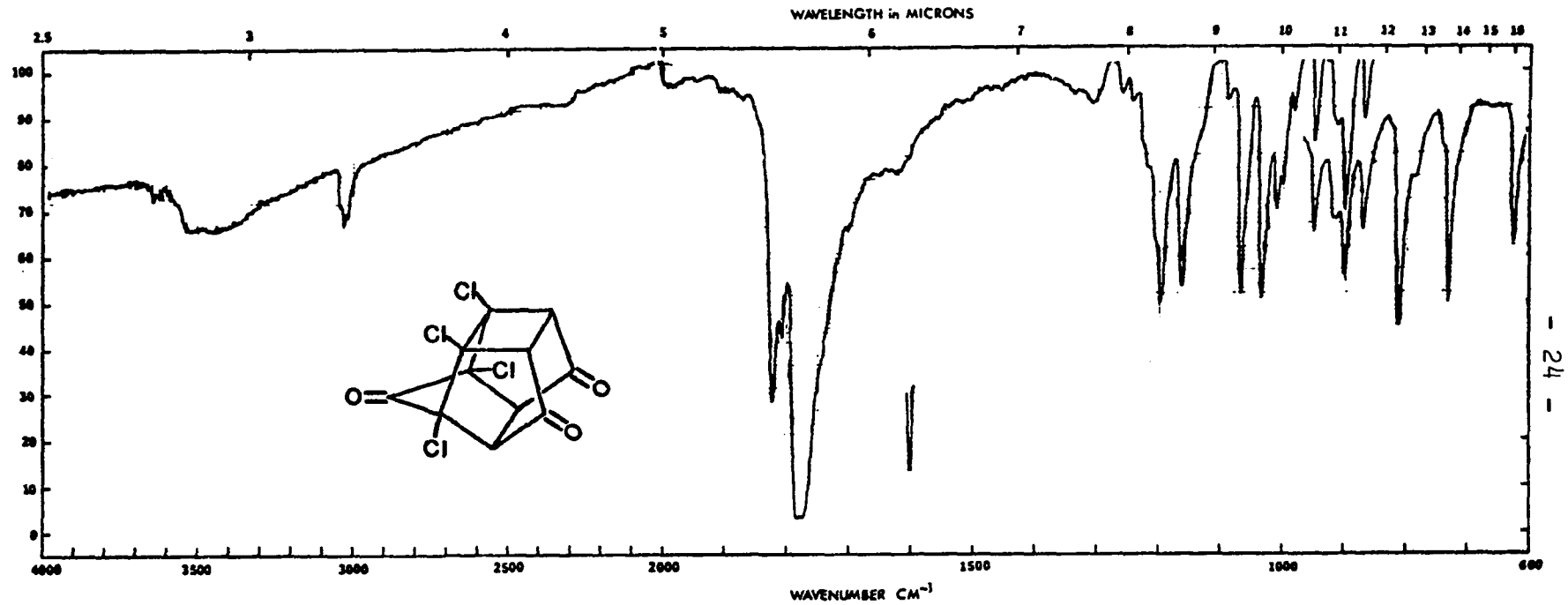


Figure 2a. Infrared spectrum (KBr) of 13.

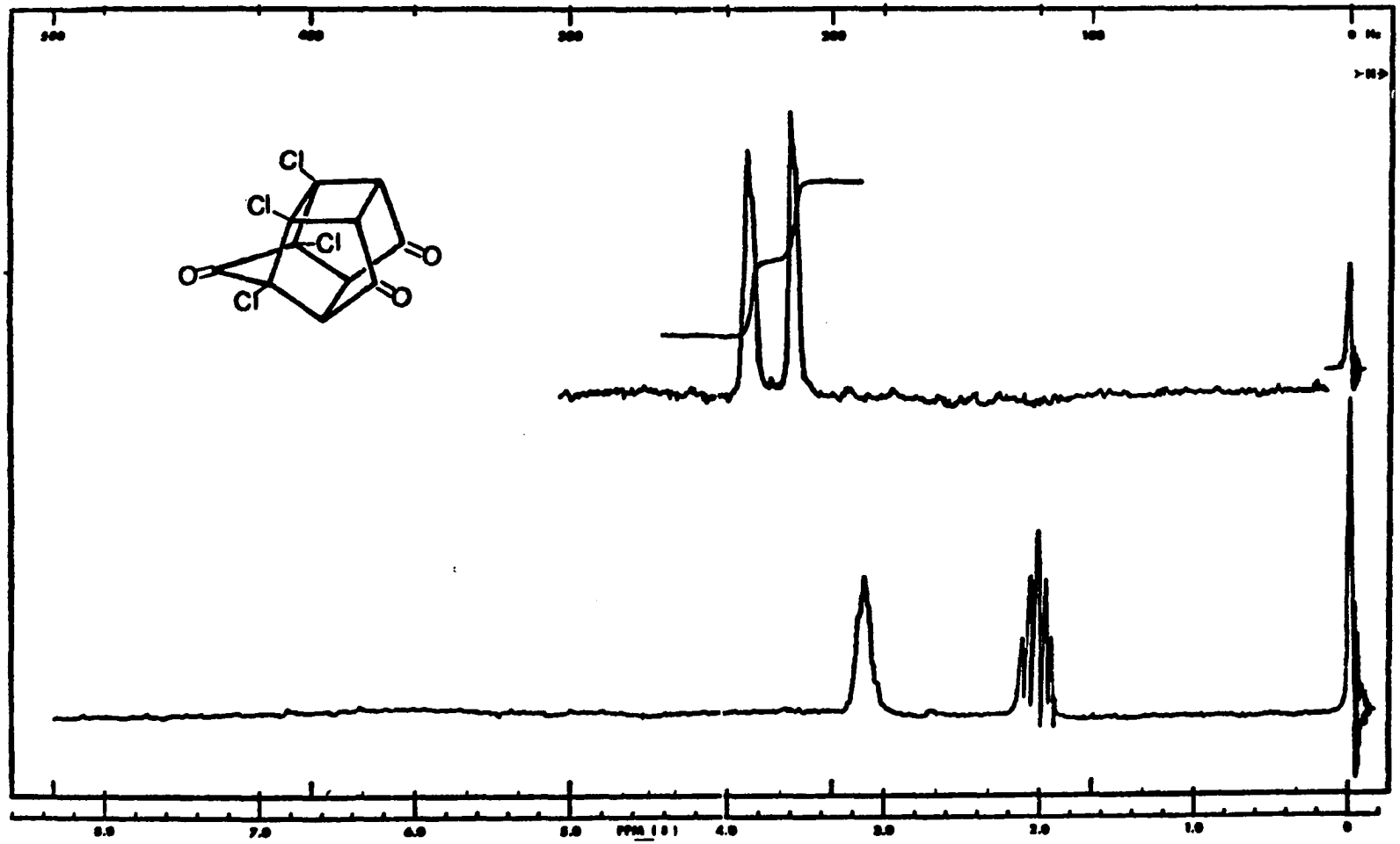


Figure 2b. Proton nmr spectrum [60mHz, (top) pyridine solvent, (bottom) acetone-d_6 solvent, TMS internal standard] of 13.

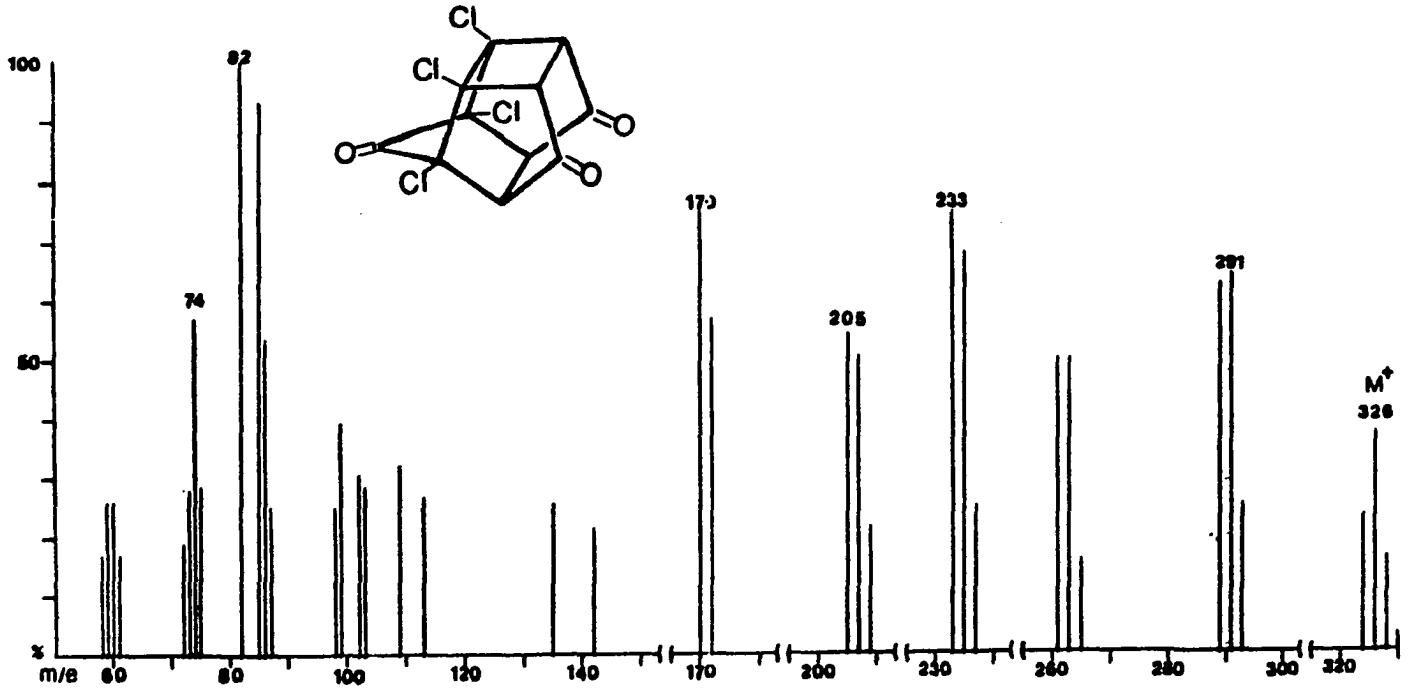
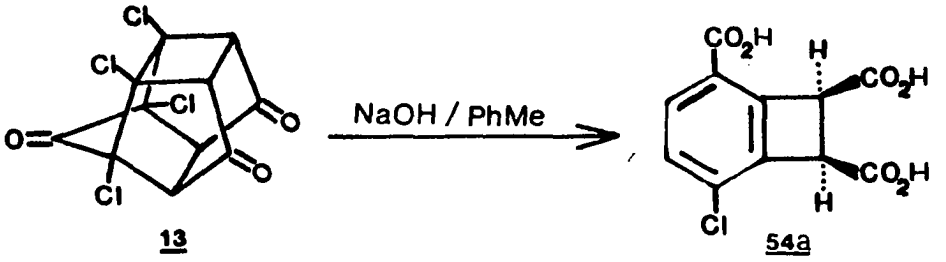


Figure 2c. Mass spectrum of 13.

recrystallized from acetone-hexane, affording colorless crystals. On the basis of spectroscopic evidence, the structure 54a was assigned to this product (equation 14).



13 54a (14)

No trace of the expected product (14) of semibenzilic acid rearrangement of 13 was detected.[50]

The infrared spectrum of 54a (Figure 3a) displays bands at 3000 (vbr) and at 1700 and 1730 cm^{-1}, suggesting the presence of both conjugated and nonconjugated carboxyl groups. The presence of 1,2,3,4-tetrasubstituted benzene ring is suggested by the pmr spectrum (in acetone-d_6, Figure 3b), which displays an AB pattern (2H) centered at δ7.63 ($\Delta\delta$25 Hz, J_{AB}=8 Hz). A sharp singlet (2H) at δ4.78 corresponds to the hydrogens on the cyclobutane ring. The adventitious equivalence of these two hydrogens can be removed by adding a few drops of benzene-d_6 to the solution;[51] an AB pattern (J=ca. 6 Hz) resulted.

Attempted sublimation of 54a afforded a mixture of 54a and the corresponding carboxylic anhydride 55, as evidenced by the presence of additional infrared absorption at 1788 and 1862 cm^{-1}; this doublet is characteristic of

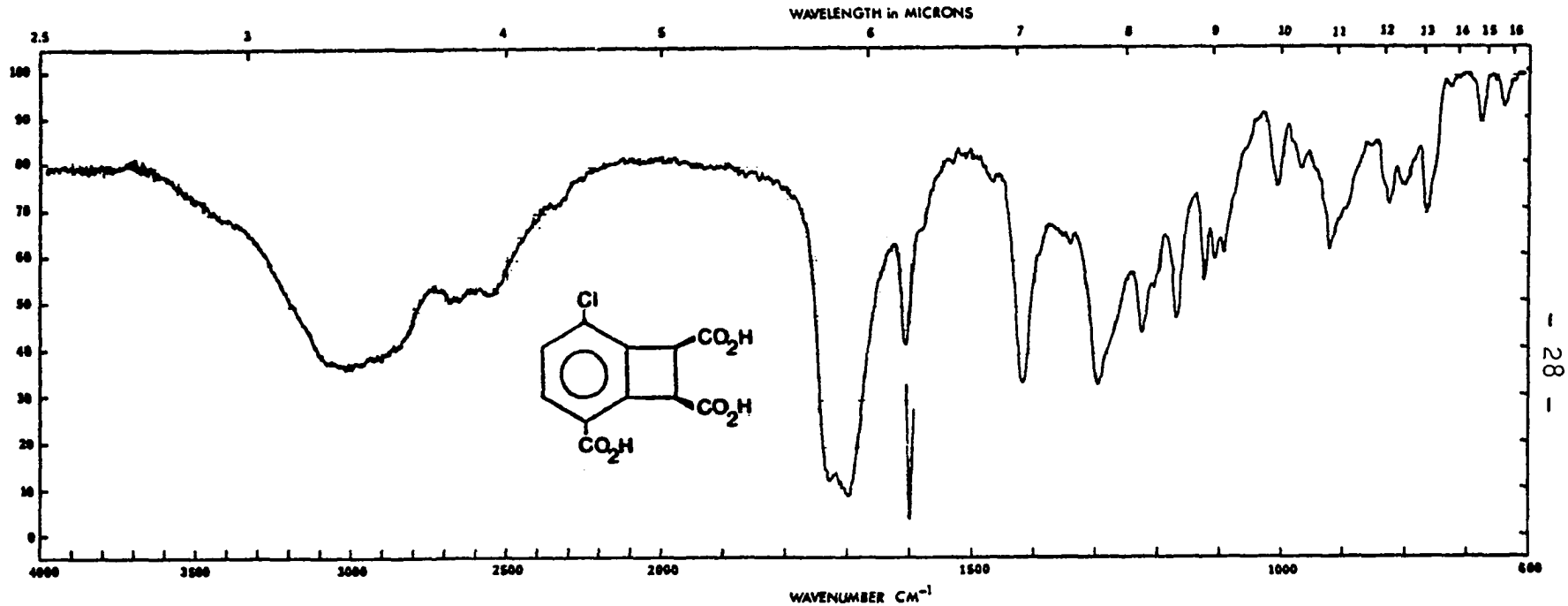


Figure 3a. Infrared spectrum (KBr) of 54a.

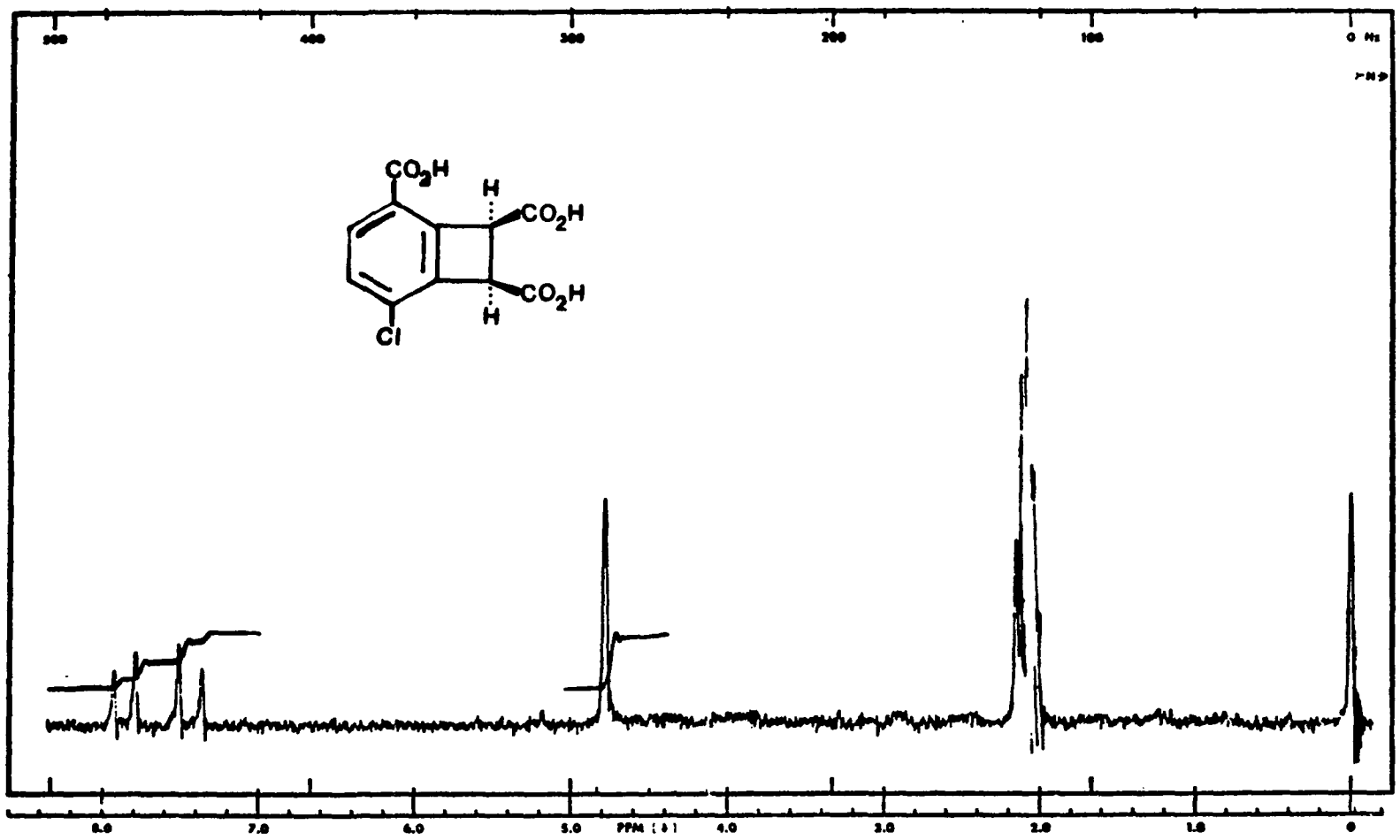


Figure 3b. Proton nmr spectrum (60 Hz, acetone-d_6 solvent, TMS internal standard) of 54a.

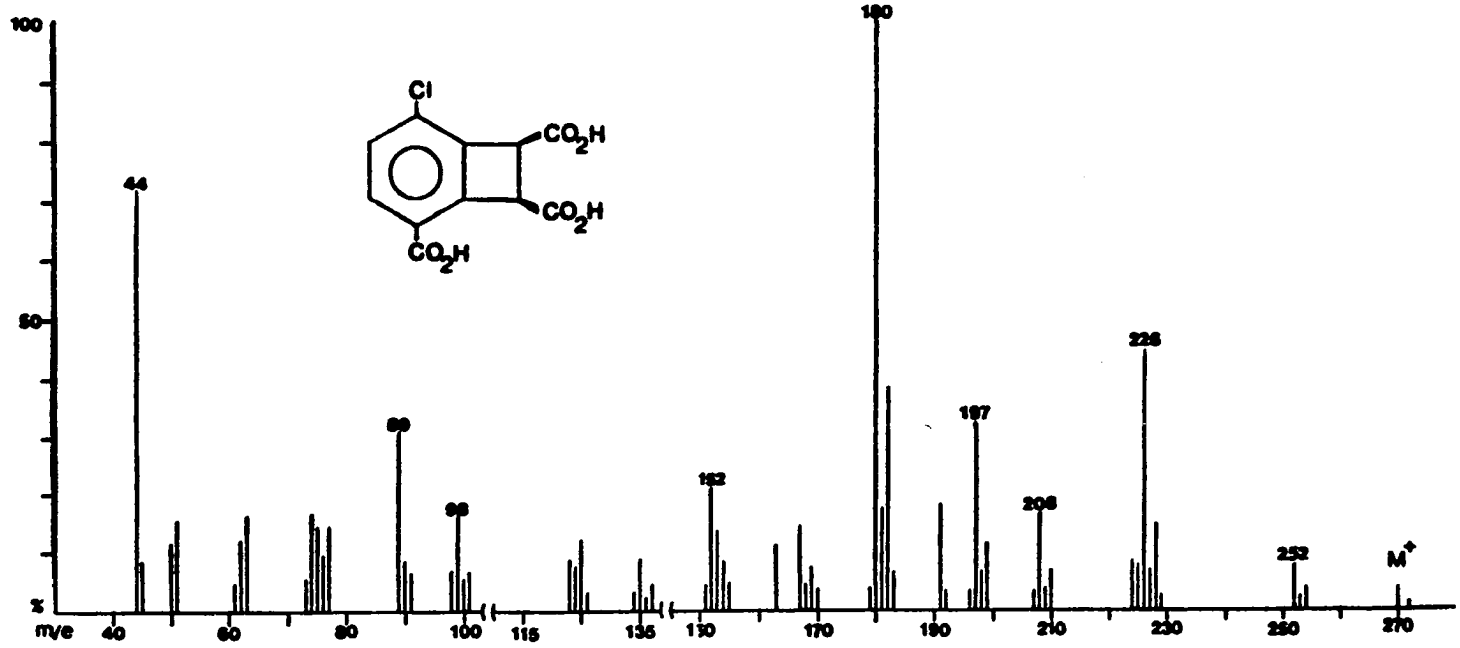
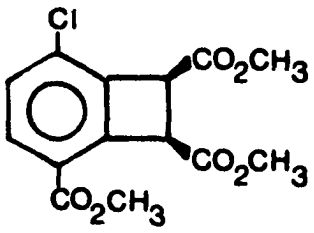
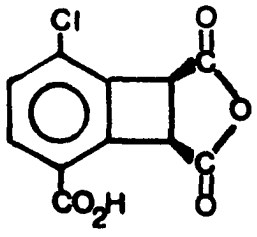


Figure 3c. Mass spectrum of 54a.

strained, cyclic acid anhydride.[52] The pmr spectrum of the mixture in acetone-d_6 exhibits two sets of signals, the upfield set being identical to those of 54a. The set appearing at lower field corresponds to the acid anhydride 55 (δ 5.05 (br s, 2H) and δ7.70 (AB system, 2H)). The peaks corresponding to the acid anhydride disappear completely from the spectrum after the solution is treated with D_2O for several days; the only peaks remaining correspond to hydrogens of 54a. Primarily on the basis of these observations, the cis stereochemistry is assigned to the vicinal carboxylic acid groups in 54a.



54b



55

The tendency of 54a to suffer thermal dehydration impeded attempts at purification of an analytical sample. Accordingly, tricarboxylic acid 54a was further characterized as its trimethyl ester (54b), obtained by treatment of 54a with diazomethane in anhydrous diethyl ether. The infrared spectrum of 54b (Figure 4a) displays carbonyl absorptions at 1750 and 1728 cm^{-1} and its pmr spectrum (Figure 4b) exhibits three singlets at δ3.70, 3.72 and 3.85 corresponding to the three methyl ester groups in 54b. In addition, the correct

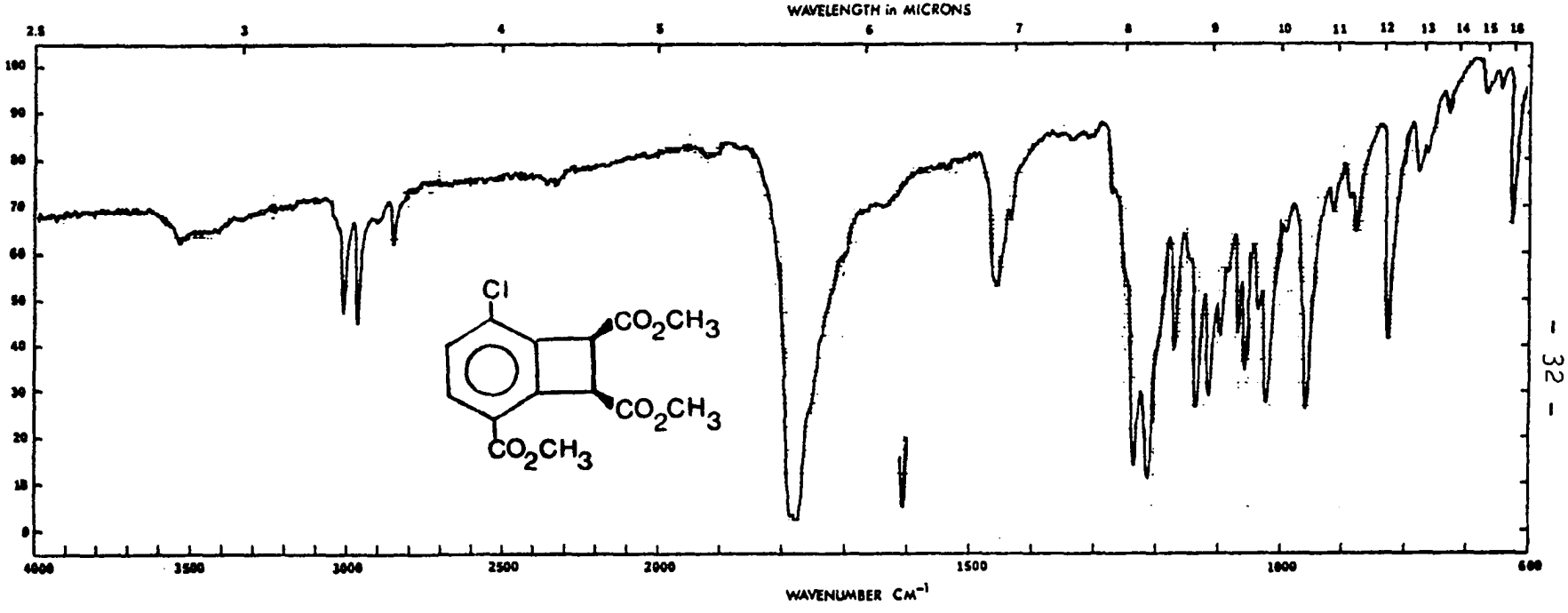


Figure 4a. Infrared spectrum (KBr) of 54b.

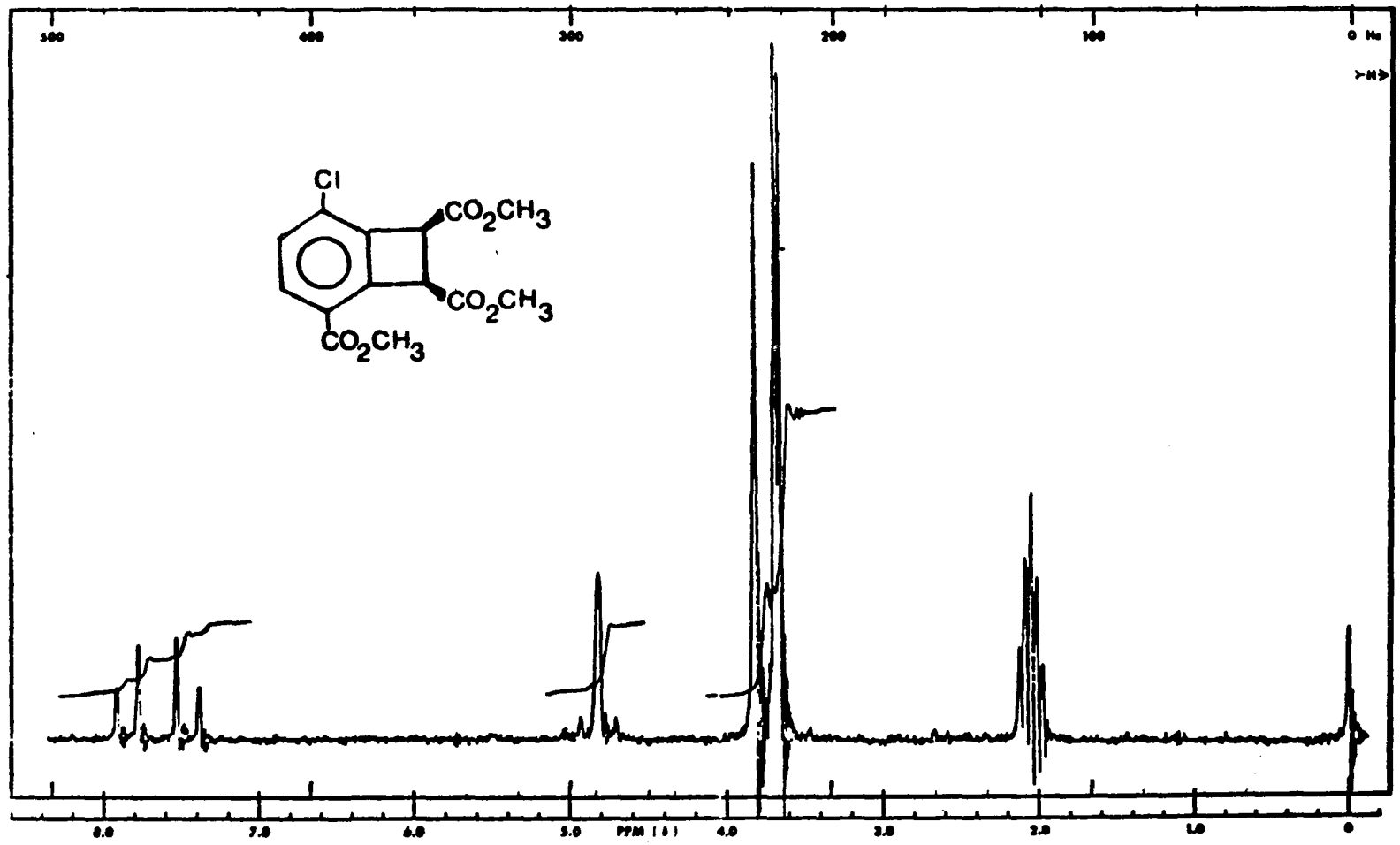


Figure 4b. Proton nmr spectrum (60MHz, acetone-d_6 solvent, TMS internal standard) of 54b.

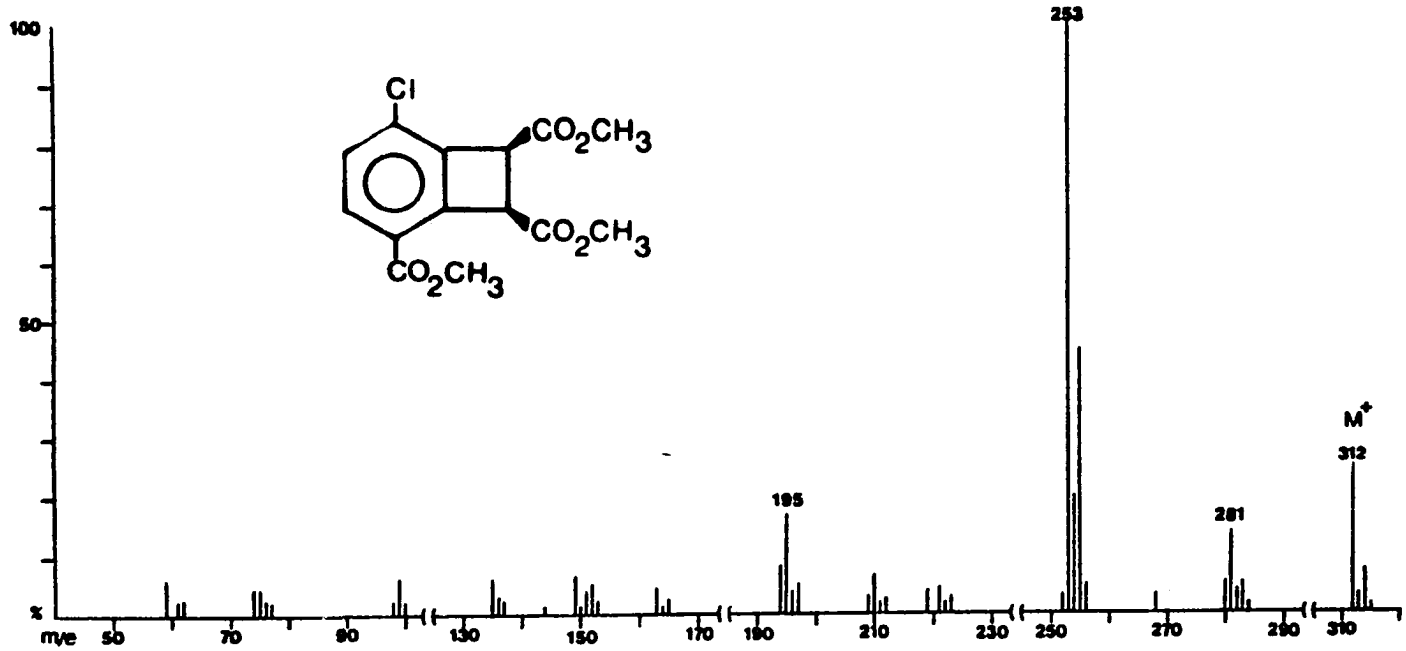
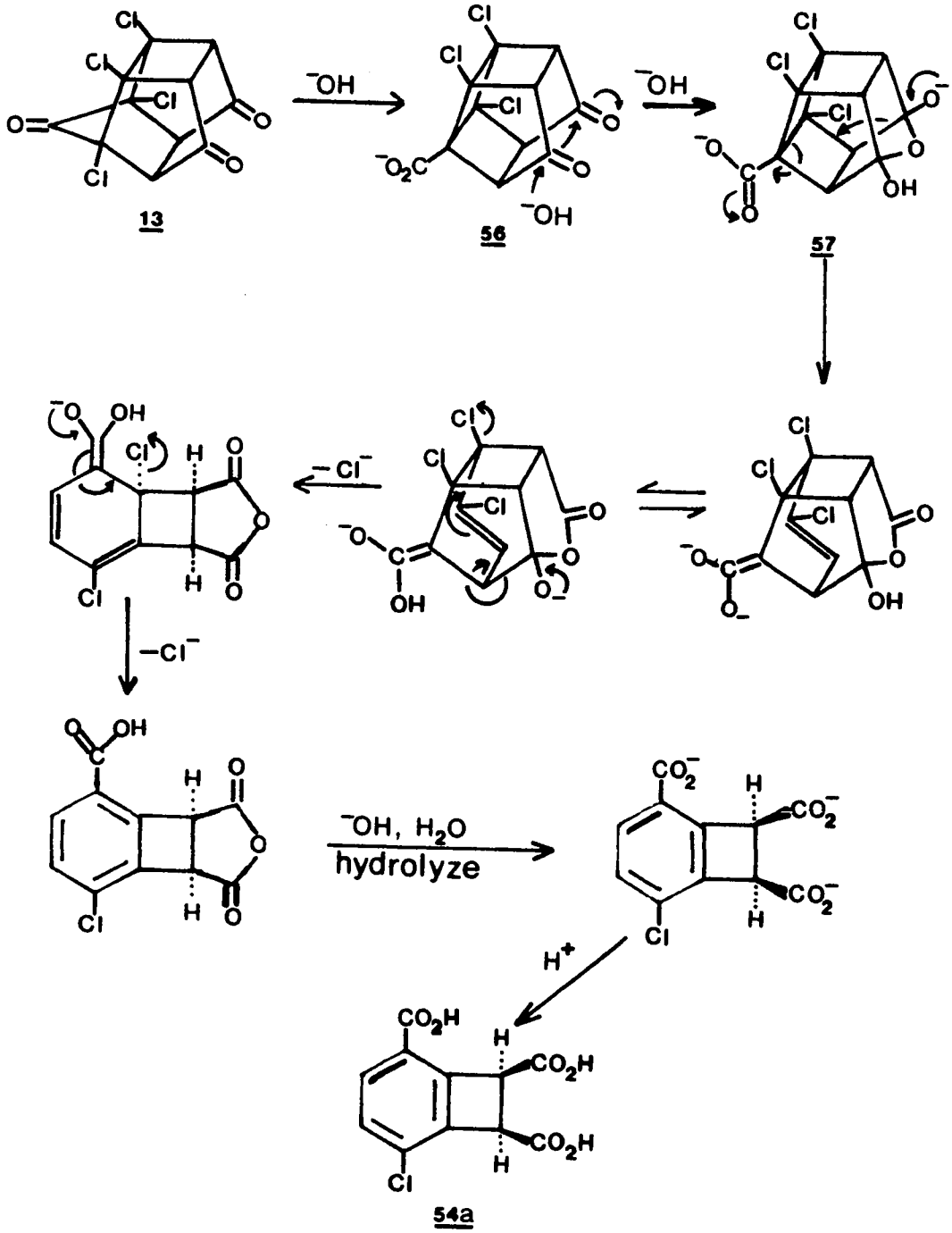


Figure 4c. Mass spectrum of 54b.

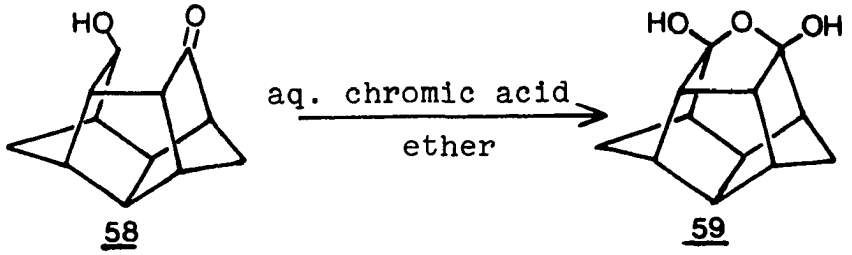
elemental analysis (corresponding to $C_{14}H_{13}ClO_6$) was obtained for trimethyl ester 54b. Structural information is further gained from the mass spectra of compounds 54a and 54b (Figure 3c and 4c). That of 54a shows the molecular ion at m/e 270/272, possessing the intensity profile characteristic of the Cl multiplet,[53] and peaks at m/e 252, 208 and 180 (base peak) which arise from dehydration (to form the corresponding acid anhydride) followed by elimination of CO_2 and cycloelimination of CO_2+CO; such fragmentation behavior is common for cis-1,2-dicarboxylic acids and their corresponding anhydrides.[54,55] The mass spectrum of 54b (Figure 4c) displays the molecular ion at m/e 312/314, with an intensity profile similar to that of 54a, and major peaks at m/e 281 (M^+-OMe), 253 (M^+-CO_2Me, base peak), and 194 (M^+-2CO_2Me); this fragmentation behavior is common for vicinal diesters.[56]

A reasonable mechanism for the formation of 54a via base-promoted rearrangement of 13 might involve the intermediacy of the normal product (14) of semibenzilic acid rearrangement of 13 (Scheme III) as suggested by the conversion 46⟶47,[31] (Table II). The carboxylate anion 56 thus formed is not stable to the reaction conditions, and, thus, cannot be isolated as 14. Instead, it continues to react with base to afford 54a; this process is facilitated by the presence of two additional carbonyl groups in 56,

SCHEME III

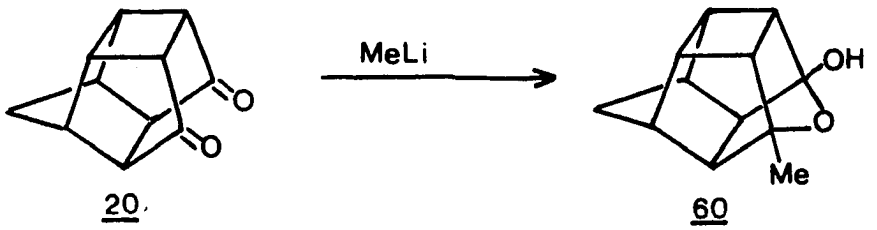


and the process of aromatization provides the driving force for the rearrangement. The intermediate 57 (Scheme III) is suggested by analogy with the previously observed formation of the dihydroxy-ether 59 via aqueous chromic acid oxidation of the keto-alchol 58 (equation 15)[57] and by analogy to the



58 59 (15)

observed transannular participation in the reaction of diketone 20 with methyllithium (which affords hemiacetal 60 (equation 16)[15]).

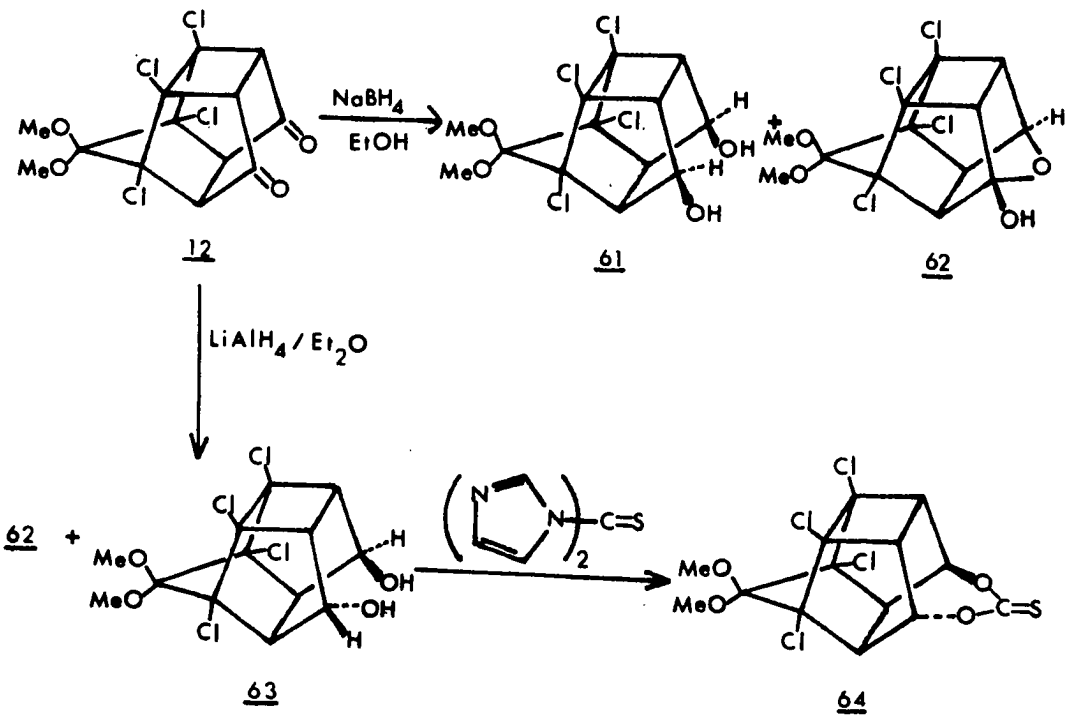


20 60 (16)

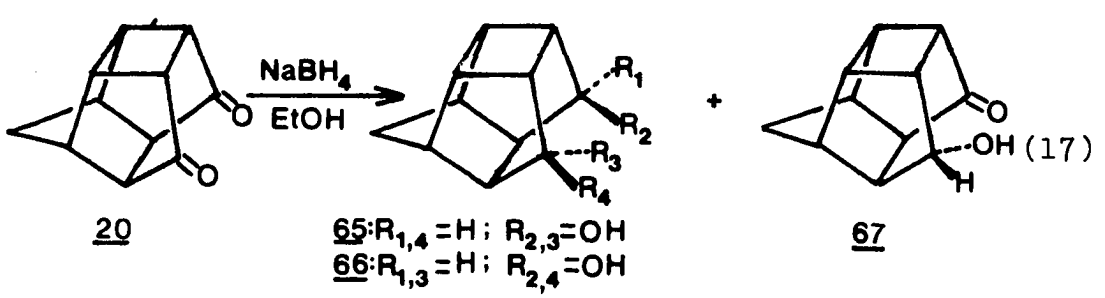
Our next attempt to synthesize pentaprismane is outlined in pathway B (12→15→16→17), Scheme I. Preparation of 15 from 12 was attempted utilizing a heterocyclic intermediate analogous to 49b (equation 13). This intermediate was synthesized from 12 by the reaction sequence shown in Scheme IV.

The reduction of pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]-

SCHEME IV



undecane-8,11-dione (20) with sodium borohydride has been investigated by Cookson and coworkers,[15] (equation 17).



When using one molar proportion of reductant, the reduction afforded the corresponding endo,exo diol 66 and ketol 67, whereas, the corresponding ketol 67 together with two

isomeric diols 65 and 66 was obtained when diketone 20 was treated with an excess of reductant. However, lithium aluminum hydride reduction of diketone 20 has been reported to afford cleanly the endo,endo diol 65.[58]

In present study, reduction of diketone 12 with sodium borohydride in 95% ethanol afforded a diol, mp 256-257°, together with a small amount of a second product which could be easily removed via recrystallization (ethyl acetate-hexane). The pmr spectrum (Figure 5b) of this diol displays two absorption signals at δ4.50 (broad singlet) and δ5.41 (broad doublet), corresponding to two hydrogens at the carbon atoms bearing hydroxyl groups; these two signals were not present in the pmr spectrum of the diol obtained from reduction of 12 with sodium borodeuteride. It also displays two absorption signals at δ3.76 (doublet) and δ4.83 (broad doublet) for the hydroxyl protons, which disappeared upon addition of D_2O. This observation suggests that the diol has endo,exo* hydroxyl groups as shown in 61. It may arise by internal reduction of the second carbonyl group by the hydroborate formed from reduction of the first.

The minor product from sodium borohydride reduction of 12 was identified as the corresponding hemi-acetal (62).

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*The stereochemistry of functional group is defined as endo or exo, if the group orients itself inward or outward, respectively, with respect to the carbon skeleton of the cage system.

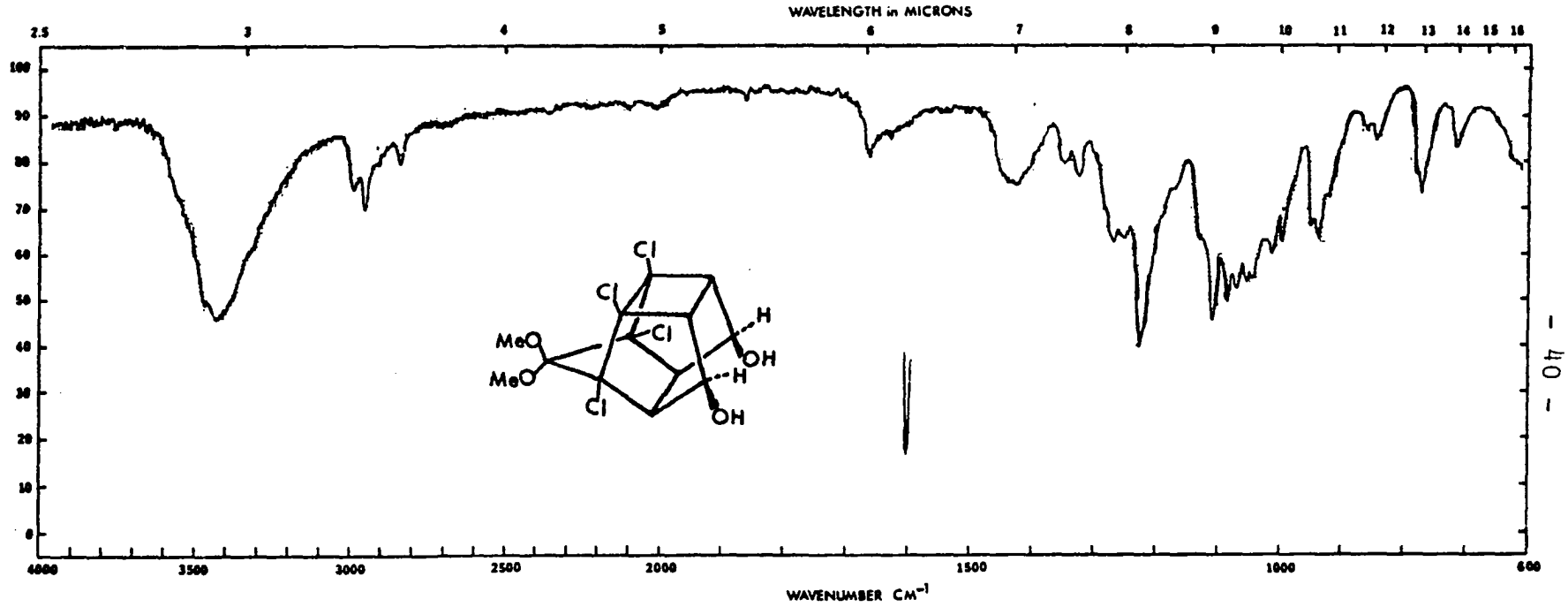


Figure 5a. Infrared spectrum (KBr) of 61.

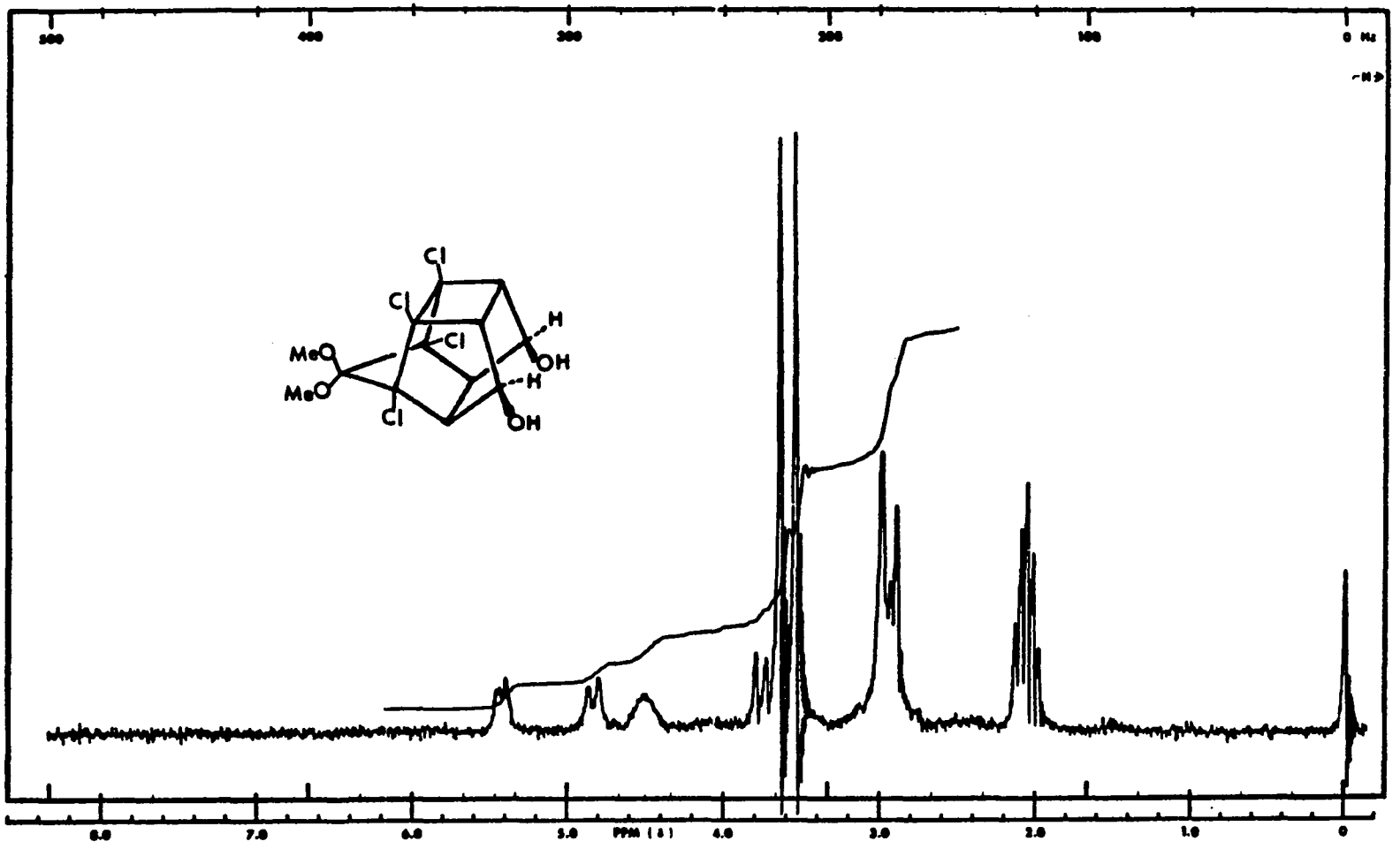


Figure 5b. Proton nmr spectrum (60MHz, acetone-d_6 solvent, TMS internal standard) of 61.

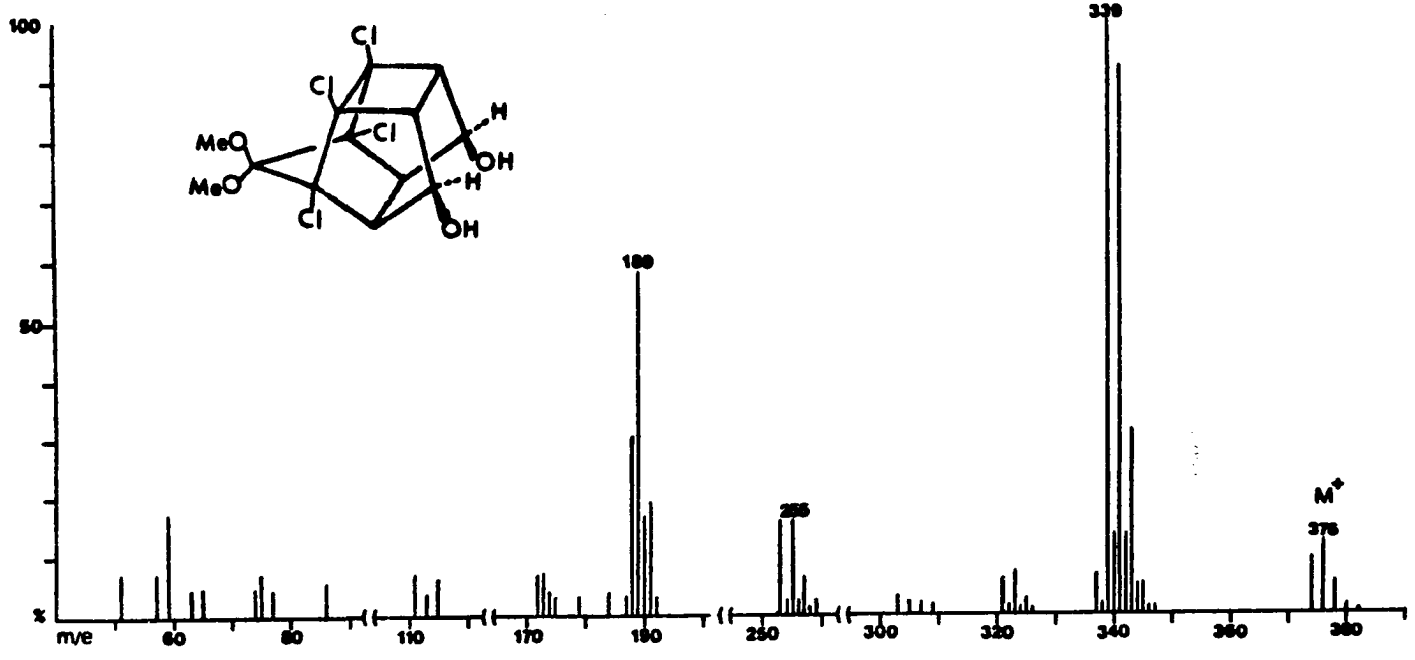
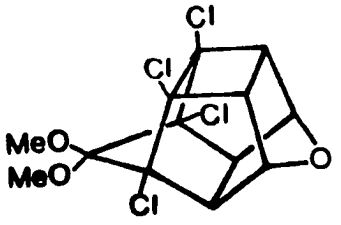


Figure 5c. Mass spectrum of 61.

The structure of 62 was assigned on the basis of spectral evidence and by the fact that it could be further reduced by lithium aluminum hydride to the corresponding endo,endo diol 63. The infrared spectrum of a sublimed sample of 62 displayed strong absorption at 3300 cm^{-1} and no absorption in the carbonyl stretching frequency region. The pmr spectrum of 62 displayed a broad triplet at δ5.0 due to the hydrogen at the carbon atom adjacent to the oxygen bridge.

Diol 61 failed to produce the corresponding cyclic 1,3-dioxolane derivatives when treated with either triethyl orthoformate or benzaldehyde. With the former reagent, diol 61 was recovered quantitatively and with the latter, the reaction afforded a dehydrated product (68) as the only



68

product. These results further establish the stereochemistry of the hydroxyl groups in 61 (i.e., endo-exo configuration of hydroxyl groups), since formation of cyclic derivatives would result in the creation of a strained bicyclo[3.2.2]heptyl ring system with a hydrogen (endo-H) disposed inside the ring.

In order to avoid internal reduction resulting in

the formation of endo,exo diol 61, the reduction of 12 was attempted using lithium tributoxyaluminum hydride[59] (prepared via addition of tert-butyl alcohol to lithium aluminum hydride). However, this reductant failed to reduce diketone 12 in two such attempts.

While the reduction of 12 with sodium borohydride afforded endo,exo diol 61, reduction of 12 with lithium aluminum hydride in diethyl ether at 0°-25°, however, did not give diol 61. Instead, the reduction product was found to consist of hemi-acetal 62 and a new diol, 63, (product ratio 62 : 63 = ca. 4 : 1, based on integration of the pmr spectrum of the product mixture). Further treatment of the mixture of 62 and 63 with lithium aluminum hydride yielded pure diol 63, mp 200.5-201.5°. If the reduction were performed at lower temperature (195-273°K), the reduction product consisted of both isomeric diols (61 and 63), along with hemi-acetal 62, (as indicated by the pmr spectrum of the crude product).

That diol 63 possesses the endo-endo configuration is suggested by the simplicity of its pmr spectrum (which exhibits a broad singlet at δ4.38 due to the two hydrogens geminal to the hydroxyl groups, Figure 6b) and by its ready formation of cyclic 1,2-dioxolane derivatives (64 and 73, vide infra). The other possibility (i.e., that the product of reduction of 12 may be the diol having exo-exo configu-

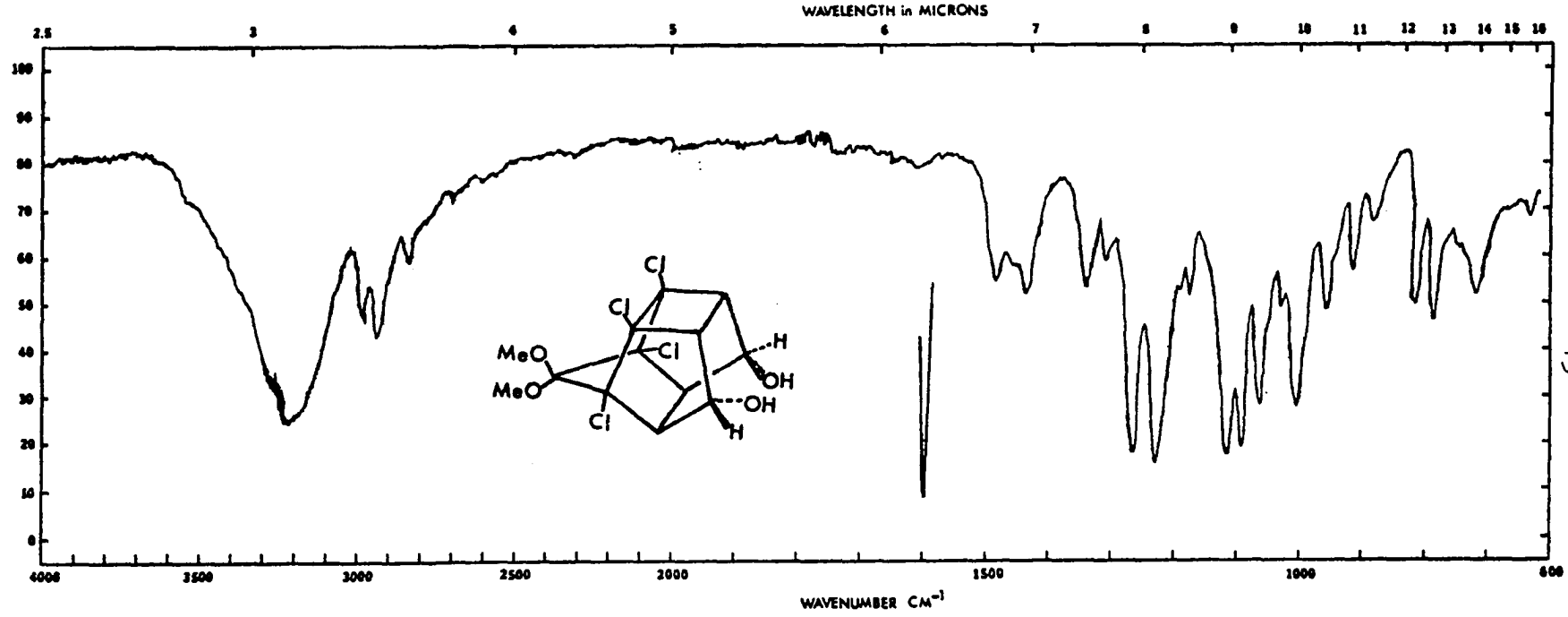


Figure 6a. Infrared spectrum (KBr) of 63.

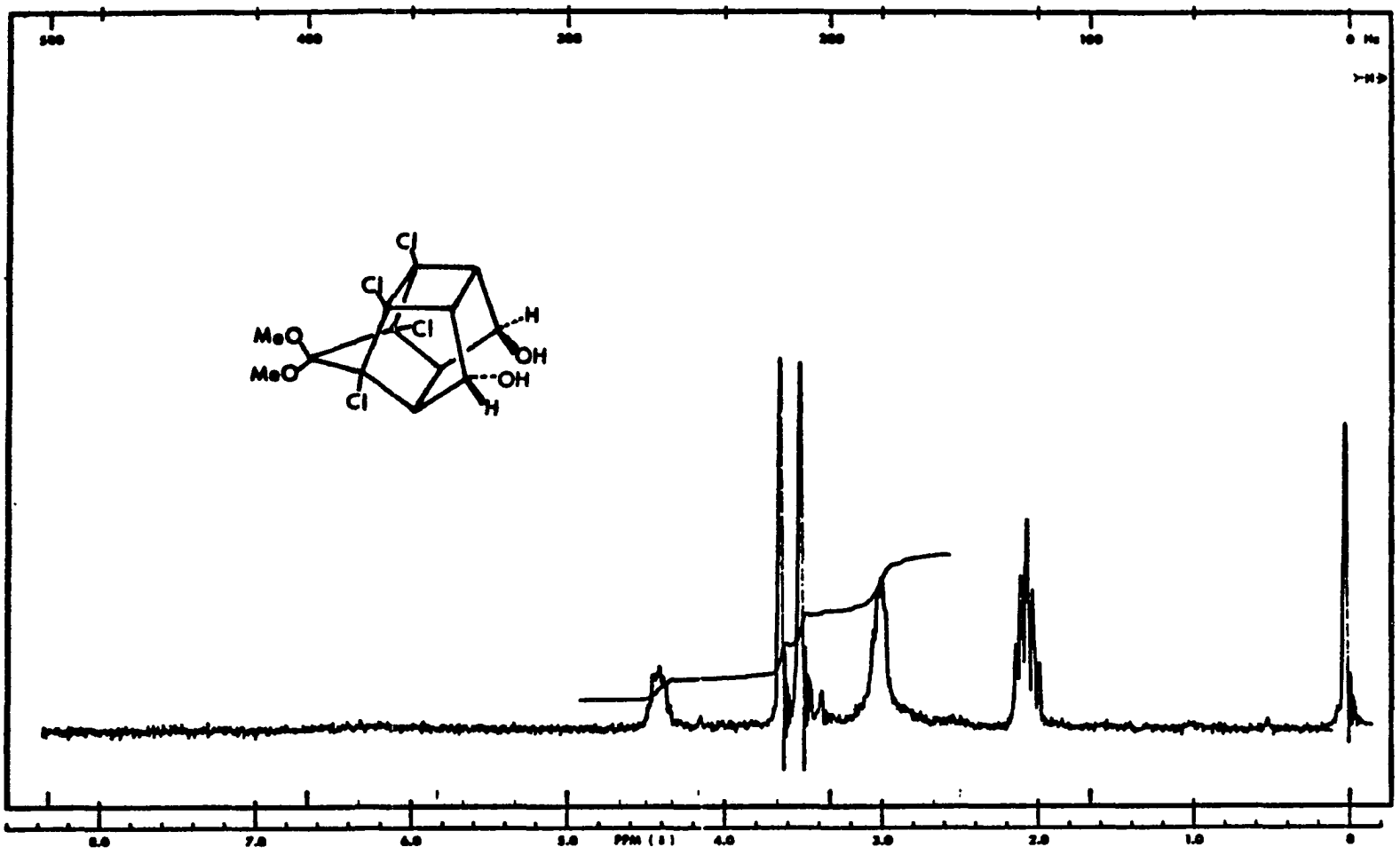


Figure 6b. Proton nmr spectrum (60MHz, acetone-d_6 solvent, TMS internal standard) of 63.

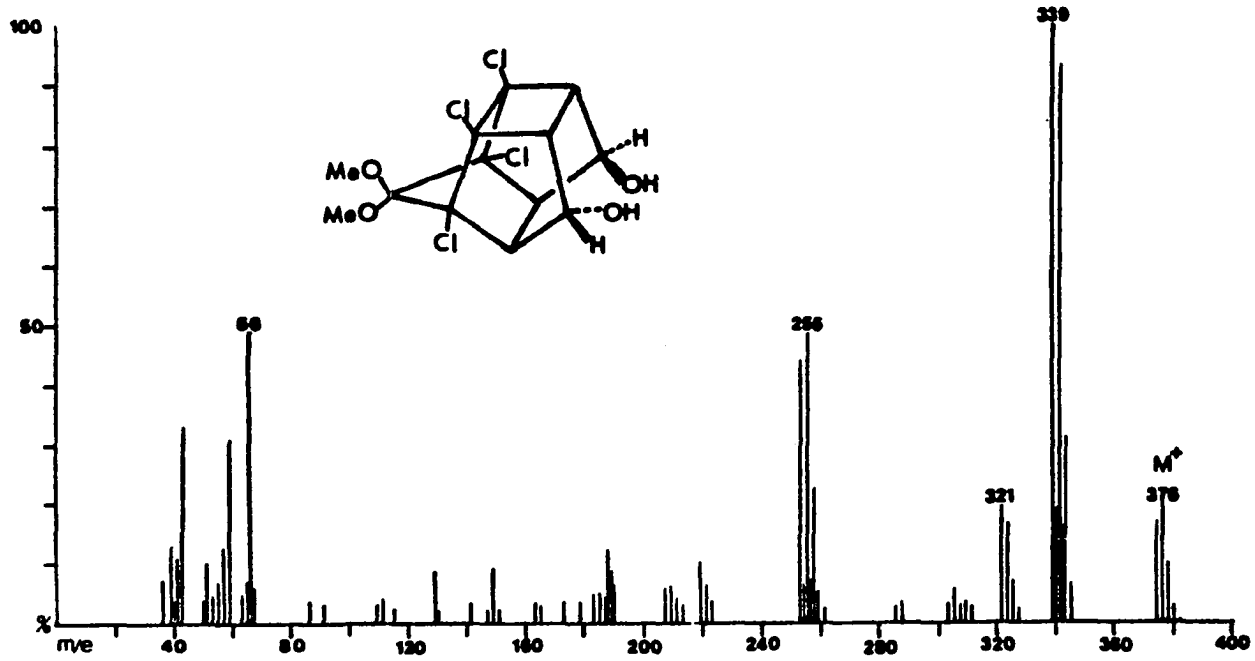


Figure 6c. Mass spectrum of 63.

ration of its hydroxyl groups) could be ruled out on the grounds of ready formation of heterocyclic compounds (64 and 73) from diol 63 and on the grounds of the known stereochemistry of lithium aluminum hydride reduction of diketone 20.[58]

Thiocarbonate 64 was prepared by refluxing a toluene solution of diol 63 and N,N'-thiocarbonyldiimidazol[60] under nitrogen for 2 hr. The infrared spectrum of 64 (Figure 7a) shows very strong absorption bands at 1305 and 1267 cm^{-1}, in the general area (1266 - 1370 cm^{-1}) of the thiocarbonyl stretching frequencies in thiocarbonate esters.[61] The pmr spectrum of 64 (Figure 7b) reveals the anisotropic deshielding effect of the thiocarbonyl groups[62] on the methine hydrogens whose absorption pattern appears at a correspondingly lower field than those of the corresponding diol 63 (i.e., δ3.43-3.72 for 64 vs. δ3.03 for 63).

In an attempt to promote cycloreversion of thiocarbonate 64, a solution of 64 in trimethylphosphite was heated at 135-145° under nitrogen for 4 days.[36,44] No trace of the desired ring-closure product (15) was obtained. The reaction afforded a material having a complex pmr spectrum which displayed a multiplet (area 4H) at δ3.1, two singlets (total area 3H) at δ3.30 and 3.33, two singlets (total area 6H) at δ3.5 and 3.6, a broad singlet (area 2H) at δ4.5, and two singlets (total area 1H) at δ5.2 and 5.3. Its infrared

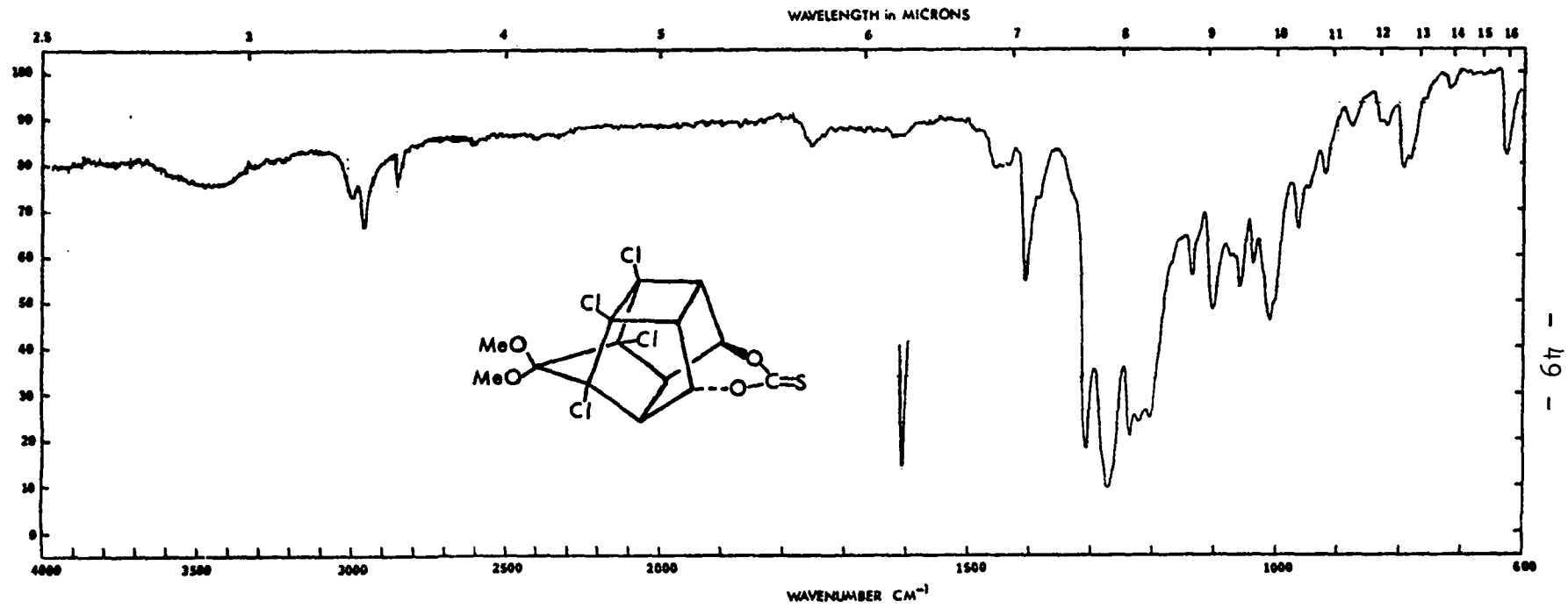


Figure 7a. Infrared spectrum (KBr) of 64.

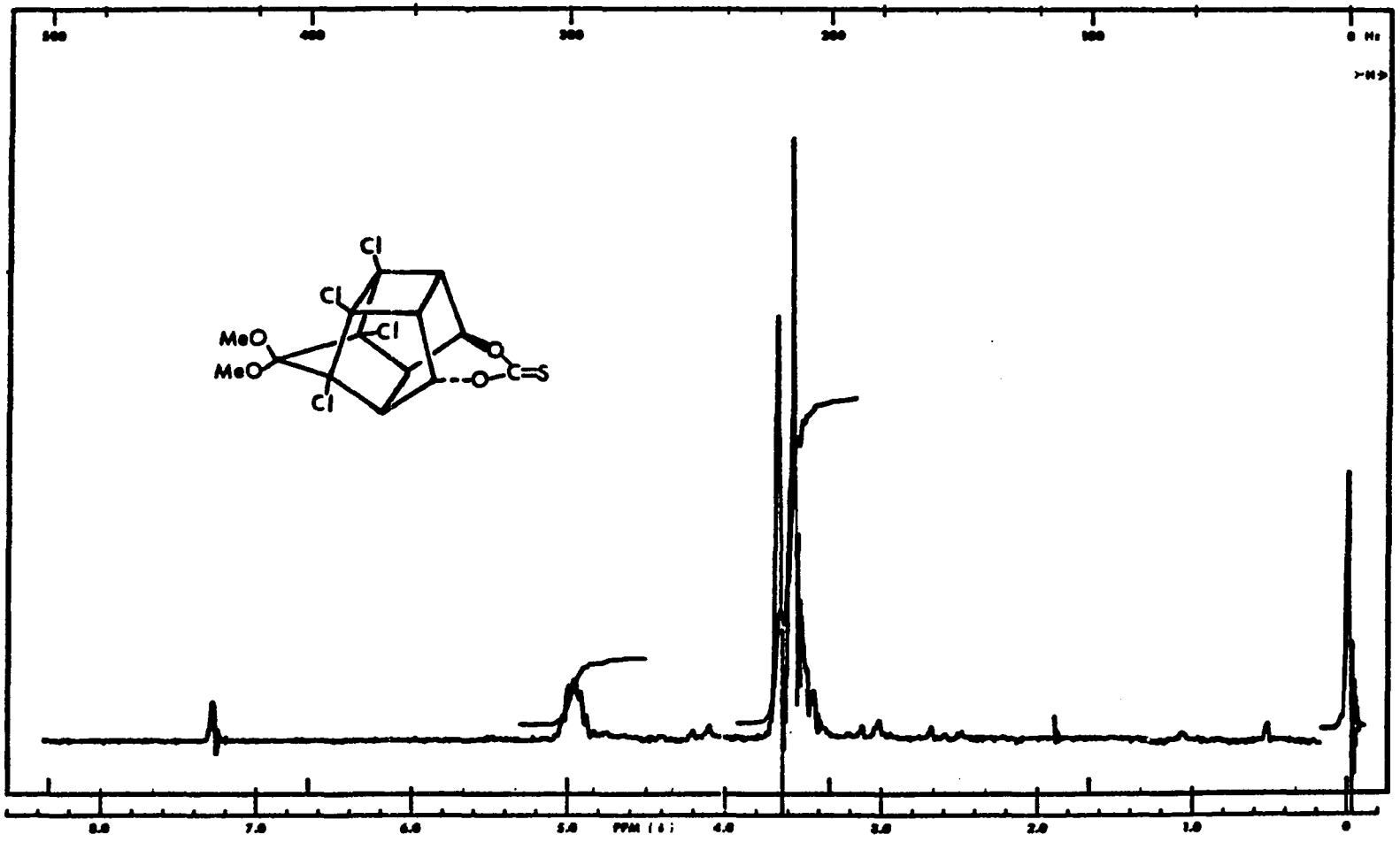


Figure 7b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 64.

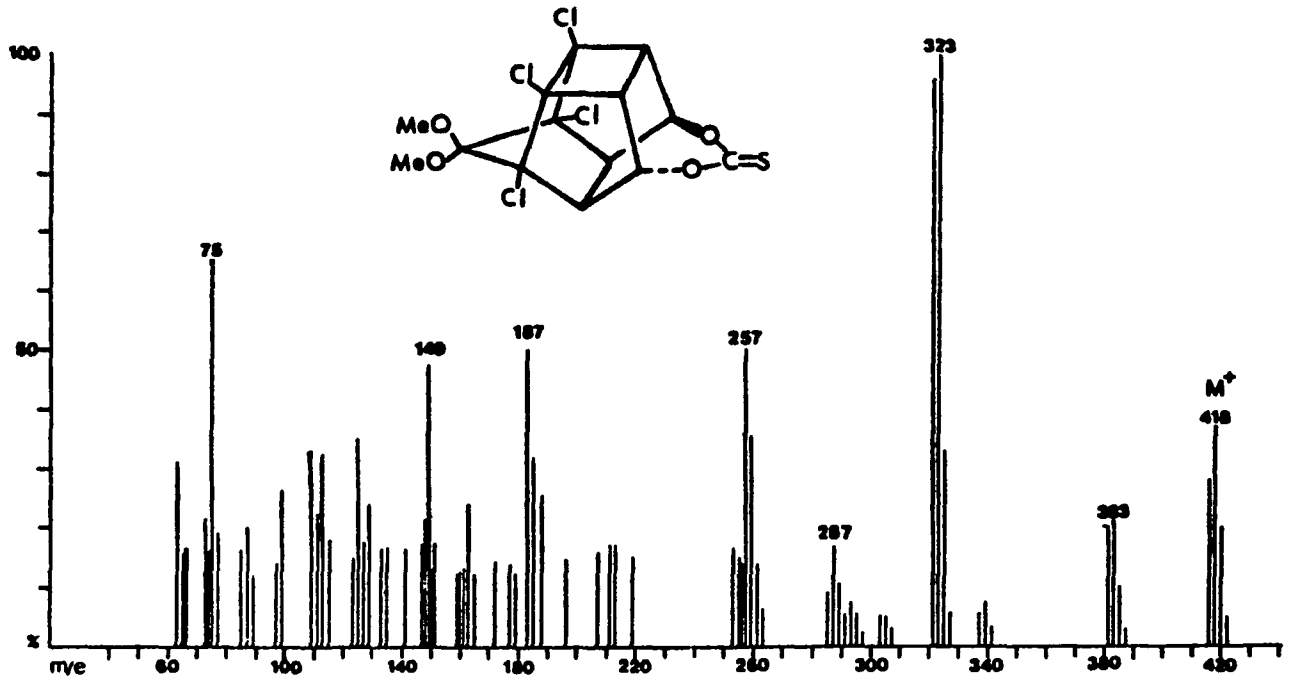
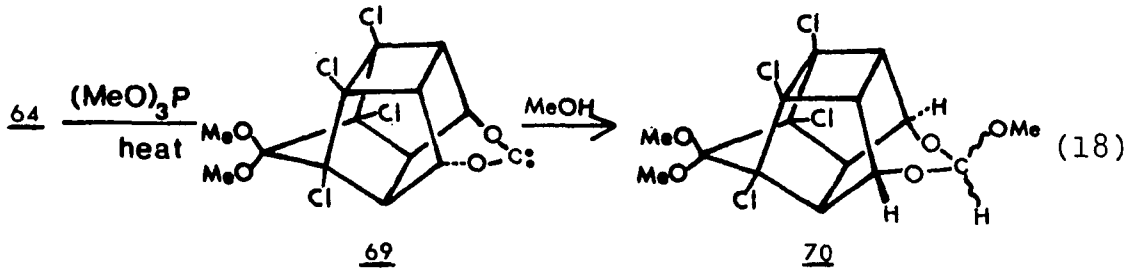


Figure 7c. Mass spectrum of 64.

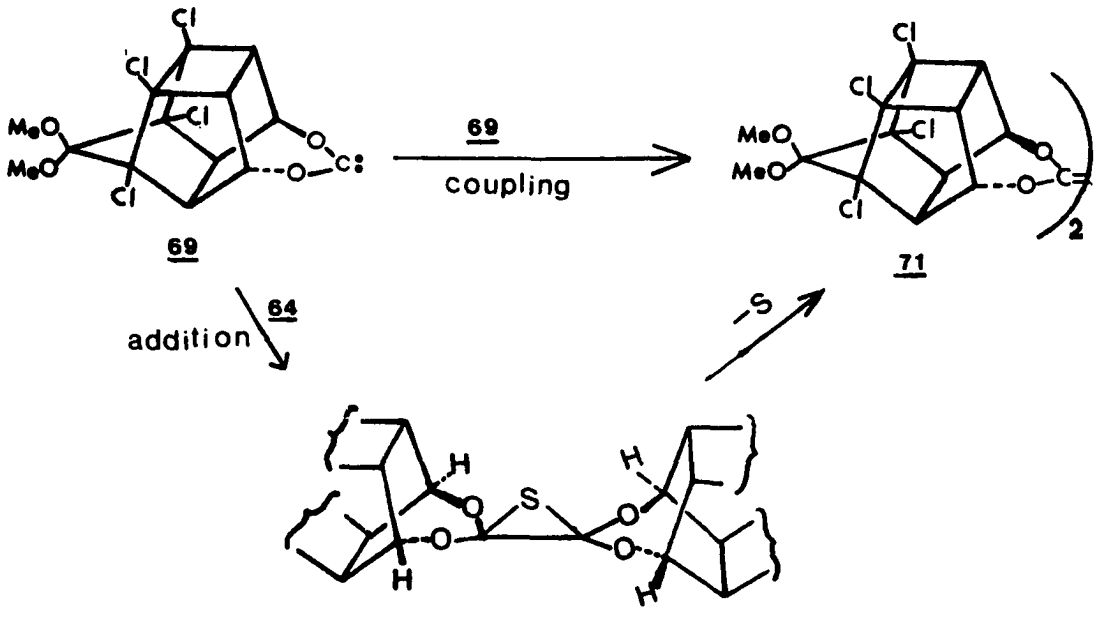
spectrum showed a strong complex absorption pattern at 950-1300 cm^{-1}. On the basis of the above spectral data and their similarities with those of ethoxydioxolane derivative 73 (to be referred to later) of diol 63, this material was thus tentatively assigned to be the corresponding methoxy-dioxolane derivative (70) of diol 63, (equation 18). The



69 70 (18)

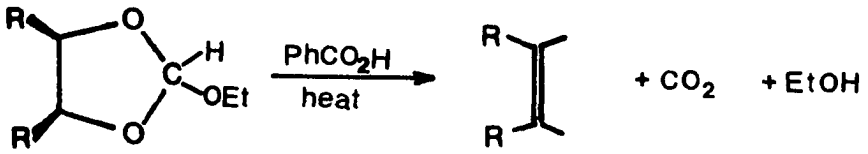
formation of compound 70 could be explained in terms of carbene-insertion into methanol by the carbene intermediate 69 generated from the action of trimethylphosphite on thiocarbonate 64. The presence of methanol in the reaction mixture must be due to impure trimethylphosphite or, more likely, to contamination by water which decomposes trimethyl-phosphite to produce methanol. This latter speculation was later confirmed. When thiocarbonate 64 was heated at 140° with trimethylphosphite which had been freshly distilled, compound 70 was not obtained. Instead, the reaction pro-duced a colorless powder (mp > 300°) which was not soluble in diethyl ether, chloroform, acetone, dimethylsulfoxide, or pyridine. This material could not be sublimed, thus making purification and identification difficult. Its

infrared spectrum (KBr) displayed strong absorption band at 1100-1300 cm^{-1} and was different from that of either 70 and 73, both of which showed additional strong bands at 950-1100 cm^{-1}. The mass spectrum of this material showed the heaviest ion at m/e 768/770/772/774/776, possessing the intensity profile characteristic of the Cl_8 multiplet.[53] Based on these observations, we suggest that this material could be a dimer 71 which might arise via the coupling of carbene intermediate 69 or via carbene-addition to C=S bond of 64 with subsequent extrusion of sulfur:



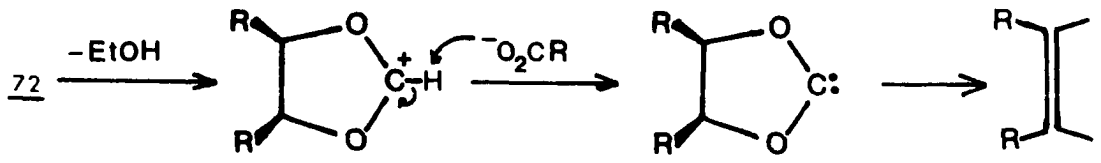
2-Ethoxy-1,3-dioxolanes (72) (derived from the corresponding 1,2-diols) have also been shown to undergo a stereospecific cis elimination to form the corresponding

olefins when 72 is heated in the presence of a carboxylic acid.[63,64] The mechanism by which the olefins are produced



72

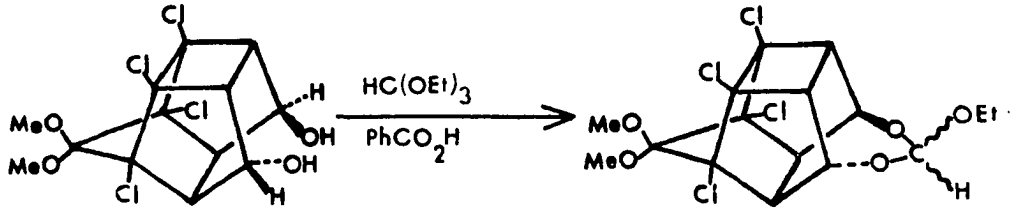
stereospecifically has not yet been established. However, the results indicate that the elimination takes place through a planar five membered intermediate. The authors[64] explained this observation on the basis of a carbene intermediate by analogy to the observed stereospecific formation of olefins from 2-thio-1,3-dioxolanes (48b). The carbene intermediate is generated from a carbonium ion by carboxylate anion-assisted removal of the proton, as indicated below:



Again, there is no precedent for the formation of sigma bonds by this procedure.

To test this method as a possible entry to the synthesis of compound 15, 2-ethoxy-1,3-dioxolane derivative 73 was prepared by heating diol 63 with an excess of triethyl

orthoformate in the presence of a catalytic amount of benzoic acid (equation 19). The infrared spectrum of 73 (Figure 8a)



63 73 (19)

displayed the absence of hydroxyl absorption but a strong absorption in the range 960-1200 cm^{-1} due to the ortho-formyl group.[63] The product consisted of a mixture of the α- and β- stereoisomers as indicated in 73, since the pmr spectrum (Figure 8b) exhibited singlets at δ5.33 and δ5.45 which together integrated for a single proton and were assigned to the proton geminal to the ethoxy group. Its mass spectrum (Figure 8c) showed the base peak at m/e 387 (4 Cl) corresponding to the ion arising *via* expulsion of an ethoxy group from the parent ion.

When a solution of 73 in dry dimethylformamide was refluxed for 22 hr in the presence of benzoic acid, compound 73 was recovered unchanged quantitatively. The failure to effect cycloreversion process on 64 and 73 as a synthetic route to convert compound 12 to 15 (Scheme I) indicated that a new approach to compound 15 had to be searched and developed.

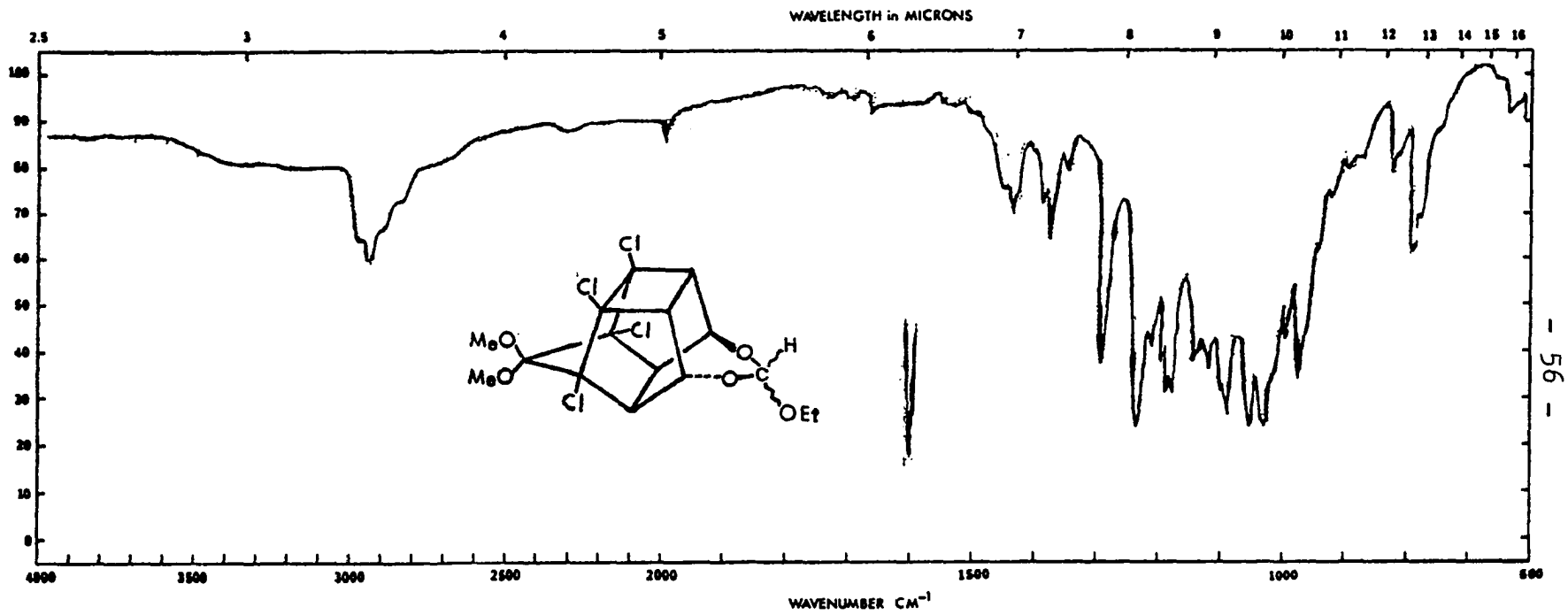


Figure 8a. Infrared spectrum (KBr) of 73.

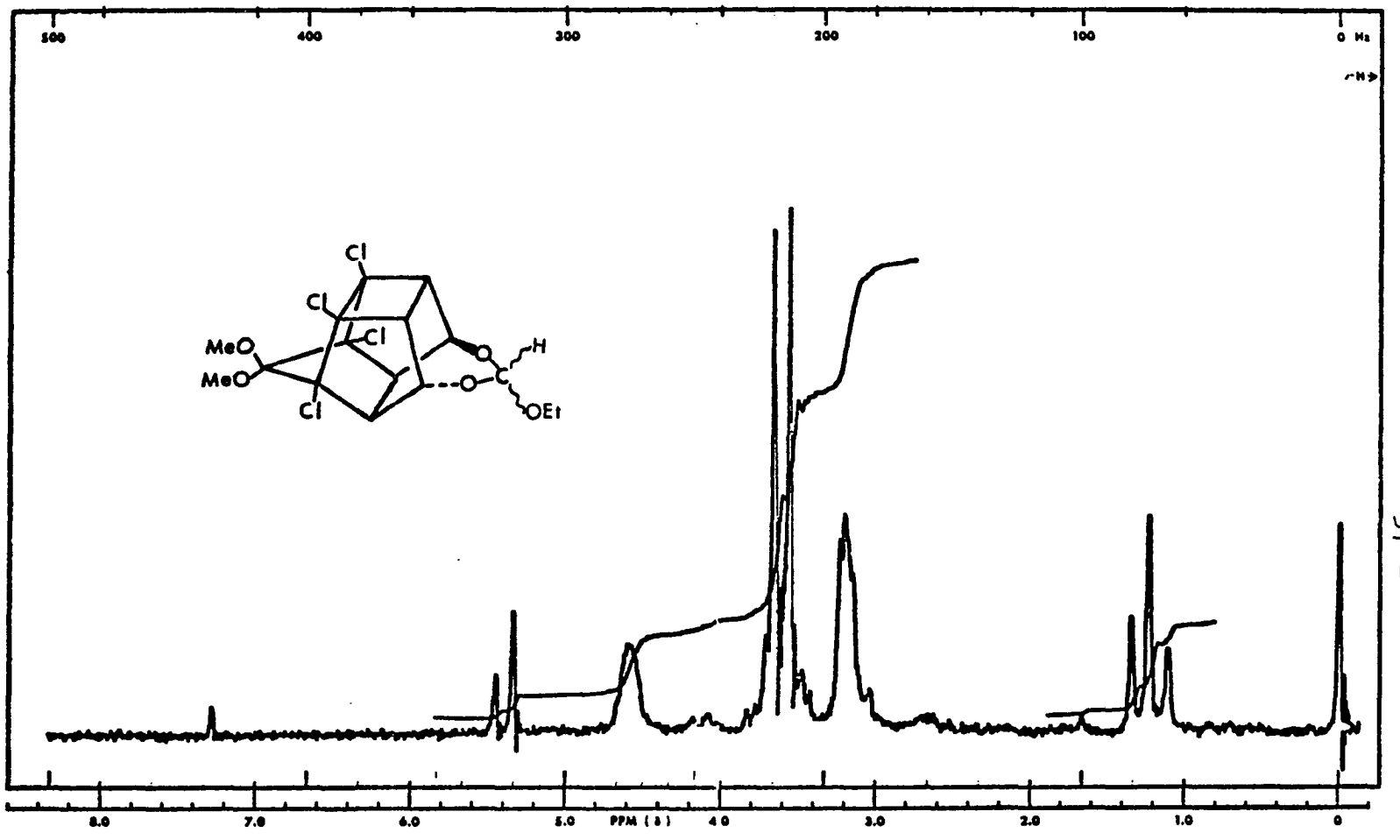


Figure 8b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 73.

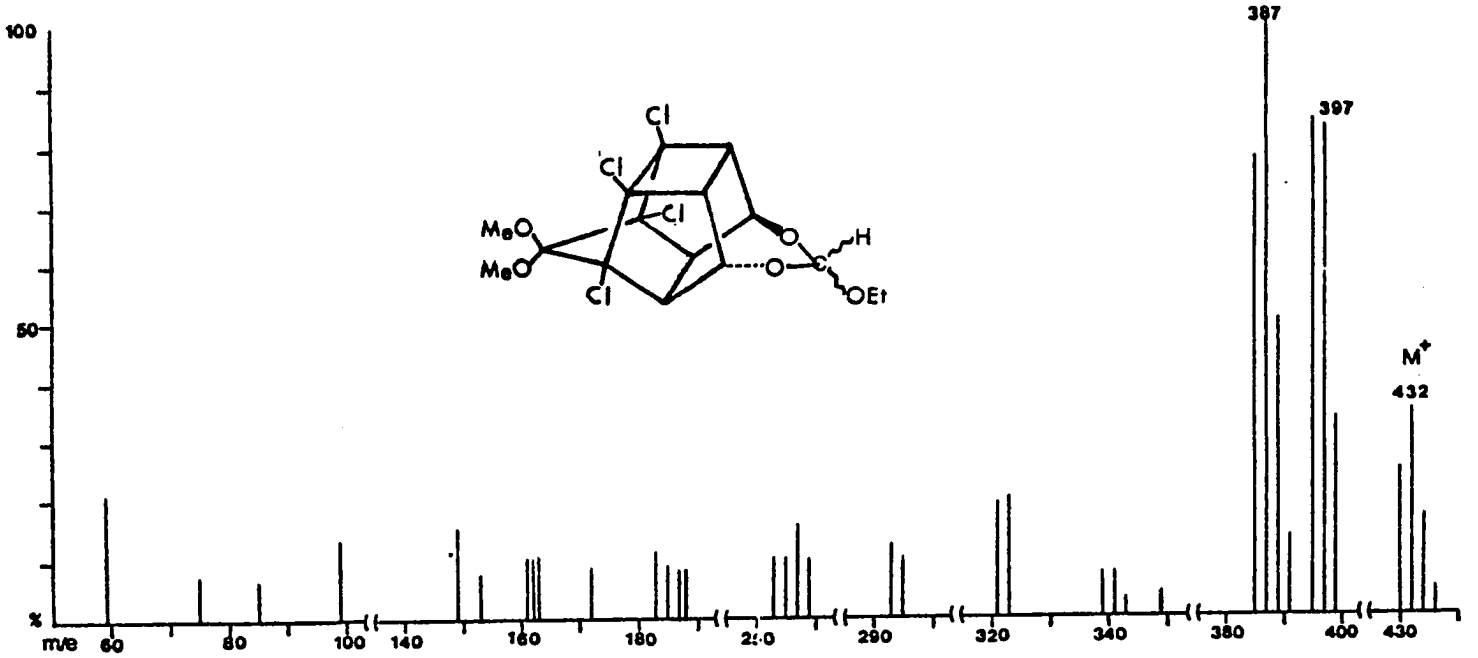
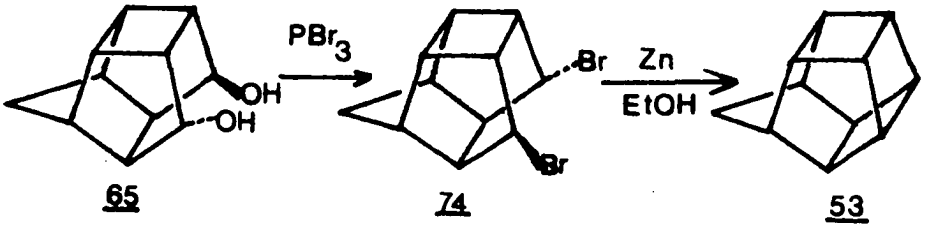


Figure 8c. Mass spectrum of 73.

Underwood and Ramamoorthy have recently reported the successful synthesis of homopentaprismane (53) by the reaction sequence shown in equation 20.[45] Diol 65, formed via



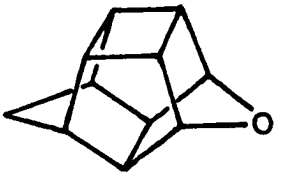
65 74 53 (20)

lithium aluminum hydride reduction of the corresponding diketone (20) was converted to dibromide 74 with phosphorous tribromide. Dibromide 74 was subsequently dehalogenated with zinc in ethanol to yield a hydrocarbon, mp 98-100°, which they reported to be homopentaprismane.

Homopentaprismane (53) is of considerable interest to the present study. The primary interest in this compound is that derivatives of this system (i.e., 15 and 16) appear in Scheme I as intermediates along the synthetic route to pentaprismane. This suggests that the successful synthesis of homopentaprismane by equation 20 might be useful both from the standpoint of being a model system for the alternative syntheses of 15 and also as potential synthetic entry leading ultimately to the pentaprismane system.

Attempts at converting diol 63 to the corresponding dibromide with phosphorous tribromide afforded only an intractable tar. Repeated attempts to prepare dibromide 74

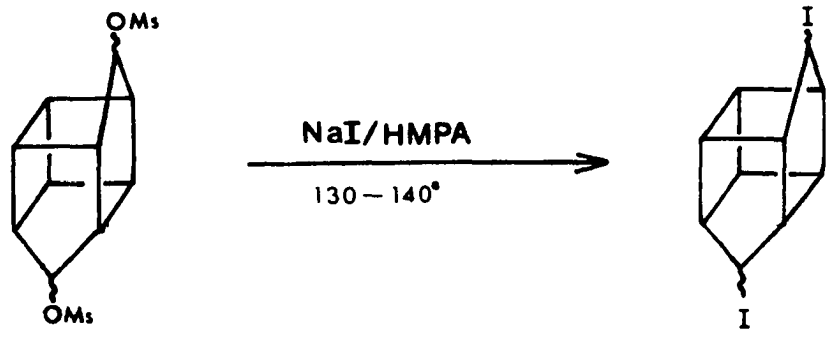
by treatment of diol 65 with phosphorous tribromide also failed. In most cases, the reactions yielded a dehydrated product 75,[58] together with some olefinic compounds as



75

indicated by the pmr spectrum. On one occasion, the reaction gave a solid product, mp 70-80°, which contained a dibromo compound as shown by the mass spectrum of this product, but its physical state was different from 74 (which was reported[45] to be a colorless liquid, bp 130-131°). The pmr spectrum of this product displayed a broad singlet due to the methylene hydrogens which would be magnetically nonequivalent and should display an AB pattern were this product to have structure 74.

The preparation of a dihalide from diol 65 was then attempted *via* the reaction of the ditosylate (76), derived from diol 65, with sodium iodide in hexamethylphosphoramide (HMPA) solvent. Paquette and coworkers[65] have extensively utilized this type of S_N2 reaction for the synthesis of halides (*e.g.*, equation 21) from the corresponding mesylate. Paquette suggested that, due to the unsolvated nature of the



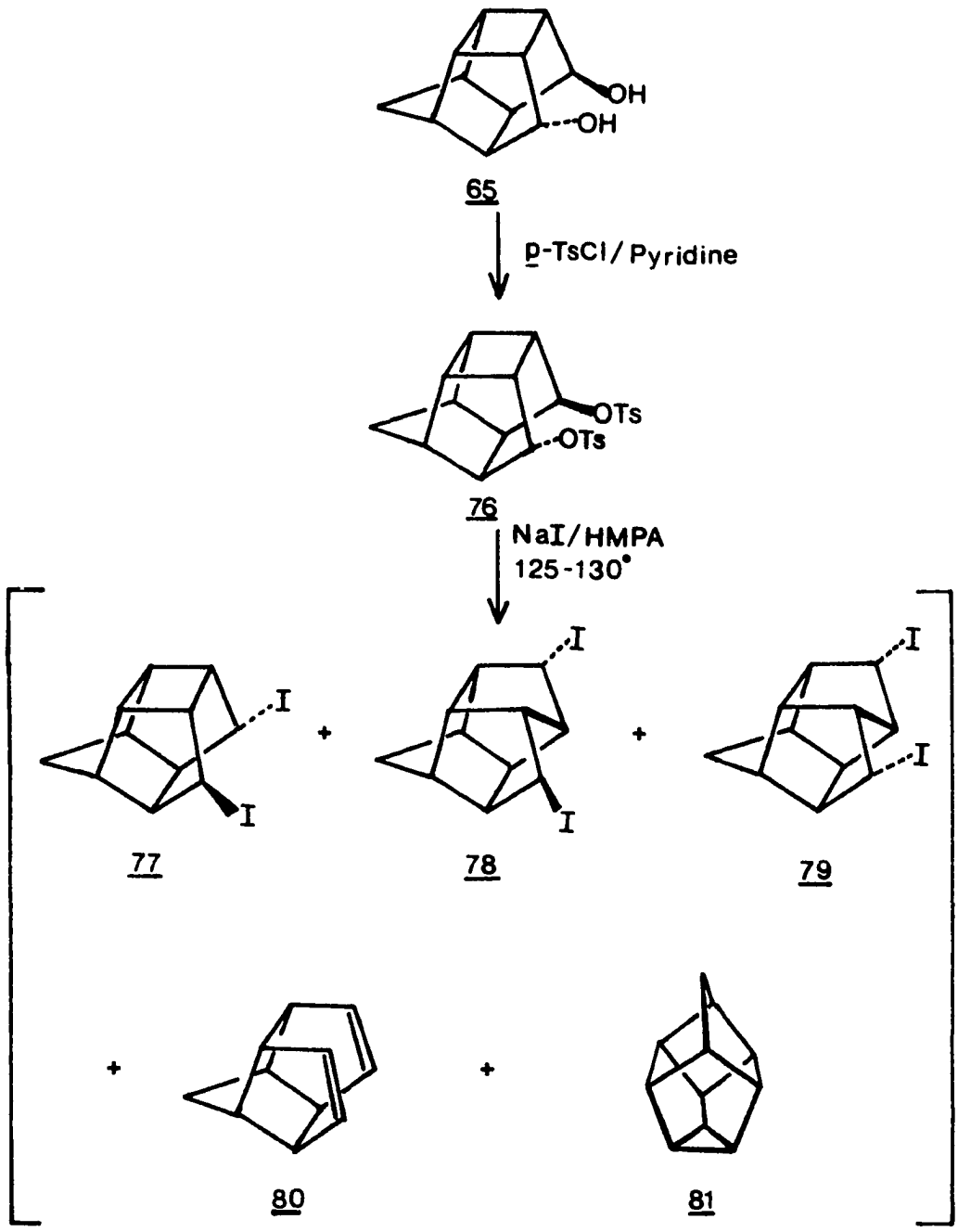
(21)

iodide ion in this medium (HMPA), its effective steric bulk is reduced and its nucleophilicity enhanced such that displacement of the mesylate groups operates at a reasonable rate and without obvious side reactions. In present study, however, the reaction of ditosylate 76 with sodium iodide in freshly distilled HMPA at 125-130° for 2 days under a nitrogen atmosphere afforded five products, as indicated in Scheme V.

Ditosylate 76 was prepared in nearly quantitative yield by treating endo,endo diol 65 with p-toluenesulfonyl chloride in dry pyridine. The pmr spectra of both diol 65 and ditosylate 76 (Figure 9b) exhibited the characteristic broad singlet at δ3.78 and δ4.47 due to the protons geminal to the hydroxyl and tosyl groups, respectively. In addition, both spectra had similar two-proton AB absorption pattern centered at δ1.33 and δ1.30 for the methylene protons in 65 and 76, respectively.

The isomeric diiodides (77, 78 and 79, $C_{11}H_{12}I_2$) were isolated in a total yield of 43.4%. Pmr analysis of

SCHEME V


OH
OH
65
p-TsCl / Pyridine
OTs
OTs
76
NaI/HMPA
125-130°
I
I
77
I
I
78
I
I
79
80
81

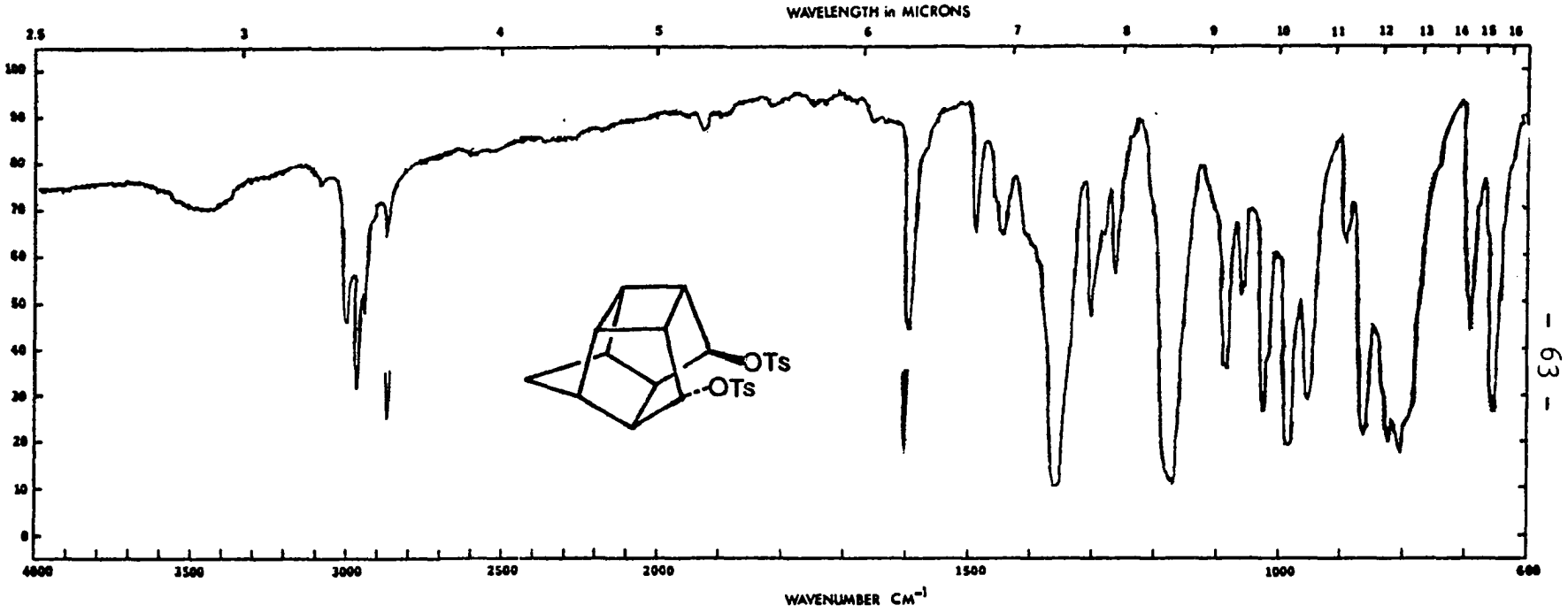


Figure 9a. Infrared spectrum (KBr) of 76.

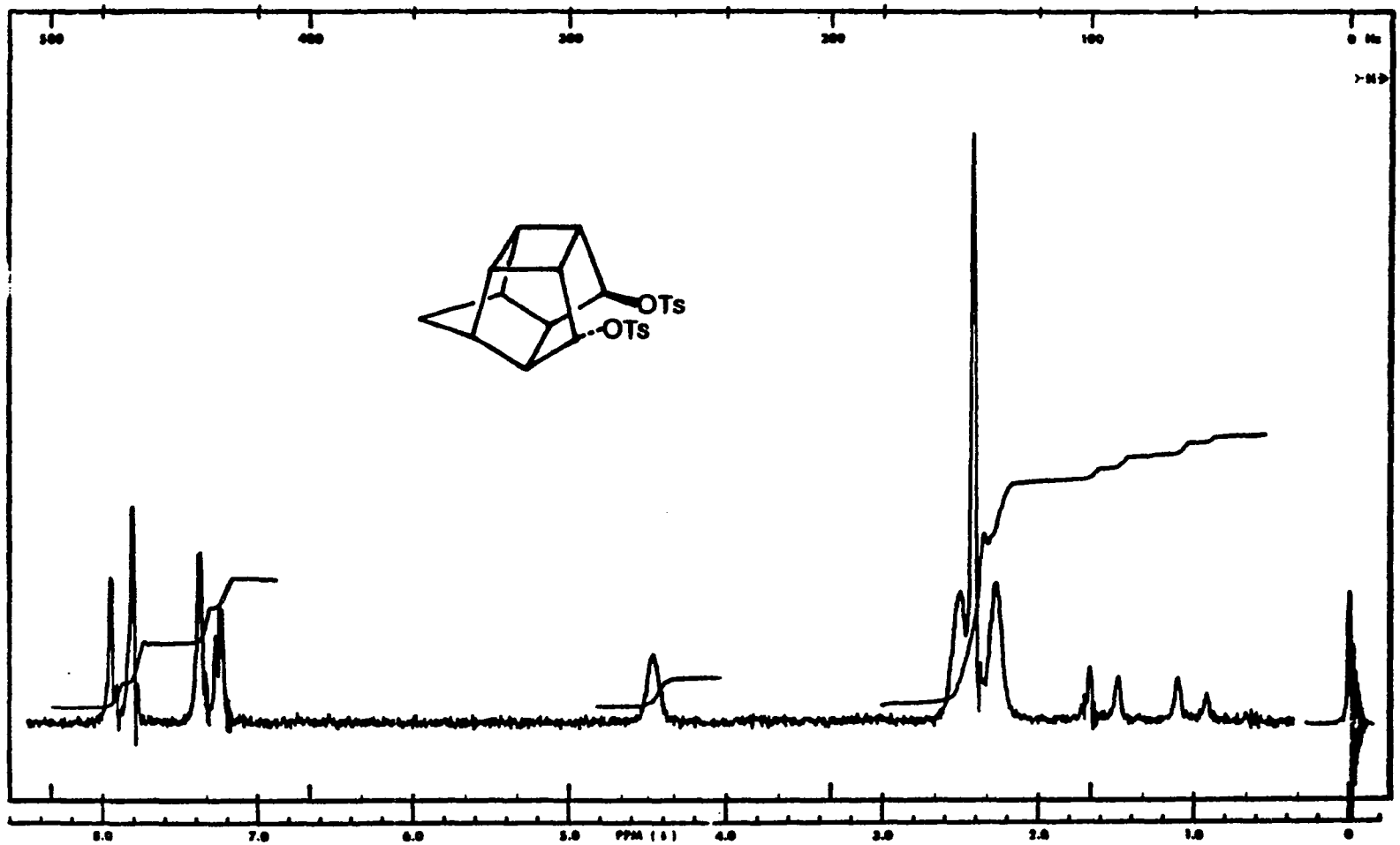


Figure 9b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 76.

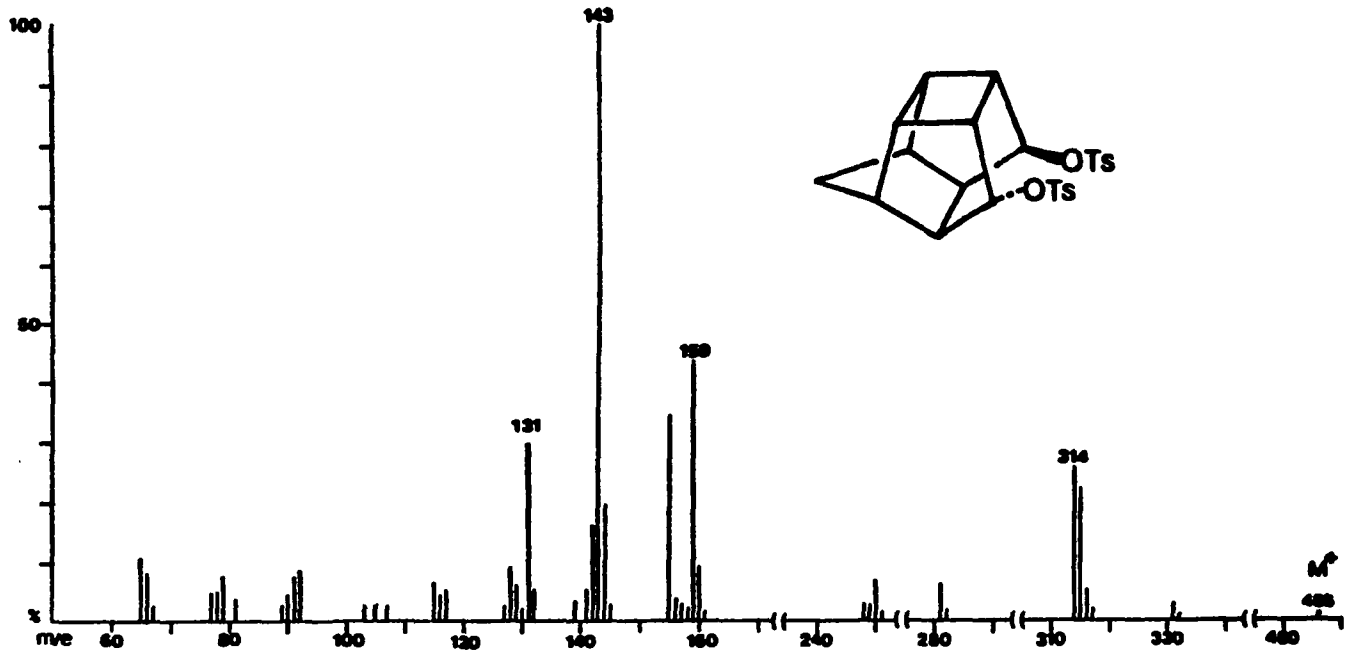


Figure 9c. Mass spectrum of 76.

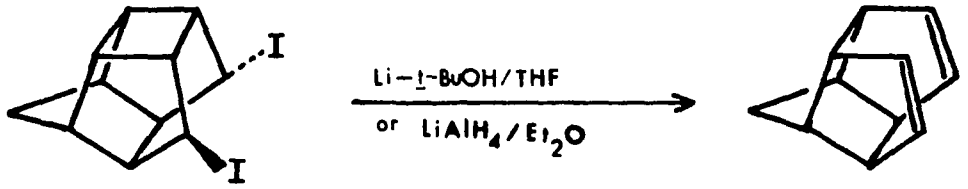
the product mixture which contained these diiodides was performed *via* integration of the broad singlets at δ4.47 and δ4.0 corresponding to the protons geminal to the iodine atoms in 77 and in the mixture of 78 and 79, respectively. This analysis revealed the presence of the isomeric diiodides in the ratio 77 : (78+79) = *ca.* 1 : 1.5. The isomeric hydrocarbons (80 and 81, $C_{11}H_{12}$) were isolated in a total yield of 11.6%. Vpc analysis of the product mixture containing 80 and 81 revealed their presence in the ratio 80 : 81 = 1 : 2.5.

The ratio of isomeric diiodides from this reaction depended upon the reaction temperature under which the reaction was performed. At reaction temperature of 160° (23 hr), the reaction yielded, in addition to hydrocarbons (80 and 81), the isomeric diiodides in a ratio 77 : (78+79) = *ca.* 1 : 35. However, diiodide 77 became the major product when the reaction temperature was kept at 100-105° (42 hr). Under these conditions, the reaction was not complete, affording isomeric diiodides in a ratio 77 : (78+79) = *ca.* 15 : 8, along with unchanged ditosylate 76 and a small amount of hydrocarbons 80 and 81.

Separation of the two isomeric hydrocarbons could be easily achieved by preparative gas chromatography. However, it was possible to separate the isomeric diiodides only *via* difficult and painstaking column chromatography

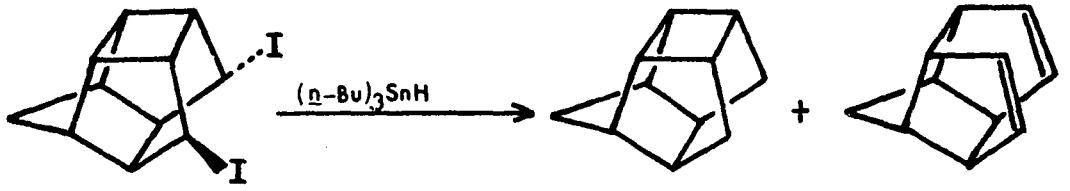
(silica gel, hexane eluant) and recrystallization (hexane). Separation via this procedure afforded, in order of increasing polarity, diiodides 77, 78, and 79 with melting points 132-133°, 151-152°, and 122-123°, respectively.

Positive identification of each of the isomeric diiodides (77, 78, and 79) was accomplished by both spectral informations and via chemical conversions. Attempts to dehalogenate diiodide 77 to the corresponding hydrocarbon, pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (82)[31,66], with either lithium and tert-butyl alcohol in tetrahydrofuran or lithium aluminum hydride in diethyl ether failed, as the reactions afforded diene 80 as the only detectable product (equation 22). Dehalogenation of diiodide 77 with freshly



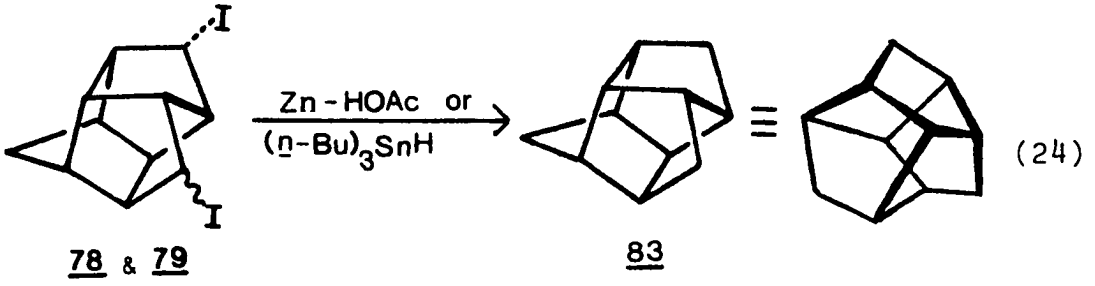
77 80 (22)

prepared tri-n-butyltin hydride, however, yielded the desired hydrocarbon (82) along with diene 80 in a ratio 82 : 80 = ca. 7 : 9, (equation 23). Dehalogenation of a



77 82 80 (23)

mixture of diiodides 78 and 79 with either zinc-acetic acid[67] or tri-n-butyltin hydride afforded the corresponding hydrocarbon, pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane ("trishomocubane", 83, equation 24), in 83.4% yield. Com-



78 & 79 83 (24)

parison of spectral and physical properties of the hydrocarbons from these dehalogenation reactions with the corresponding literature values for 82[66] and 83[67,68] permitted unambiguous assignments of the carbon skeleton of each of the diiodides (77 and 78-79, respectively). These assignments were substantiated by their proton nmr spectra.

The pmr spectrum of 77 (Figure 10b) displays an AB quartet at δ_A 1.37 and δ_B 1.78 (2H, J_{AB}=12 Hz, methylene protons), a broad singlet at δ2.57 (2H), a complex multiplet at δ2.70-3.10 (4H), a multiplet at δ3.43 (2H), and a singlet at δ4.47 (2H, $W_{1/2}$=ca. 2 Hz). The above AB-quartet absorption pattern reveals that the methylene bridge protons are distinctly nonequivalent, as anticipated for methylene protons in diiodide 77. The pmr spectrum of 78 (Figure 11b) contains two two-proton singlets at δ1.53 and δ4.0 due to the methylene protons and the protons geminal to the iodine

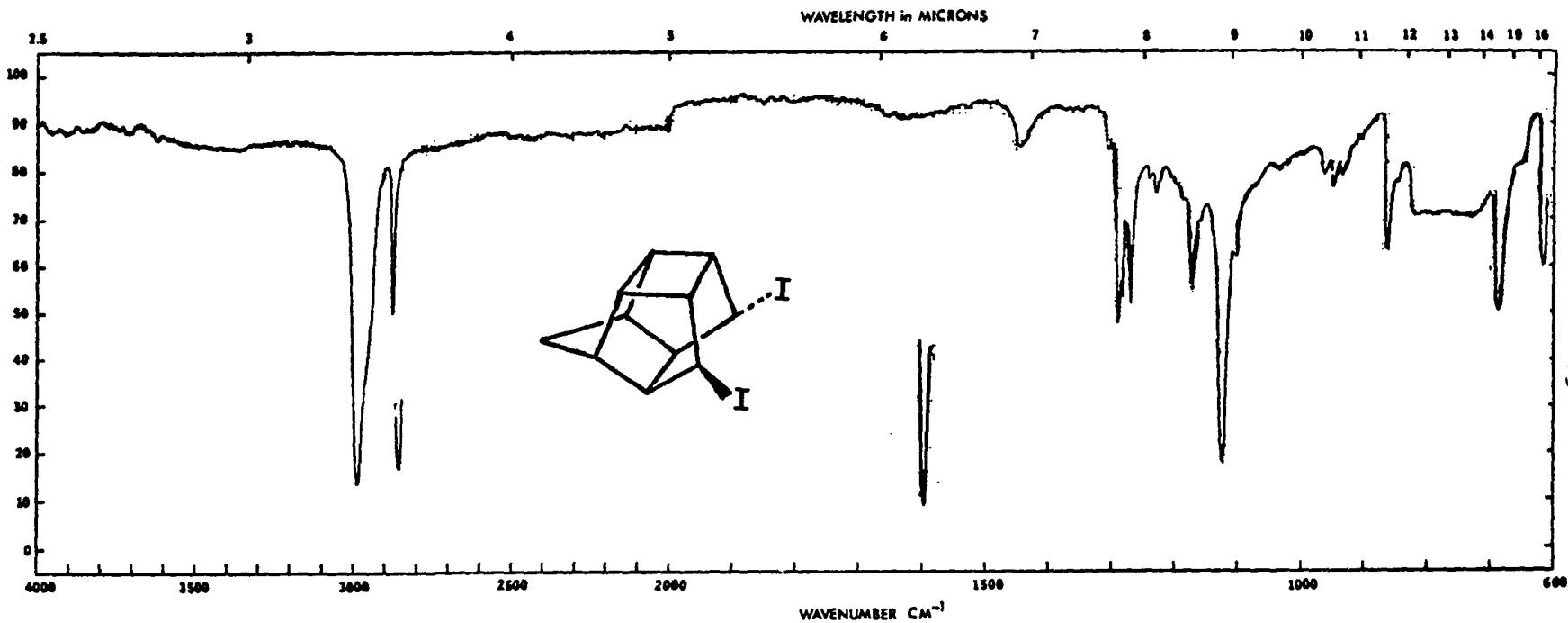


Figure 10a. Infrared spectrum (CCl_4) of 77.

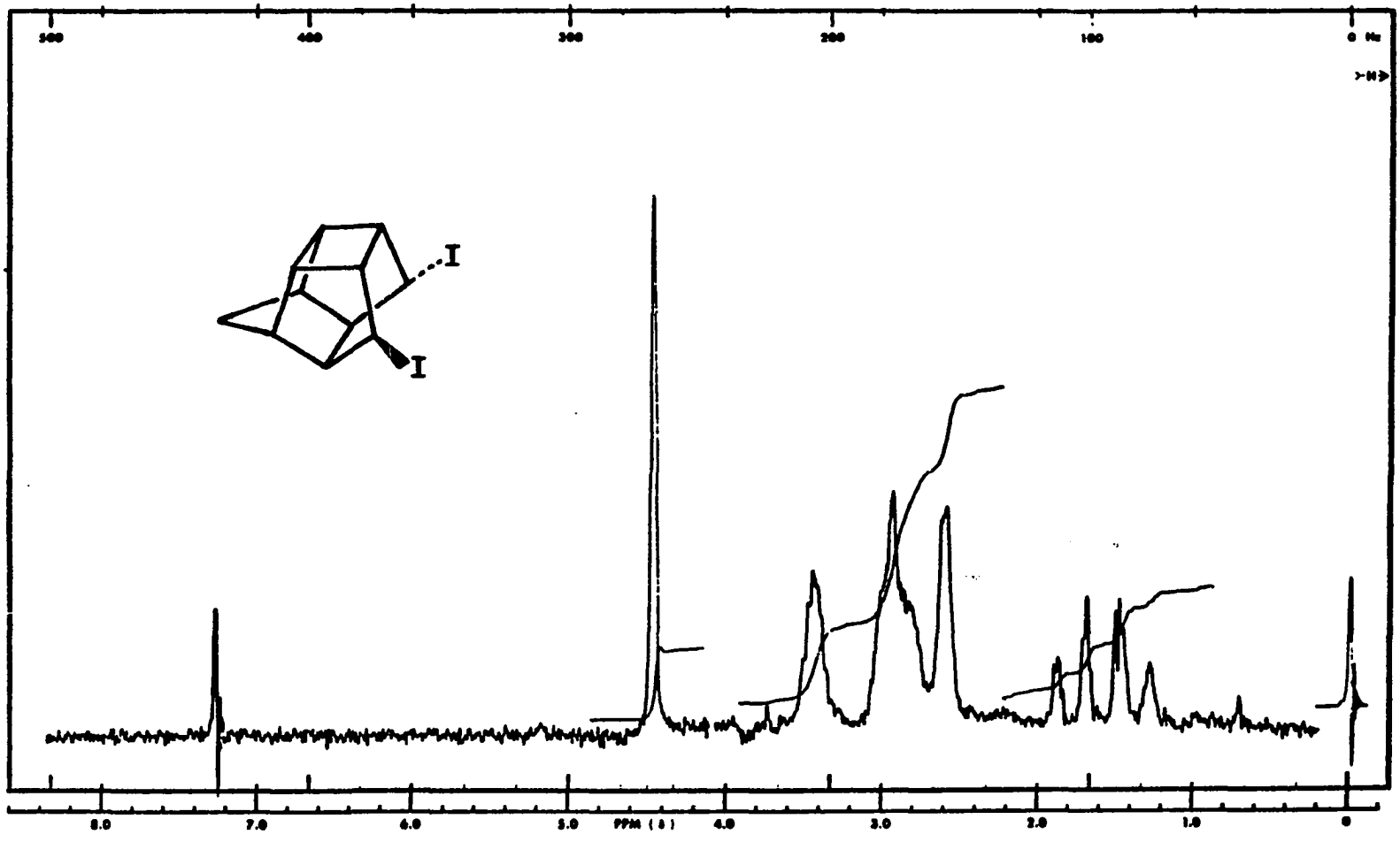


Figure 10b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 77.

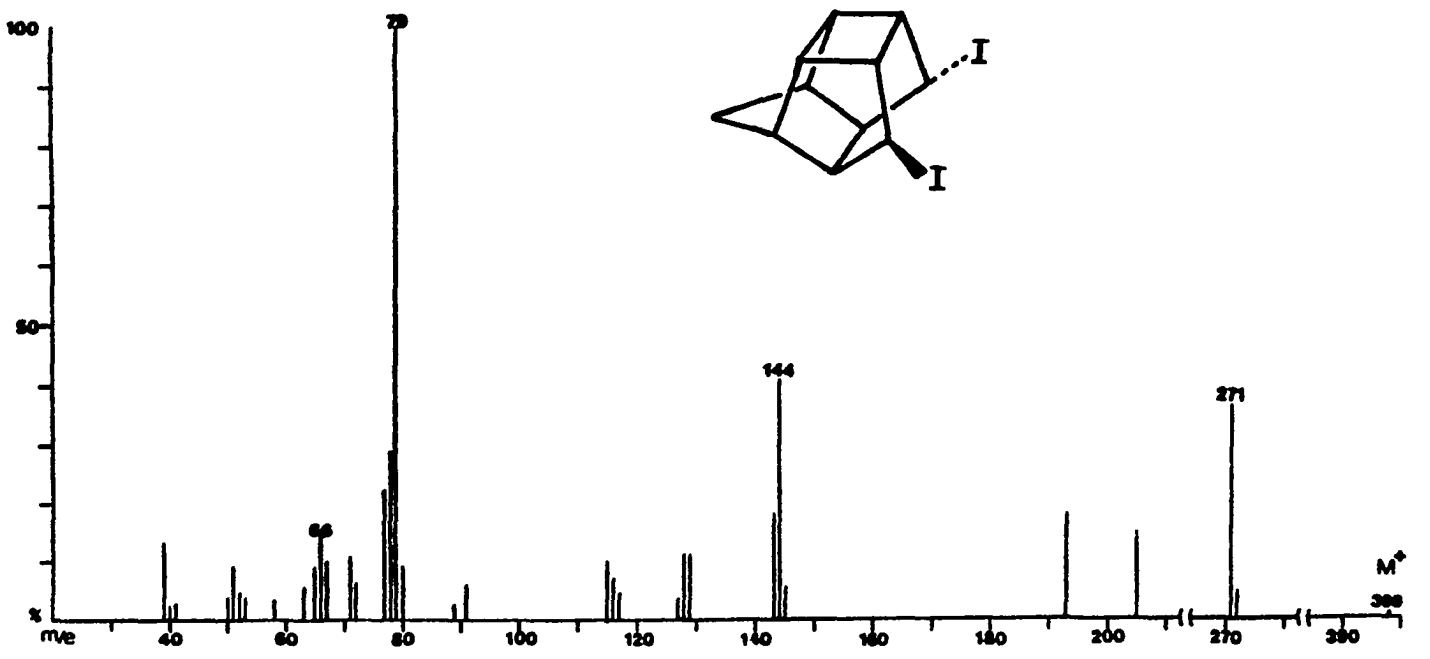


Figure 10c. Mass spectrum of 77.

atoms, respectively. The methine protons in 78 give three broad singlets (total eight protons) centered at δ2.23, 2.73, and 3.07 with intensity ratio of 2 : 1 : 1, respectively. The pmr spectrum of 79 (Figure 12b) displays a doublet at δ1.5 (2H, J=ca. 1 Hz), a singlet, $W_{1/2}$=ca. 5 Hz, at δ4.0 (2H), and complex multiplets at δ1.93-2.8 (6H) and δ2.8-3.3 (2H). The lack of a complex absorption pattern observed for the methine protons of 78 suggests that the carbon-iodine bonds in 78 are exo,exo and those in 79 are exo,endo, as shown.

The carbon-iodine bond stereochemistries in 77, 78, and 79 were further established via analysis of their ^{13}C nmr spectra. The proton noise-decoupled ^{13}C nmr spectrum of 77 (Figure 13a) consists of six peaks; the chemical shifts relative to benzene are 73.9, 78.3, 79.3, 86.4, 97.1, and 97.2 ppm (upfield). The off-resonance decoupled ^{13}C nmr spectrum of 77 (Figure 13b) displayed five doublets and one triplet. These spectra are consistent with 77 having carbon-iodine bonds either endo,endo or exo,exo. Sterically and mechanistically (i.e., S_N2 displacement of the endo-tosylate groups in 76 by iodide), the latter would appear to be the more likely of the two choices.

The proton noise-decoupled ^{13}C nmr spectrum of a mixture containing diiodides 78 and 79 displays seventeen peaks (Inset, Figure 14a). Among them, six lines at 68.9,

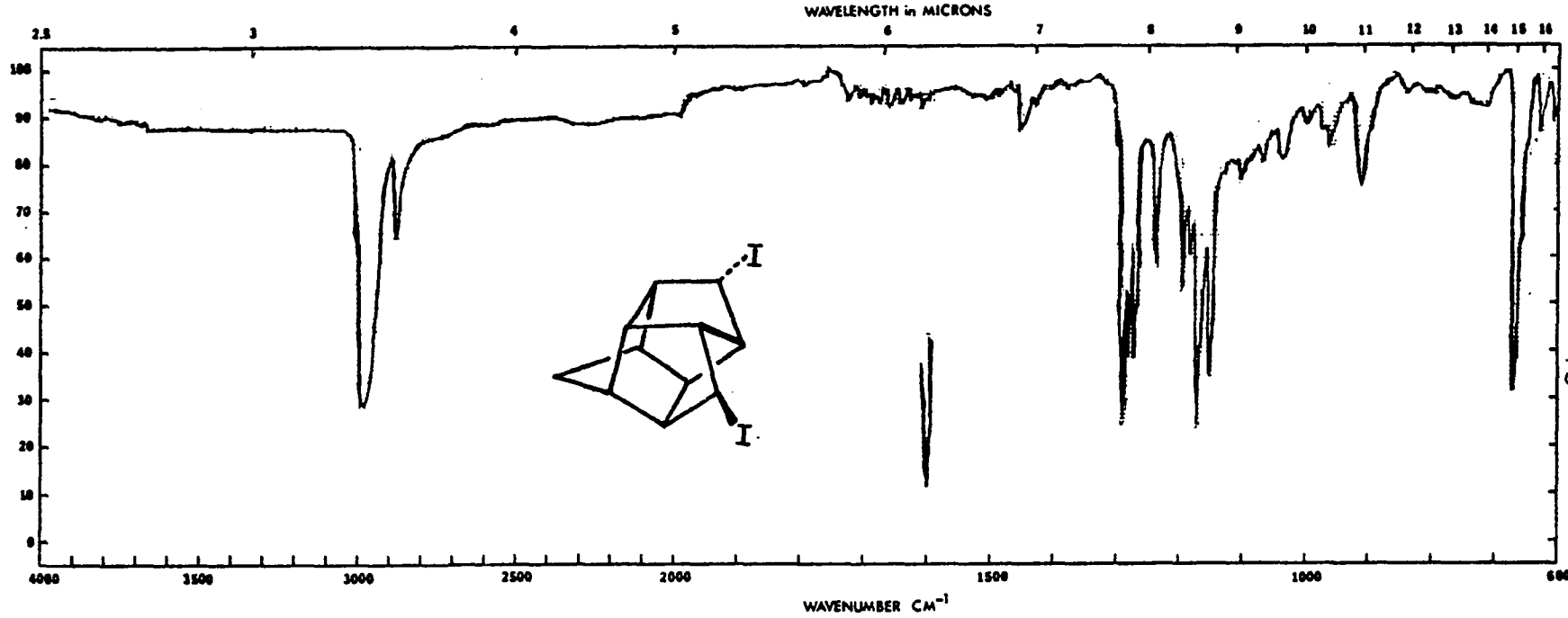


Figure 11a. Infrared spectrum (CCl_4) of 78.

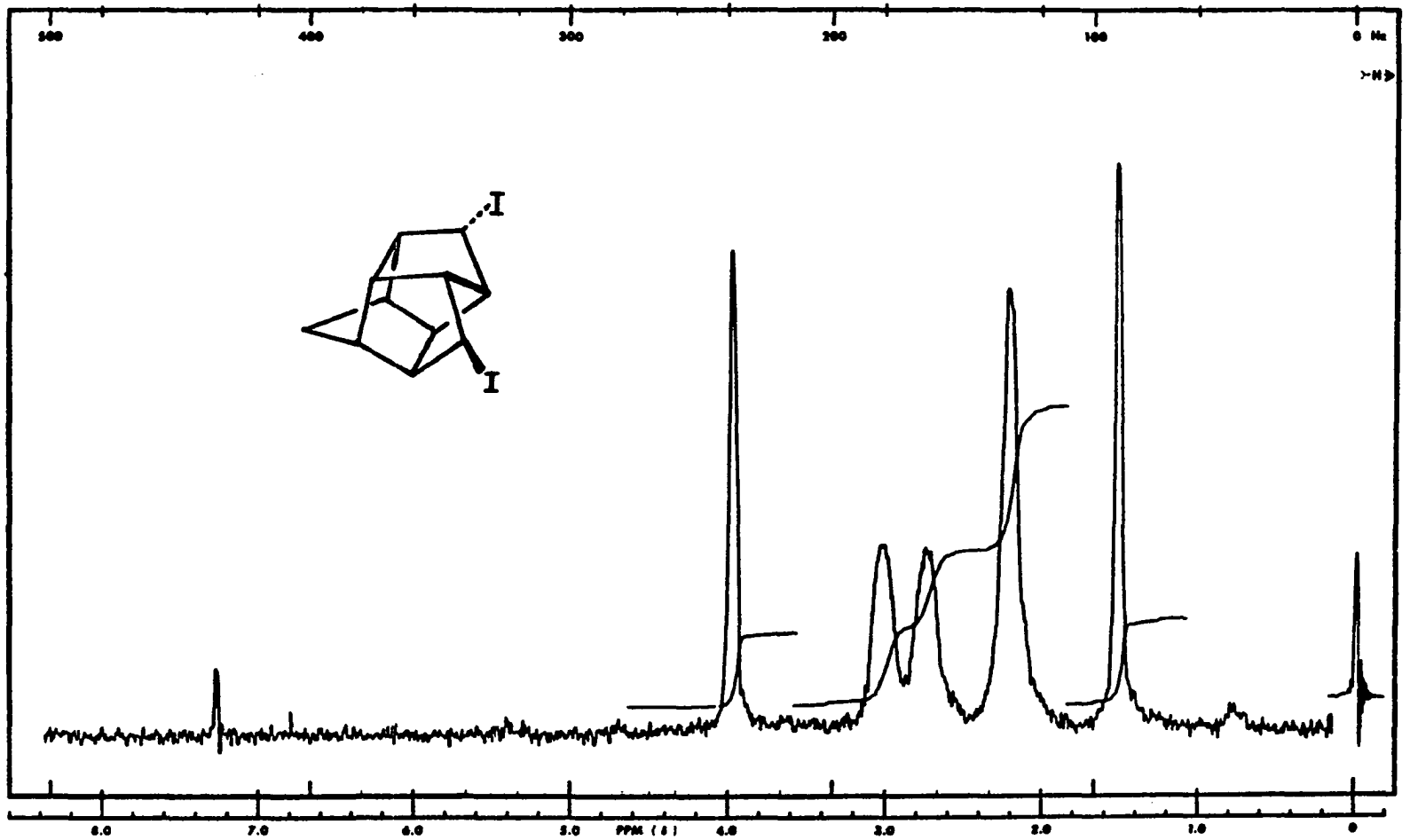


Figure 11b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 78.

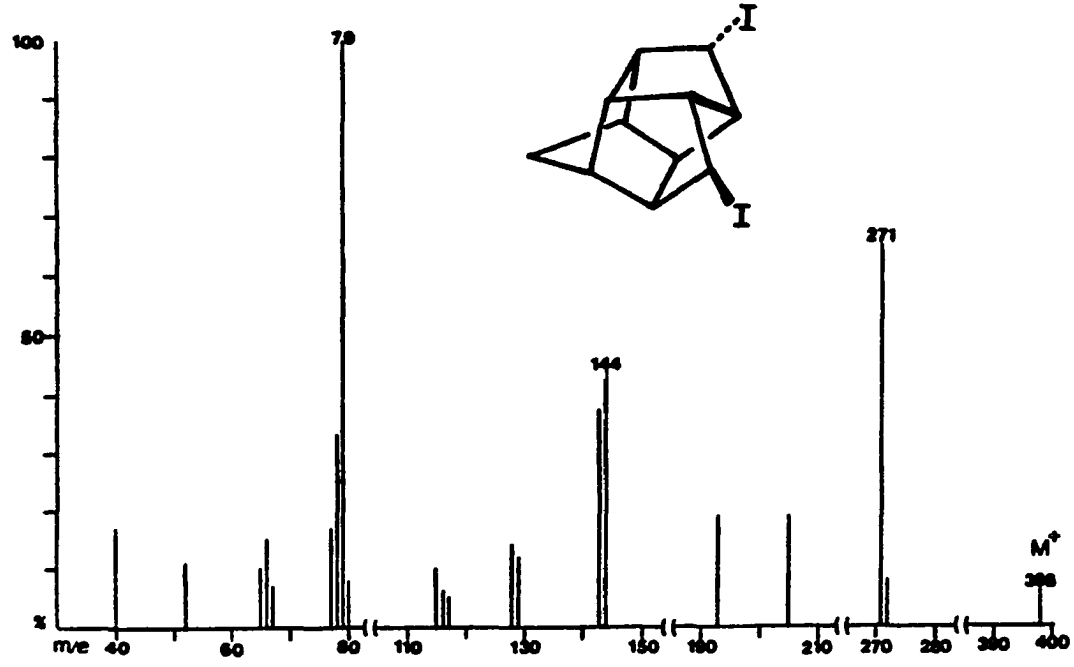


Figure 11c. Mass spectrum of 78.

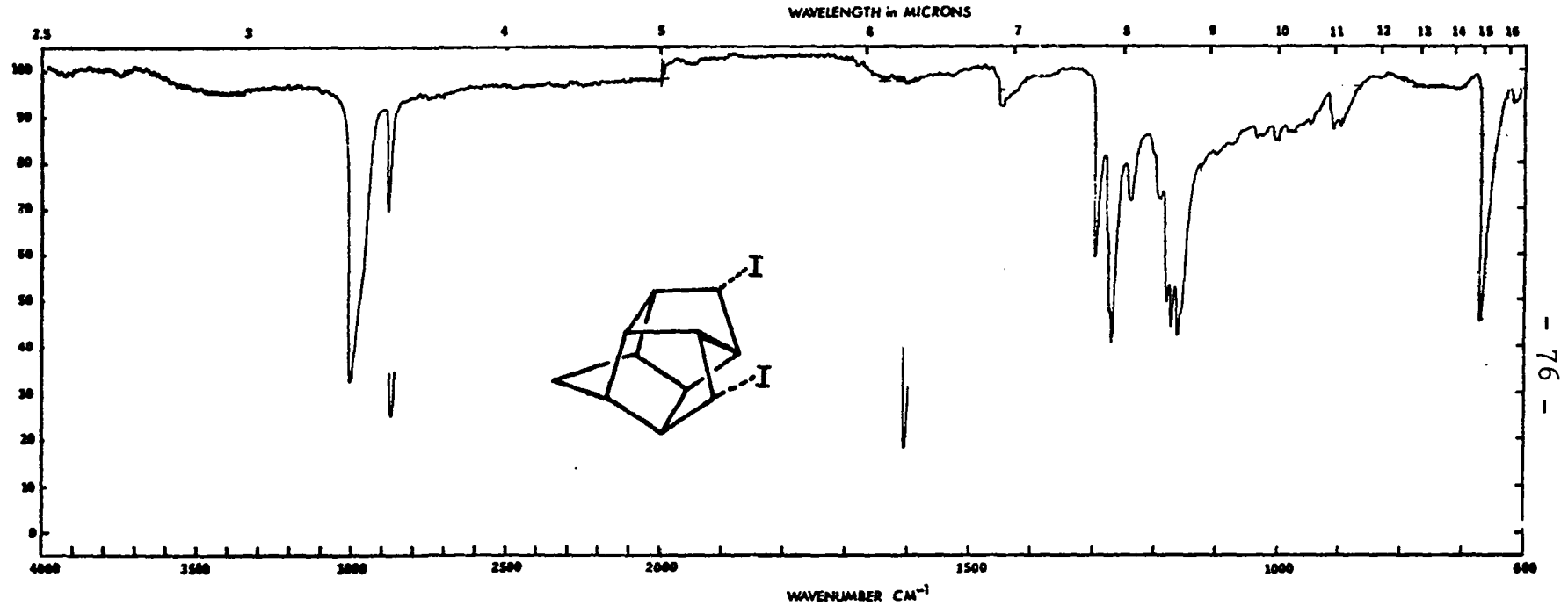


Figure 12a. Infrared spectrum (CCl_4) of 79.

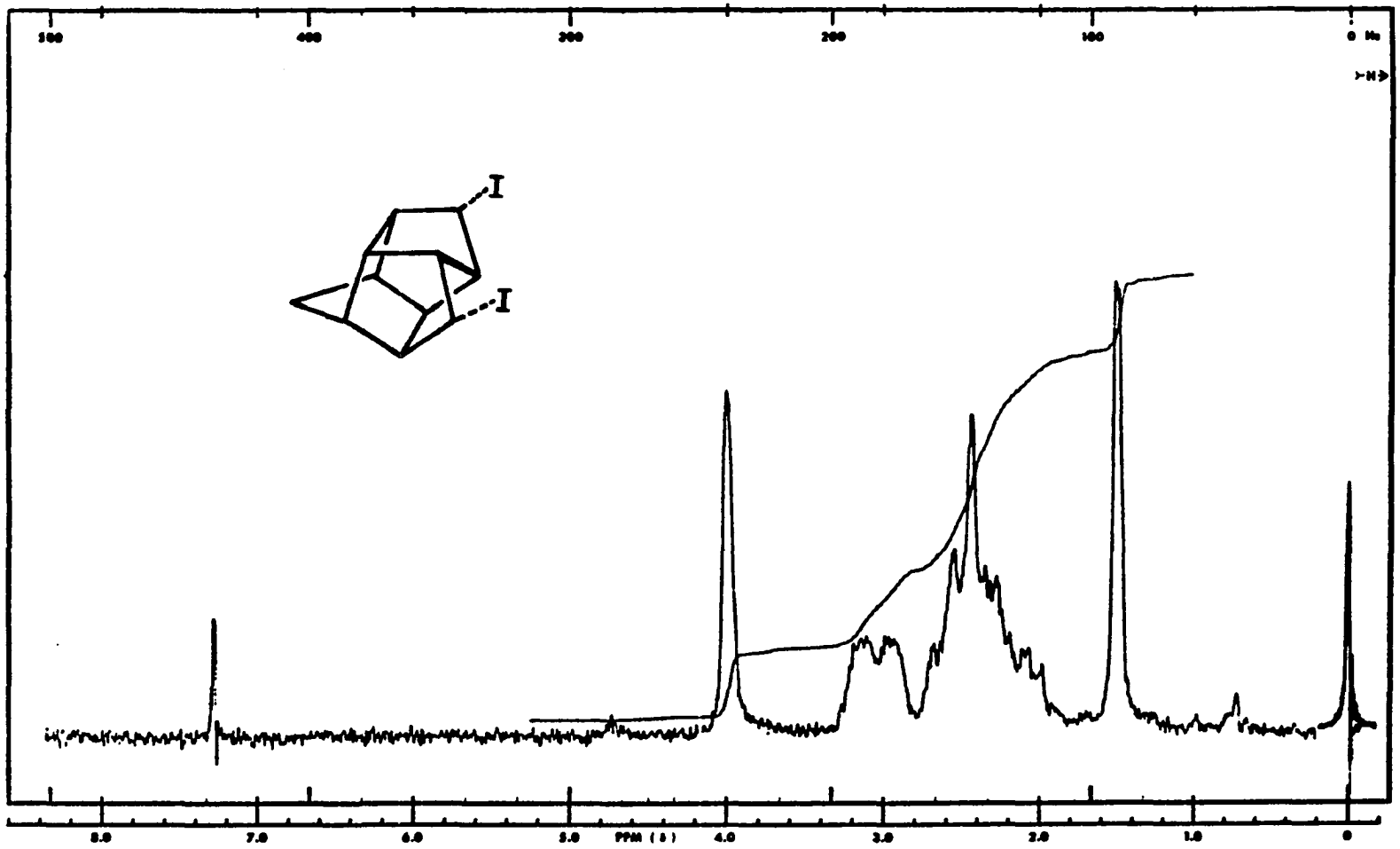


Figure 12b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 79.

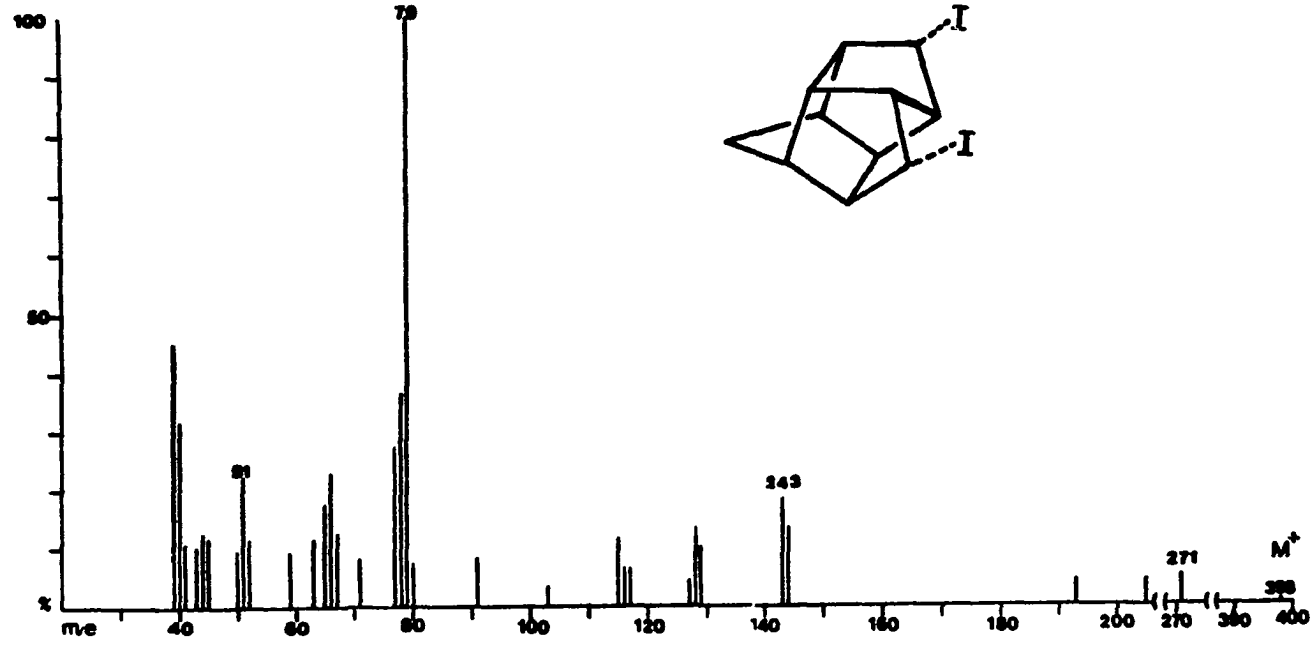


Figure 12c. Mass spectrum of 79.

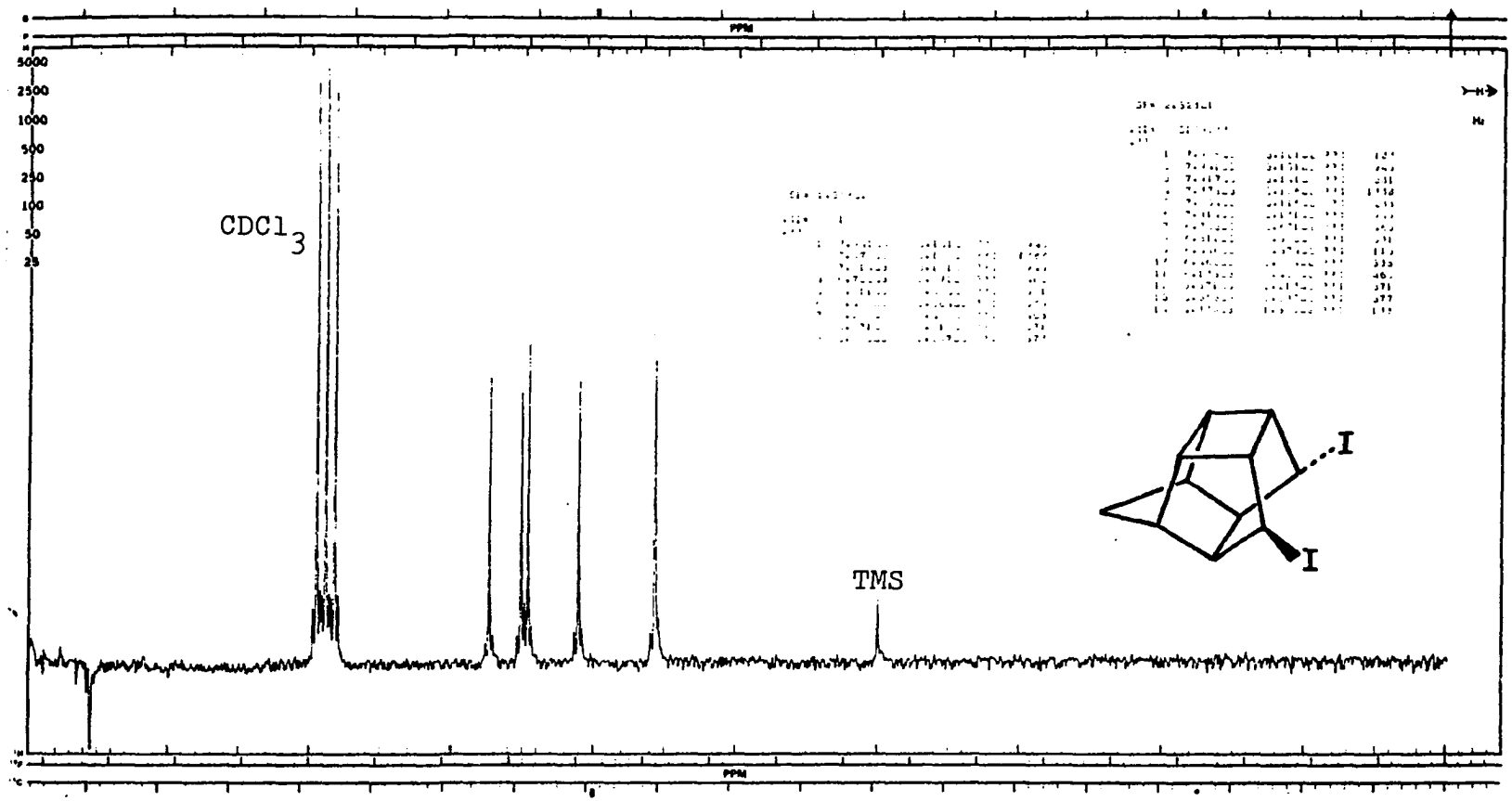


Figure 13a. Proton noise-decoupled ^{13}C nmr spectrum (25.2MHz, $CDCl_3$ solvent, TMS and benzene standards) of 77.

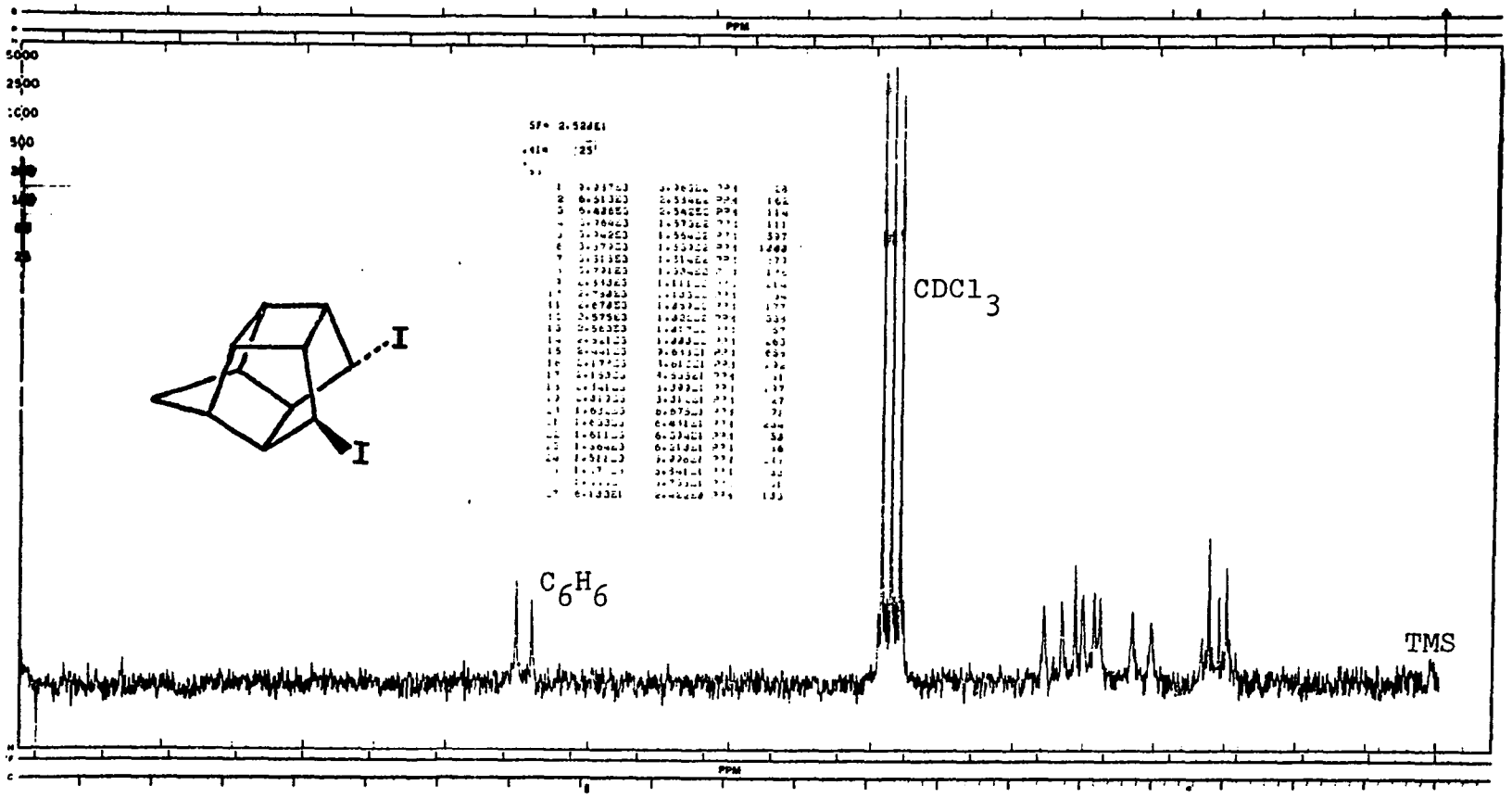


Figure 13b. Off-resonance decoupled ^{13}C nmr spectrum (25.2MHz, $CDCl_3$ solvent, TMS and benzene internal standards) of 77.

72.2, 81.9, 87.7, 94.3, and 99.2 ppm upfield from benzene (indicated by *) are due to diiodide 78 which has five different groups, each containing two equivalent carbon atoms and one additional carbon atom which is different from the foregoing five groups. This result is consistent with 78 having the carbon-iodine bonds either exo,exo or endo,endo. Sterically and mechanistically, the former would appears to be more likely of the two choices. The proton noise-decoupled ^{13}C nmr spectrum of 79 (Figure 14a) consists of eleven peaks; the chemical shifts relative to benzene are 69.1, 70.7, 71.7, 75.0, 79.0, 79.9, 87.2, 88.1, 95.9, 98.2, and 98.7 ppm (upfield). The off-resonance decoupled ^{13}C nmr spectrum of 79 (Figure 14b) displays twenty-three peaks resulting from ten doublets and one triplet. These observations require the endo,exo configuration of the carbon-iodine bonds in diiodide 79.

Assignment of the structure of diene 80 was obtained by comparison of its spectral (ir, pmr, mass) and physical properties with literature values.[69] The assigned structure of 80 is further supported via analysis of its ^{13}C nmr spectrum. The proton noise-decoupled ^{13}C nmr spectrum of 80 exhibits four peaks; the chemical shifts relative to benzene are 96.8, 79.5, 63.6 ppm

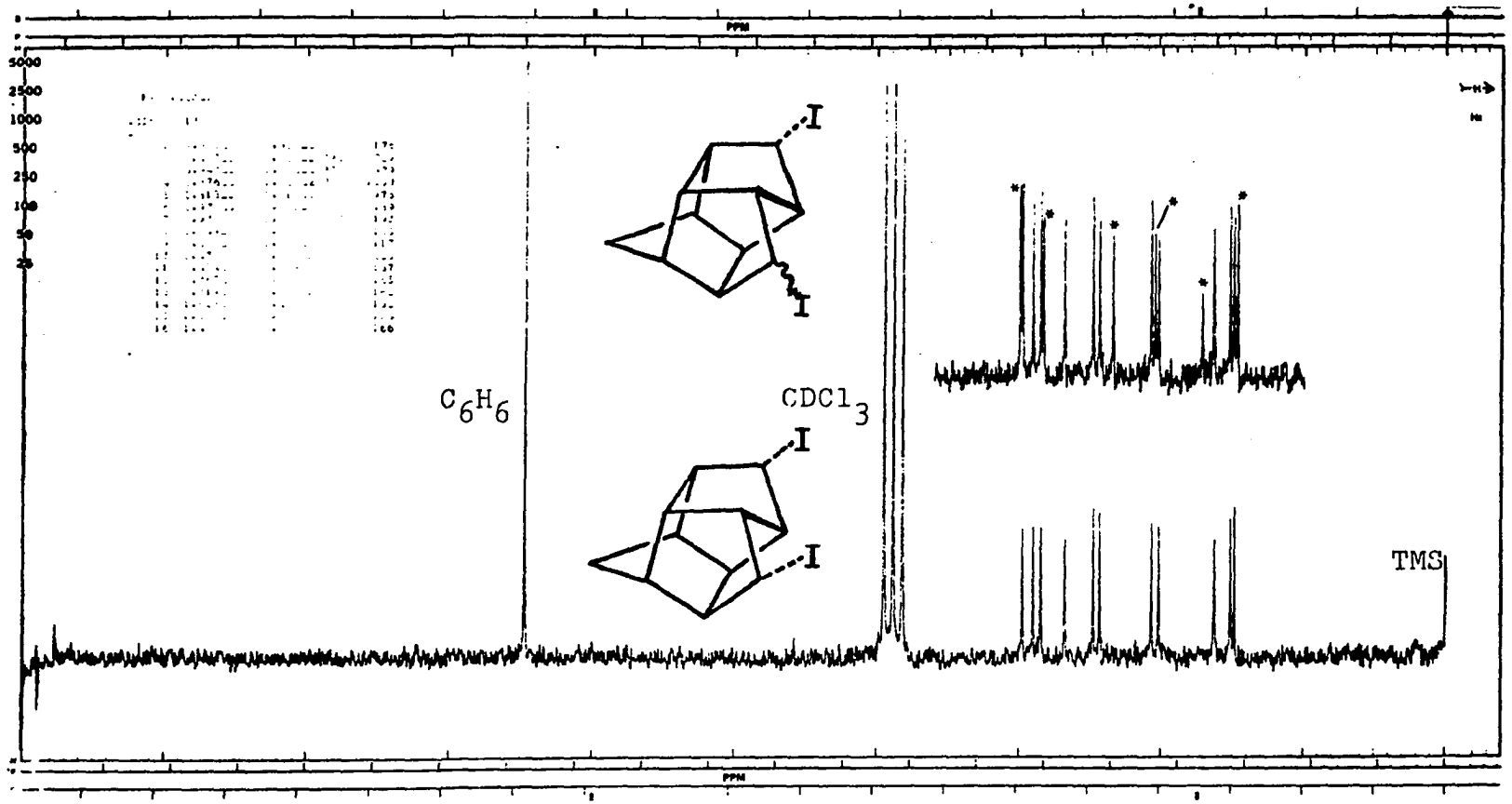


Figure 14a. Proton noise-decoupled ^{13}C nmr spectrum (25.2MHz, $CDCl_3$ solvent, TMS and benzene internal standards) of 79 (bottom spectrum) and a mixture of 78 and 79 (Inset, asterisk indicates the peaks corresponding to 78).

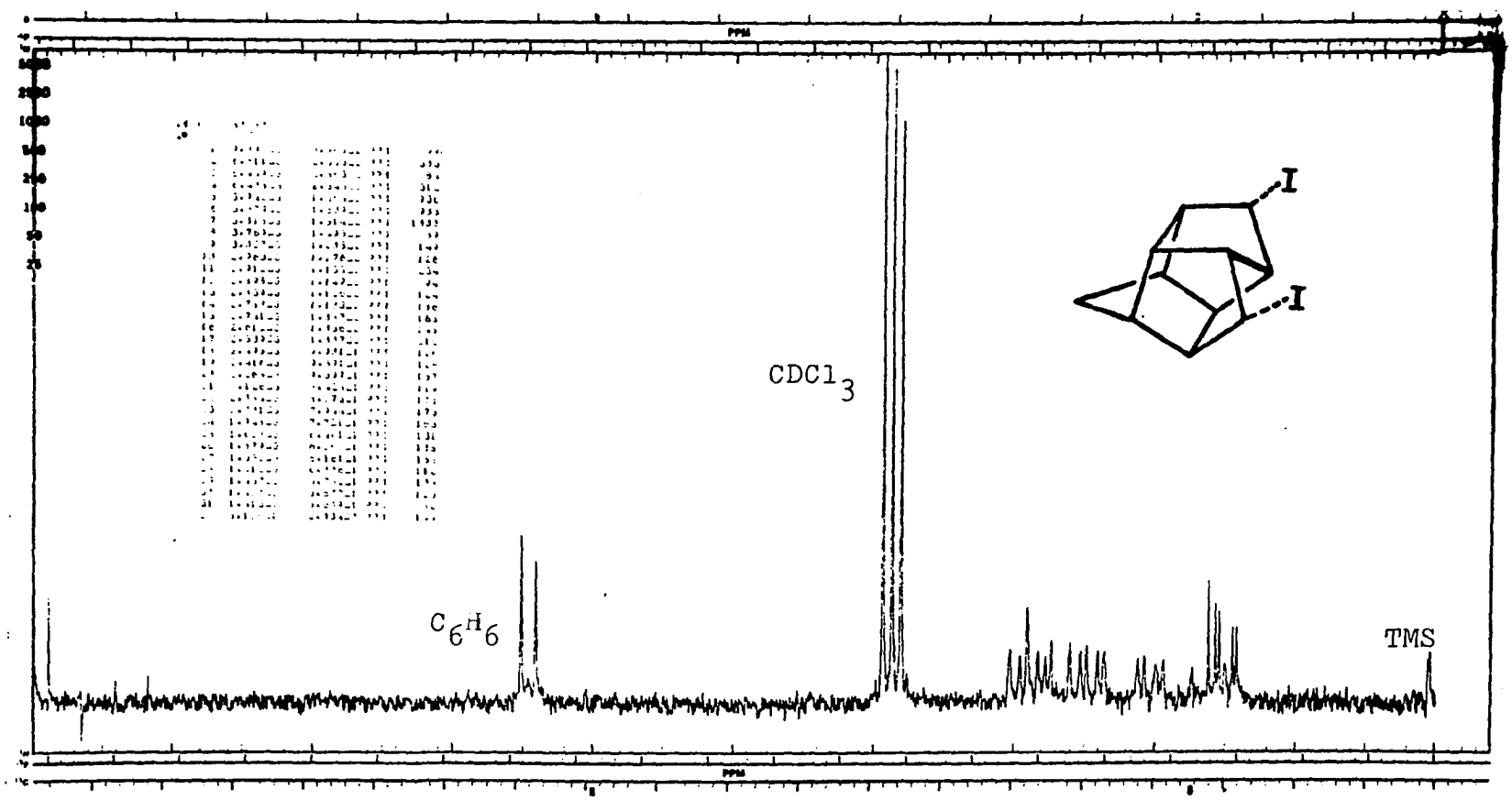


Figure 14b. Off-resonance decoupled ^{13}C nmr spectrum (25.2MHz, $CDCl_3$ solvent, TMS and benzene internal standards) of 79.

(upfield), and 8.6 ppm (downfield)[#]. The off-resonance decoupled ^{13}C nmr spectrum of 80 displays nine peaks resulting from three doublets and one triplet (the latter occurring at 96.8 ppm upfield from benzene).

Hexacyclo[5.4.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$.$0^{8,11}$]undecane (81), a new $C_{11}H_{12}$ hydrocarbon, was identified via analysis of its ir, pmr, and mass spectra (Table III). The infrared spectrum of 81 (Figure 15a) is characterized by the presence of an absorption band at 3040 cm^{-1} which is diagnostic of a cyclopropane moiety.[70] The pmr spectrum (Figure 15b), which exhibits two complex multiplets at δ1.83-2.48 (4H) and δ2.48-3.17 (6H), and a doublet (J=ca. 1 Hz) at δ1.43 (2H), eliminates $C_{11}H_{12}$ structures having olefinic hydrogens. The occurrence of the cyclopropyl pmr absorption below δ2 has ample precedent.[71-73] For example, hexacyclo[4.4.0.$0^{2,4}$.$0^{3,9}$.$0^{5,8}$.$0^{7,10}$]decane (8), the parent compound of 81, displays only two complex multiplets centered at δ3.5 (6H) and δ2.6 (4H).[73] That 81 contains only one cyclopropane ring is suggested by the fact that it reacts with bromine in chloroform solution to afford a mixture of isomeric dibromides (ratio ca. 1 : 2.5). Cleavage of cyclopropane ring by bromine in polar solvents is a rather general

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[#]The chemical shifts relative to TMS [δ(TMS)=128.2-δ(benzene)] are 31.4, 48.7, 64.6, and 136.8 ppm. Professor Eaton has informed us (personal communication) that the chemical shifts of 80 relative to TMS are 31.8, 49.0, 64.9, and 137.1 ppm.

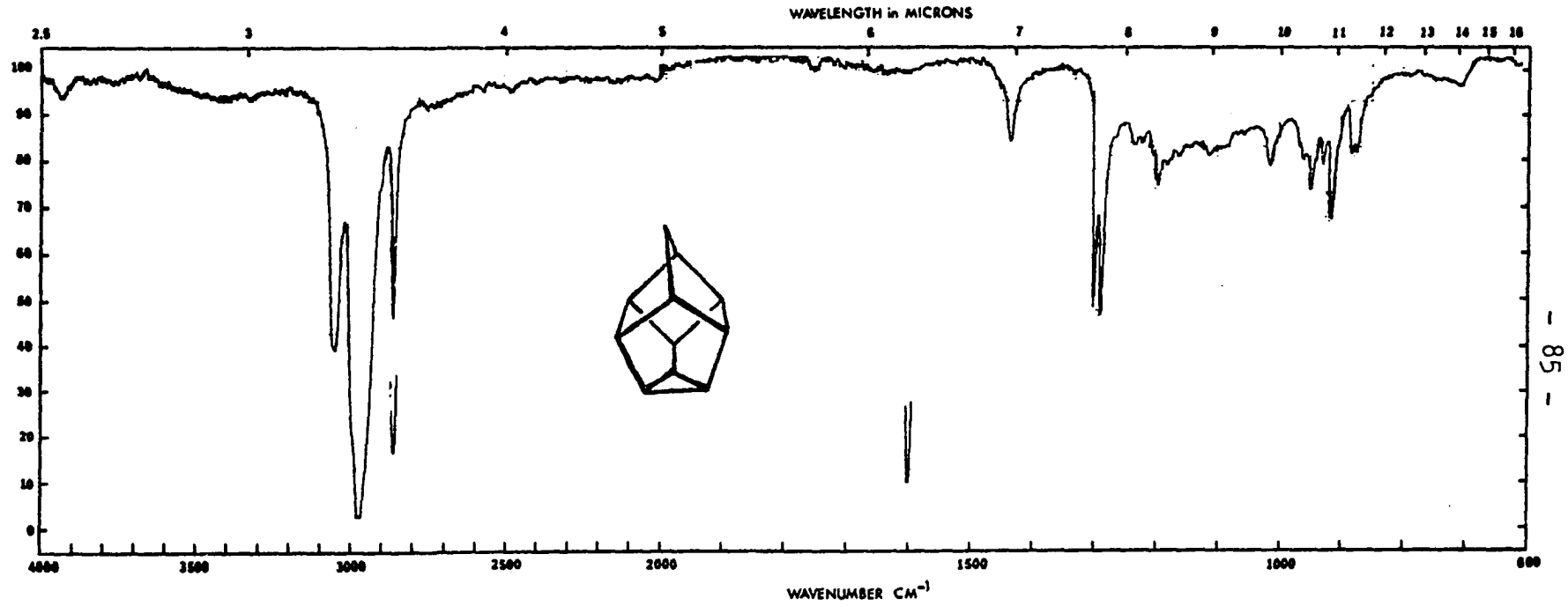

Figure 15a. Infrared spectrum (CCl_4) of 81.

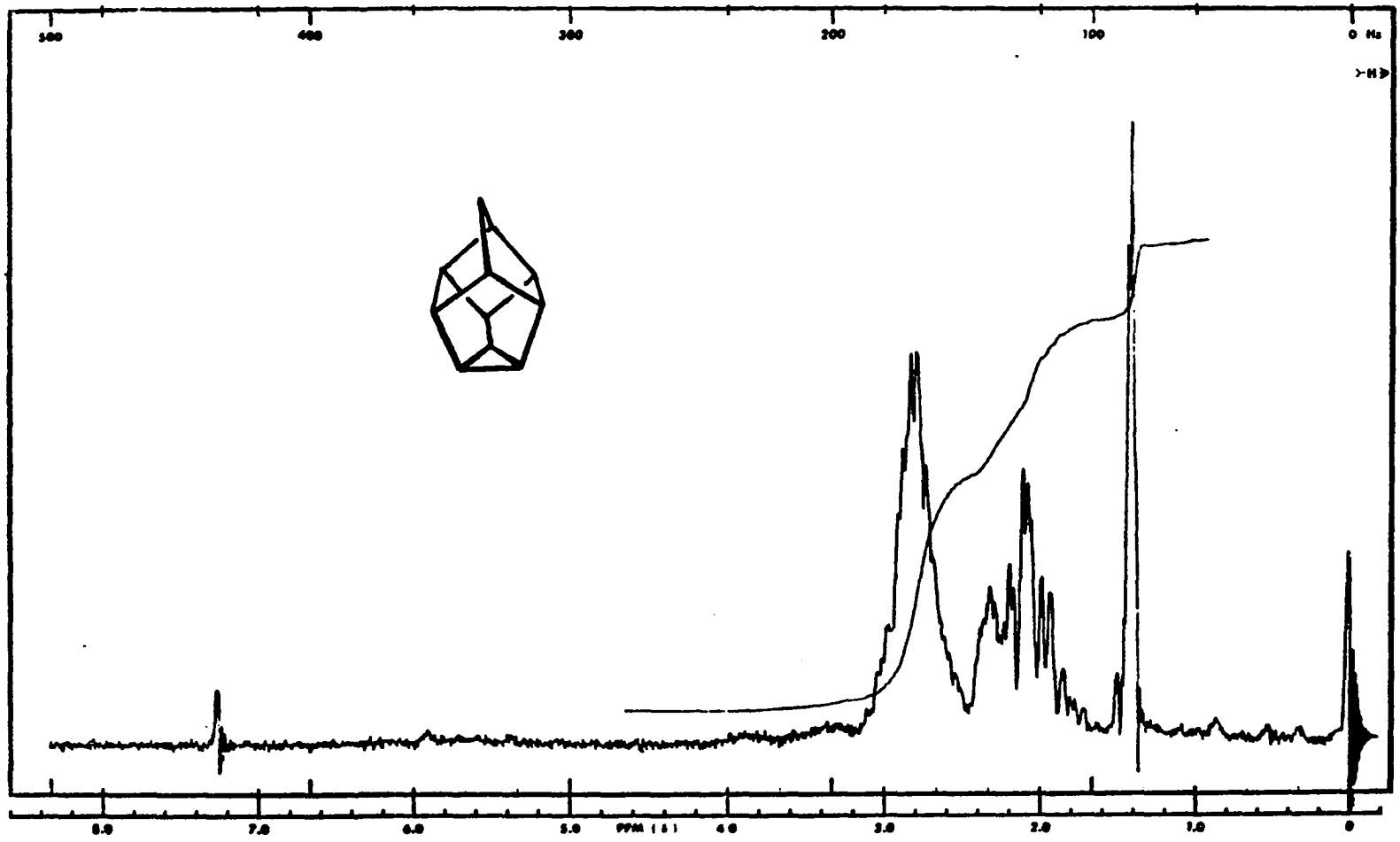

Figure 15b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 81.

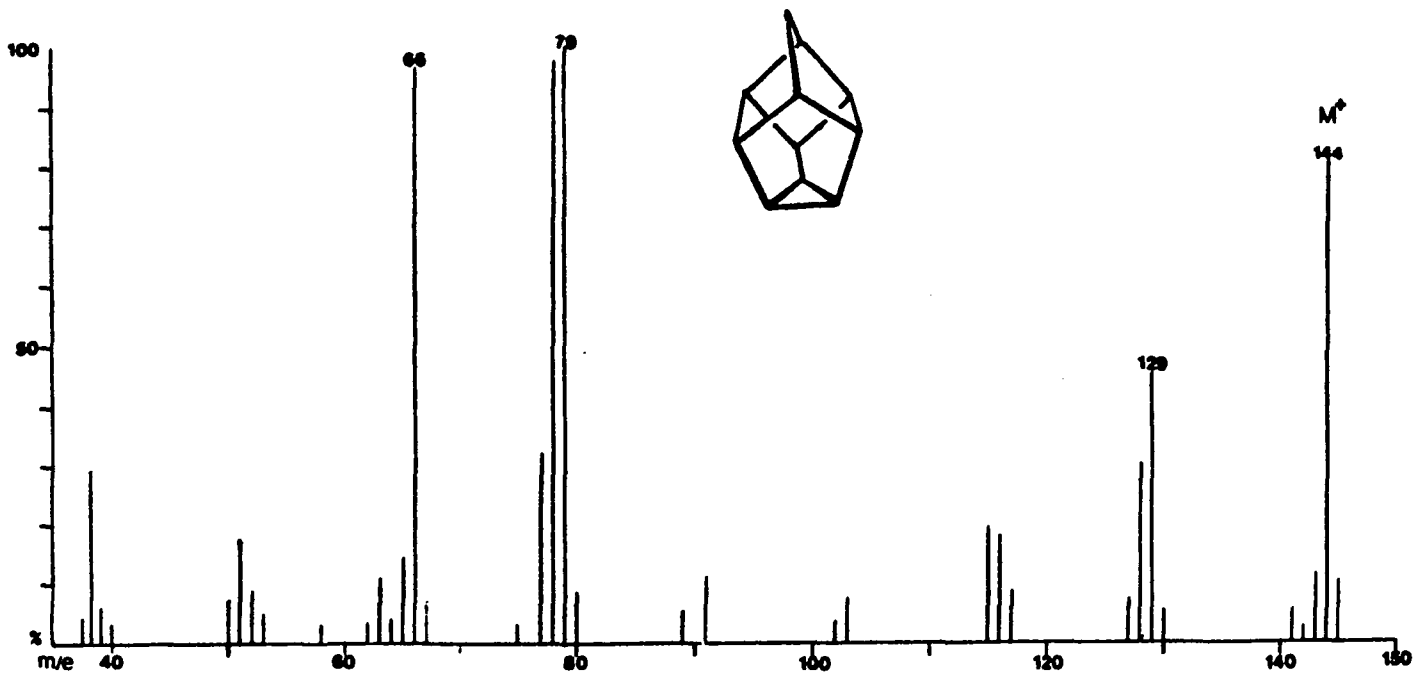

Figure 15c. Mass spectrum of 81.

phenomenon.[74,75] The mass spectrum (10eV) of the mixture of dibromides exhibits the molecular ion at 302/304/306, with intensity profile characteristic of the Br_2 multiplet.[53] This result requires a molecular formula $C_{11}H_{12}Br_2$ for the dibromides. Its infrared spectrum displays no absorption band above 3000 cm^{-1}, suggesting the absence of a cyclopropane moiety.[70] The pmr spectrum of dibromides displays absorption signals at δ1.5 (br s) and 1.6 (center of an AB pattern, J_{AB}=ca. 1.5 Hz), the integral corresponding to two protons (methylene protons), δ2.0-3.2 (complex multiplet, 8H), δ4.2 (br s) and δ4.35 (br s), the integral corresponding to two protons (ratio ca. 2.5 : 1, respectively) (protons geminal to the bromine atoms in the mixture of dibromides).

Assignment of the structure of 81 was further substantiated via the analysis of its ^{13}C nmr spectrum. The proton noise-decoupled ^{13}C-FT nmr spectrum of 81 (Figure 16a) displays eight lines, five arising from distinct carbon atoms and three arising from pairs of equivalent carbon atoms; the chemical shifts relative to benzene are 66.4 (1C), 72.2 (2C), 75.8 (2C), 79.8 (1C), 87.6 (1C), 88.5 (2C), 88.7 (1C), and 92.4 (1C) ppm (upfield). The off-resonance decoupled ^{13}C-FT nmr spectrum (Figure 16b) consisted of seven doublets and one triplet (at 88.7 ppm upfield from benzene).

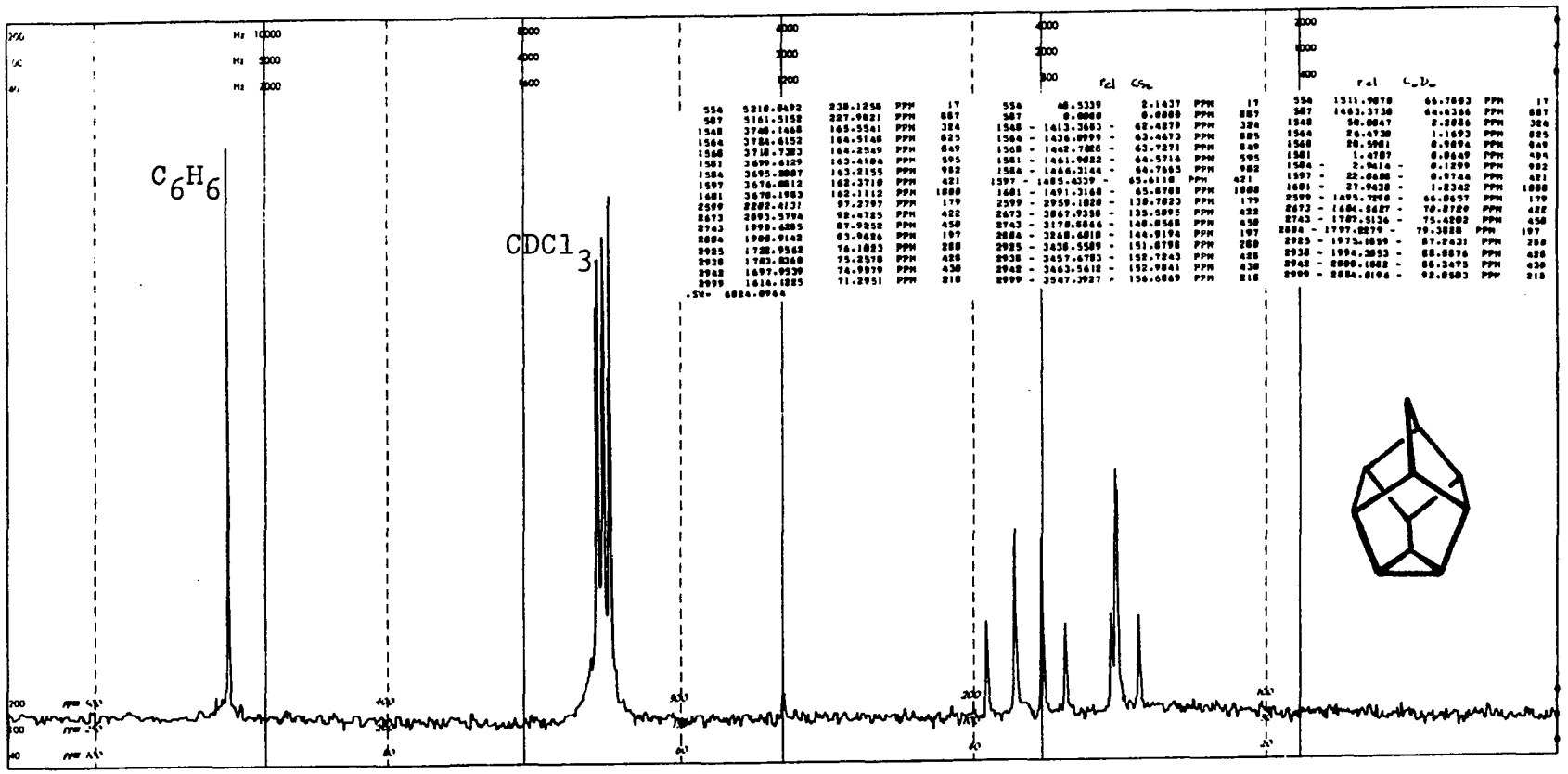

Figure 16a. Proton noise-decoupled ^{13}C-FT nmr spectrum (22.63 MHz, CCl_4 solvent, CS_2 internal standard, C_6D_6 lock) of 81.

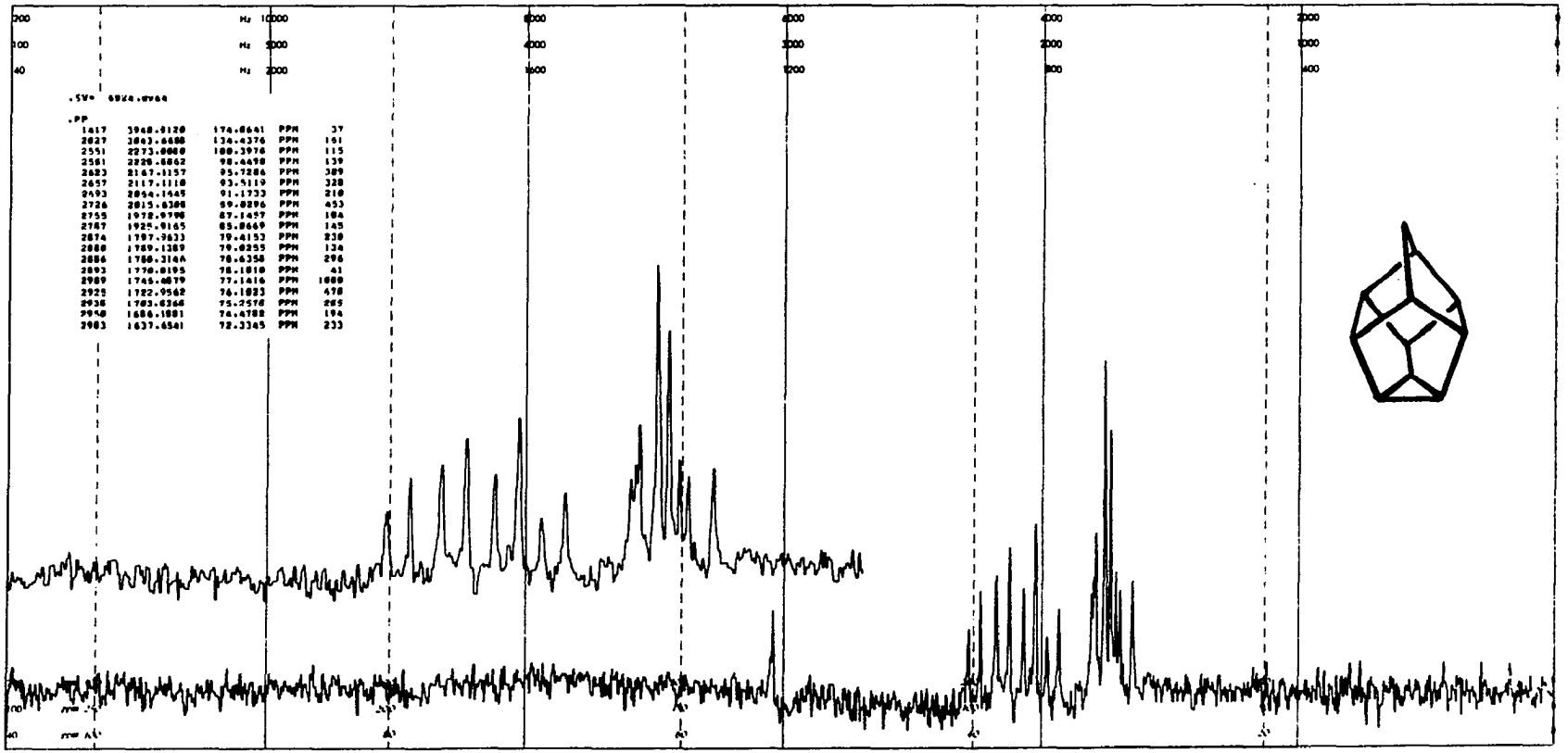

Figure 16b. Off-resonance decoupled ^{13}C-FT nmr spectrum (22.63 MHz, CCl_4 solvent, CS_2 internal standard) of 81.

There are three significant points to come out of the investigation of the reaction shown in Scheme V. The first relates to diiodides 78 and 79. Schleyer and co-workers[67] have reported the synthesis of 78 and 79 as a "mixture of trishomocubyl diiodides" having mp 82-84°. They did not attempt to separate the isomeric diiodides; positive assignment of structure was derived from dehalogenation of this mixture to trishomocubane (83) with zinc in acetic acid. In our study, these two trishomocubyl diiodides were separated and fully characterized.

Secondly, Underwood and Ramamoorthy[45] have previously reported the synthesis of homopentaprismane (53) via the reaction sequence shown in equation 20. Later, this result has been corrected by the authors in an Erratum[76] which states that the product of dehalogenation of 74 with zinc-ethanol was not homopentaprismane. However, no further characterization of that product has appeared. In this connection, it is of interest to compare the physical and spectral (ir, pmr, mass) properties of compound 81 (from this study) with the corresponding properties of Underwood and Ramamoorthy's hydrocarbon (Table III). From examination of the data in Table III, it appears that material prepared by Underwood and Ramamoorthy was very likely impure 81.*

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*Underwood & Ramamoorthy's "homopentaprismane" has 3040 cm^{-1} peak in the infrared spectrum and ^{13}C nmr spectrum identical to that of 81 (personal communication from Professor Underwood, 4 April 1975).

TABLE III. Comparison of Physical and Spectral Properties between Two $C_{11}H_{12}$ Hydrocarbons.

	Compound 81[a]	Compound 53[b]
Melting point	132 - 134°	98 - 100°
Infrared spectrum (cm^{-1}, CCl_4 solvent)	3040 2960 2850 1438 1301 1290 1190 1050 950 931	(3040)[c] 2958 2854 1549 1308 1296 1250 1208 1006 931
Pmr spectrum (ppm)[d]	δ1.43 (br d, 2H) δ1.83-2.48 (complex mult, 4H) δ2.48-3.17 (complex mult, 6H)	δ1.43 (t, 2H) complex mult centered at δ2.1 (4H) complex mult centered at δ2.8 (6H)
Mass spectrum, m/e (% of base peak)	144 (M^+, 81) 129 (45) 128 (30) 115 (19) 79 (100%) 78 (98) 66 (97) 38 (30)	144 (39) 129 (36) 79 (100%) 78 (75) 66 (91)

[a] $C_{11}H_{12}$ saturated hydrocarbon from present study

[b] $C_{11}H_{12}$ saturated hydrocarbon reported by Underwood and Ramamoorthy[45]

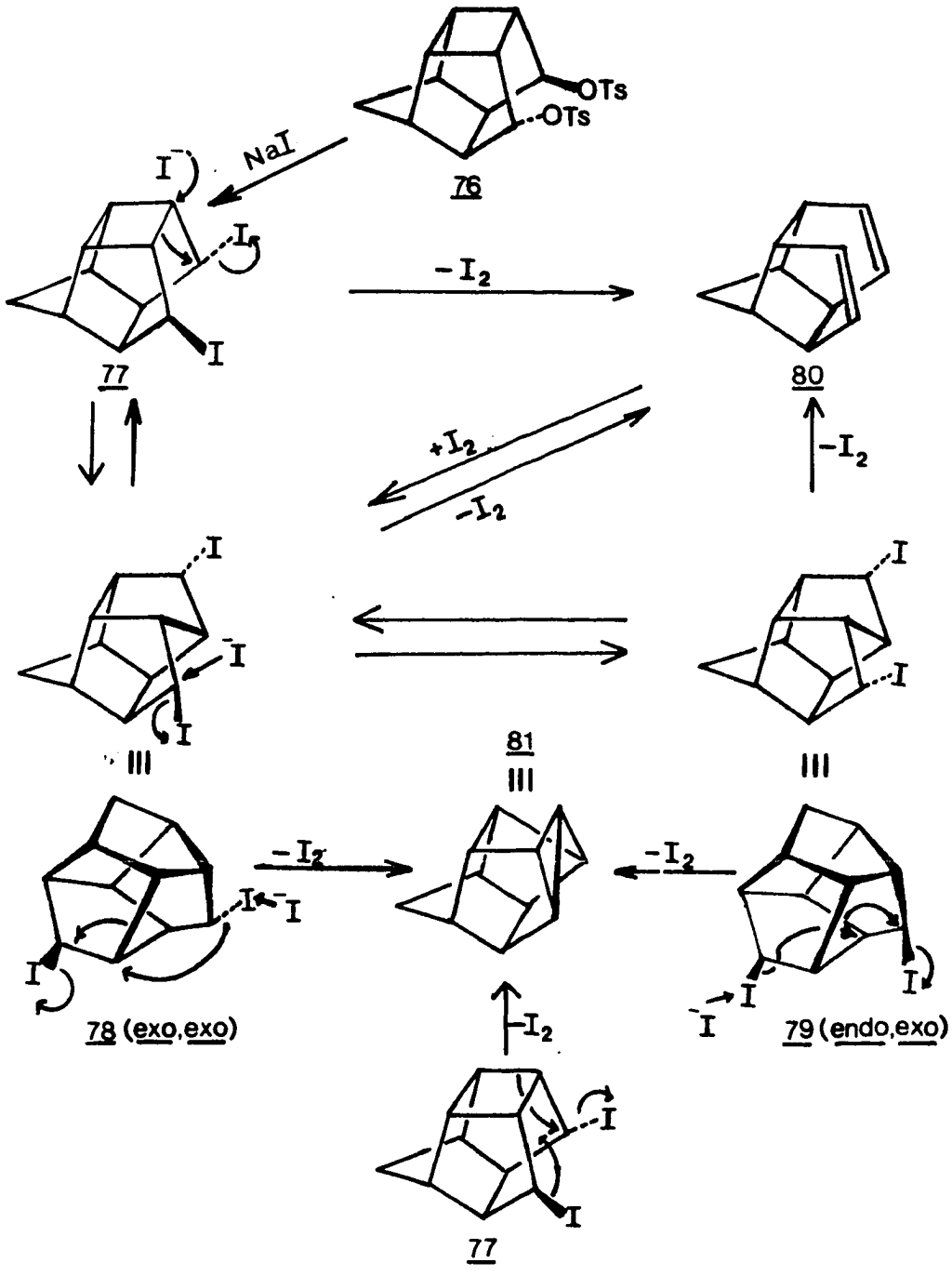
[c] Value obtained *via* personal communication with Professor Underwood

[d] $CDCl_3$ solvent, TMS internal standard (This Study); Solvent and internal standard used in obtaining nmr spectrum of 53 not indicated[45]

The third and final point relates to the mechanism of formation of products 77 - 81 (Scheme V). A plausible sequence is shown in the Scheme VI. Mechanistically, it is conceivable that the formation of exo,exo diiodide 77 follows directly via S_N2 displacement of endo-tosylate groups in 76 by iodide ion. Displacement of iodide in 77 by incoming I^- in the manner shown in Scheme VI then occurs, affording exo,exo trishomocubyl diiodide, 78. Compound 78 is then subsequently converted to exo,endo trishomocubyl diiodide 79 as indicated in Scheme VI. Formation of diene 80 might be envisioned as a result of 1,4-elimination of I_2 from any of the three diiodides (77, 78, and 79).

A particularly salient feature is that a mechanism involving an iodide-promoted 1,4-dehalogenation leading to the formation of a new, highly strained carbon-carbon sigma bond via reductive cyclization is required to account for the formation of 81 from either 77 or 78 (or 79). Such reductive cyclization of α,ω-dihalides are commonly encountered when promoted either electrolytically or by powerful nucleophiles.[77] However, it is unusual to encounter iodide-promoted reductive cyclization in a 1,4-dihalide which must necessarily lead to the formation of such a highly strained cage system as 81. This iodide-promoted reductive cyclization, however, did not promote cyclization of diiodide 77 leading to the formation of

SCHEME VI


OTs
OTs
76
NaI
I⁻
77
-I₂
80
+I₂
-I₂
-I₂
III
81
III
III
-I₂
-I₂
78 (exo,exo)
79 (endo,exo)
-I₂
77

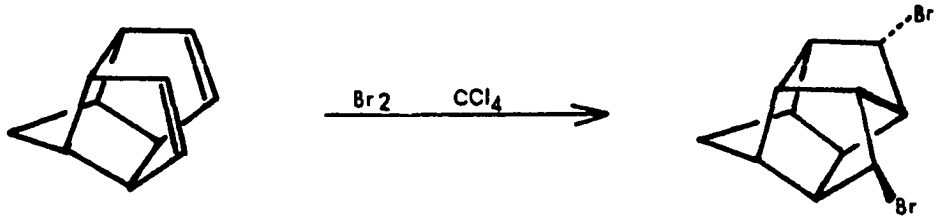
homopentaprismane 53. This observation might indicate that homopentaprismane which possesses four cyclopentane and three cyclobutane moieties is even more strained than 81 which consists of five cyclopentane, one cyclobutane and one cyclopropane moieties.

The question concerning the nature of the intermediates leading to the formation of trishomocubyl diiodides (78 and 79), and particularly the hydrocarbons 80 and 81 remains to be answered. In order to determine whether 77 and/or 78 might be intermediate(s) in the formation of hydrocarbons 80 and 81 from ditosylate 76, control experiments were carried out with each of the pure isomeric diiodides.

When diiodide 77 was subjected to the same experimental condition by which ditosylate 76 was converted to products shown in Scheme V, it afforded a mixture of products. Pmr spectral analysis indicated that the product mixture contained unchanged 77 and trishomocubyl diiodides (78 and 79) in approximately equal amount. Vpc analysis of this product mixture revealed the presence of hydrocarbons 80 and 81 in a ratio 80 : 81 = 9.5 : 1. Diiodide 77 was shown to be stable to the conditions under which this vpc analysis was performed, thus ruling out the possibility of decomposition of diiodide 77 to hydrocarbons 80 and 81 in the vpc column. In the similar control experiment, both

pure trishomocubyl diiodides 78 and 79 produced a mixture of 78 and 79 as the only detectable products (pmr analysis). Vpc analysis revealed the absence of any other volatile materials.

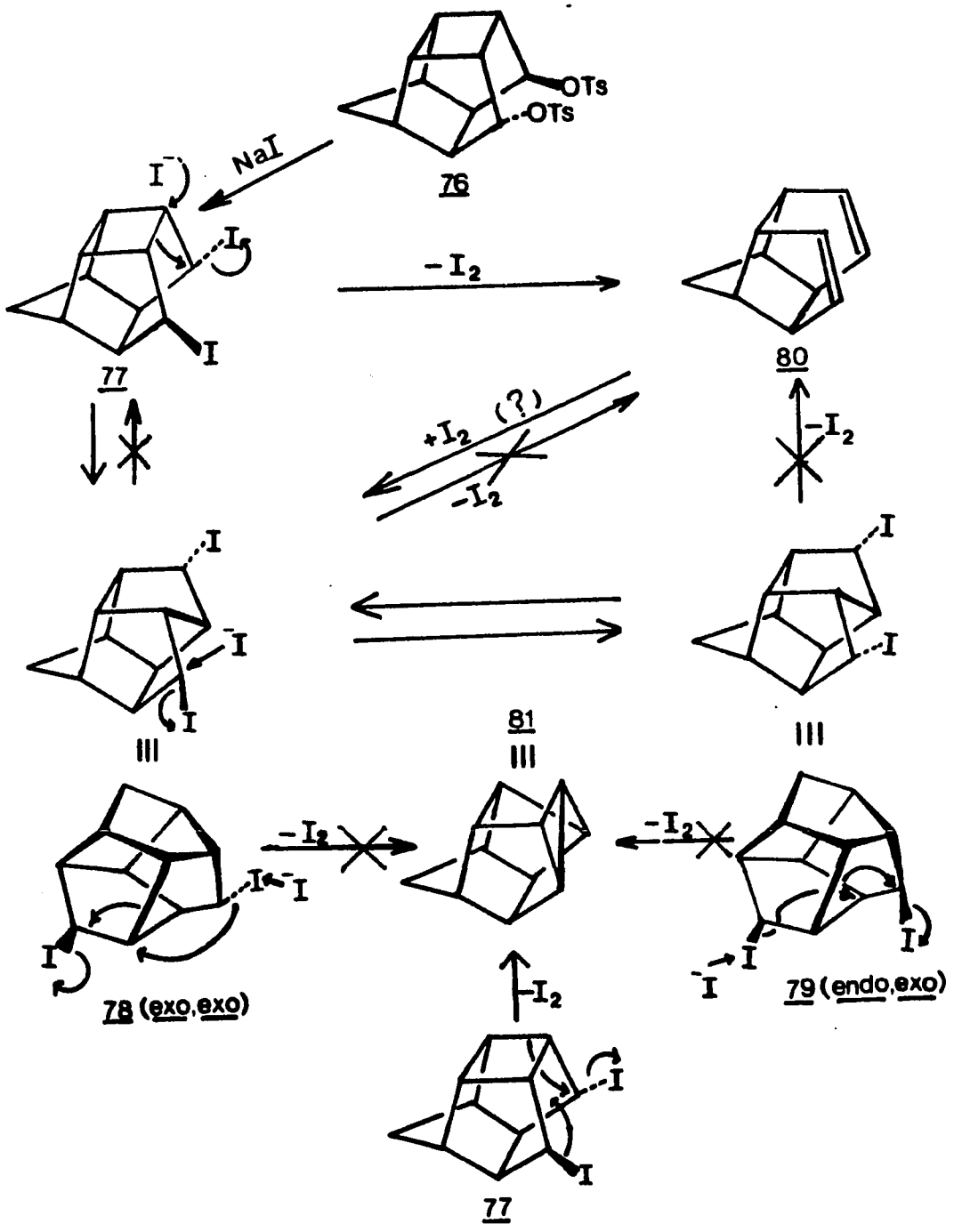
Examination of the results of control experiments reveals that diiodide 77 is the only intermediate responsible for the formation of trishomocubyl diiodides (78 and 79) and hydrocarbons (80 and 81). Under the reaction conditions, two isomeric trishomocubyl diiodides 78 and 79 mutually interconvert without being involved in the formation of either 77, 80 or 81. Based on the control experiments, the mechanism for the formation of 77 - 81 from ditosylate 76 shown in Scheme VI is thus revised, and is shown in Scheme VII. Addition of iodine to diene 80 leading to the formation of exo,exo trishomocubyl diiodide is suggested by the previously observed bromination of diene 80 (equation 25).[69]



80 (25)

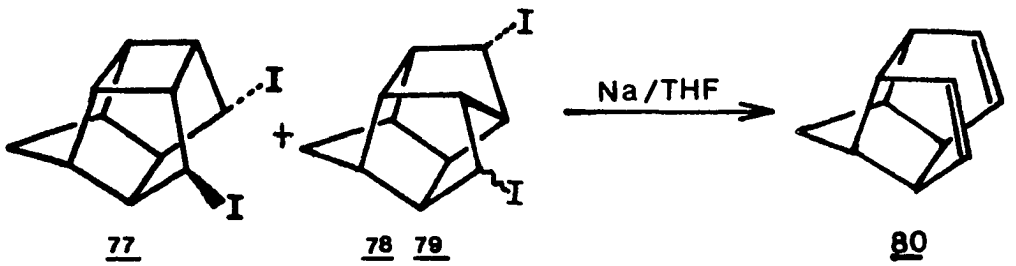
The primary object of investigating the reaction of ditosylate 76 with sodium iodide was to synthesize the corresponding diiodide 77 for use as a possible precursor to homopentaprismane (53), and as a model system for ex-

SCHEME VII


OTs
OTs
76
NaI
I⁻
77
-I₂
80
+I₂
(?)
-I₂
-I₂
81
III
III
III
-I₂
-I₂
78 (exo,exo)
79 (endo,exo)
-I₂
77

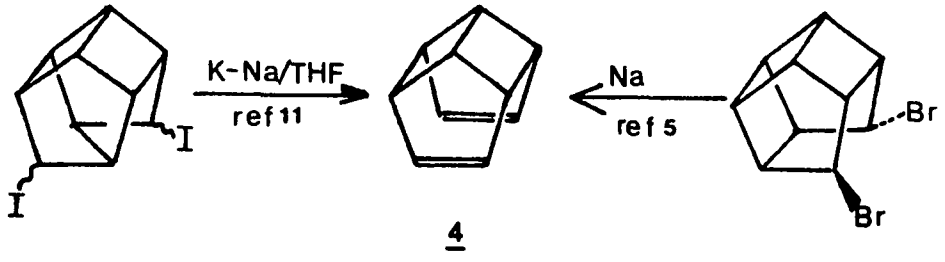
ploring the synthetic route leading to homopentaprismane derivatives, such as 15 shown in Scheme I. The results of this investigation clearly indicate that the reaction was not useful for synthesizing diiodide 77. Also, when a mixture of diiodides containing 77, 78 and 79 was dehalogenated with zinc-ethanol, the product was found to consist of only 80, 82 and 83. This result suggested that dehalogenation of diiodide 77 by this method was not useful for synthesizing homopentaprismane (53). However, in addition to the interesting outcome of the reaction of ditosylate 76 with sodium iodide mentioned earlier, the reaction produced diene 80, which, possessing the two nonconjugated double bonds in a close face-to-face relationship, could be an immediate precursor to homopentaprismane (53) via a $[_{\pi}2_s + _{\pi}2_s]$ photocyclization.[33]

In order to obtain diene 80 in quantity for the photochemical synthesis of homopentaprismane (53), a mixture of isomeric diiodides (77, 78, and 79) was subject to dehalogenation by exposure of diiodides to sodium metal in refluxing tetrahydrofuran (equation 26). The desired diene



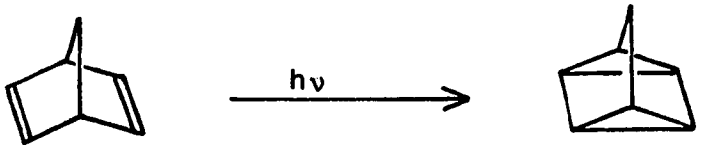
77 78 79 80 (26)

80 so produced could be isolated by sublimation in 75% yield and was free of contaminants. An analogous 1,4-elimination of halogen has been demonstrated in the synthesis of hypostrophene (4) as illustrated in equation 27.



4 (27)

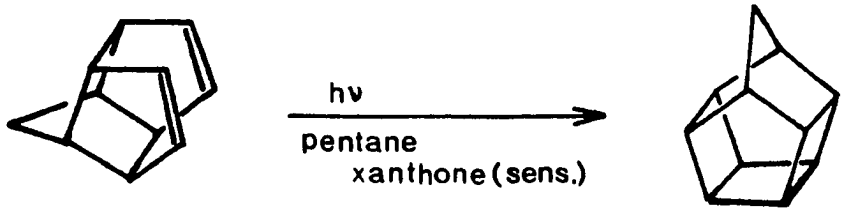
Intramolecular photocyclization of nonconjugated dienes has been extensively utilized in the field of photosynthetic organic chemisty,[78-83] and is represented by the well known norbornadiene-quadricyclane (84⟶85) photoisomerization reaction shown in equation 28.[82,83] The



84 85 (28)

conversion 84---85 can be brought about either by direct[82] or sensitized excitation.[83] In the presence of acetophenone as sensitizer, the yield of the conversion of norbornadiene to quadricyclene was 57% after irradiation for 5 hr.[84] In the present study irradition of a pentane solution of diene 80 for 18 hr using 9-xanthenone (xanthone) as sensitizer

produced homopentaprismane (53) in a yield of 30% (42% based on unrecovered diene, equation 29).[85] The yield of



80 53 (29)

this reaction was not optimized. Vpc analysis of the progress of reaction (see Table IV in Experimental) indicated that a maximum yield of 53 could be obtained if 80 were irradiated for about 10 to 13 hr. Longer irradiation times led not only to reduced yields of 53 but also caused polymerization.

The structure assigned to 53 followed directly from the spectral data. The elemental analysis and mass spectrum (Figure 17c) indicated that 53 is isomeric with diene 76. The pmr spectrum of 53 (Figure 17b) exhibits a triplet (J = ca. 1.5 Hz) at δ1.73 due to the methylene protons, a broad singlet at δ2.67 assigned to the methylene bridgehead protons, and a singlet ($W_{1/2}$=ca. 3 Hz) at δ3.03 corresponding to the eight protons in cyclobutane rings. The infrared spectrum (Figure 17a) is quite simple, displaying a strong absorption peak at 2985 cm^{-1} and no absorption above 3000 cm^{-1}.

The synthesis of homopentaprismane was thus ac-

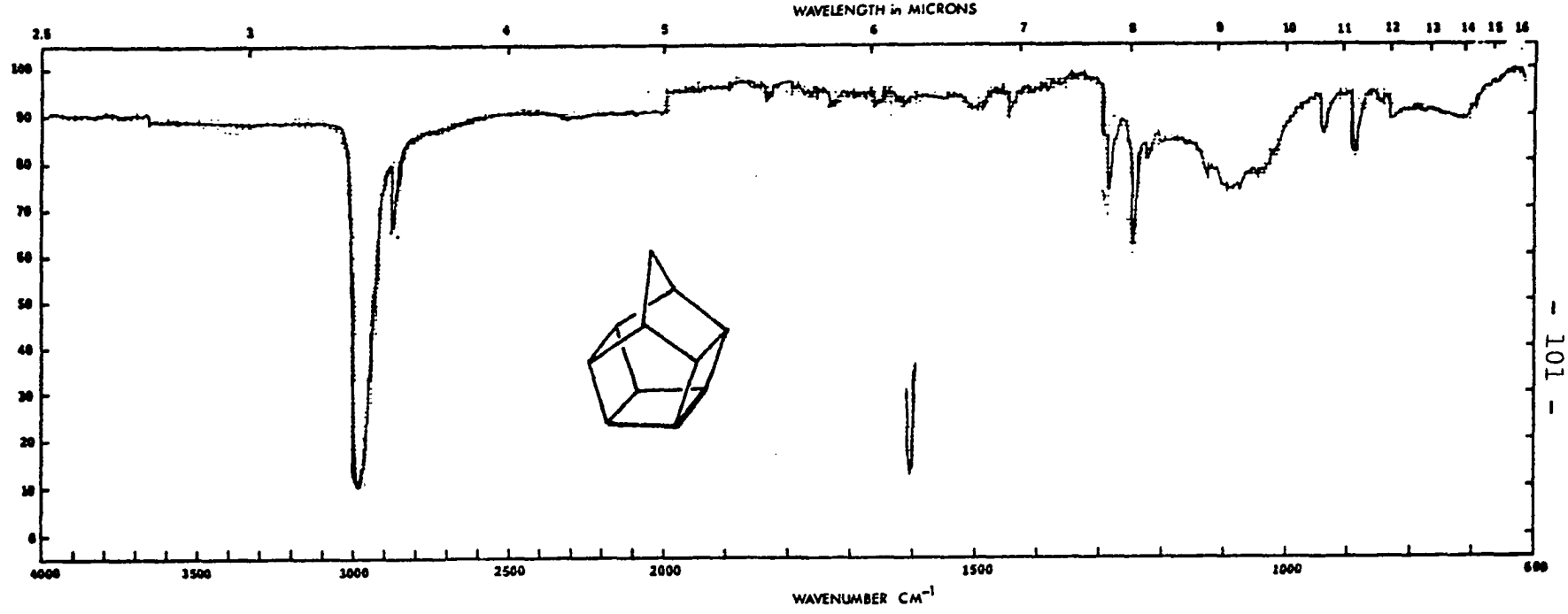


Figure 17a. Infrared spectrum (CCl_4) of homopentaprismane (53).

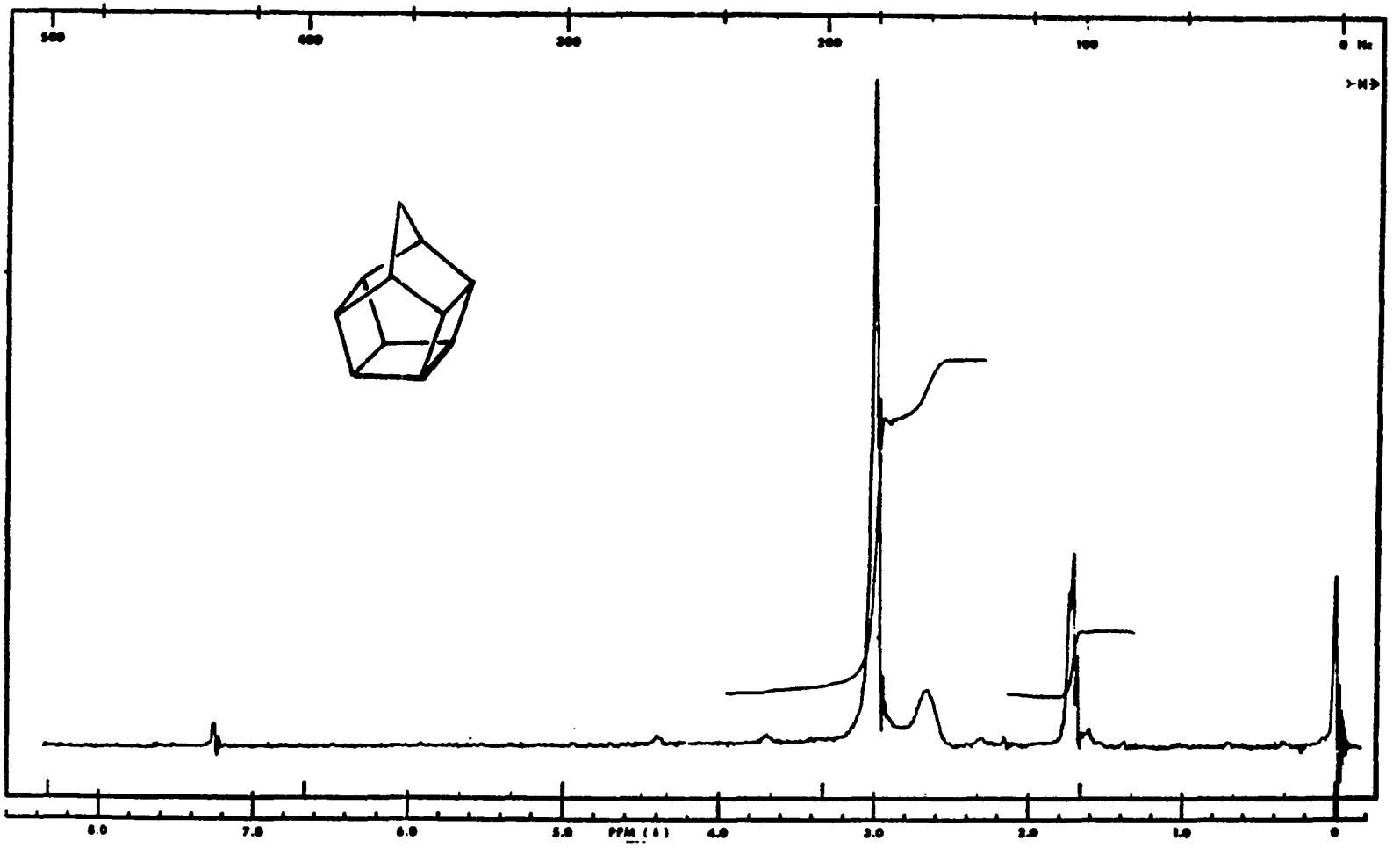


Figure 17b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of homopentaprismane (53).

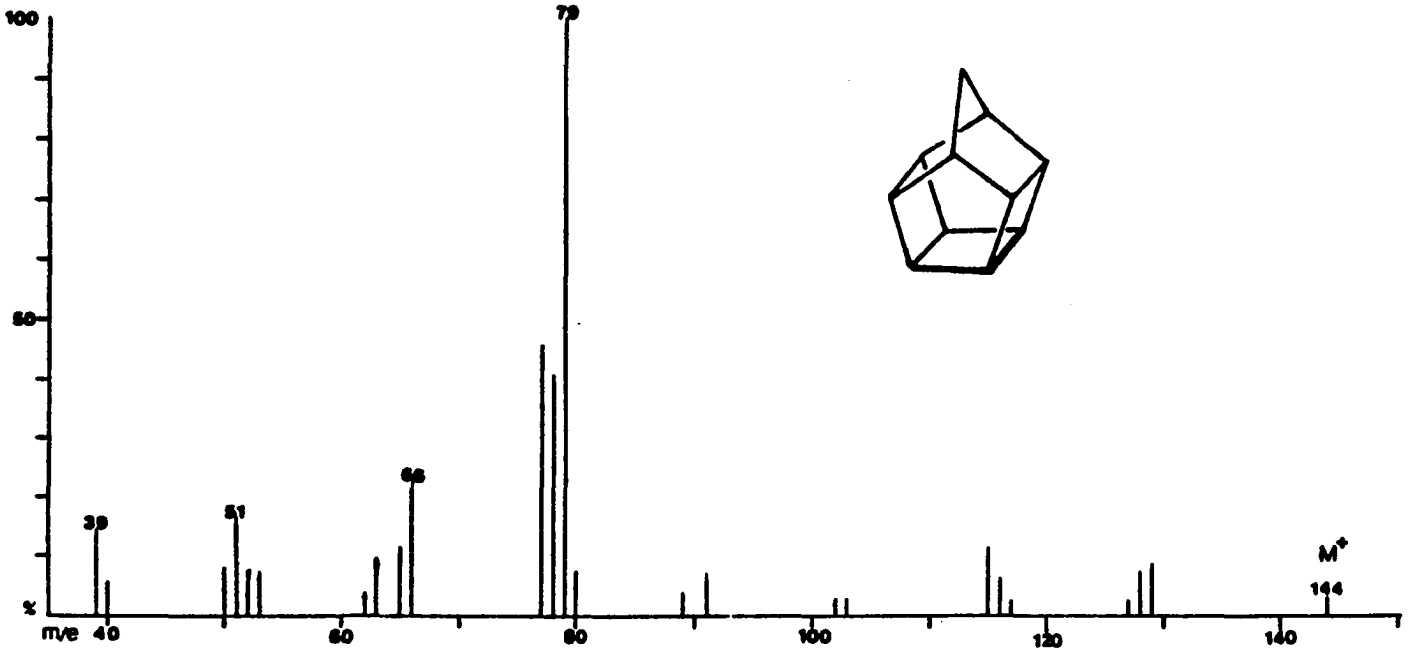
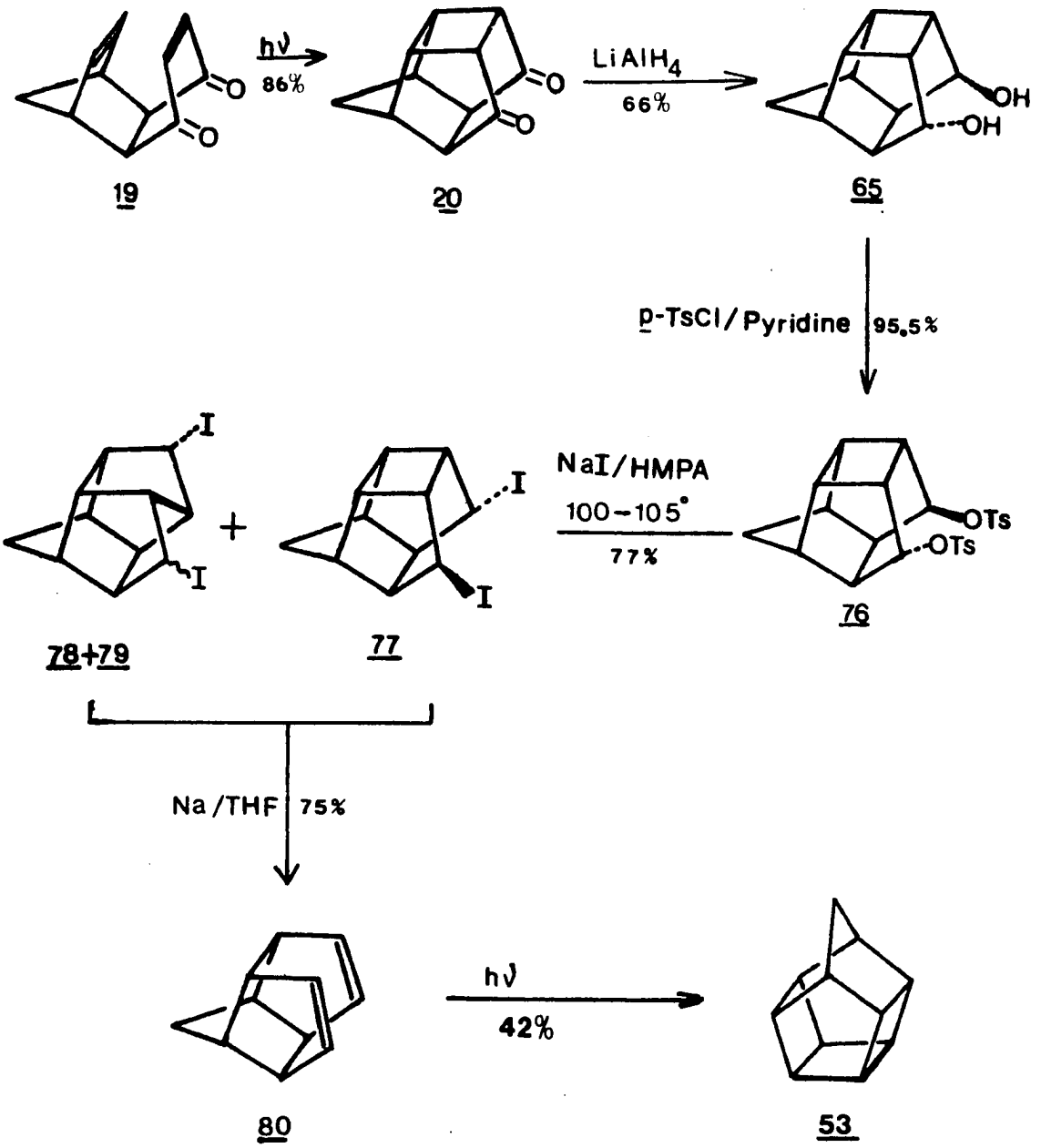


Figure 17c. Mass spectrum of homopentaprismane (53).

complished by the series of reactions illustrated in Scheme VIII. The cage compound 20, produced in 86% by photo-

SCHEME VIII



cyclization of the cyclopentadiene-p-benzoquinone Diels-Alder adduct 19,[15,86,87] was reduced with lithium aluminum hydride to endo,endo diol 65[57] in a yield of 66%. Conversion of diol 65 to its corresponding ditosylate 76 was easily achieved in nearly quantitative yield. A 77% yield of the mixture of diiodides 77 - 79 could be obtained from the reaction of ditosylate 76 with sodium iodide in anhydrous hexamethylphosphoramide at 100-105° under nitrogen for 2 days. This mixture of diiodides was dehalogenated with sodium in dry tetrahydrofuran to produce diene 80 in 75% yield. Photocyclization of diene 80 afforded homopentaprismane (53) in 42% yield. This reaction sequence thus furnished homopentaprismane* in an overall yield of 13% from compound 19.

The synthesis of oxahomopentaprismane (52), a cage system relating to homopentaprismane (53) and pentaprismane (1), was attempted following the sequence shown in Scheme IX. The successful synthesis of oxahomopentaprismane again hinges upon the success of effecting a semibenzilic acid rearrangement on ketone 86 to the corresponding ring-contraction carboxylic acid 87.

Ketone 86 could be synthesized from either endo,exo diol 61 or endo,endo diol 63 via dehydration of diol to 68

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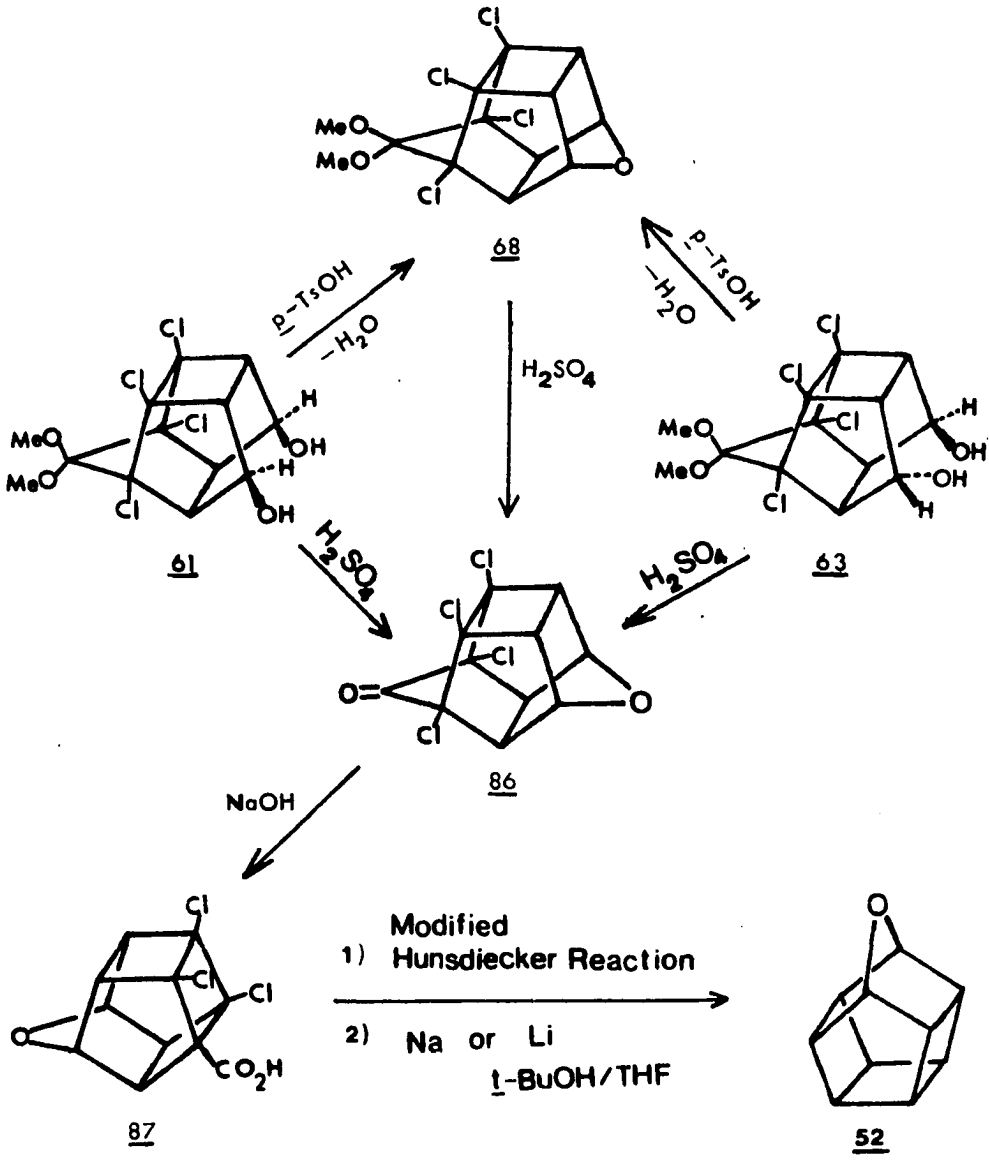
*The study of the transition metal promoted isomerizations of homopentaprismane will be presented at the end of this chapter.

SCHEME IX



followed by acid hydrolysis of 68. Treatment of 61 or 63 with concentrated sulfuric acid resulted in simultaneous

dehydration and hydrolysis to afford ketone 86. However, yield of 86 prepared in this manner was poor (13-36%) owing to difficulties encountered during extraction of the product from the reaction mixture. Alternatively, 86 could be prepared in stepwise fashion from 61 by first dehydrating 61 to 68 (75%) and then hydrolyzing 68 with concentrated sulfuric acid (87%). Compound 86 was thereby obtained in an overall yield of 65%. Endo,endo diol 63 was found to be less easily dehydrated to 68 than was endo,exo diol 61, as evidenced by the incomplete dehydration of 63 under the conditions used to dehydrate 61.

The pmr spectra of both 68 and 86 (Figure 18b and 19b) exhibited the characteristic quintet (J=ca. 2 Hz) at δ5.18 and δ5.25, respectively, assigned to the protons geminal to the oxygen bridge. The infrared spectrum of ketone 86 (Figure 19a) displayed a band at 1795 cm^{-1} which is characteristic of strained perchlorinated norbornanone-type ketones.[47] Ketone 86 was also found to hydrate rapidly on contact with moist air.

In an attempt to promote semibenzilic acid rearrangement, ketone 86 was treated with base under a variety of conditions. In no case was the desired semibenzilic acid rearrangement product 87 obtained. The results of these attempts are summarized in Scheme X. When ketone 86 was treated with powdered sodium hydroxide or potassium

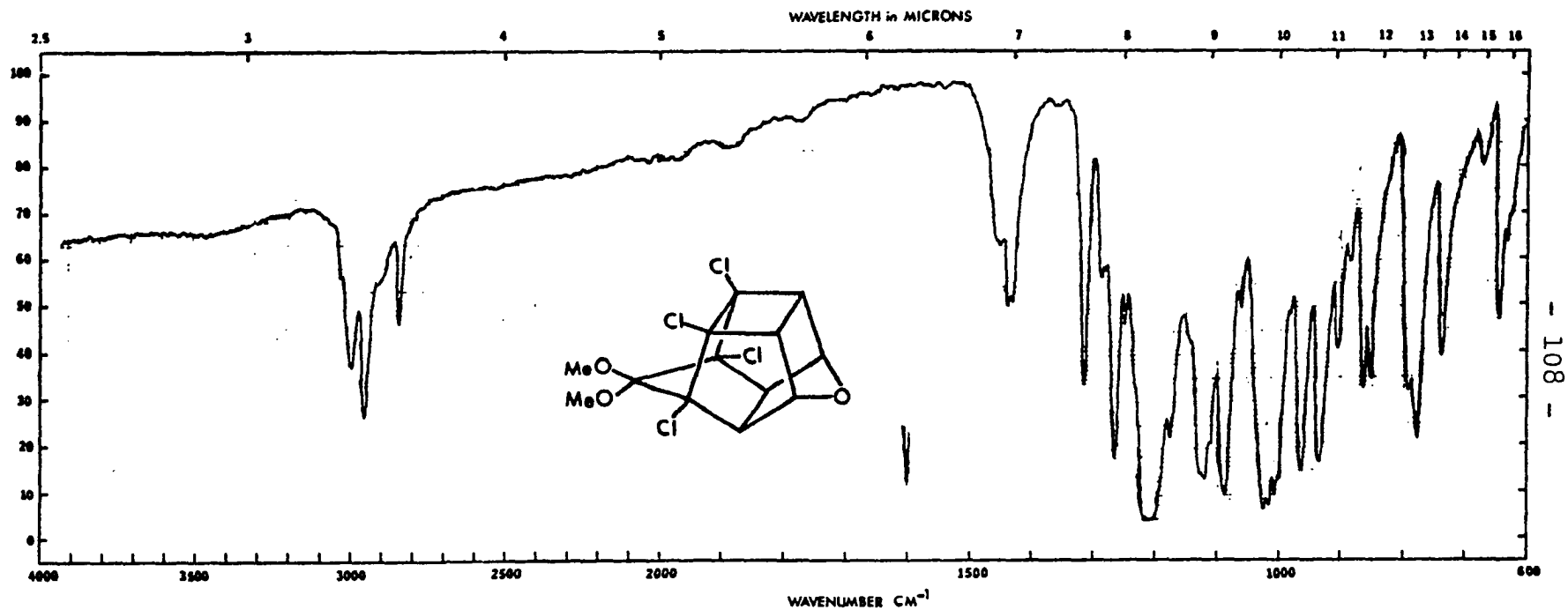


Figure 18a. Infrared spectrum (KBr) of 68.

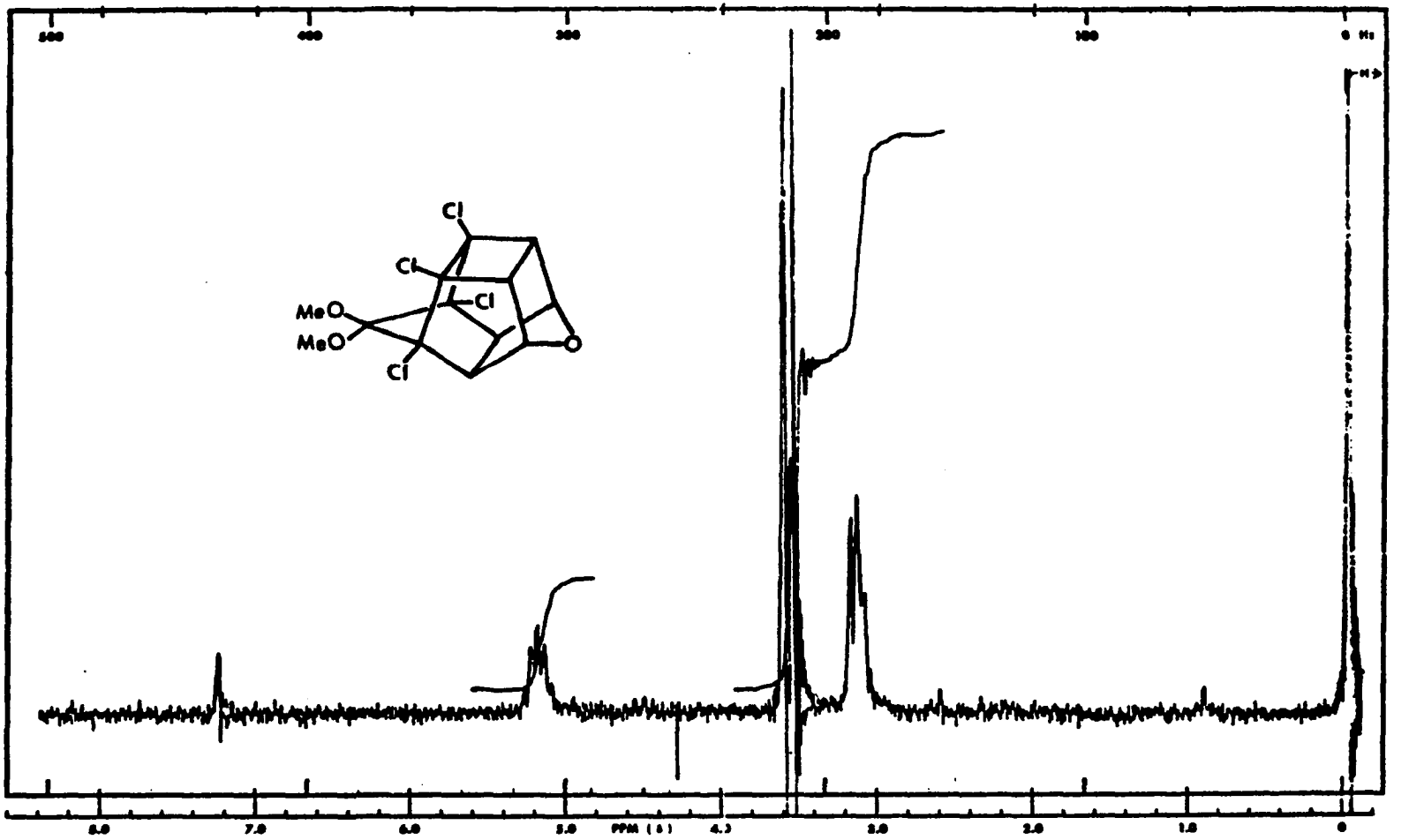


Figure 18b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 68.

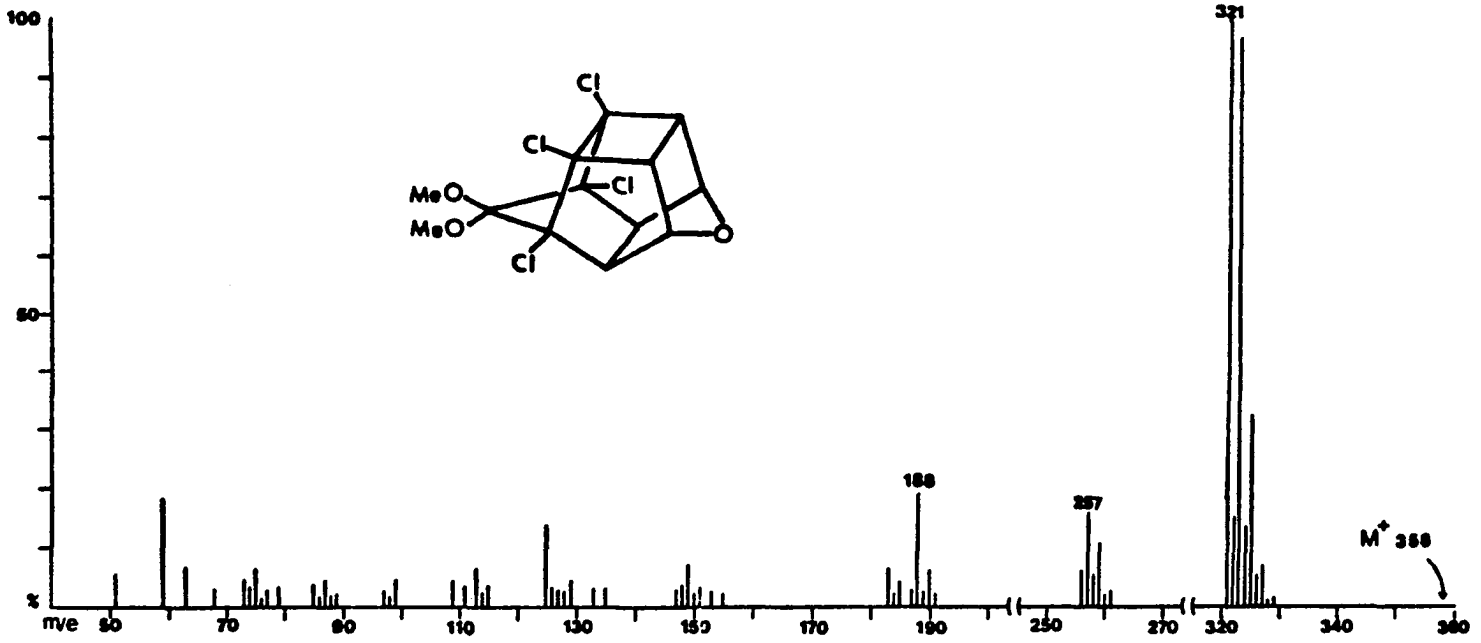


Figure 18c. Mass spectrum of 68.

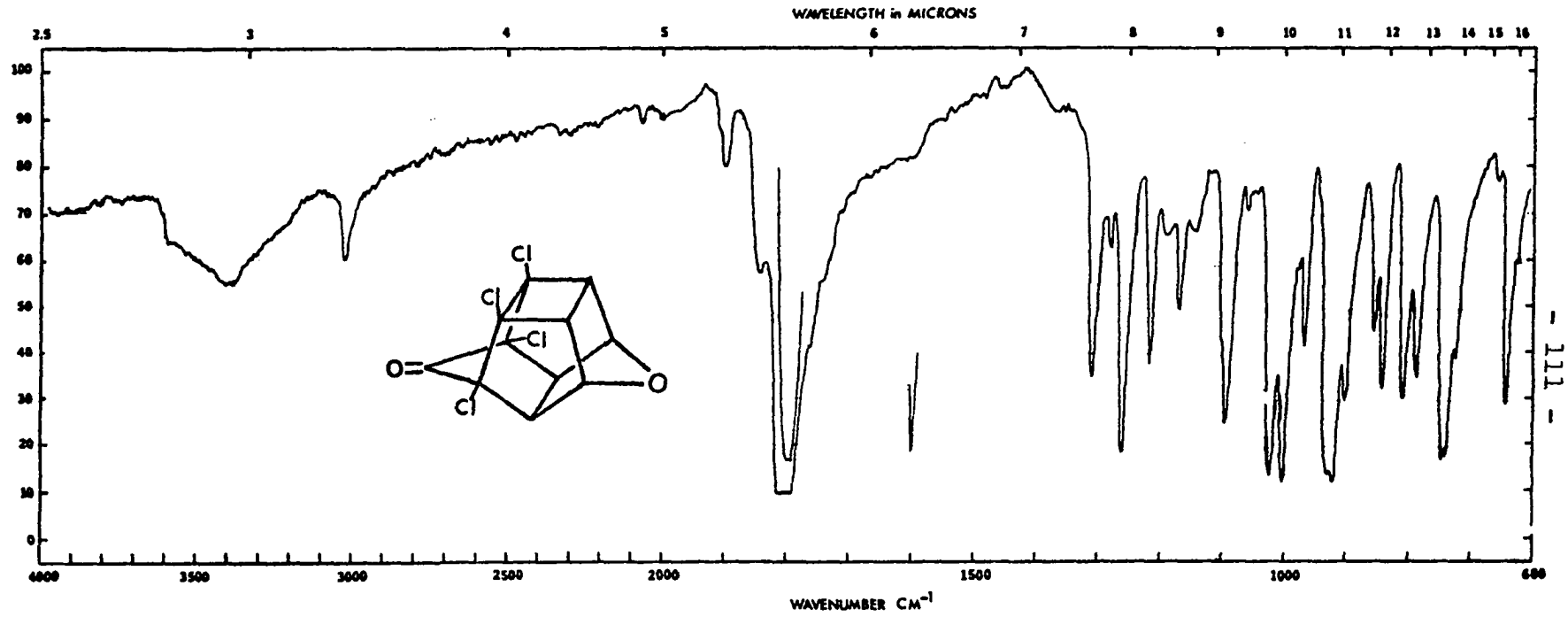


Figure 19a. Infrared spectrum (KBr) of 86.

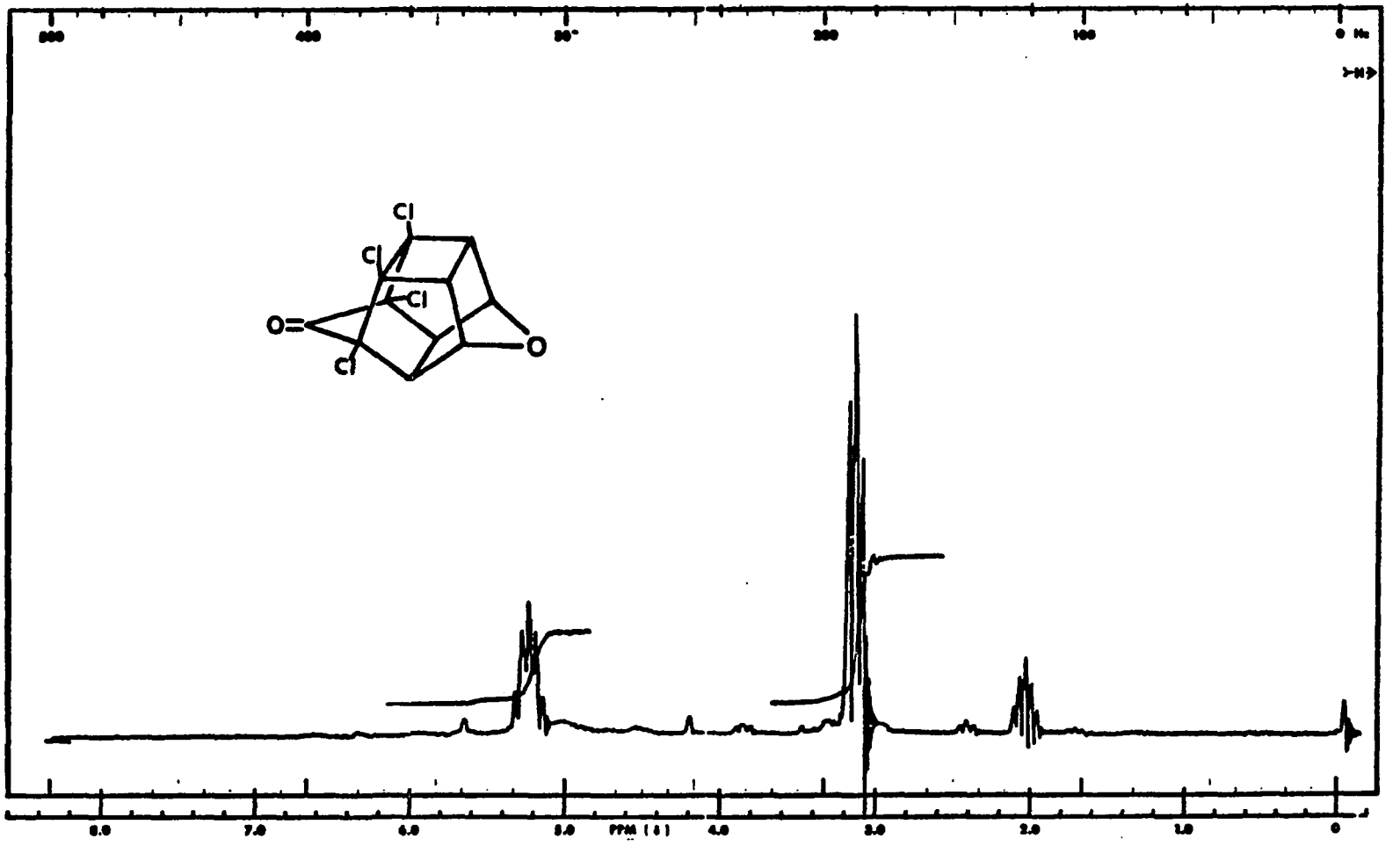


Figure 19b. Proton nmr spectrum (60MHz, acetone-d_6 solvent, TMS internal standard) of 86.

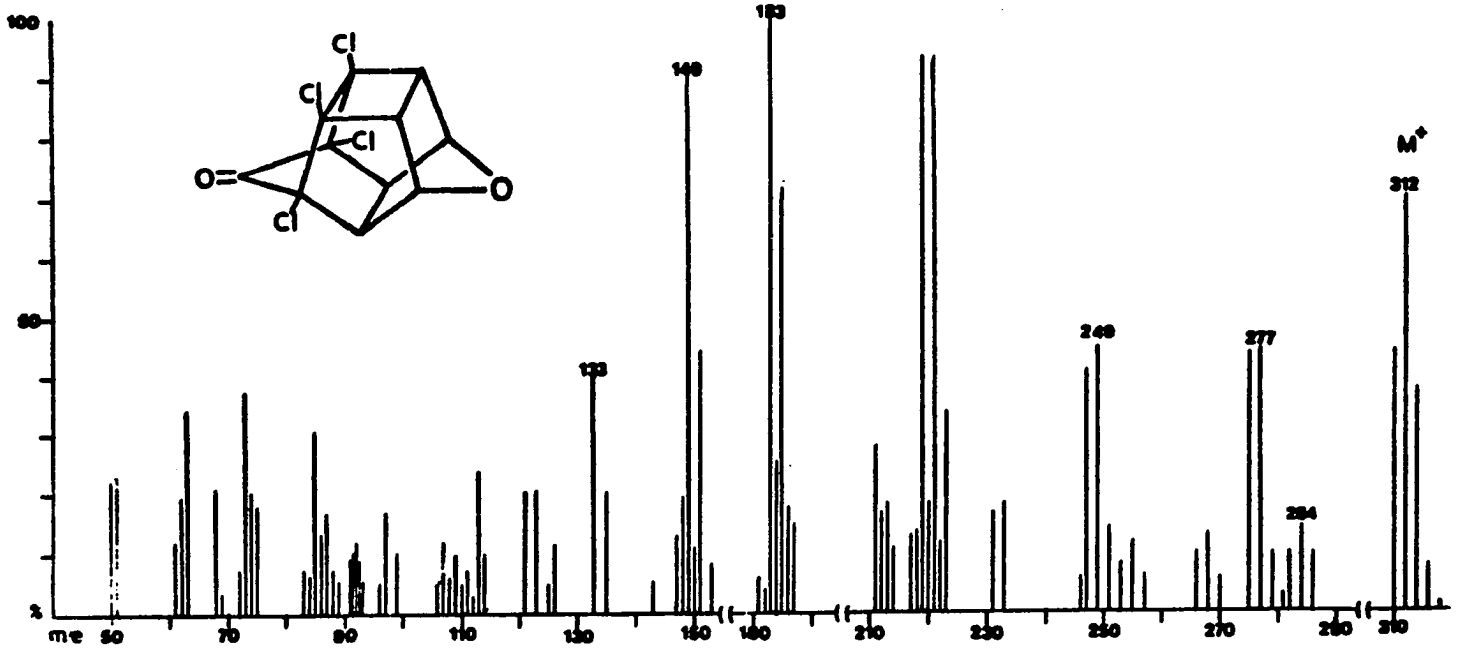
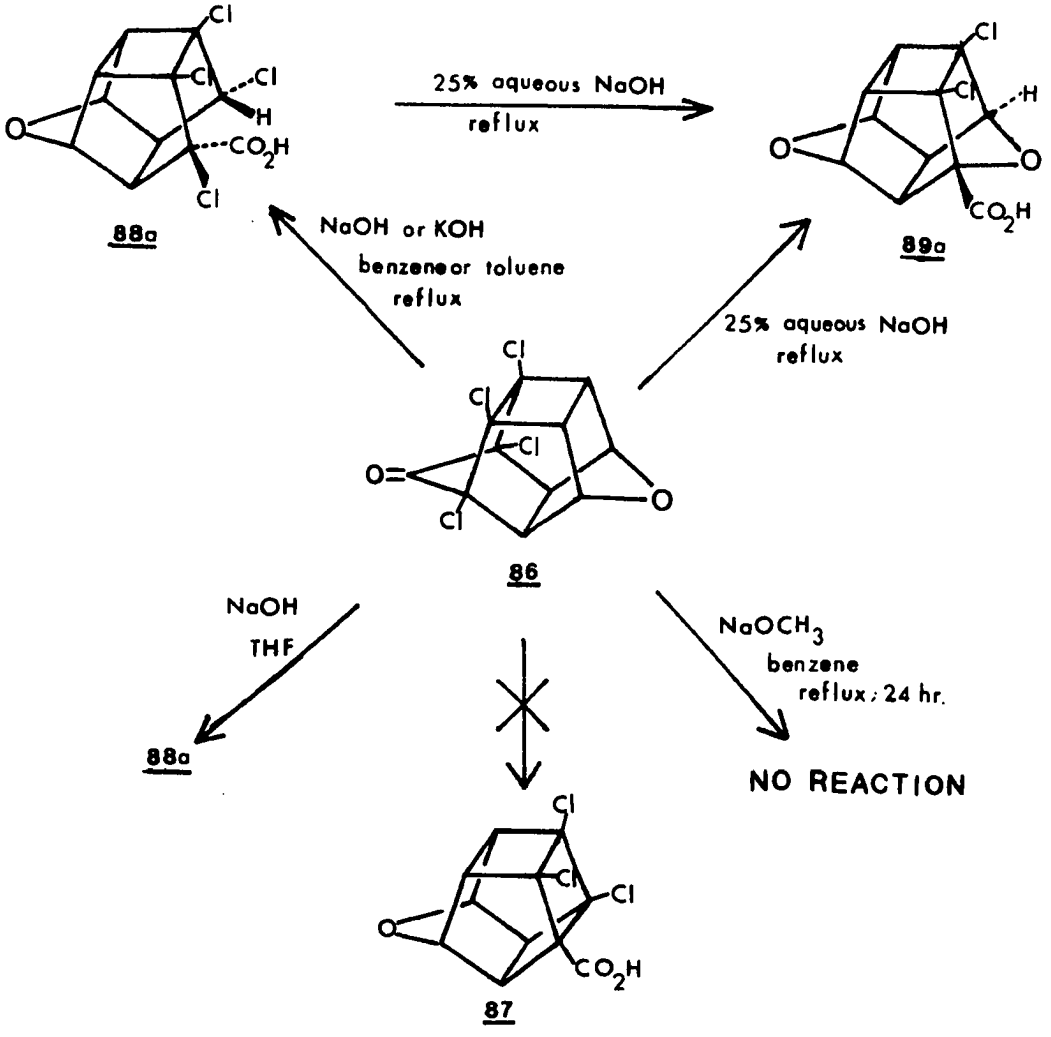


Figure 19c. Mass spectrum of 86.

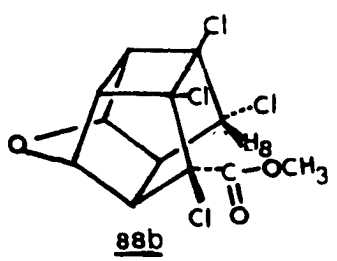
SCHEME X



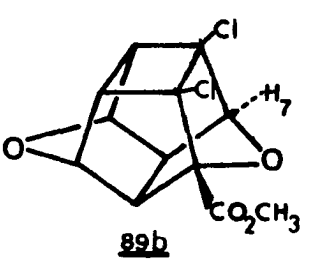
hydroxide in refluxing toluene for 2 - 4 hr or benzene for 24 hr,[31] a ring-cleaved carboxylic acid 88a was produced in 79 - 80% yields. A considerable amount (ca. 25%) of unchanged ketone 86 was recovered from those reactions having shorter refluxing time. Carboxylic acid 88a was also obtained in 90% yield from the reaction of 86 with crushed sodium hydroxide pellets in tetrahydrofuran at room

temperature overnight.[27,28] However, 86 could be recovered unchanged (in its hydrate form) essentially quantitatively from its reaction with sodium methoxide in refluxing benzene for 24 hr. When ketone 86 was treated with 25% aqueous sodium hydroxide solution at reflux,[88] an oxygen-bridged carboxylic acid 89a was isolated in 66% yield. This carboxylic acid 89a was also formed when 88a was treated with 25% aqueous sodium hydroxide solution (Scheme X). Primarily on the basis of this observation, the stereochemistries of carboxyl group at C(3) and chlorine atom at C(6) in 88a are assigned to be endo and exo, respectively. This observation also indicated that 88a is an intermediate in the conversion of ketone 86 to 89a.

The carboxylic acids 88a and 89a were further characterized as their corresponding methyl esters 88b and 89b; the structural assignments are supported by spectral and elemental analyses. Attempts to esterify 88a by using



88b



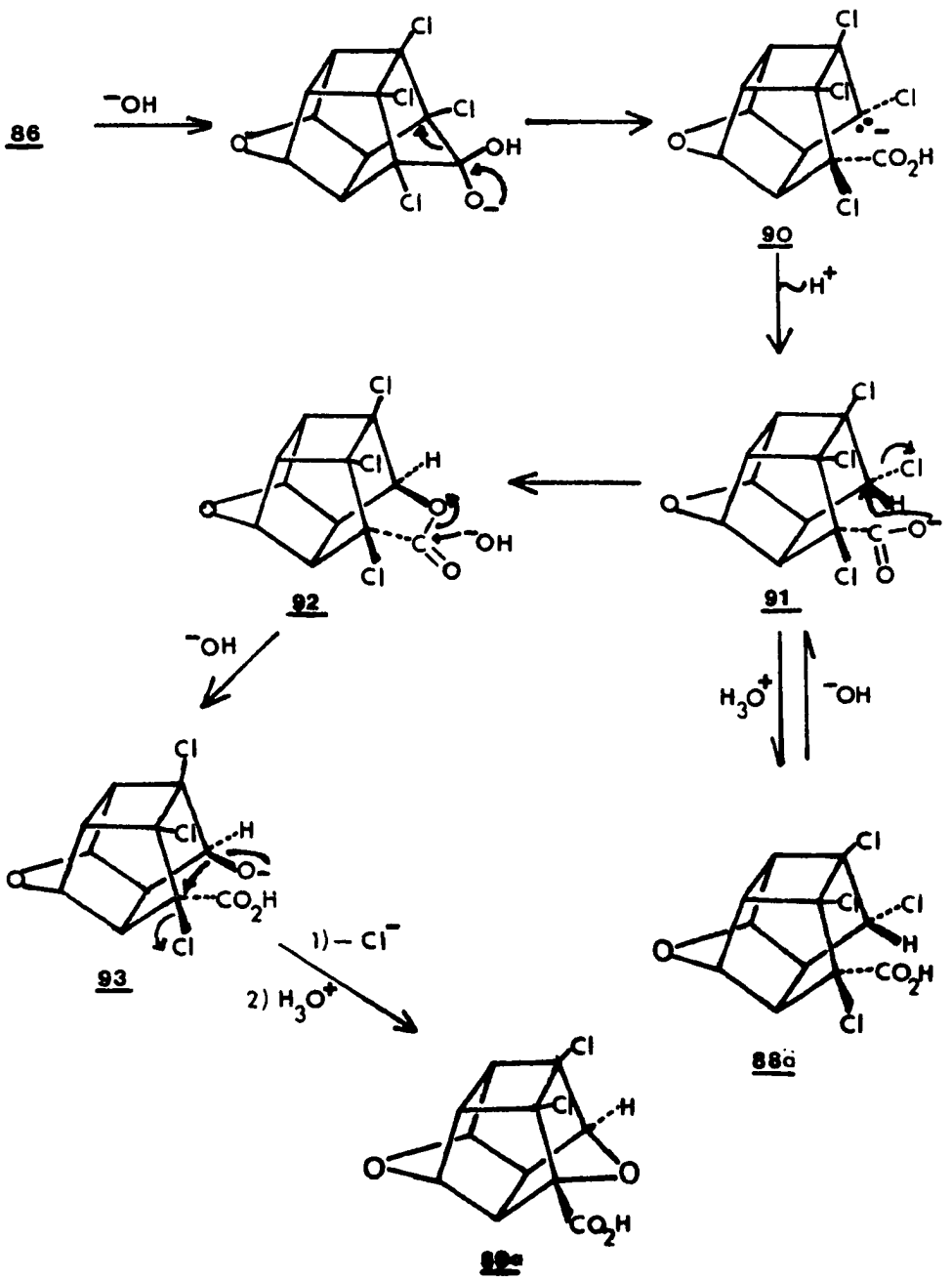
89b

hydrochloric acid-methanol, sulfuric acid-methanol or trifluoacetic anhydride-methanol[89] were unsuccessful. Esterification of 88a was achieved by converting 88a to its

acid chloride with thionyl chloride followed by treatment of the acid chloride with anhydrous methanol *in situ*. These results might reflect the steric hindrance which the *endo* carboxyl group in **88a** experiences. The pmr spectra of both esters **88b** (Figure 20b) and **89b** (Figure 21b) were similar with exception of a doublet (J=*ca*. 1 Hz) at δ4.10 for the *endo* proton (H_8) geminal to chlorine atom in **88b** and a broad triplet (J=*ca*. 2 Hz) at δ4.90 for the *exo* α-oxy proton (H_7) of **89b**. The lack of complex splitting observed for the *endo* proton (H_8) of **88b** is a rather general phenomenon which has been observed in other cage compounds.[90,91]

A reasonable mechanism for the formation of **88a** and **89a** from the base-promoted rearrangement of ketone **86** is shown in Scheme XI. The action of alkali on **86** leads to the ring-opened chlorocarbanion **90** which abstracts a proton from the carboxyl group to form a carboxylate anion **91**. Apparently, the carboxylate anion **91** survives when the reaction is carried out in nonpolar solvent and is isolated during acidic work-up as **88a**. The orientation of the carbon-chlorine bond away from the carboxyl group in **88a** may result from avoiding both congestion and unfavorable dipole-dipole interaction. In polar solvent, further intramolecular displacement of chloride ion by the carboxylate anion proceeds in the manner shown to afford the chlorolactone **92**. Saponification of the lactone-bridge in **92**

SCHEME XI



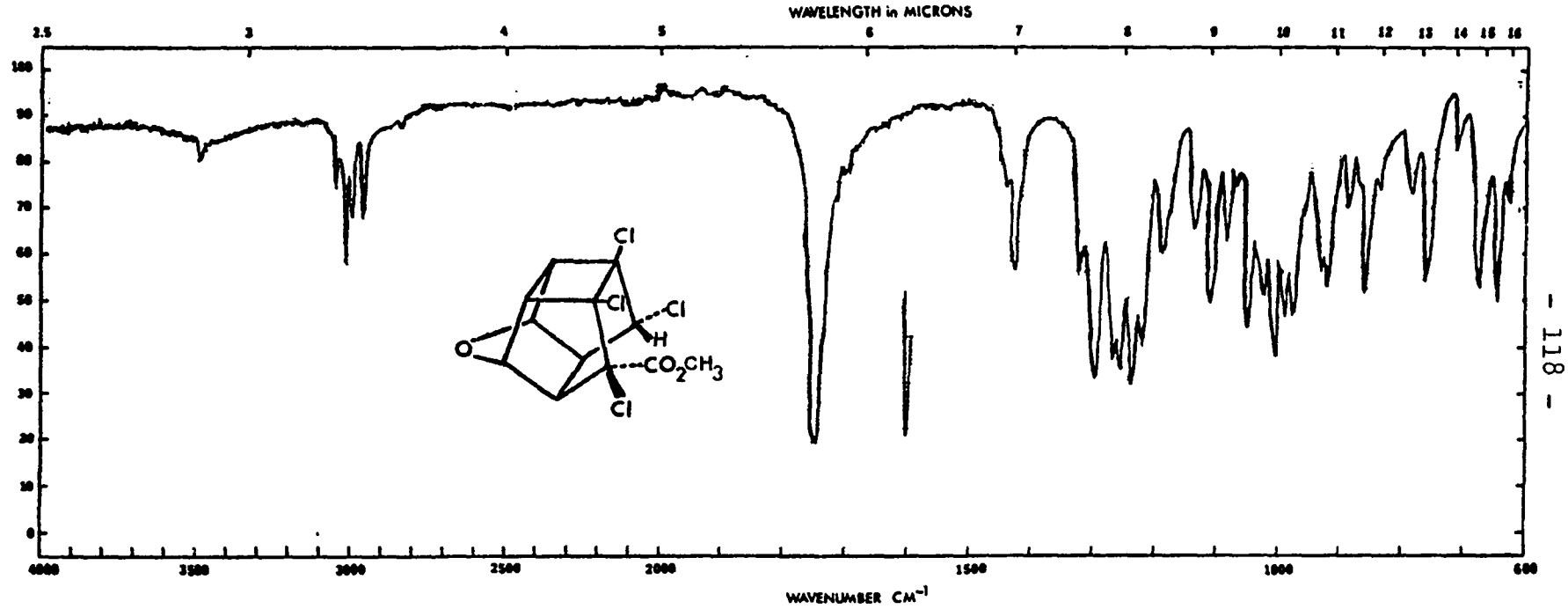


Figure 20a. Infrared spectrum (KBr) of 88b.

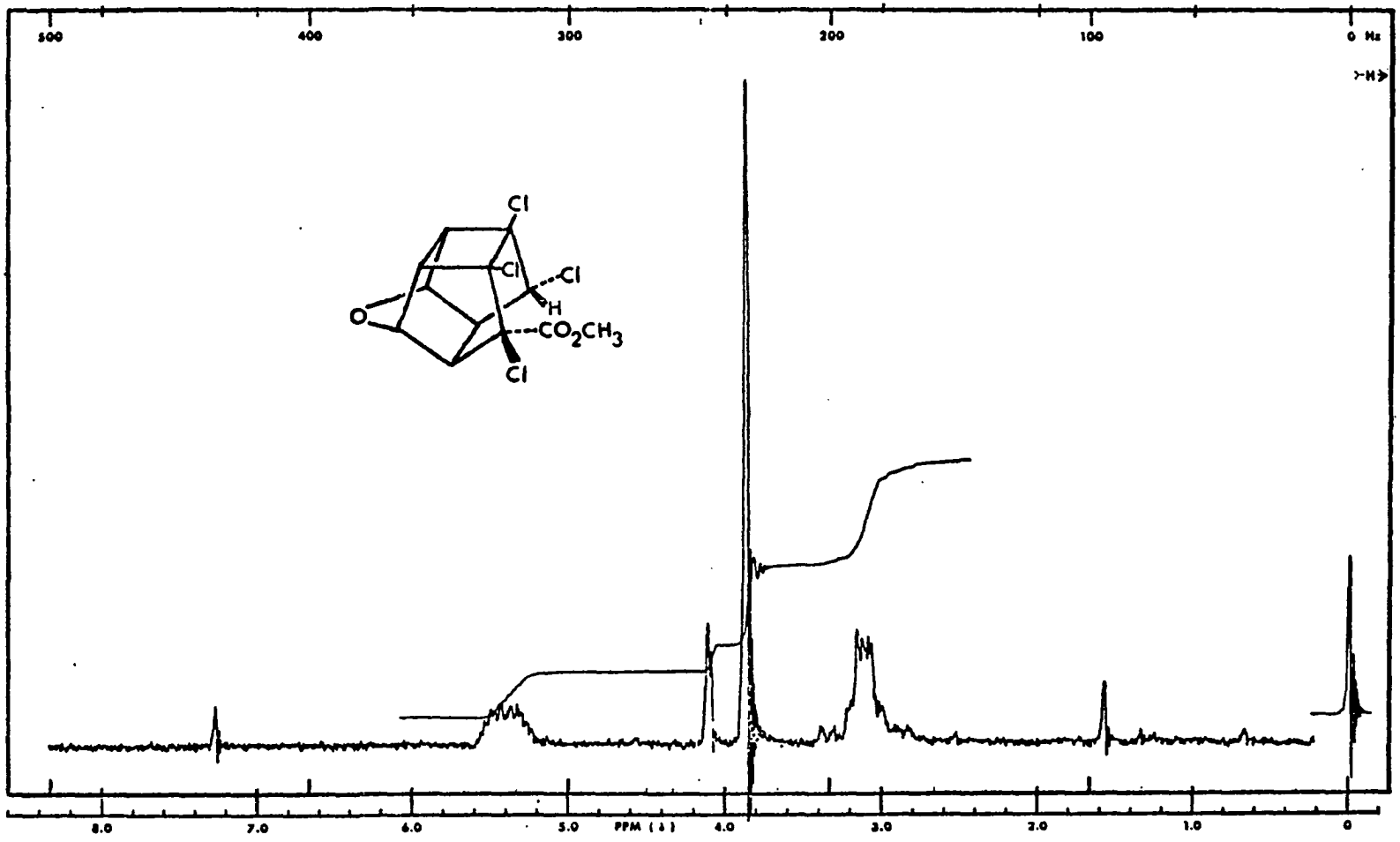


Figure 20b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 88b.

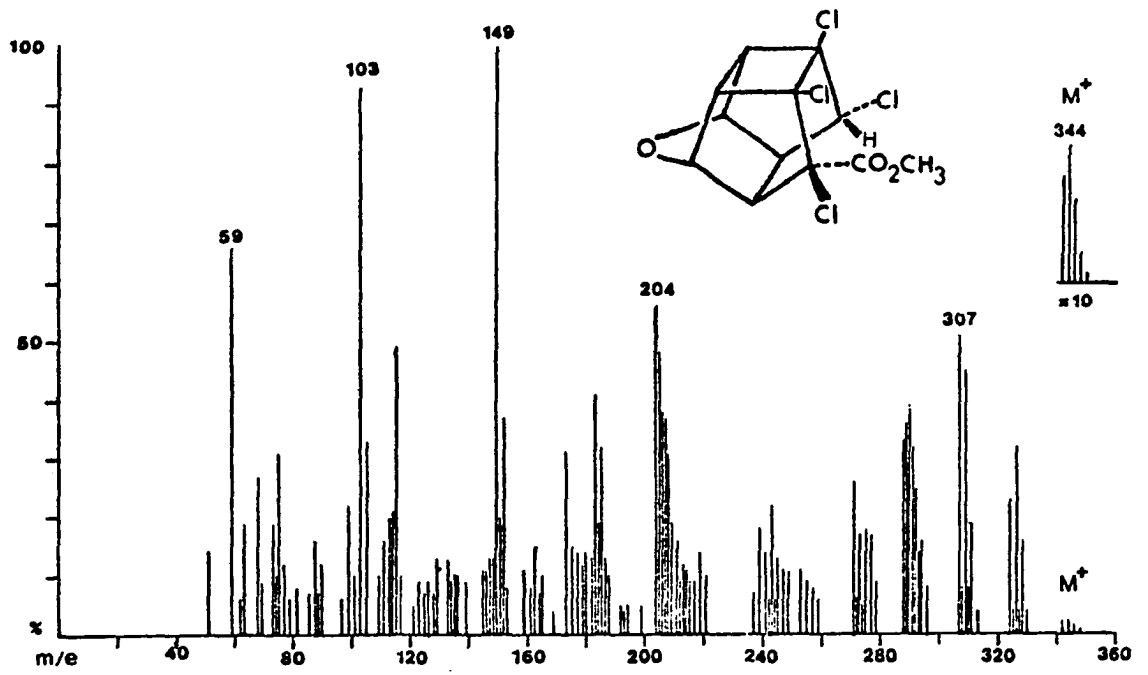


Figure 20c. Mass spectrum of 88b.

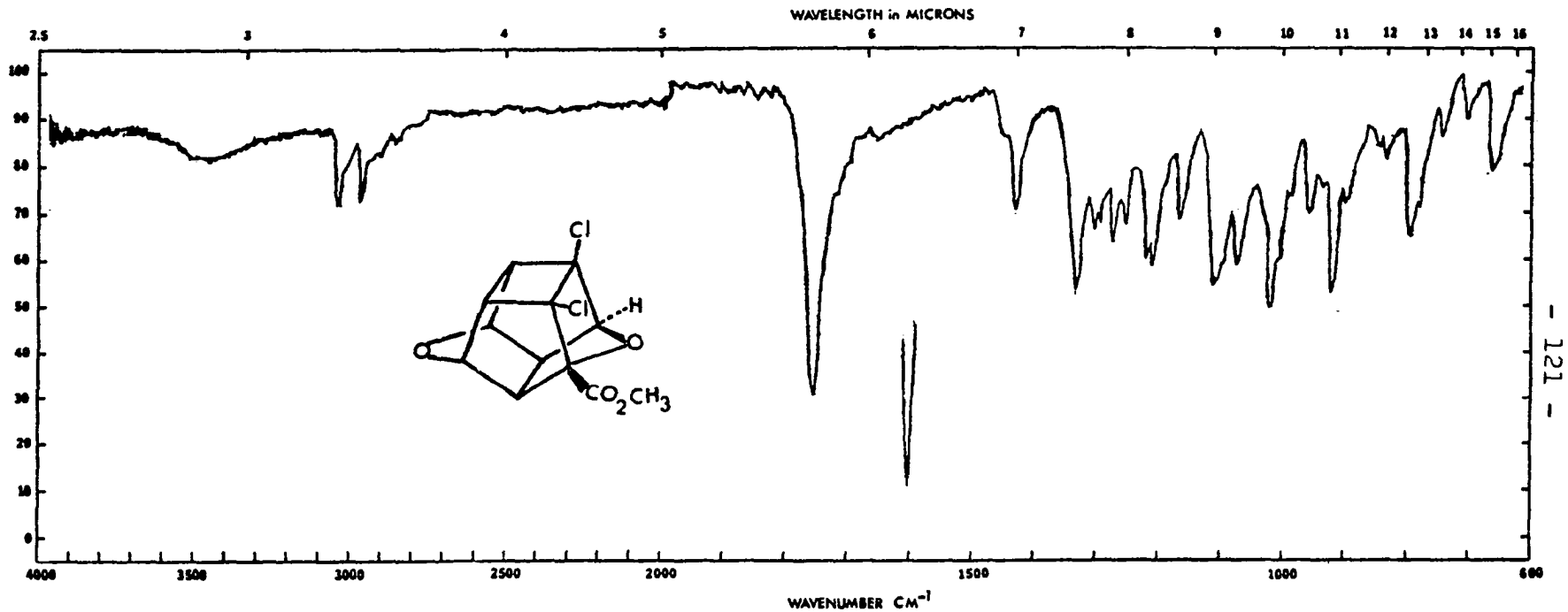


Figure 21a. Infrared spectrum (KBr) of 89b.

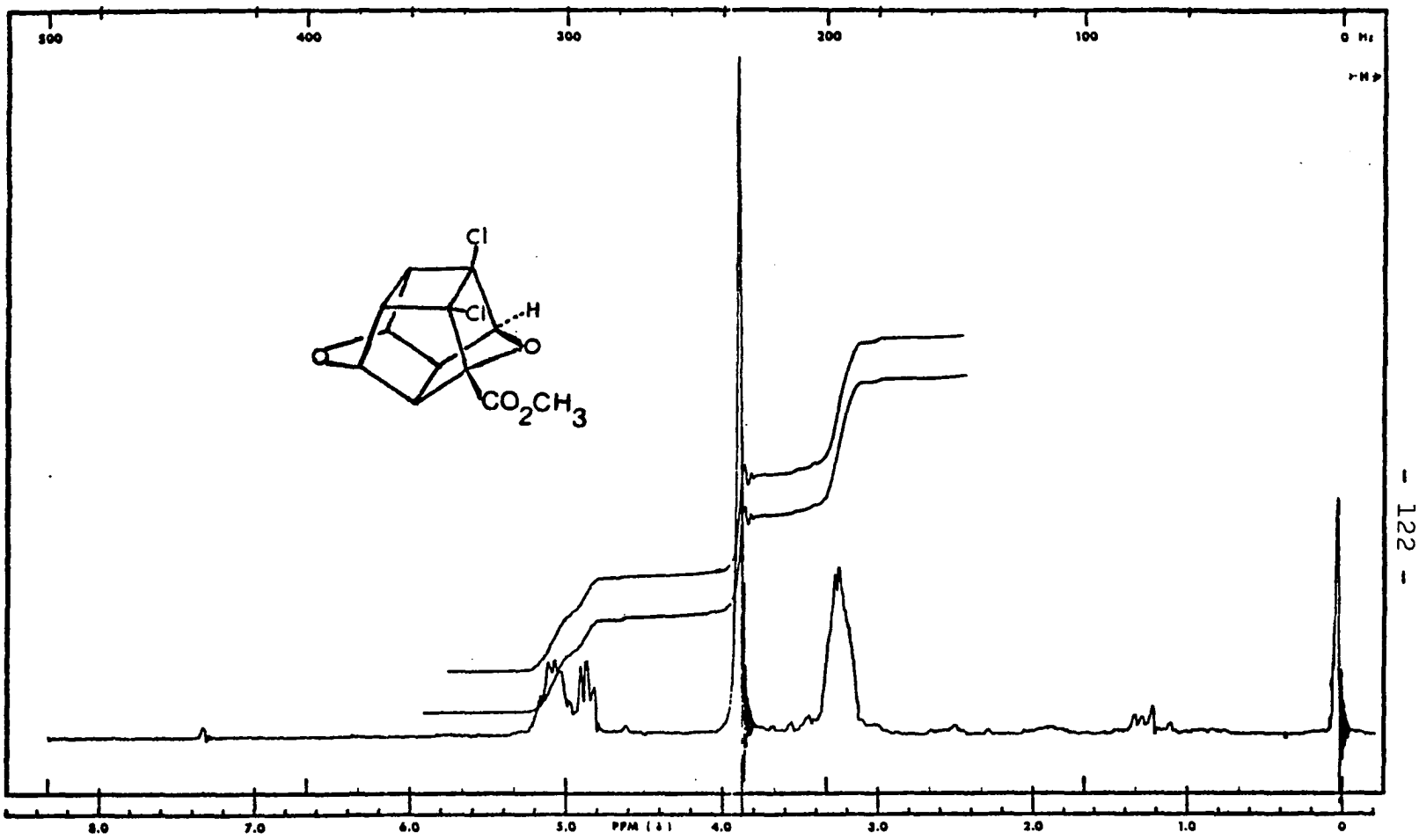


Figure 21b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 89b.

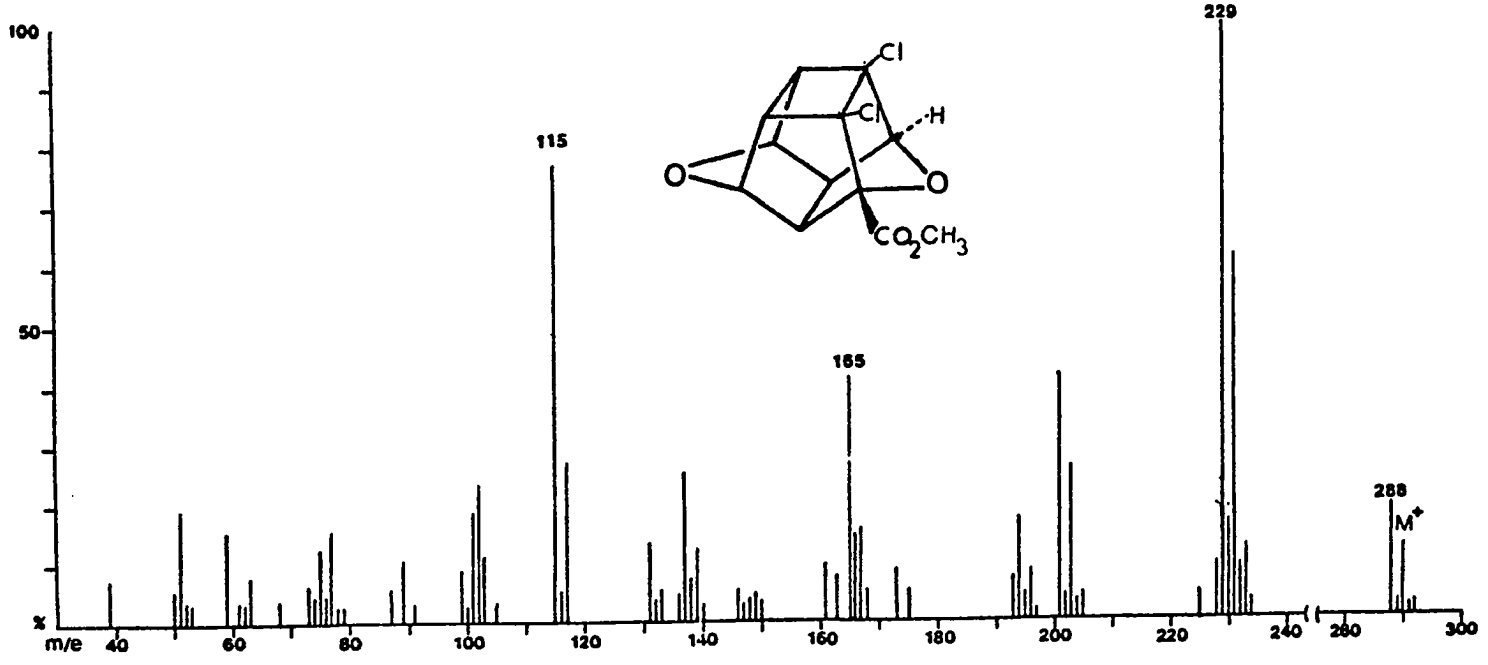
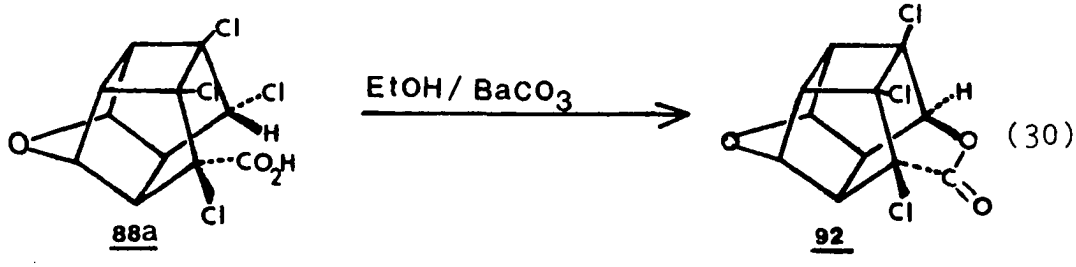


Figure 21c. Mass spectrum of 89b.

affords ring-opened anion 93, which undergoes an internal nucleophilic substitution to yield oxygen-bridged carboxylic acid 89a.

In support of the postulated mechanism (Scheme XI), two intermediates (88a and 92) have been separately synthesized and characterized. Compound 88a was prepared in the manner indicated in Scheme X. Lactone 92 was prepared in 78% yield by refluxing an ethanolic solution of 88a over solid barium carbonate for 44 hr (equation 30). In the



88a 92 (30)

absence of barium carbonate, 88a was not completely converted to lactone 92 after the same period of refluxing. The structure of 92 was assigned on the basis of its elemental analysis for molecular formula $C_{11}H_7Cl_3O_3$ and on the basis of the following spectral data: ir (KBr, Figure 22a) 1778 cm^{-1}; pmr (DMSO-d_6, Figure 22b) δ3.07-3.53 (m, 4H) and δ5.10-5.53 (m, 3H, α-oxy protons).

When subjected to the same experimental conditions by which ketone 86 was converted to 89a (i.e., refluxing 25% aqueous sodium hydroxide), both 88a (Scheme X) and 92 (equation 31) could be converted to 89a. These results

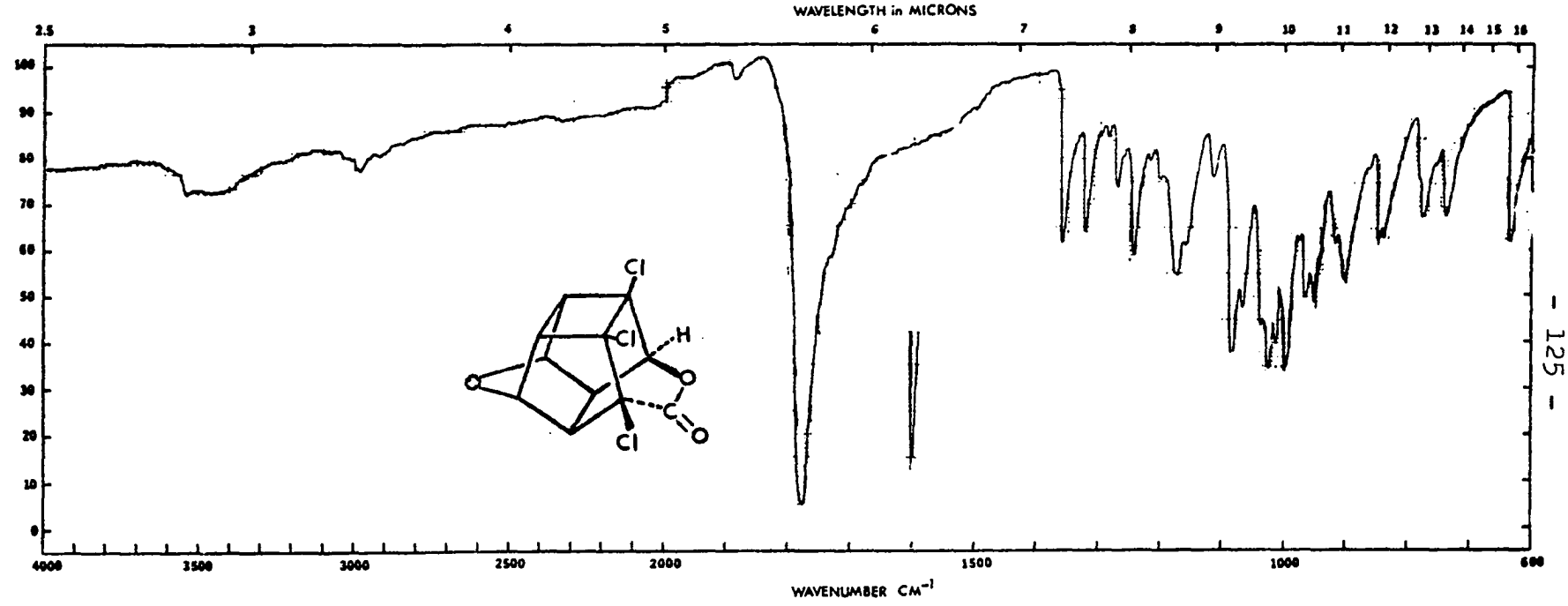


Figure 22a. Infrared spectrum (KBr) of 92.

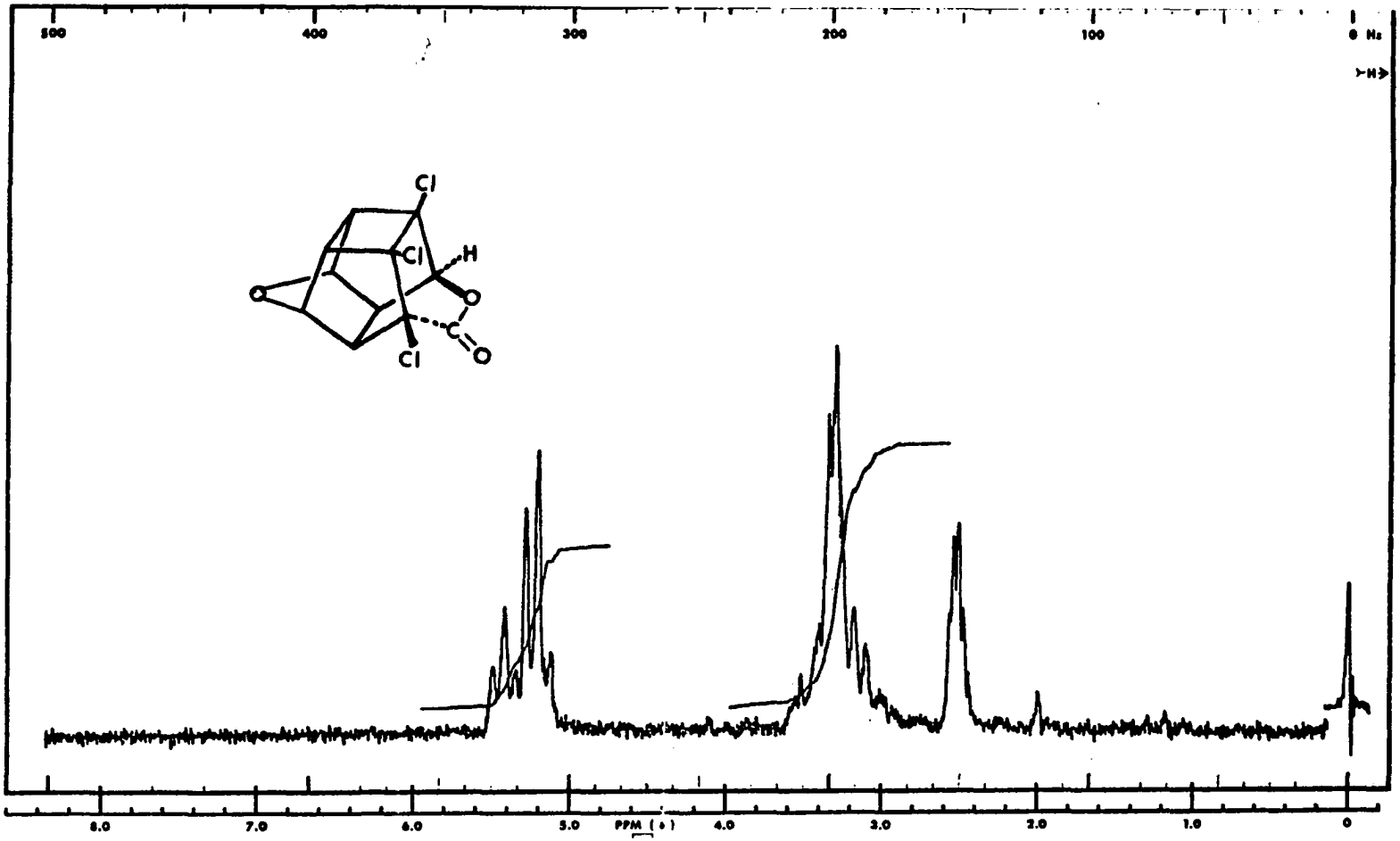


Figure 22b. Proton nmr spectrum (60MHz, DMSO-d_6 solvent, TMS internal standard) of 92.

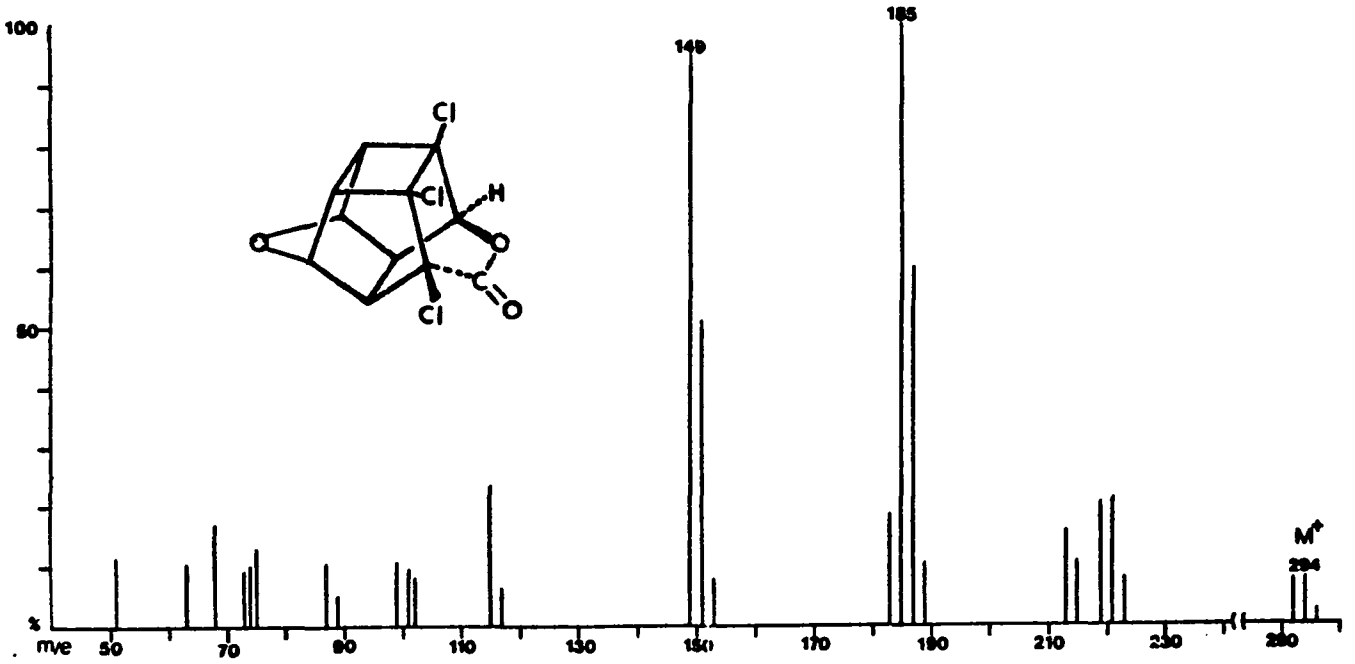
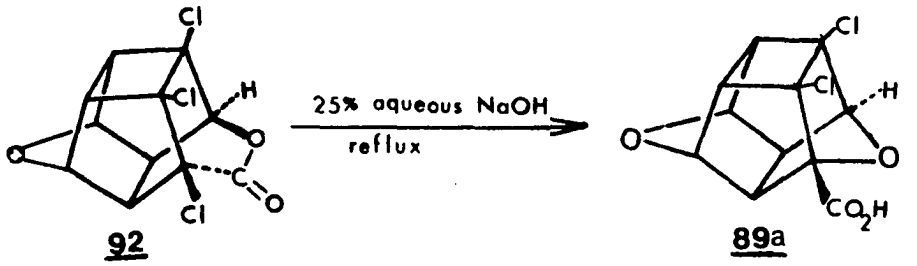


Figure 22c. Mass spectrum of 92.

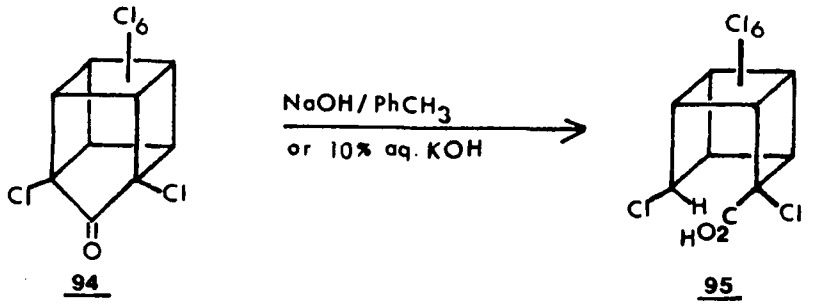


92 89a (31)

argue strongly for the involvement of intermediate 88a (or 91) and 92 in the mechanism illustrated in Scheme XI.

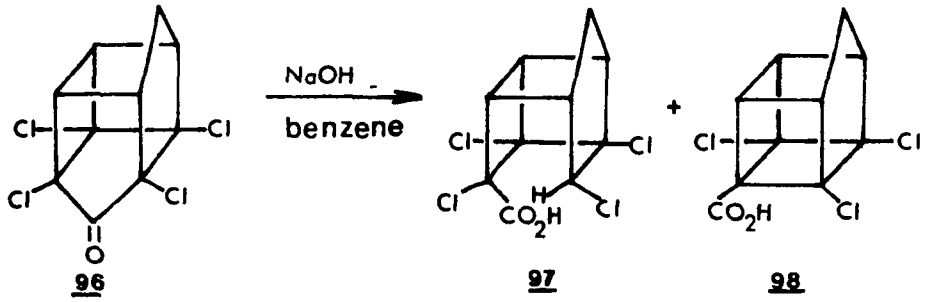
The reaction pathways for ketone 86 shown in Scheme X have not been observed previously in the reaction of ketone 46 with sodium hydroxide in refluxing toluene, (which was reported[31] to give only ring-contracted carboxylic acid 47, Table II). While this result is less readily rationalized in the light of results of the present study, it is apparent that changes in strain and steric factors due to the extra oxygen-bridge in ketone 86 must play a major role in determining what reaction pathways are open to the molecule.

Other workers have also described several products from the attempted semibenzilic acid rearrangement of polychlorinated ketones of cubane cage systems. Perchlorohomocubanone (94) was reported to give, stereospecifically, a ring-cleaved product 95 when treated with either 10% aqueous potassium hydroxide or with sodium hydroxide in toluene (equation 32).[30] The reaction of tetrachloro ketone 96 with sodium hydroxide in benzene was found to



94 95 (32)

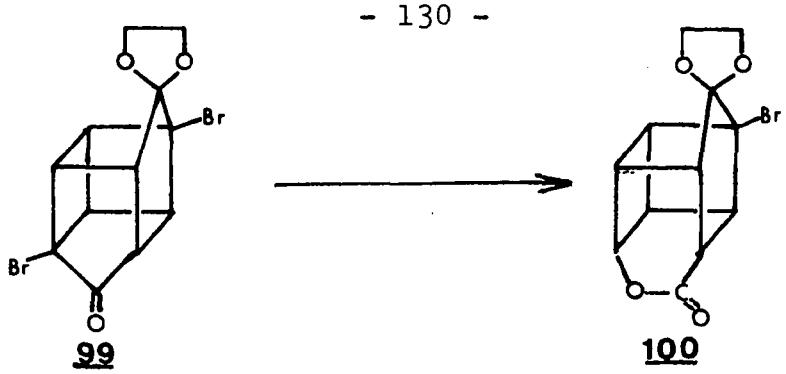
give a mixture of ring-cleaved product 97 and the ring-contracted product 98 in a ratio of 2 : 3; ring cleavage occured almost exclusively when 96 was treated with aqueous alkali (equation 33).[21] In none of these reactions did the



96 97 98 (33)

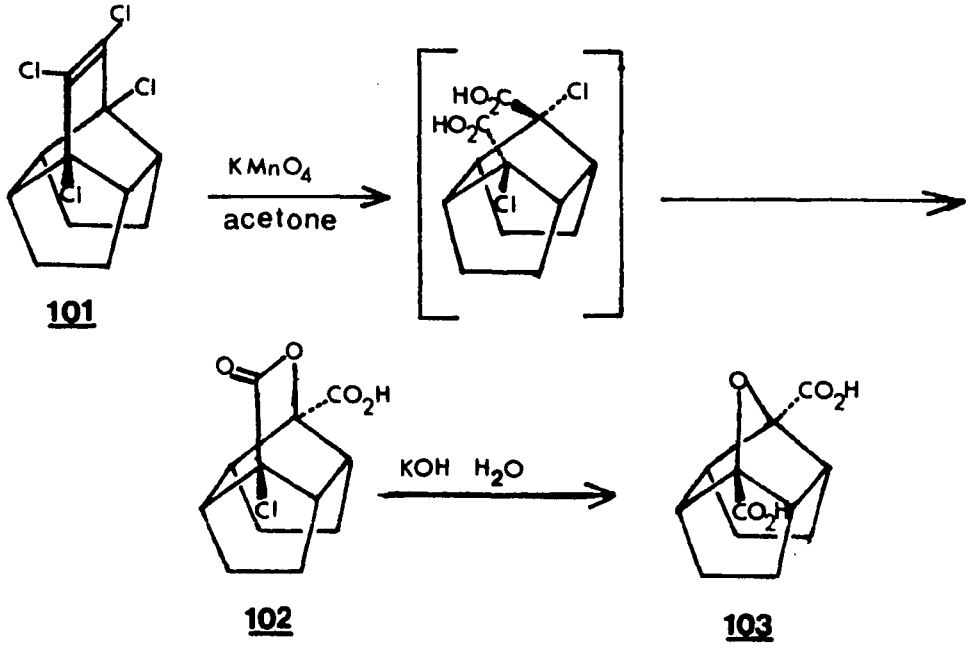
carboxylate anion group in the cleaved product displace chloride ion to yield chloro-lactone (and, ultimately, the oxygen-bridged carboxylic acid, resembling the conversion 91⟶92⟶89a illustrated in Scheme XI).

The formation of lactone 92 is not without precedent; a similar intramolecular displacement to form lactone 100 has been observed in the attempted ring contraction of bromo-ketone 99 in dimethyl sulfoxide (equation 34).[92] Also, the similar intramolecular displacement of halogen has been observed in the oxidation of tetrachloro-olefin 101 with potassium permaganate in refluxing acetone to



99 100 (34)

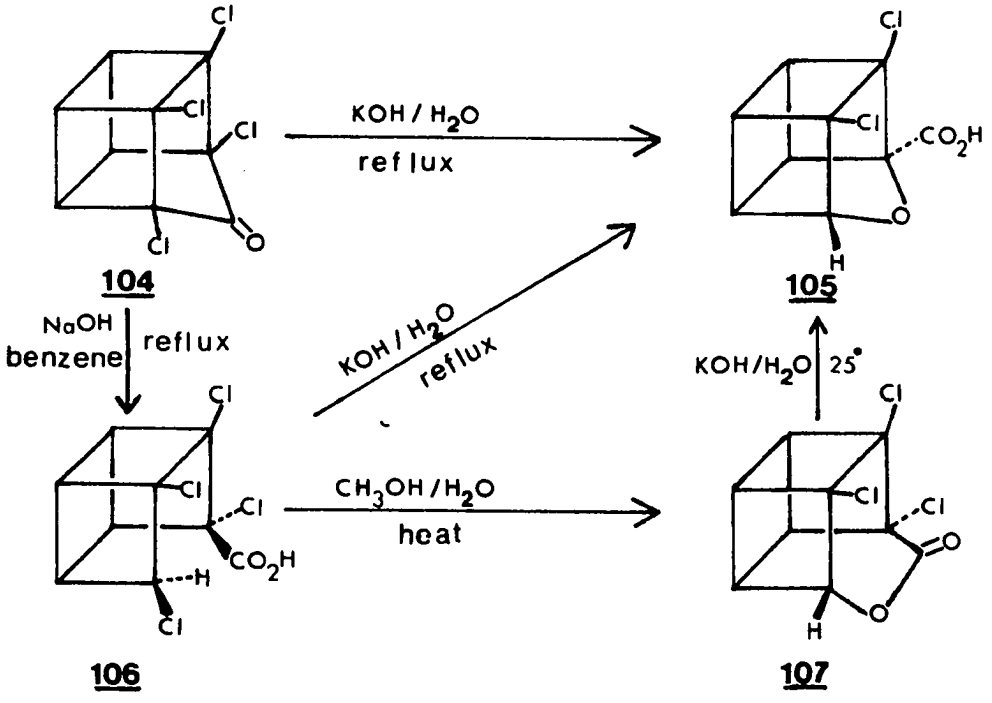
produce 102. Upon heating with aqueous potassium hydroxide, 102 was converted to an oxygen-bridged dicarboxylic acid 103 (equation 35),[93] in the manner analogous to the conversion of chloro-lactone 92 to 89a shown in Scheme XI.



101 102 103 (35)

Most recently, the analogous reaction pathways for ketone 86 illustrated in Scheme X have been observed in the base-promoted rearrangement of 1,2,3,4-tetrachloro[4.3.0.$0^{2,5}.0^{3,8}.0^{4,7}$]nonan-9-one (104), as outlined in Scheme XII.[91] Treatment of 104 with aqueous base afforded the

SCHEME XII

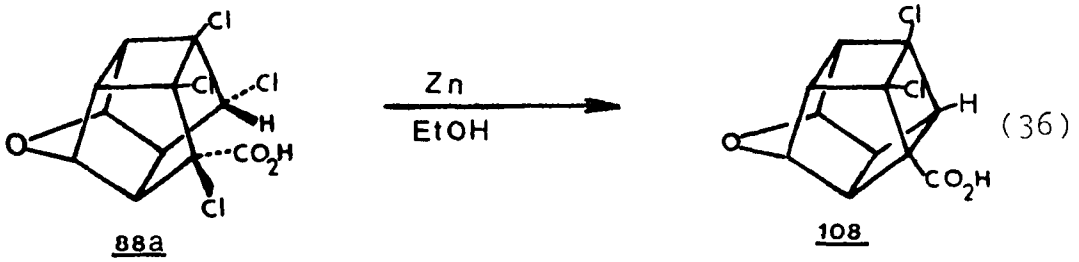


oxahomocubane acid 105, while treatment of 104 with sodium hydroxide in benzene gave tetrachlorosecocubanecarboxylic 106. That conversion of 104 to 105 proceeds through 106 via a sequence of intramolecular displacements was shown by the isolation of intermediate 107.

The formation of ring-cleaved and rearranged products instead of the normal ring-contracted products in these reactions can be attributed to a combination of factors due to ring strain, steric interaction, and to the added stability of the chlorocarbanion intermediates. Apparently, the preferences for different reaction pathways observed for ketones 94 and 104 (equation 32 and Scheme XII)

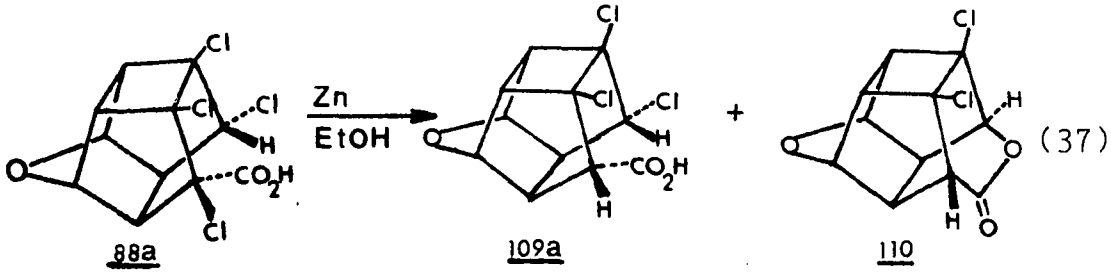
must be due to the presence of the four additional chlorines in 94 which stabilize the carbanion intermediate derived from 94 sufficiently to prevent it from reacting further in the manner observed for 104. In case of ketones 96 and 104 (as well as 46 and 86) each of which bears only four chlorine substituents, the different reaction pathways observed among them are most likely the results of differences in ring strain and differences in the degree of steric interactions between the crowded endo substituents in the ring-opened intermediates. Apparently, steric strain is less severe in the ring-opened intermediate derived from 96 (and 46) than it is in the ring-opened intermediates derived from 104 (and 86). In both the formation of lactone 107 (and 92) and its conversion to acid 105 (and 89a) steric strain can be relieved by closure of that intermediate to afford cyclized product.

In a continued effort to search for methods which would permit the synthesis of oxahomopentaprismane (52), carboxylic acid 88a was taken as a starting compound. We first attempted to dehalogenate 88a with zinc metal in refluxing ethanol in the hope that a Wurtz-type coupling reaction would produce an oxahomopentaprismane derivative 108 (equation 36). This reaction was also employed by Underwood and Ramamoorthy to synthesize homopentaprismane from dibromide 74 (equation 20). However, when an ethanolic



88a 108 (36)

solution of 88a was refluxed with zinc dust for 44 hr, the reaction produced one acidic and one neutral compound in 84.8% and 13% yield, respectively (equation 37). The acidic



88a 109a 110 (37)

compound was not the desired carboxylic acid 108. It was instead identified as being acid 109a on the basis of spectral data of 109a and of its corresponding methyl ester 109b. The mass spectra of both 109a and 109b (Figure 23c) displayed a molecular ion whose intensity profile required three chlorine substituents.[53] Ester 109b had a carbonyl absorption at 1730 cm^{-1} in the infrared spectrum (Figure 23a), and its pmr spectrum (Figure 23b) was similar to that of 88b with the exception of an additional one-proton absorption appearing, together with the methine protons, at δ 3.0 for the proton geminal to the carbomethoxy group in 109b. The neutral compound was assigned the lactone

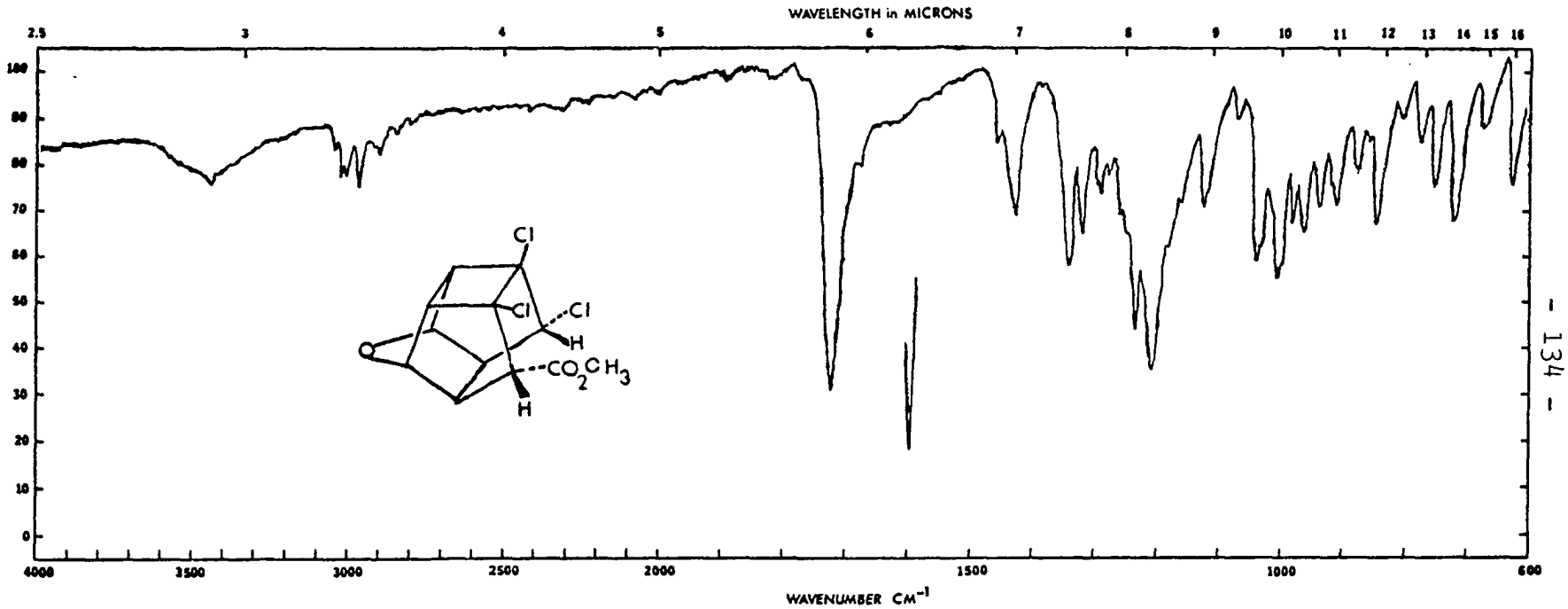


Figure 23a. Infrared sepctrum (KBr) of 109b.

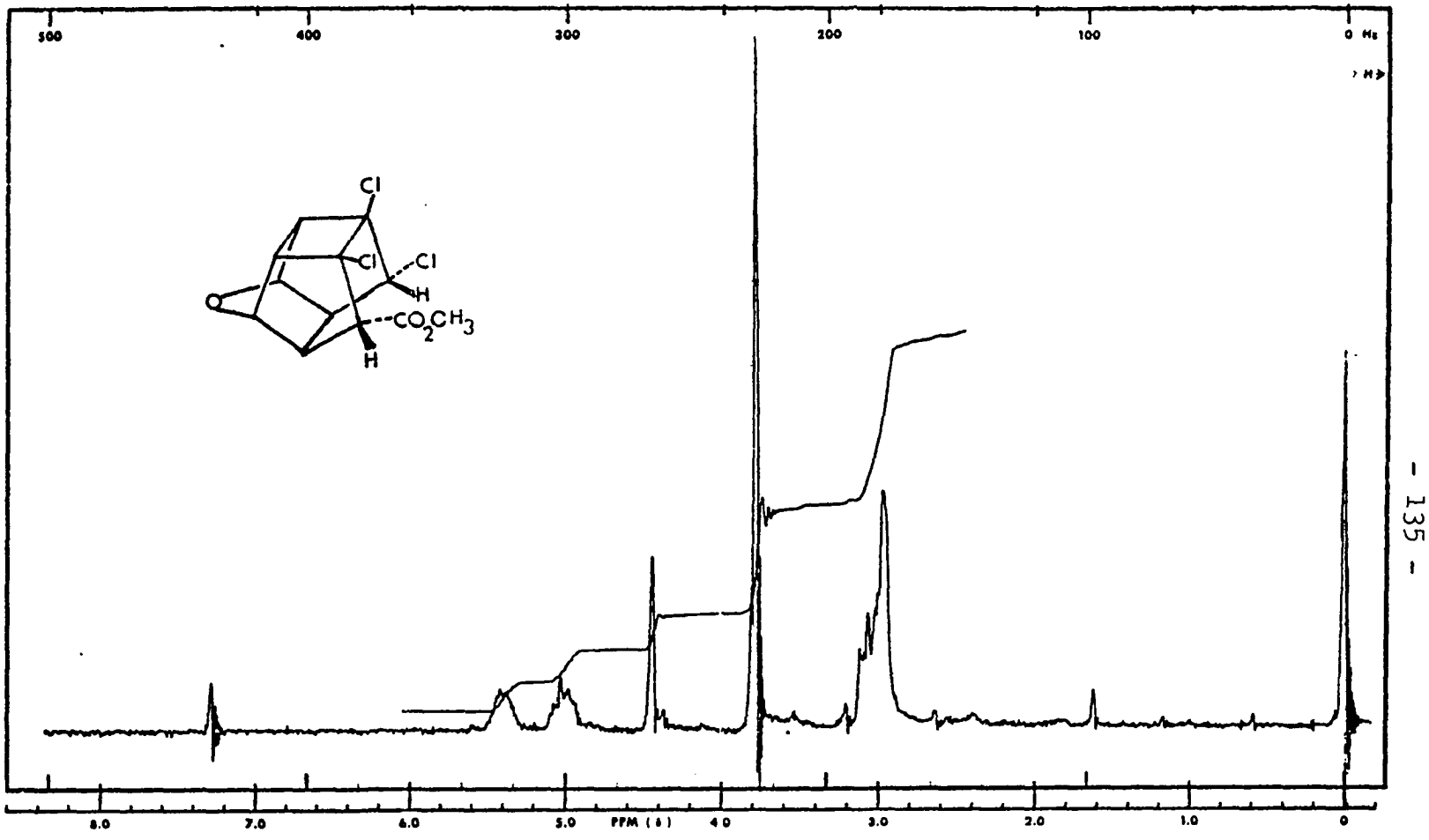


Figure 23b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 109b.

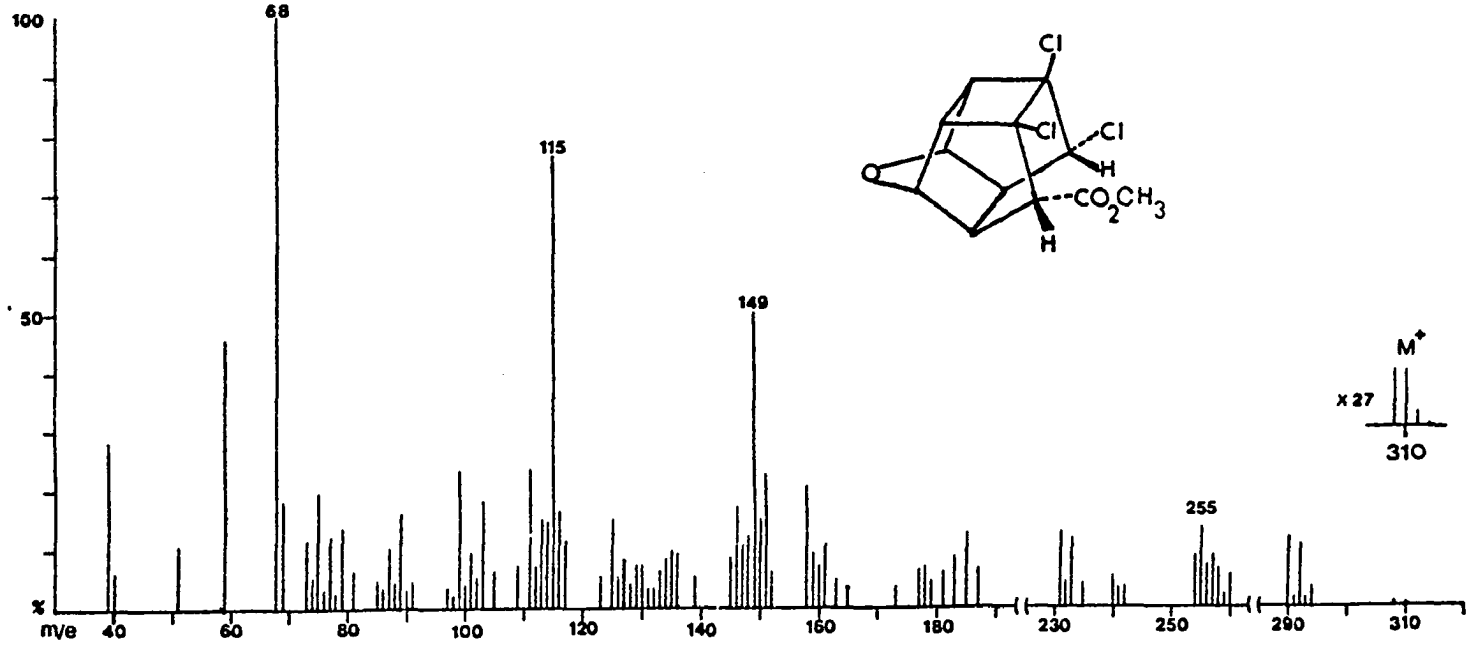
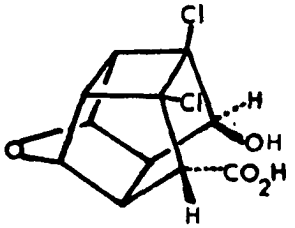


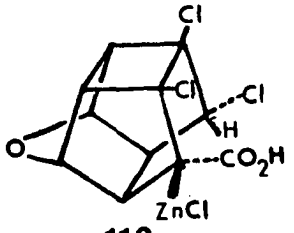
Figure 23c. Mass spectrum of 109b.

structure 110 on the basis of its elemental analysis for molecular formula $C_{11}H_8O_3Cl_2$ and on the basis of the following spectral data: ir (KBr, Figure 24a) 1768 cm^{-1}; pmr ($CDCl_3$, Figure 24b) δ2.8-3.3 (m, 5H) and δ4.8-5.3 (m, 3H), resembling that of lactone 92 which had multiplets at δ3.07-3.53 and δ5.10-5.53 (integration ratio 4 : 3).

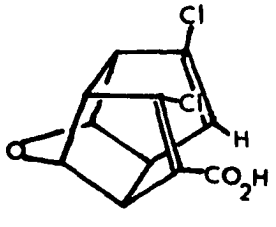
The formation of lactone 110 must arise from 109a via an intramolecular displacement of chloride ion by the carboxyl group (as discussed earlier). Lactone 110 is not able to undergo another internal displacement analogous to the conversion 92⟶89a (equation 31) because of the absence of a leaving group geminal to the carbonyl group. No hydrolyzed product 111 was observed in this reaction, suggesting the operation of a severe steric interaction between the endo hydroxyl and carboxyl groups in 111. This steric strain is relieved by closure to the cyclic product, 110. The formation of acid 109a could result from hydrolysis of 112 generated from the reaction of α-chloroacid 88a with zinc metal. Apparently, the presence of a geminal carboxyl group stabilizes 112 and prevents further reaction leading



111



112



113

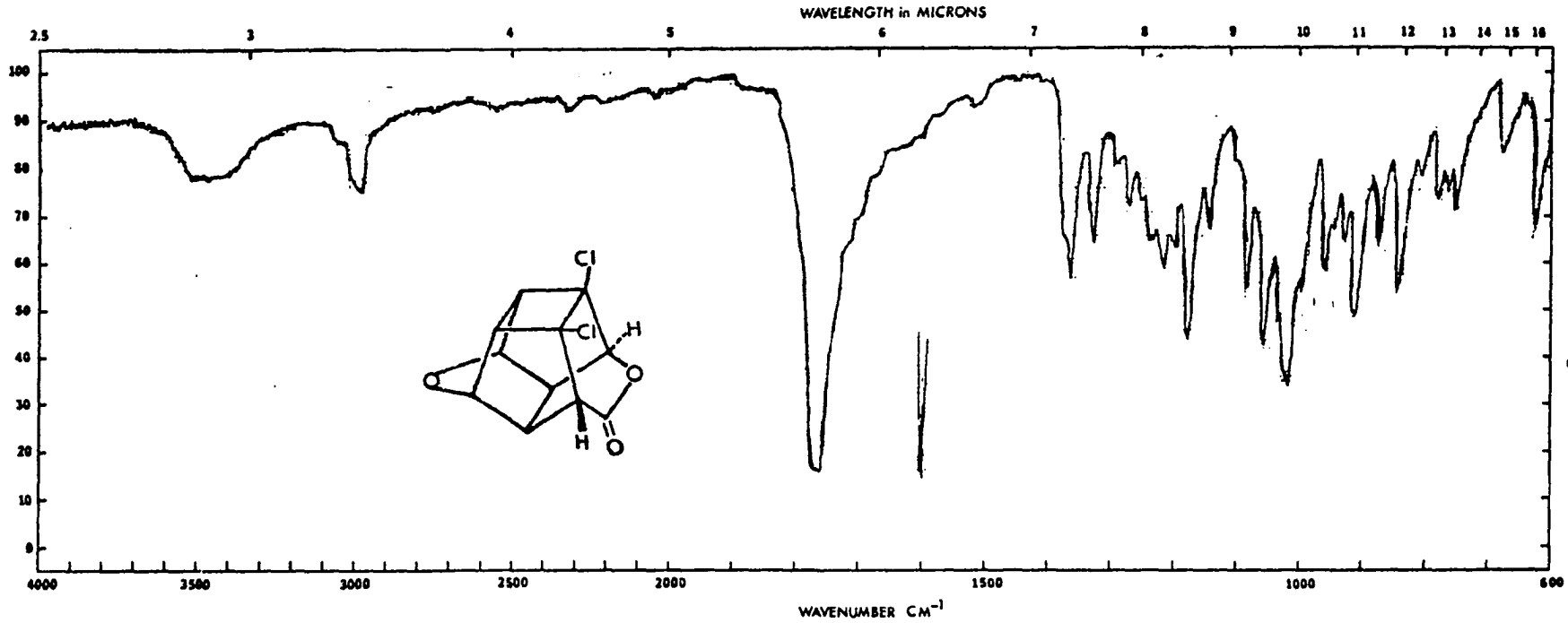


Figure 24a. Infrared spectrum (KBr) of 110.

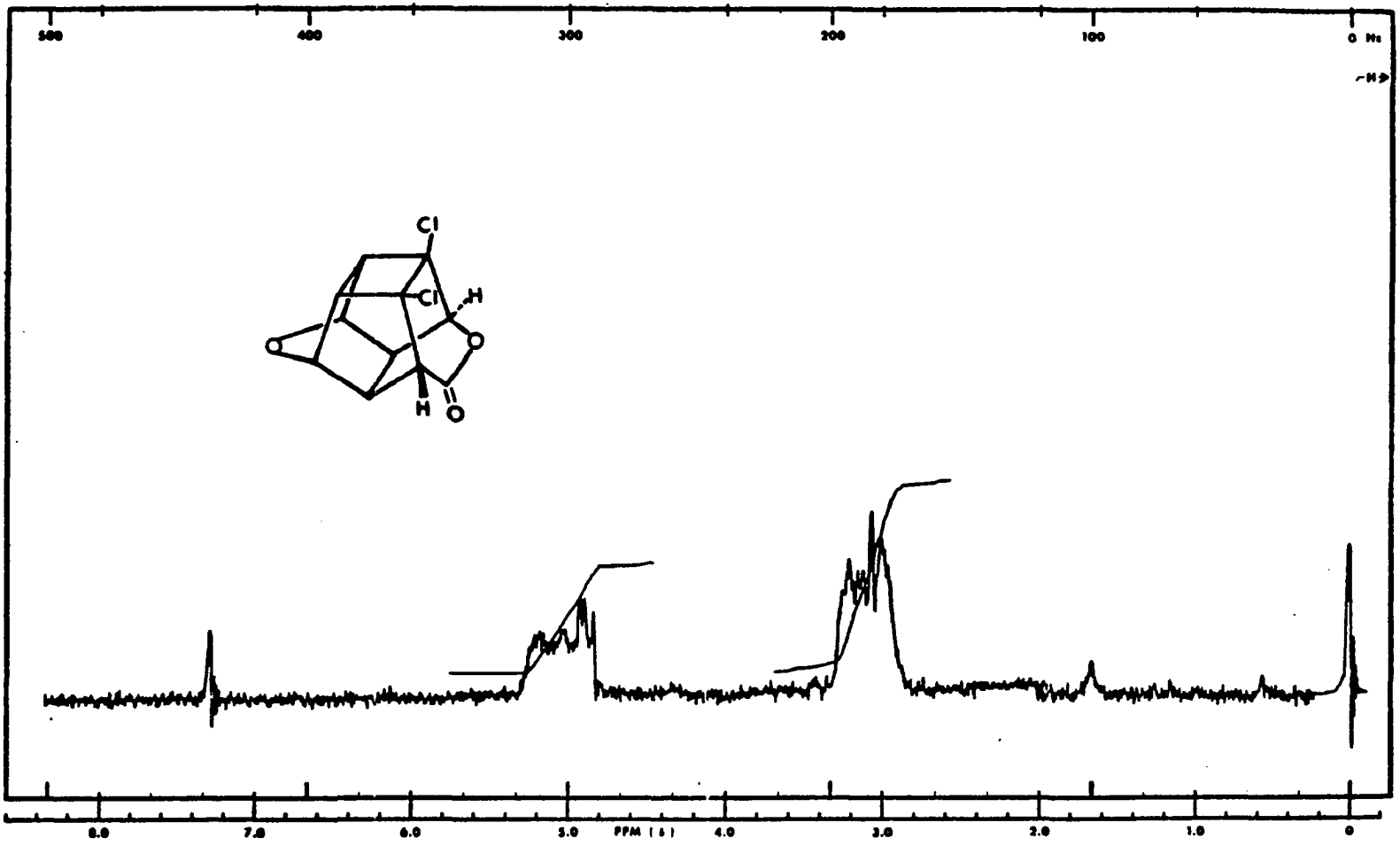


Figure 24b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 110.

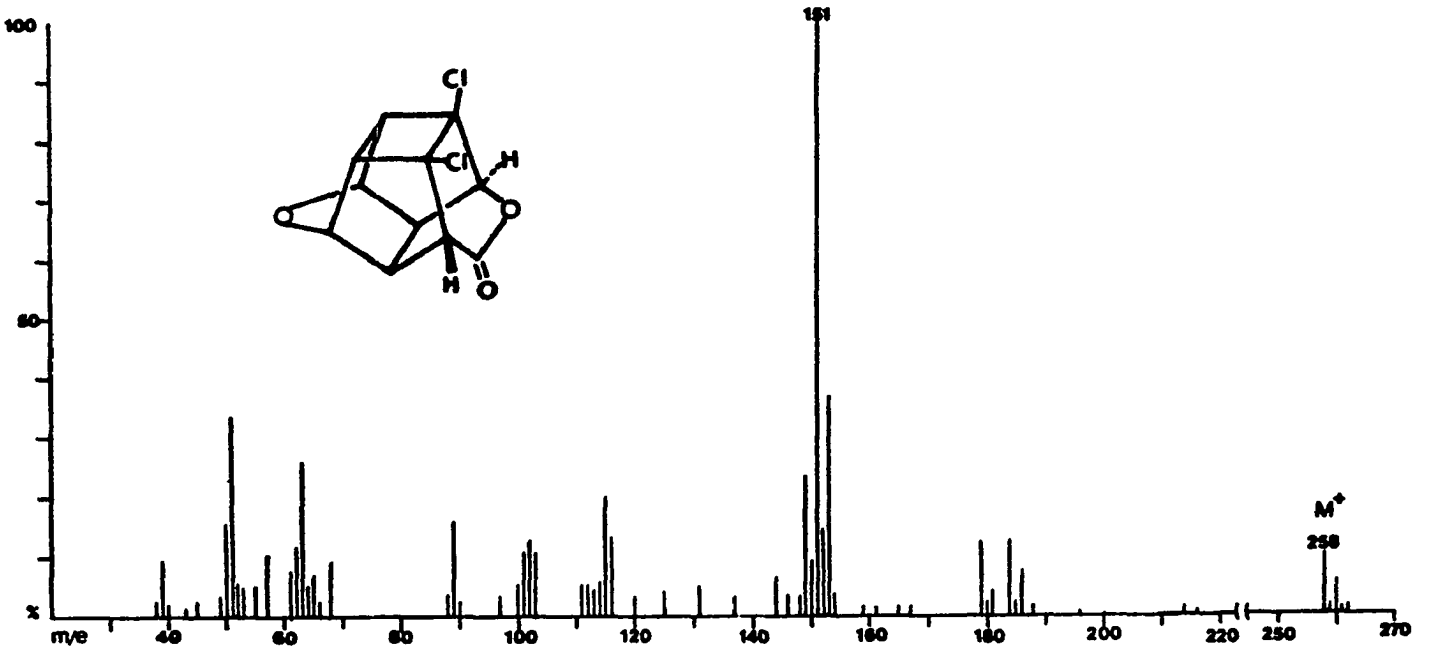
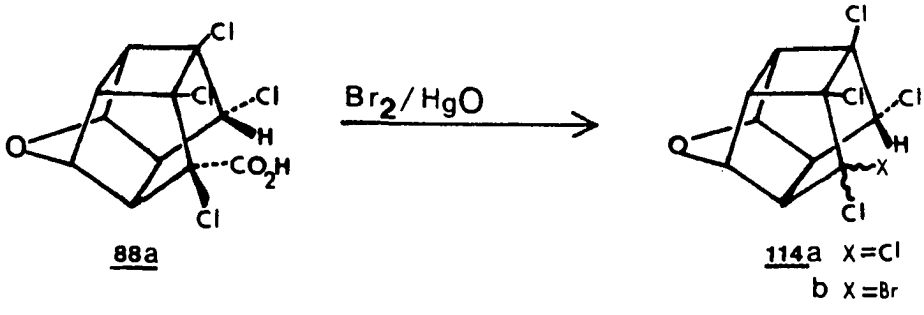


Figure 24c. Mass spectrum of 110.

to the formation of diene 113 via 1,4-elimination of chlorine. Such a process has been frequently encountered in analogous cage compounds.[94]

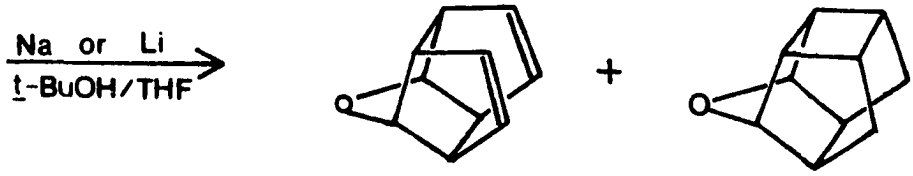
In view of the successful synthesis of homopentaprismane (53) via the photocyclization of diene 80 (equation 29), the corresponding oxa-diene 115 was prepared following the reaction sequence illustrated in equation 38. The



88a

114a X=Cl
b X=Br

(38)



115 116

Cristol-Firth modification of the Hunsdiecker reaction[16] was employed for the decarboxylative halogenation of acid 88a. The attempts of this reaction using purified bromoform as solvent afforded 114b in low yields due to the formation of an intractable tarry product. However, when carbon tetrachloride was used as solvent,[95] the reaction proceeded smoothly to give the desired product 114 in good yield.

Subsequent dehalogenation of 114 with lithium metal and tert-butyl alcohol in tetrahydrofuran[17] afforded a mixture of products which was shown by vpc analysis to consist of oxa-diene 115 (46%), a saturated compound 116 (38%), and three unidentified products.

Modified Hunsdiecker reaction of carboxylic acids in carbon tetrachloride have been shown to afford both the decarboxylative bromination and chlorination products,[96-99] and, in some cases, the latter predominate.[96] In the present study, the formation of a mixture of products 114a and 114b was suggested by the observations that the bromine color persisted during the entire course of reaction and the melting point of 114 remained broad after several recrystallizations from hexane. Consequently, no further attempts were made to obtain an analytical sample of 114. The assigned structure 114 was gained from the spectral data and the isolation of the corresponding dehalogenated compound 116 from the lithium reduction of 114 (equation 38).

The infrared spectrum of 114 (Figure 25a) displays no absorption between 1350-3000 cm^{-1}. The pmr spectrum (Figure 25b) exhibits only two complex multiplets at δ2.8-3.6 (4H) and δ5.3-5.7 (3H). The downfield multiplet contains a doublet (J=ca. 2 Hz) at δ5.32 which is assigned to the endo proton alpha to the chlorine substituent in 114. This endo proton appears at much lower field than the corre-

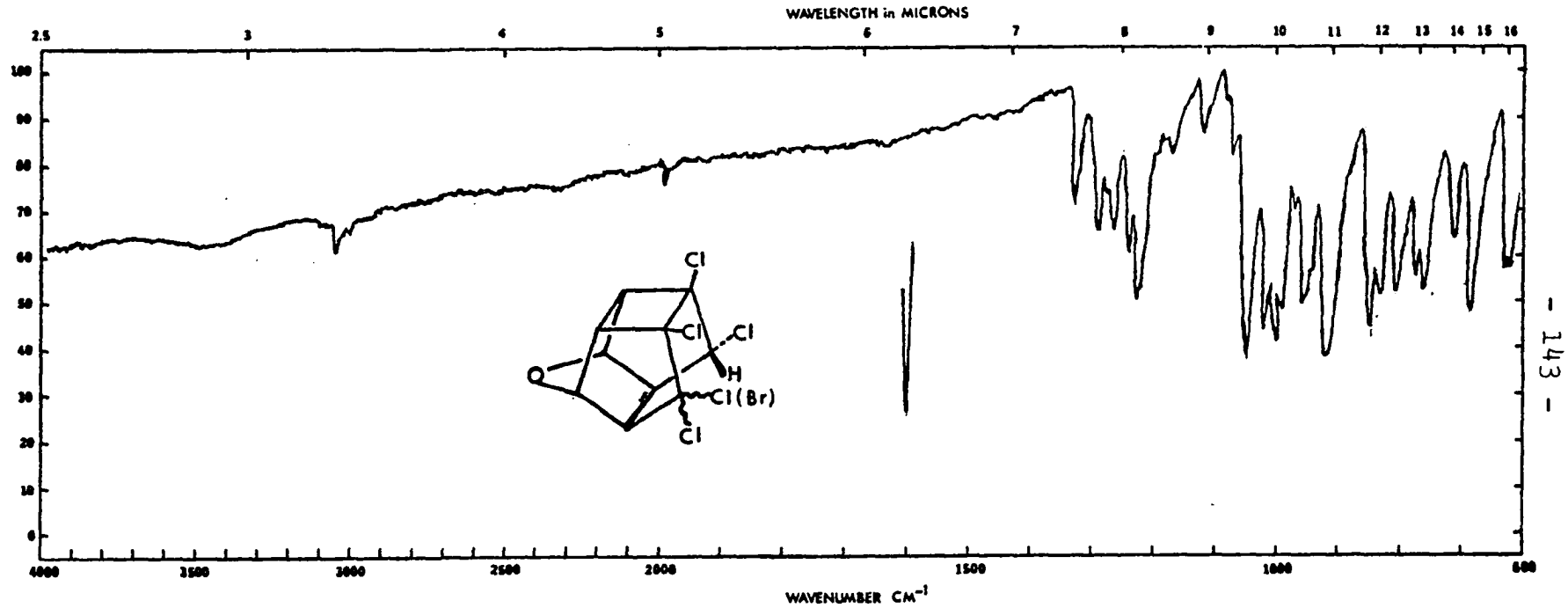


Figure 25a. Infrared spectrum (KBr) of 114.

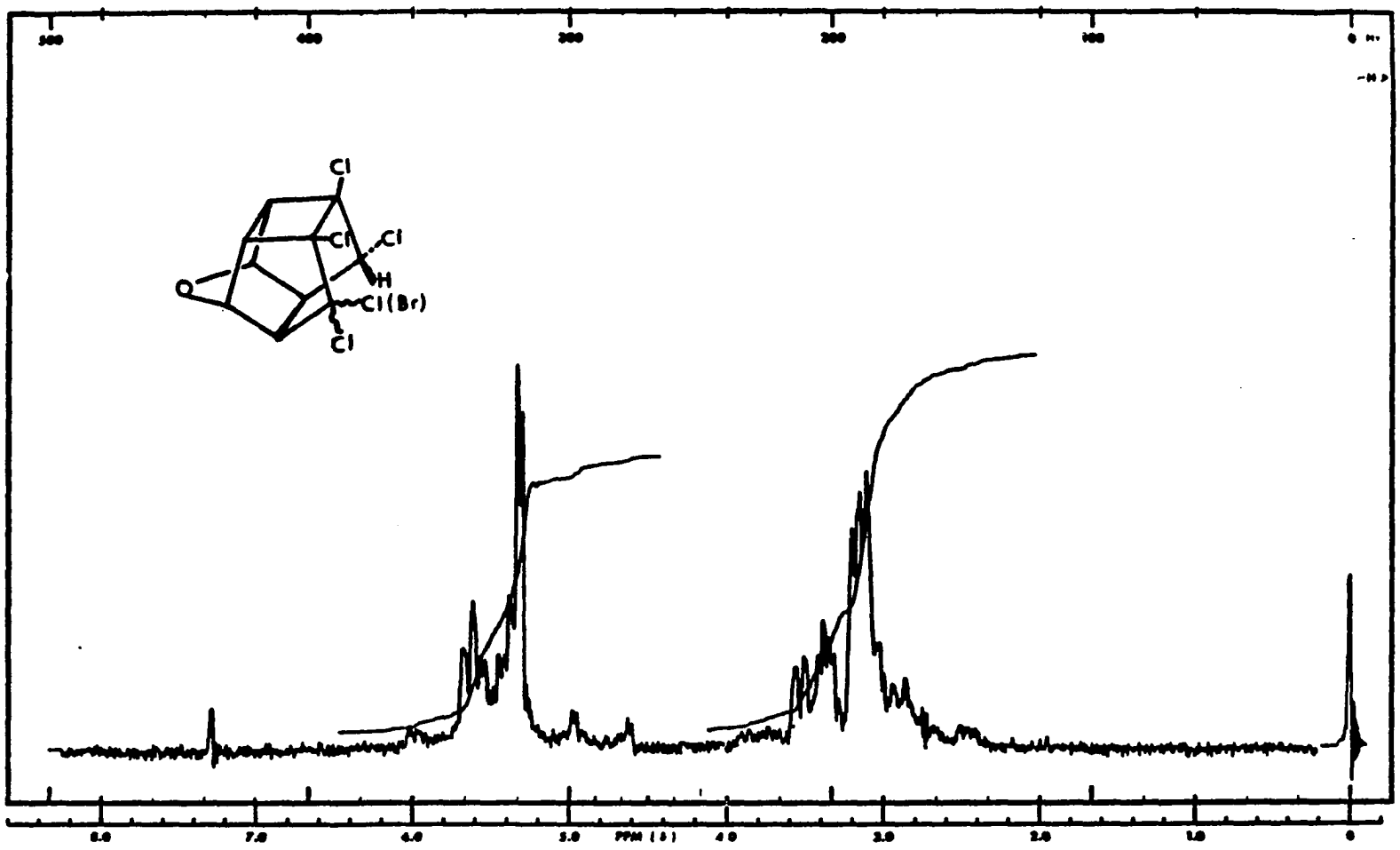


Figure 25b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 114.

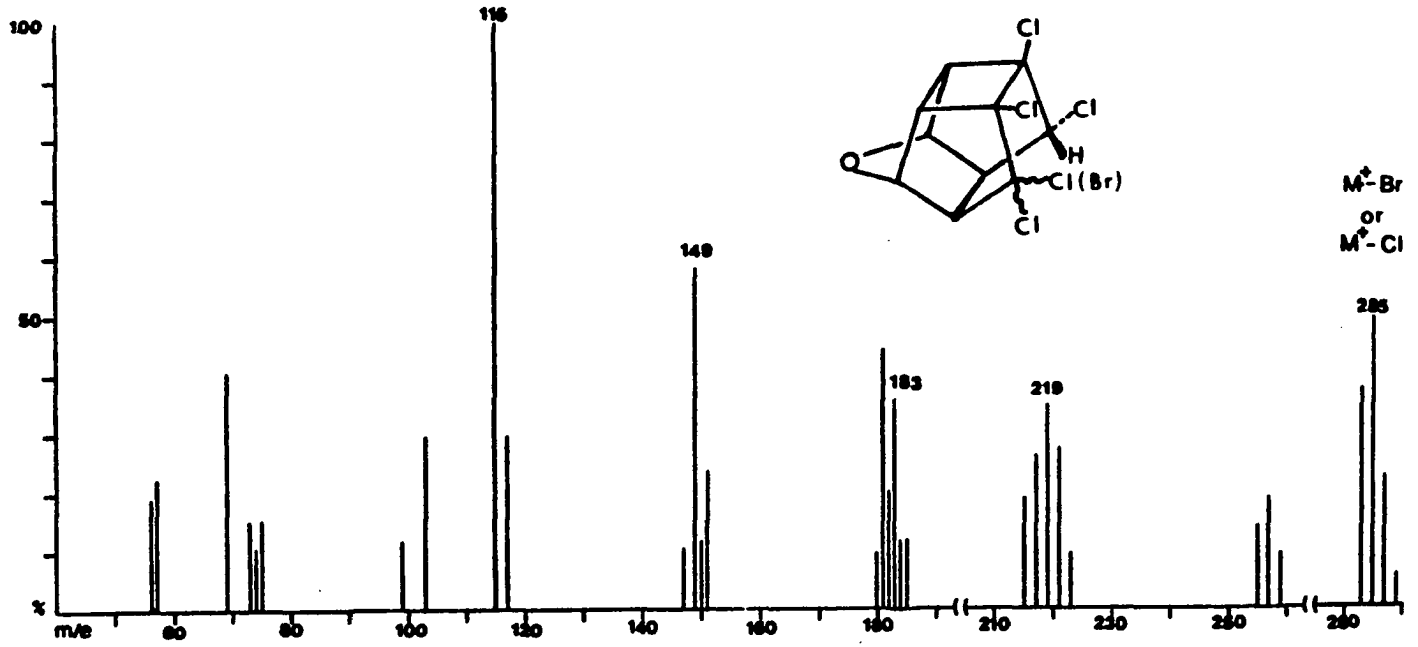
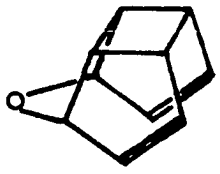


Figure 25c. Mass spectrum of 114.

sponding proton (at δ4.50) in acid 88a. The molecular ions corresponding to both 114a (X = Cl) and 114b (X = Br) were not observable in the mass spectrum of 114 (Figure 25c). The heaviest ion appeared at m/e 285 (with intensity profile characteristic of Cl_4 multiplet[53]) which could arise from the parent ion of 114a or 114b via loss of a chlorine or a bromine radical, respectively.

The structures of 115 and 116 follow unmistakably from analytical and spectral data. The infrared spectrum of oxa-diene 115 (Figure 26a) exhibits absorptions at 3050 (m) and 1575 cm^{-1} (w) suggesting the presence of the C = C double bond.[100] The pmr spectrum of 115 (Figure 26b) displays three signals at δ2.46 (broad singlet, 4H), δ5.41 (center of a quintet, J=ca. 3Hz, 2H), and δ5.88 (s, $W_{1/2}$= ca. 2Hz, 4H, olefinic protons). The simplicity of pmr spectrum eliminates the other possible structure 117 which



117

contains five pairs of chemically nonequivalent protons. This diene 115 is sensitive to air and gradually forms an insoluble material upon standing. The pmr spectrum of 116 (Figure 27b) shows the characteristic AB pattern at δ1.13

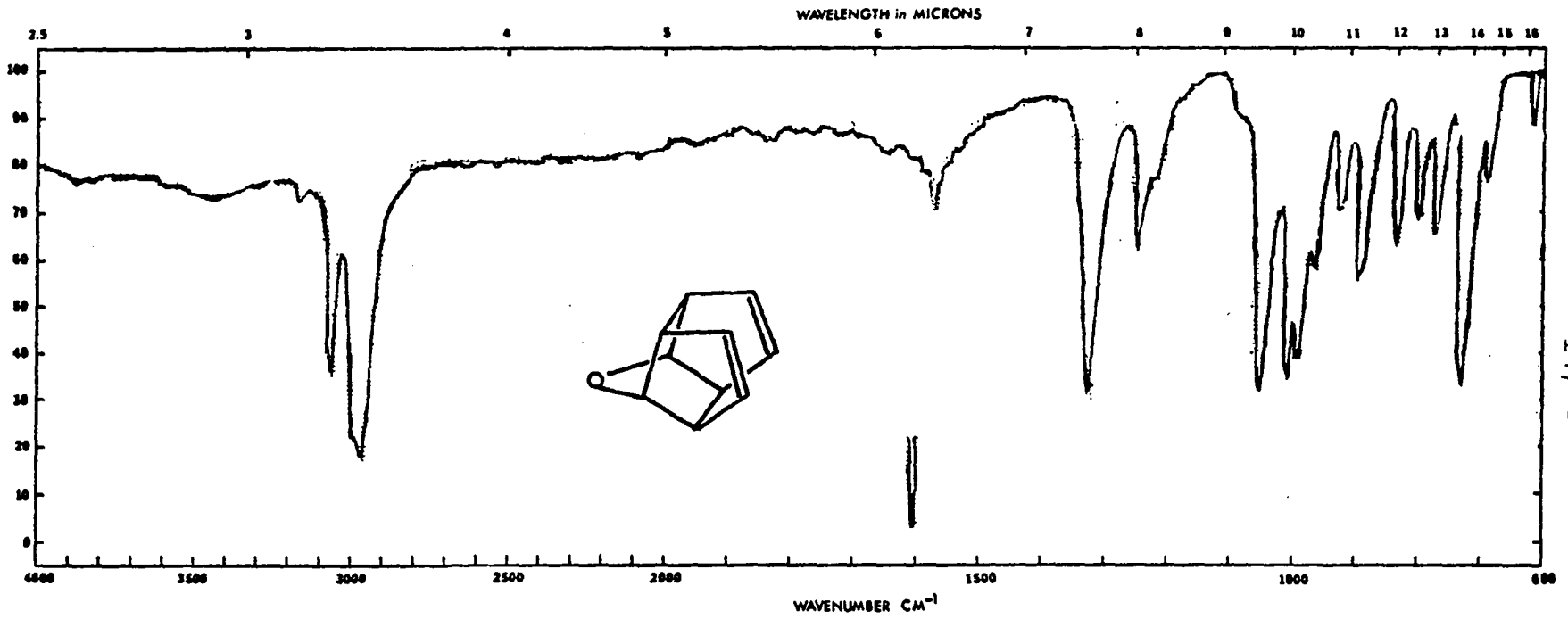


Figure 26a. Infrared spectrum (KBr) of 115.

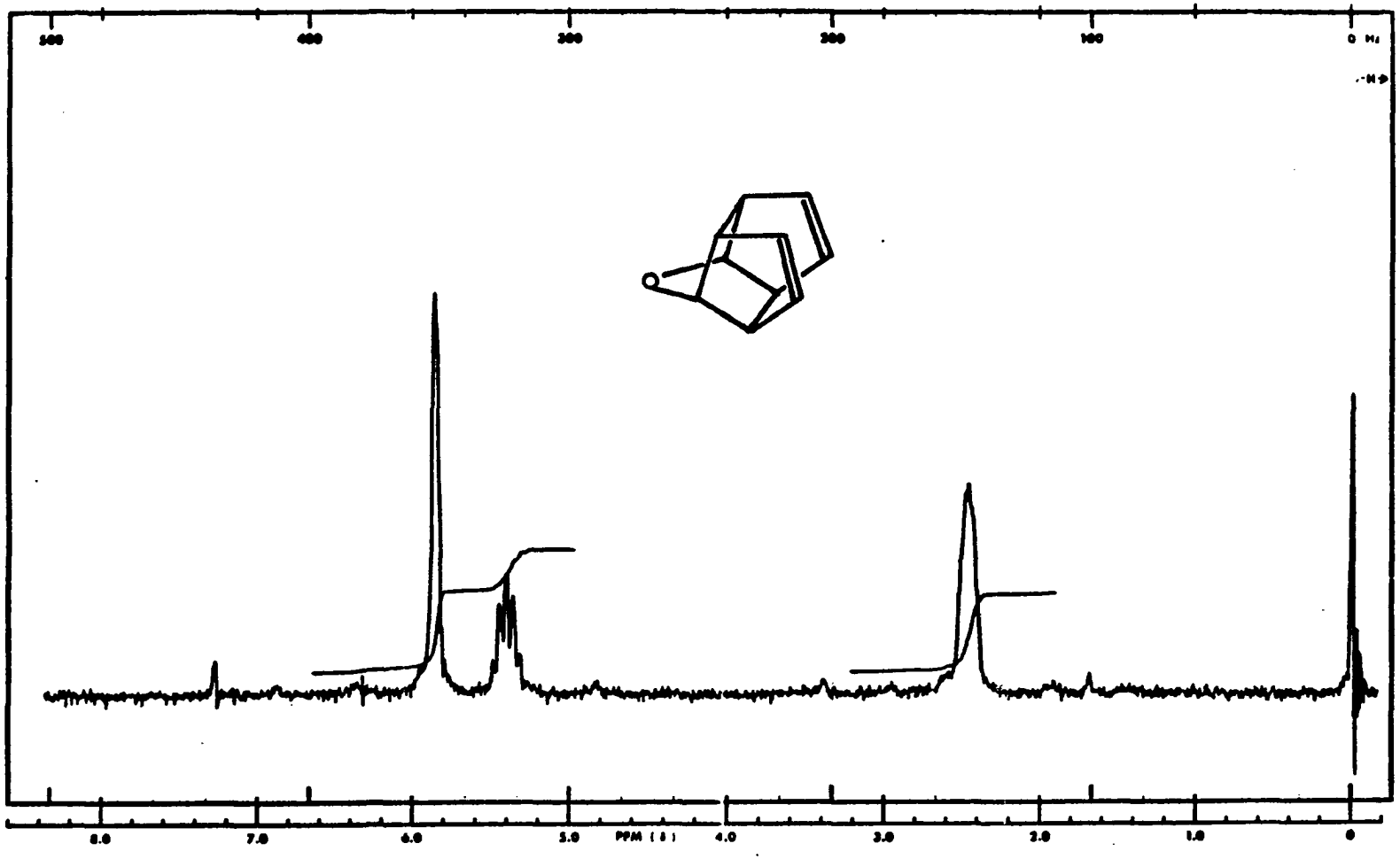


Figure 26b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 115.

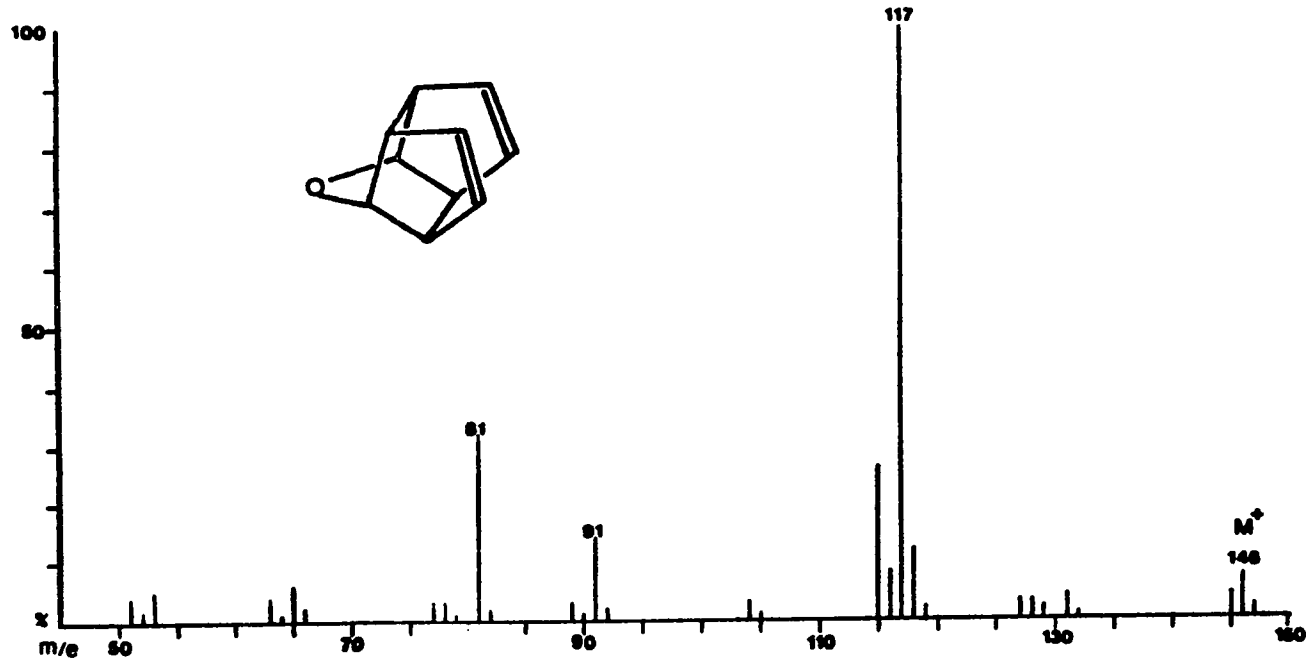


Figure 26c. Mass spectrum of 115.

(multiple doublet) and δ_B 1.50 (doublet) with coupling constant ca. 12 Hz, corresponding to the exo,exo and endo,endo methylene protons, respectively. The assignment of the downfield absorption pattern to the endo methylene proton in 116 is in accord with results found for other cage and half-cage compounds; this downfield shift has been attributed to steric compression.[101] In addition, the lack of complex splitting observed for the endo proton is consistent with previous observations in other cage compounds.[90]

Photocyclization of oxa-diene 115 to oxahomopentaprismane (52) could not be effected. We have attempted the photolysis of 115 under various conditions as follows: acetone (solvent and sensitizer), low-pressure mercury lamp (quartz filter), 0°-25° (5 hr), or 195°-273°K (15 hr), no product; pentane (solvent), acetophenone (sensitizer), low-pressure mercury lamp (quartz filter), 0°-25° (10 hr), no product; pentane (solvent), xanthone (sensitizer), low-pressure mercury lamp (quartz filter), 0°-25° (10 hr), no product; pentane (solvent), xanthone (sensitizer), Hanovia 200 watt medium-pressure mercury lamp, 10°-15° (10-63 hr), no product; pentane (solvent), xanthone (sensitizer), Hanovia high-pressure mercury lamp, 10°-15° (20 hr), no product; pentane (solvent), direct (no sensitizer), high-pressure mercury lamp, 10°-15° (20 hr), no product. The irradiated reaction mixture from each attempt was analyzed

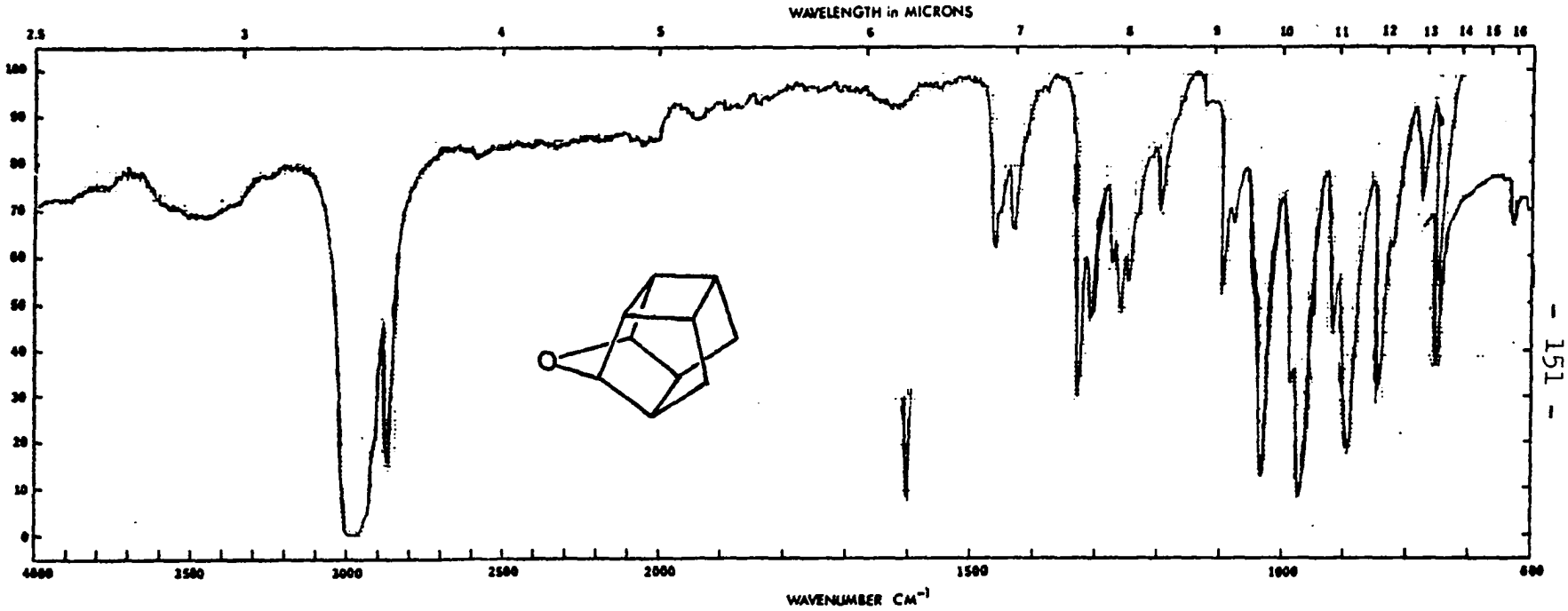


Figure 27a. Infrared spectrum (KBr) of 116.

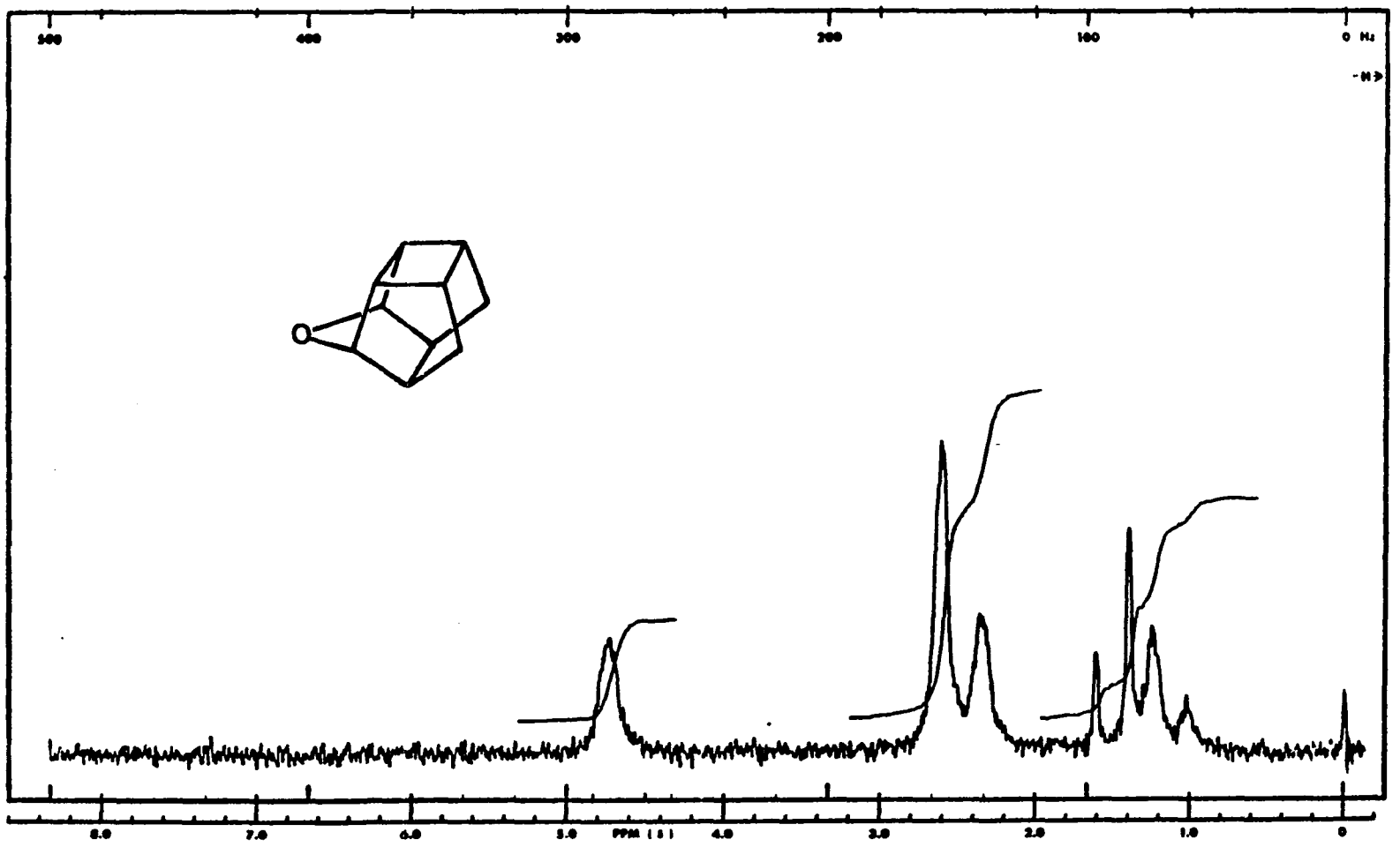


Figure 27b. Proton nmr spectrum (60MHz, $CDCl_3$ solvent, TMS internal standard) of 116.

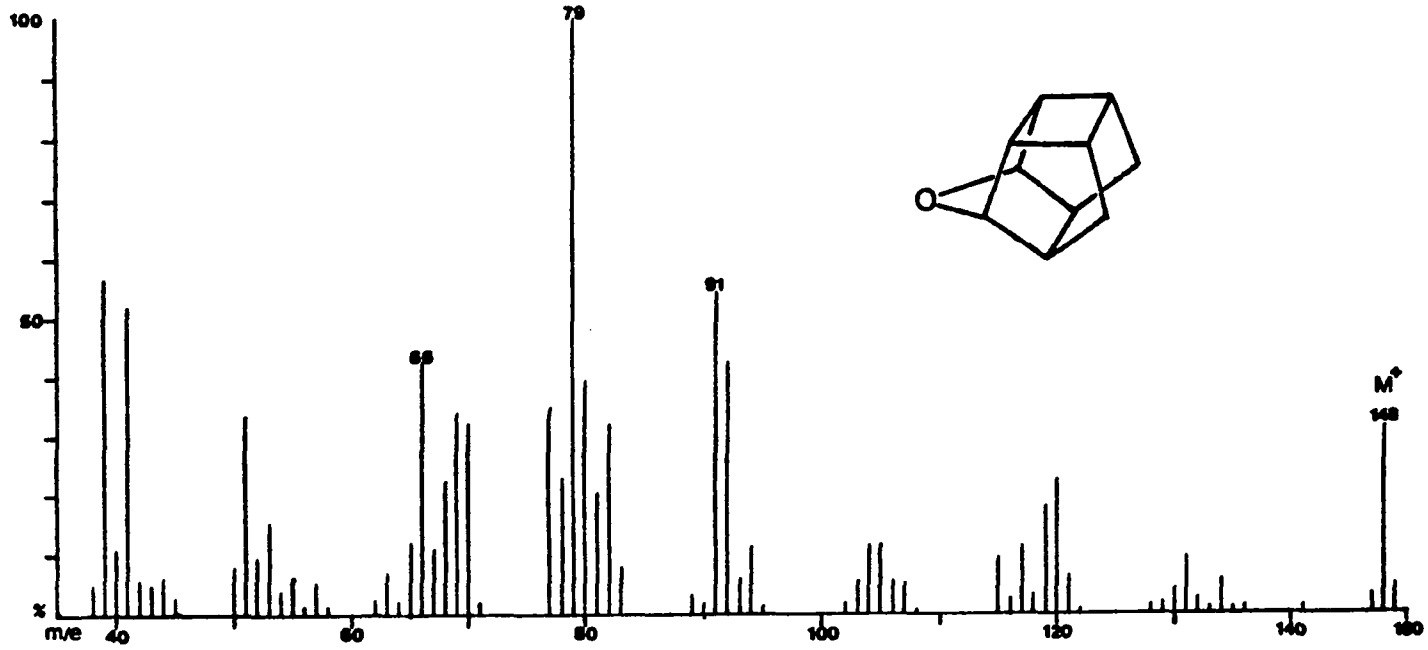


Figure 27c. Mass spectrum of 116.

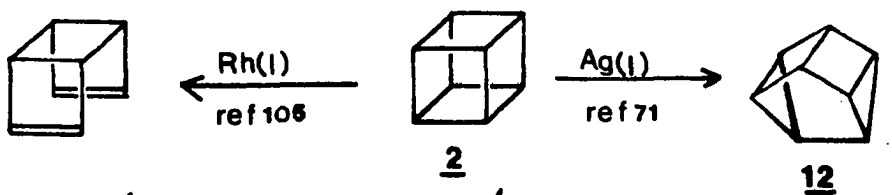
by vpc and shown to contain oxa-diene 115 as the only volitile material (except solvent).

The results of attempting photocyclization of oxa-diene 115 were rather puzzling in view of successful photocyclization of its 10-methylene analogue. In general, replacement of a CH_2-group by an oxygen atom does not alter very drastically the structurally imposed close proximity of the two ethylene bond. In fact, photochemical cyclization reactions in oxanorbornadiene derivatives have been investigated and shown to undergo photoisomerization to the corresponding oxaquadricyclanes.[78,102] However, on same occassions the yields were lower than those of 7-methylene analogues, due to side reactions and interaction with sensitizers used. In the present case, the unsuccessful photocyclization of oxa-diene 115 was probably due to its proneness to polymerize, as evidenced by noticeable amount of insoluble material formed in the irradiated reaction mixture.

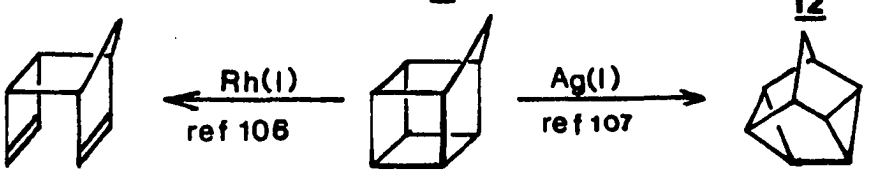
Transition Metal Catalyzed Rearrangements of Homopentaprismane.

Transition metal catalyzed isomerization of highly strained cyclobutane compounds is currently a subject of intensive pursuit by a number of investigators.[103-115] The bond reorganizations are of two extreme types: (a) that

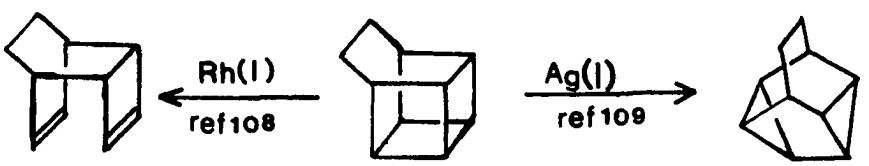
induced by transition metals such as Rh(I) ($4d^8$) with capacity for oxidative addition which results in cleavage of one of the four-membered rings to a diolefin; (b) that promoted by Ag(I) ($4d^{10}$) and related metal ions having appreciable σ electron acceptor ability which effects dicyclobutane-dicyclopropane bond switching. Some typical examples of these types of rearrangements are shown in equation 39-43:



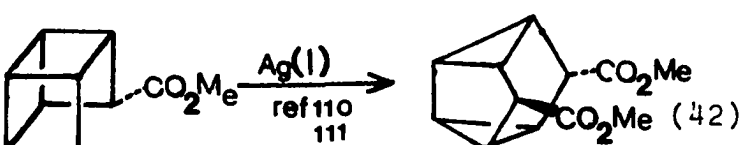
2 12 (39)



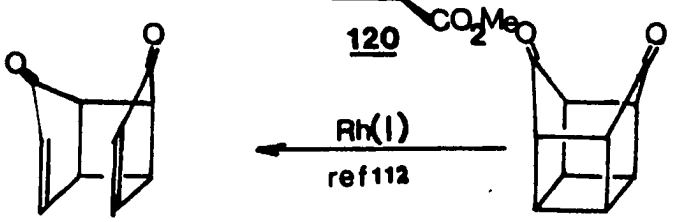
118 122 (40)



119 123 (41)

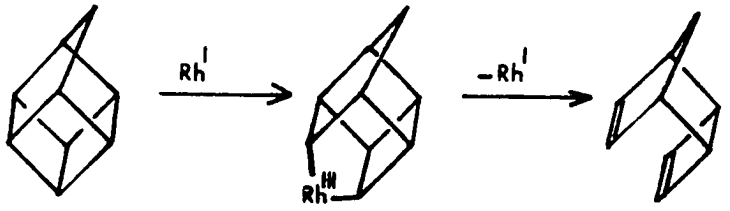


120 124 (42)



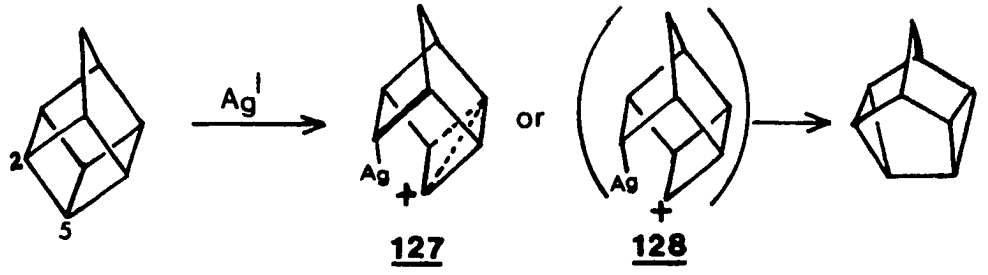
125 (43)

A reasonable mechanism for the Rh(I)-promoted cyclobutane-diolefin transformation has been advanced by Cassar, Eaton, and Halpern.[105] The reaction proceeds in a stepwise fashion via an intermediate such as 126 where the



126 (44)

transition metal has entered into oxidative addition in the rate-determining step. Based on the intensive studies[107,109,113-115] of silver(I)-promoted rearrangements of homocubane and 1,8-bishomocubane systems, Paquette has argued strongly in favor of a stepwise mechanism involving a delocalized argente carbonium ion species such as 127 (instead of a nondelocalized carbonium ion intermediate such as 128) which is generated by electrophilic attack of



127 128 (45)

Ag^+ at the C_2-C_5 bond.

With regard to reactivity of cage molecules toward this type of bond reorganization, it would appear that ring

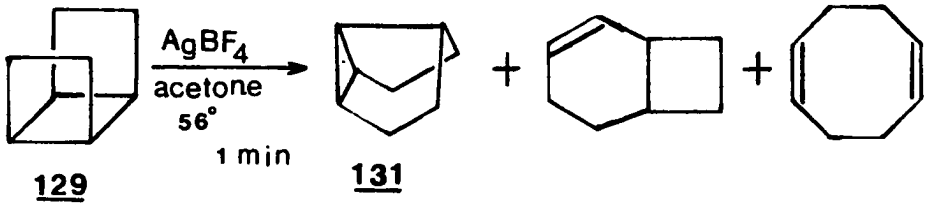
strain must be present in the molecule under consideration. The consequence of ring strain is to create high levels of p character in the C-C bond necessary to bring the substrate into the metal coordination sphere. Furthermore, relief of strain provides the ultimate driving force for rearrangement. Reported kinetic data of cubane (2)[71], homocubane (118)[107], 1,8-bishomocubane (119)[109], and seco-cubyl diester (120)[104] with $AgClO_4$ solution in benzene at 40° are cited in Table V, along with estimated strain energies relieved in the formation of corresponding products (121-124). This Table reveals that the relief of strain in these isomerizations is estimated to be in order of 30-50 kcal/mol. However, the lack of apparent correlation between the strain energies and the rate constants (e.g., 118 vs. 119) indicates that relief of ring strain alone is not sufficient to account for the course of the isomerizations.

In a recent review, Paquette[104] has pointed out that ". . .the lower limit of inherent ring strain required for rearrangement is yet to be established". The least strained, entirely sigma-bonded systems to be studied appear to be the syn- and anti-tricyclooctanes (129 and 130).[115] The inertness of anti-tricyclooctane (130) to silver(I) ion has been interpreted[104,115] to indicate that, in addition to ring strain, the substrate must possess

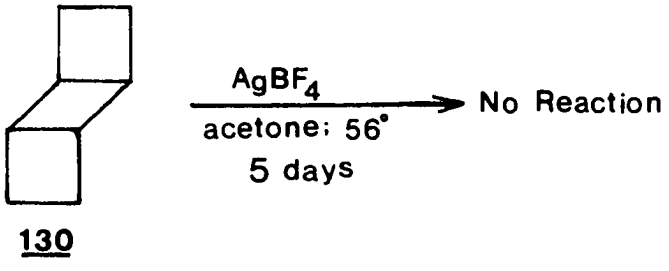
TABLE V. Isomerization Rate Data and Estimated Relief of Strain Energies for Cubane and Its Homologs ($AgClO_4$, benzene, 40°)

Substrate	k_{Ag}	$(E_s)^a_{substrate}$ (kcal/mol)	$(E_s)^b_{product}$ (kcal/mol)	ΔE_s (kcal/mol)
cubane (2)	3.0×10^{-1}	165.87	118.49[c]	47.38
homocubane (118)	7.36×10^{-4}	118.13	84.80[d]	33.33
bishomocubane (119)	2.85×10^{-2}	112.75	80.77[e]	31.98
seco-cubyl diester (120)	4.3×10^{-5}	111.98[f]	69.25[f]	42.73

(a) Data taken from ref. 2. (b) This estimate is based on the assumption that the total strain energy should approximate the sum of strain energies of the composite fused rings [ref. 74]. (c) One bicyclo[2.2.0]hexane (E_S = 50.67 kcal/mol) plus two bicyclo[3.1.0]hexane (E_S = 2 x 33.91 kcal/mol). (d) One norbornane (E_S = 16.98 kcal/mol) plus two bicyclo[3.1.0]hexane. (e) One bicyclo[2.2.0]octane (E_S = 12.95 kcal/mol) plus two bicyclo[3.1.0]hexane. (f) Estimated, assuming that two exo,exo carbomethoxy groups do not appreciably alter the strain energies of the parent (unsubstituted) compounds. The strain energy of the product is estimated by summing the strain energy of cyclohexane (E_S = 1.43 kcal/mol) with that of two bicyclo[3.1.0]hexanes.



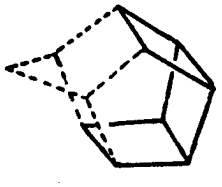
(46)



(47)

the "proper geometry" for interaction with metal ion along the reaction pathway.

Homopentaprismane (53), which contains the syn-tricyclooctane system (heavy outline in the figure below)



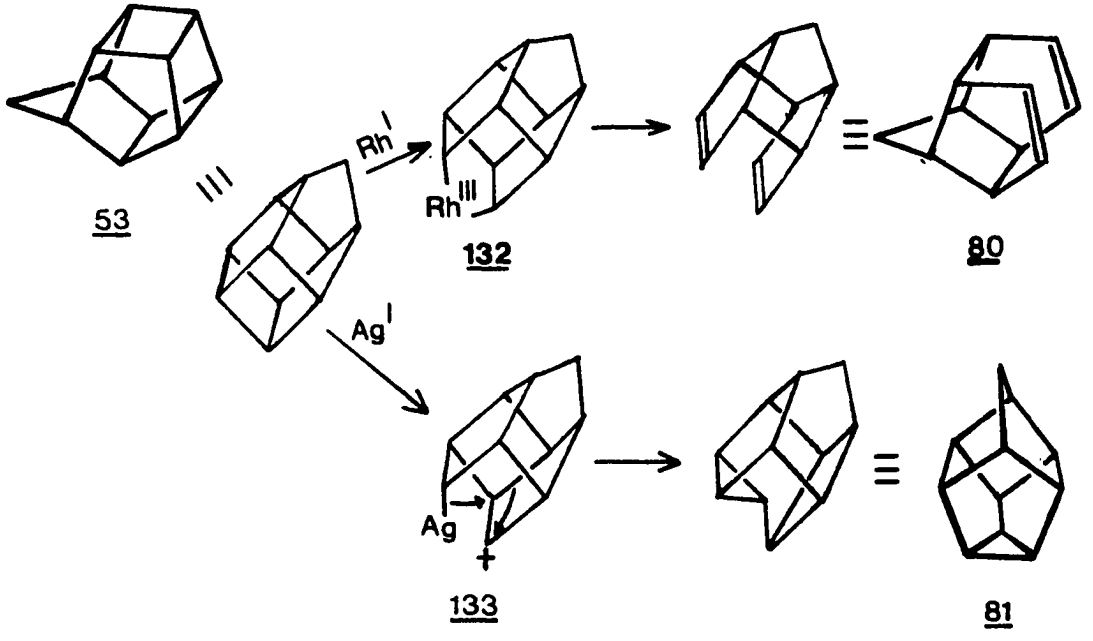
and an estimated strain energy of 110 kcal/mol*, might a priori be expected to undergo transition metal catalyzed rearrangement processes analogous to the type of rear-

---

*Estimated by the sum of the strain energies of the composite rings: syn-tricyclooctane (E_S = 79.45 kcal/mol), norbornane (E_S = 16.98 kcal/mol), and two cyclopentane (E_S = 2 x 7.28 kcal/mol).

rangements shown in equation 39-43 and 46. If we utilized the mechanisms which are analogous to those shown by equation 44 and 45, we might expect to find the products shown in Scheme XIII resulting from Rh(I) and Ag(I) catalyzed

SCHEME XIII



rearrangement of homopentaprismane (53).

When a solution of homopentaprismane (53) in chloroform was allowed to react with catalytic amount of bis(triphenylphosphine)rhodium carbonyl chloride, $[(C_6H_5)_3P]_2Rh(CO)Cl$, 53 was cleanly converted to diene 80. The rearrangement did not proceed at room temperature, but was achieved at 70-75° within 16 hr (pmr analysis). The structural assignment of the rearranged product (80) was confirmed by its pmr spectrum which was identical to an

authentic sample prepared according to the reaction shown in Scheme V. Kinetic study of this rearrangement, performed with $[(C_6H_5)_3P]_2Rh(CO)Cl$ in chloroform solution and using pmr spectroscopy to follow the reaction, showed the rate of disappearance of 53 to be linear for at least two half-lives when $\ln [53]_o/[53]_t$ was plotted vs. time (Figure 28). Least-squares treatment of the kinetic data gave a slope 0.07. A second-order rate constant could then be calculated ($k_2 = 5.7 \times 10^{-5}$ M^{-1} sec^{-1}), which corresponds to a half-life of 9.8 hr for the Rh(I)-promoted ring opening process. Kinetic measurements performed with rhodium(I) norbornadiene chloride dimer $[Rh(NOR)Cl]_2$ in anhydrous benzene solution at 40°, however, did not yield a linear relationship for $\ln [53]_o/[53]_t$ vs. time as shown in Figure 29. Although rearrangement was observed within 30 min, the half-life was found to be about 7.5 days!

While homopentaprismane undergoes the Rh(I)-promoted cyclobutane-diolefin transformation (although at a much slower rate than do cubyl systems), it is virtually inert to silver(I). Addition to homopentaprismane (53) of catalytic amounts of $AgBF_4$ in chloroform solution did not bring about rearrangement after heating at 58-62° for 4 days (after which time 53 could be recovered quantitatively). Homopentaprismane was also found to be inactive to $AgClO_4$ in benzene solution at 78° (10 days) or 83-110° (1 day).

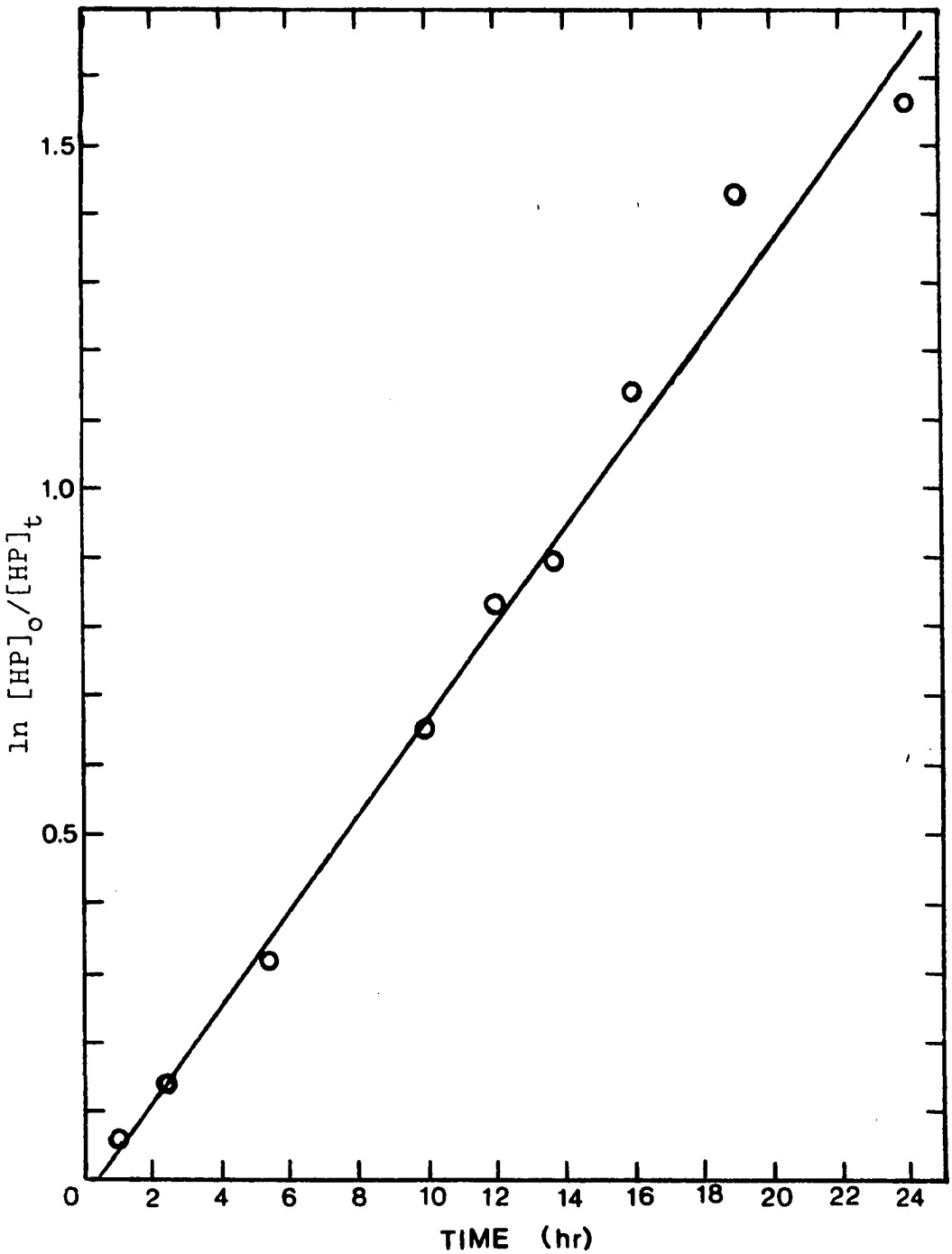


Figure 28. Plot of ln $[53]_o/[53]_t$ *vs.* time (t). Reaction was performed with 0.514M of 53 and 0.171M of $[(C_6H_5)_3P]_2Rh(CO)Cl$ in $CDCl_3$ at 67°. HP = homopentaprismane (53).

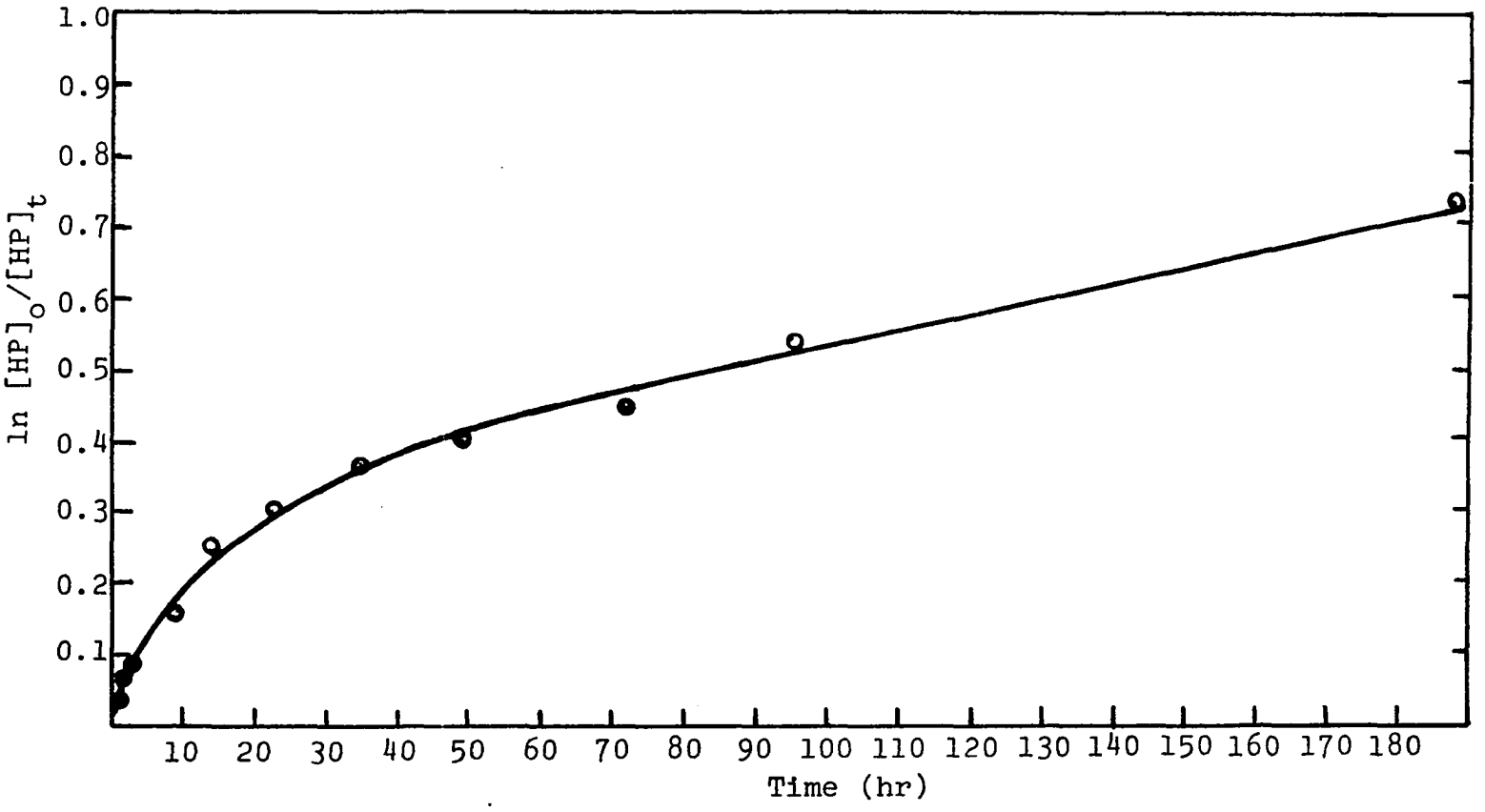
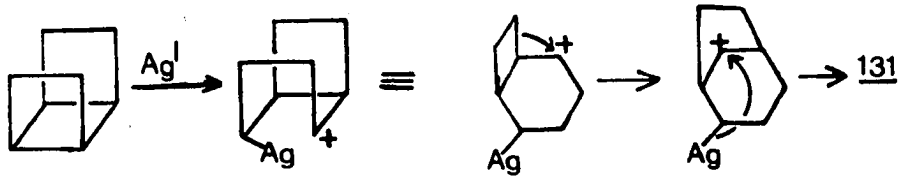


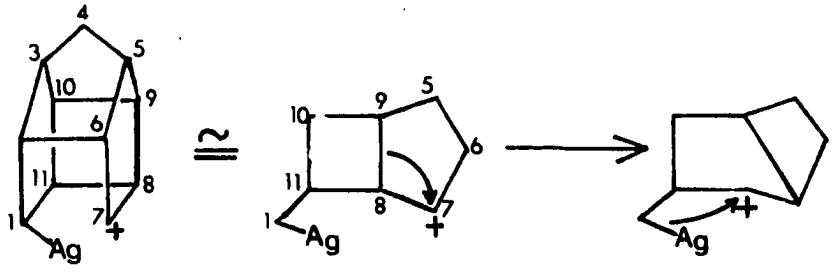
Figure 29. Plot of ln $[\underline{53}]_o/[\underline{53}]_t$ *vs.* time (t). Reaction was performed with 4.556×10^{-1} M of *53* and 1.354×10^{-2} M of $[Rh(NOR)Cl]_2$ in benzene-d_6 at 40°. HP = homopentaprismane (*53*).

The different catalytic activity of Rh(I) and Ag(I) toward homopentaprismane might be ascribed to the distinct nature of transition states. Paquette and coworkers[106] have pointed out that development of positive charge does not take place in the rate-limiting step for isomerizations proceeding by oxidative addition (i.e., Rh(I)-catalyzed reactions), whereas a transient carbonium intermediate is generated in the bond switching process catalyzed by Ag(I). The possibility exists that Rh(I)-induced isomerization of 53 arises because oxidative addition into a strained sigma-bond is kinetically favored and the formation of diene is thermodynamically favored. However, the failure of 53 to undergo Ag(I)-catalyzed rearrangement might be due to the rather high energy of activation needed to develop the transient carbonium intermediate (133) which lacks stabilization via bond delocalization analogous to that in cubyl systems (e.g., 127, equation 45). This explanation, however, cannot account for the rapid isomerization of syn-tricyclooctane (129) to 131, where this type of stabilization is also absent in the carbonium ion intermediate. In a formal sense, the rearrangement of syn-tricyclooctane to 131 corresponds to well-documented cyclobutyl⟶cyclopentyl ring expansion (equation 48),[116] where relief of strain energy (E_s = ca. 19 kcal/mol) provides the driving force for ring expansion. In case of homopentaprismane, this



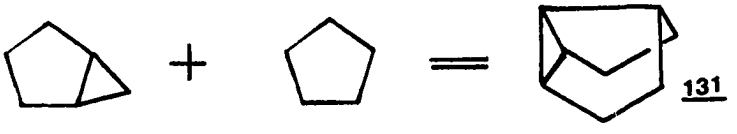
(48)

type of bond switching corresponds to a combination of cyclobutyl⟶cyclopentyl ring expansion and its reverse process. The cyclopentyl⟶cyclobutyl ring contraction



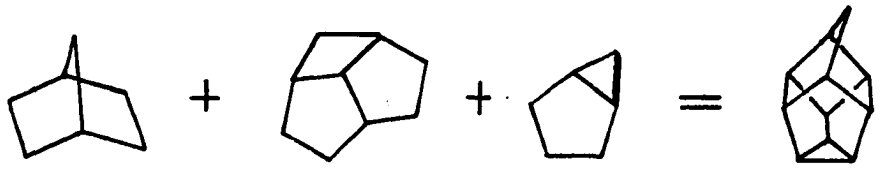
(49)

introduces considerable ring strain (E_S = ca. 19 kcal/mol), and consequently such ring contractions by a Wagner-Meerwein rearrangement are uncommon.[117] The foregoing results can be further understood via consideration of the strain energies of homopentaprismane (53) and syn-tricyclooctane (129) and their corresponding products (81 and 131). If the strain energies of 81 and 131 are estimated by the sum of the strain energies[2] of the composite fused rings as shown below:



(50)

E_S (kcal/mol)	33.91	7.28	41.14



(51)

81

E_s 16.98 36.28 33.91 87.17 (kcal/mol)

A estimated 38.26 kcal/mol (79.45 - 44.14 kcal/mol) of strain energy could thereby be expected to be relieved when syn-tricyclooctane (129) rearranges to 131. This value of relief of strain energy falls in the region (35 - 50 kcal/mol, Table IV) usually observed for Ag(I)-catalyzed rearrangement of cyclobutane compounds. However, the relief of strain energy from homopentaprismane (53) to 81 is estimated to be only 23.82 kcal/mol (110.99 - 87.17 kcal/mol). Apparantly, this amount of strain being relieved is not sufficient to provide the driving force necessary for homopentaprismane to undergo Ag(I)-catalyzed rearrangement to 81. This single consideration, of course, may not provide the whole explanation, since the impact of other factors such as structral features required for developing the transition state[104] and the electronic energy levels of the hydrocarbon responsable for the interaction with Ag(I)[118] have yet to be determined.

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover Capillary melting point apparatus and are uncorrected. Infrared (ir) spectra were recorded on a Perkin-Elmer IR-8 infrared spectrophotometer and were calibrated against the 1601 cm^{-1} band of polystyrene film. Strong, medium and weak intensities are denoted by (s), (m) and (w), respectively. Spectra were generally determined for dispersions in potassium bromide or for solutions in carbon tetrachloride. Proton nuclear magnetic resonance (pmr) spectra were recorded at 60 MHz with a Varian Model T-60 spectrometer, with tetramethylsilane as internal standard. Peak position are reported in parts per million (δ) downfield from tetramethylsilane. The center of gravity of a broad singlet (br s) or a multiplet (m) absorption is given as the peak position; however, complex multiplets are reported as a range between the highfield and lowfield ends of the multiplet. Carbon-13 nuclear magnetic resonance (^{13}C nmr) spectra were obtained on either a Bruker WH-90 FT nmr spectrometer operating at 22.63 MHz (Univeristy of Arizona) or a Varian XL-100-15 nmr spectrometer operating at 25.2

MHz, with benzene as internal standard and deuteriochloroform or carbon tetrachloride as solvent. Mass spectra were recorded on the Hitachi Perkin-Elmer Model RMU-6E mass spectrometer, operating at 70eV. M/e values of each significant peak in the mass spectra are reported, followed parenthetically by the intensity of that peak expressed as a percent of the intensity of the base peak (where the intensity of the base peak = 100). Analytical vapor-phase chromatography (vpc) was performed on a Varian-Aerograph Model 90-P3 instrument fitted with a column (60 in. x 1/4 in.) packed with 3% SE 30 on Chromosorb P 45/60. Column temperatures and helium flow rates are indicated in each case. Elemental microanalyses were performed by Chemalytics, Inc., Tempe, Arizona.

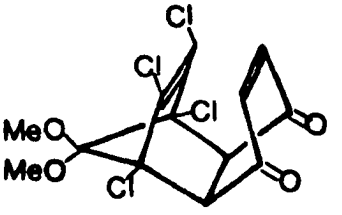
Solvents for recrystallization purpose were distilled. In the use of solvent pairs for recrystallization, the solvent in which the substance is more soluble is given first.

Unless otherwise noted, all reagents and solvents were reagent grade and used without additional purification. Reagent grade acetone was refluxed with and distilled from potassium permanganate. Bromoform (Aldrich Chem. Co.) was shaken with concentrated sulfuric acid several times and thoroughly washed with distilled water, stored over potassium carbonate in the dark, and then distilled under

reduced pressure immediately before use. Carbon tetrachloride was refluxed with potassium hydroxide for several days, distilled and stored over Linde 3A Molecular sieves. anhydrous diethyl ether was distilled from lithium aluminum hydride immediately before use. Dimethylformamide was refluxed with anhydrous cupric sulfate for 24 hr, distilled, and stored over Linde 3A Molecular sieves. Hexamethylphosphoramide (Aldrich Chem. Co.) was distilled under reduced pressure from calcium hydride and a center cut was used immediately. Pentane (36°) for photolysis was purified by stirring with concentrated sulfuric acid overnight and then distilling from potassium permagnate and drying over anhydrous sodium sulfate. Pyridine was either obtained from freshly opened bottles, or it was purified by distillation from potassium hydroxide. Anhydrous tetrahydrofuran was distilled from lithium aluminum hydride immediately before use. Toluene was dried by azeotropic distillation (Dean-Stark trap) for several days and then distilled and stored over Linde 3A Molecular sieves.

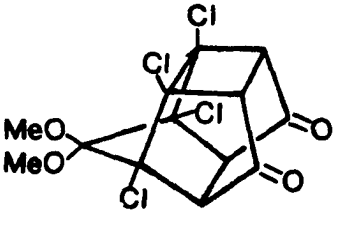
Tetrachlorocyclopentadiene dimethyl ketal (10).--was prepared by the reaction of hexachloropentadiene with methanolic potassium hydroxide following the procedure of Gassman and Marshall.[13]

1,2,3,4-Tetrachloro-9,9-dimethoxy-1,4,4a,5,8,8a-hexahydro-endo-1,4-methanonaphthalene-5,8-dione (11).--



A mixture of tetrachlorocyclopentadiene dimethyl ketal (10) (132g, 0.5 mole) and para-benzoquinone (54g, 0.5 mole) in dry toluene (300 ml) was gently refluxed for 48 hr. At the conclusion of the reflux period, the reaction mixture was concentrated to give an oily residue which was recrystallized from benzene-hexane to afford 11 (146.6g, 68%) as pale yellow crystals: mp 160-164° (lit.,[14] 162-164°); ir (KBr) 1677 (conj. C=O), and 1601 cm^{-1} (C=C); pmr ($CDCl_3$) δ3.60 (s, 3H, $-OCH_3$), δ3.63 (s, 2H, 4a,8a-methine protons), δ3.64 (s, 3H, $-OCH_3$), and δ6.7 (s, 2H, 6,7-olefinic protons).

4,4-Dimethoxy-2,3,5,6-tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (12).-- A solution of



11 (15g, 0.04 mole) in acetone (600 ml) was irradiated under nitrogen with a 200 watt Hanovia medium pressure mercury lamp (pyrex shield) for 8 hr. The solution was then concentrated to give tan solids. The total product from six such irraditions

was recrystallized from acetone-hexane to afford 12 (83.7g, 93%), mp 148-150°. An analytical sample was obtained by further recrystallization of this material from benzene-hexane followed by sublimation (125°/0.1 mm). The compound 12 thus obtained had mp 151.5-152.5°. Ir (KBr, Figure 1a) 1770 (s), 1780 (sh), 1455 (m), 1230 (s), 1210 (s), 1020-1170 cm^{-1} (complex absorption pattern, s); pmr (acetone-d_6, Figure 1b) δ3.56 (s, 4H, 1,7,9,10-methine protons), δ3.70 (s, 3H, $-OCH_3$), and δ3.74 (s, 3H, $-OCH_3$); mass spectrum (Figure 1c) m/e (%) 378/376/374/372/370 (molecular ion, with intensity profile characteristic of the Cl_4 multiplet[53]), 341(13), 339(53), 337(100), 335(88), 311(10), 309(23), 307(28), 189(20), 187(55), 172(10), 170(18).

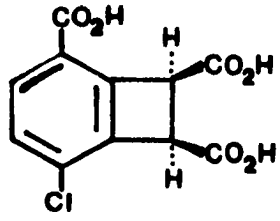
Anal. Calcd for $C_{13}H_{10}Cl_4O_4$: C, 41.97; H, 2.71.
Found: C, 41.80; H, 2.58.

2,3,5,6-Tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4,8,11-trione (13).-- A suspension of 12 (17g, 0.046 mole) in concentrated sulfuric acid (170 ml) and methylene chloride (170 ml) was stirred at room temperature for 48 hr. The brown reaction mixture was then transfered to a separatory funnel. The organic layer was separated and the sulfuric

acid layer was extracted with methylene chloride (100 ml) and then hexane (100 ml). The combined extracts were filtered through glasswool to remove sulfuric acid, and the filtrate was concentrated to yield 13 (11.4g, 80%) as a white, powdery solid, mp 195-205°, which hydrates readily on exposure to air. Successive recrystallization of this material from diethyl ether followed by sublimation gave pure 13 as a colorless microcrystalline solid, mp 211-212°: ir (KBr, Figure 2a) 1824 (m), 1809 (sh), 1785 (s), and 1775 cm^{-1} (s); pmr (acetone-d_6, Figure 2b) δ3.18 (br s, 1,7,9,10-methine protons; they exhibit as two broad singlets at δ3.87 and δ3.58 with equal intensity in pyridine solution); mass spectrum (Figure 2c) m/e (%) 332/330/328/326/324 (molecular ion, with intensity profile characteristic of the Cl_4 multiplet[53]), 291(64), 289(63), 263(50), 261(50), 235(68), 233(75), 207(61), 205(64), 172(57), 170(75), 86(54), 85(93), 82(100), 74(57).

Anal. Calcd for $C_{11}H_4Cl_4O_3$: C, 40.53; H, 1.24.
Found: C, 40.13; H, 1.24.

Attempted Semibenzilic Acid Rearrangement on Triketone 13. 6-Chloro-cis-1,2-dihydrobenzocyclobutene-1,2,3-tricarboxylic acid (54a).-- A suspension of 13 (6.0g, 18.4 mmole) in dry toluene (150 ml) was concentrated by careful distillation to 100 ml. Crushed sodium hydroxide



pellets (4g, 0.1 mole) were added, and the mixture was refluxed for 45 min, then poured into ice-water (300 ml). The aqueous layer was separated and washed with diethyl ether (100 ml x 3). The combined extracts yielded unchanged triketone 13 (0.15g). The aqueous layer was acidified with hydrochloric acid and then extracted with diethyl ether (liquid-liquid extraction apparatus) for 3 days. The extract was washed with water (50 ml), dried (Na_2SO_4), filtered, and concentrated, affording a brown oil (3.8g). Chromatography an silica gel (diethyl ether eluant) followed by recrystallization from acetone-hexane afforded a white crystalline solid (54a) (0.75g, 13.1%), mp 264-265.5° (dec.); ir (KBr, Figure 3a) 3000 (br s), 1730 (s), 1700 (s), 1610 (m), 1420 (s), 1300 (s), and 770 cm^{-1} (m); pmr (acetone-d_6, Figure 3b) δ4.78 (s, 2H, 1,2-methine protons), and δ7.63 (center of an AB pattern, $\Delta\delta$=25 Hz, J_{AB}=8 Hz, 2H, benzene ring protons); mass spectrum (Figure 3c) m/e (%) 272/270 (molecular ion, with intensity profile characteristic of the Cl multiplet[53]), 252(7), 226(45), 208(17), 197(32), 191(19), 182(38), 180(100), 152(23), 89(31). The residual oil (ca. 2g) resisted attempts at purification, however, its ir and pmr spectra were essentially similar to those of 54a.

Anal. Calcd for $C_{11}H_7ClO_6$: C, 48.82; H, 2.61.
Found: C, 48.81; H, 3.39.

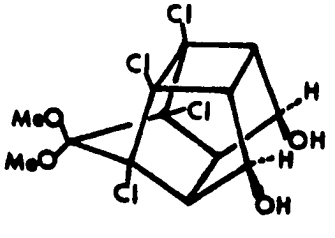
Tricarboxylic acid 54a could not be purified *via* sublimation, due to dehydration of 54a to the corresponding carboxylic acid anhydride 55. Sublimation of 54a at 150° (1 mm) overnight afforded a mixture of 54a and 55 as indicated by the additional absorptions at 1862 and 1788 cm^{-1} in the infrared spectrum (KBr) of the sublimate; these two bands are due to the presence of strained, cyclic acid anhydride 55.[52] The pmr spectrum (acetone-d_6) of the sublimate displayed two sets of spectra closely resembling that of 54a. The set appearing at lower field corresponds to the acid anhydride, and it contains a broad singlet (area 2H) at δ5.05 and an AB absorption pattern centered at δ7.70. To this pmr spectral solution was added few drops of D_2O and after several days, the spectrum was taken and shown to contain only the peaks corresponding to those of 54a.

Tricarboxylic acid 54a was further characterized *via* its trimethyl ester 54b. Ethereal diazomethane was added dropwise to a solution of 54a (310 mg) in anhydrous diethyl ether (50 ml) until the yellow color of the diazoalkane persisted. The mixture was set aside overnight; several drops of hydrochloric acid were then added to destroy unreacted diazomethane. The solution was washed

with dilute sodium bicarbonate solution, and the organic layer was dried over sodium sulfate, filtered, and concentrated to afford crude trimethyl ester 54b (290 mg, 81%). Recrystallization from diethyl ether afforded pure 54b (171 mg, 48%) as a colorless, microcrystalline solid, mp 109.5-110.5°; ir (KBr, Figure 4a) 3020 (w), 1750 (s), 1728 (s), 1605 (m), 1435 (m), 1290 (s), 1162 (s), and 769 cm^{-1} (m); pmr (acetone-d_6, Figure 4b) δ3.70 (s, 3H, $-OCH_3$), δ3.72 (s, 3H, $-OCH_3$), δ3.85 (s, 3H, $-OCH_3$), δ4.83 (center of an AB system, Δδ=7 Hz, J_{AB}=6 Hz, 2H, 1,2-methine protons), and δ7.65 (center of an AB pattern, Δδ=23 Hz, J_{AB}=8 Hz, 2H, benzene ring protons); mass spectrum (Figure 4c) m/e (%) 314/312 (molecular ion, with intensity profile characteristic of the Cl multiplet[53]), 281(13), 255(45), 253(100), 195(17), 194(8).

Anal. Calcd for $C_{14}H_{13}ClO_6$: C, 53.77; H, 4.19.
Found: C, 54.07; H, 4.13.

Sodium Borohydride Reduction of 12. 4,4-Dimethoxy-2,3,5,6-tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-endo-8-exo-11-diol (61).-- A solution of 12 (82g, 0.22 mmole) in 95% ethanol (450 ml) was cooled in an ice bath. Sodium borohydride (17g, 0.45 mole) was added portionwise, with stirring,



to the cooled solution of 12 in ethanol. After the exothermic reaction subsided, the reaction mixture was allowed to gradually warm to room temperature, and stirring was continued for an additional 3 hr. After this period, the reaction mixture was heated under reflux for 30 min, whereupon water (200 ml) was added. The resulting solution was heated to boiling for 15 min, diluted with water (500 ml), and then extracted with diethyl ether (500 ml x 4). The combined extracts were washed with water (500 ml x 3), dried ($MgSO_4$), filtered, and then concentrated. The pmr spectrum of the crude product thereby obtained displayed a triplet centered at 5.00, suggesting that a small amount of 62 was formed along with 61; (details of the pmr spectrum of 62 are presented in the section which deals with the lithium aluminum hydride reduction of 12). The crude product was recrystallized from ethyl acetate-hexane to afford 61 as a colorless microcrystalline solid (68g, 82%), mp 244-255°. Further recrystallization (ethyl acetate) followed by sublimation (175°/0.1 mm) afforded pure 61, mp 256-257°; ir (KBr, Figure 5a) 3420 (br), 2840 (w), 1425 (m), 1225 (s), 1110-1000 (complex absorption pattern, s), and 775 cm^{-1} (s); pmr (acetone-d_6, Figure 5b) δ2.83-3.13 (m, 4H, methine protons), δ3.55 (s, 3H, $-OCH_3$), δ3.65 (s, 3H, $-OCH_3$), δ3.76 (d, 1H, OH), δ4.50 (br s, 1H, CHOH), δ4.83 (br d, 1H, OH), and δ5.41 (br d, 1H, CHOH); (assignment of the various

signals in the pmr spectrum of 61 was facilitated through examination of the pmr spectrum of 8,11-dideuterated 61 which was prepared *via* reduction of 12 with excess $NaBD_4$ utilizing the procedure described above); mass spectrum (Figure 5c) m/e (%) 382/380/378/376/374 (molecular ion, with the intensity profile characteristic of the Cl_4 multiplet[53]), 343(32), 341(93), 339(100), 255(16), 253(16), 191(19), 190(17), 189(58), 188(31), 59(17).

Anal. Calcd for $C_{13}H_{14}O_4Cl_4$: C, 41.52; H, 3.75. Found: C, 41.20; H, 3.63.

Lithium Aluminum Hydride Reduction of 12. 4,4-Dimethoxy-2,3,5,6-tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-endo,endo-8,11-diol (63).-- A stirred slurry of lithium aluminum hydride (8.90 g, 0.234 mole) in anhydrous diethyl ether (200 ml) was cooled in an ice bath. To this cooled solution was added dropwise, under nitrogen atmosphere, a solution of 12 (21.6 g, 0.058 mole) in diethyl ether (350 ml). After the addition had been completed, the reaction mixture was stirred at room temperature for 24 hr and then refluxed for ca. 30 min. The reaction mixture was then cooled to 0°; to the cooled solution, the following were successively added

dropwise: water (10 ml), 15% aqueous sodium hydroxide solution (10 ml), and water (100 ml). The inorganic residue was removed by filtration, and the residue was then washed with ethyl acetate. The combined organic layers were washed with water (200 ml x 3) and then dried (Na_2SO_4), filtered, and concentrated, affording a colorless oil (19.1g) which solidified on standing. This material was found to contain 63 and 62 in the ratio (by pmr) of ca. 1 : 4. Compound 62 could be isolated from the product mixture via fractional recrystallization (ether-hexane). The material thus isolated had mp 189-191°. Compound 62 was characterized via its ir, pmr, and mass spectra: ir (KBr) 3320 (s), 1340 (s), 1210 (s), and 1200-970 cm^{-1} (complex absorption pattern, s); pmr (acetone-d_6): δ2.83-3.30 (m, 5H, OH and methine protons), δ3.53 (s, 3H, $-OCH_3$), δ3.62 (s, 3H, $-OCH_3$), and δ5.00 (br t, 1H, CHOH); mass spectrum m/e (%) 380/378/376/374/372 (molecular ion, with the intensity profile characteristic of the Cl_4 multiplet[53]), 341(65), 339(98), 337(100), 305(6), 303(9), 301(4), 273(8), 257(8), 183(8), 147(9), and 59(29). Compound 62 could be further reduced by lithium aluminum hydride to afford 63. When the mixture of 62 and 63 was further reduced with excess lithium aluminum hydride in the manner described above, crude 63 (18.2g, 96%) was produced free from contamination by 62 (as determined by the absence of absorption at δ5.00 in the pmr spectrum of

this crude product). Recrystallization from chloroform afforded 63 as colorless needles (15.8g, 82%), mp 190-197°. An analytical sample was obtained via further recrystallization of this material from benzene followed by sublimation (140°/0.1 mm). The material thus obtained had mp 200.5-201.5°: ir (KBr, Figure 6a) 3220 (br), 2840 (w), 1440 (m), 1270 (s), 1235 (s), 1120 (s), 1100 (s) and 1010 cm^{-1} (s); pmr (acetone-d_6, Figure 6b) δ3.03 (m, 6H, hydroxyl and methine protons; the hydroxyl proton absorptions disappeared upon addition of D_2O), δ3.57 (s, 3H, $-OCH_3$), δ3.63 (s, 3H, $-OCH_3$), and δ4.45 (br s, 2H, 8,11- protons); mass spectrum (Figure 6c) m/e (%) 382/380/378/376/374 (molecular ion, with the intensity profile characteristic of the Cl_4 multiplet[53]), 343(31), 342(16), 341(94), 340(20), 339(100), 323(17), 321(20), 257(23), 255(49), 253(44), 66(49), 59(31), and 43(33).

Anal. Calcd for $C_{13}H_{14}O_4Cl_4$: C, 41.52; H, 3.75.
Found: C, 41.32; H, 3.73.

Attempted Reduction of 12 Using Lithium Tri-t-butoxyaluminum Hydride.-- The reductant was prepared by the reaction of lithium aluminum hydride with tert-butyl alcohol[59] and was reacted in situ, without additional purification. To a suspension of lithium aluminum hydride (1.33g, 35 mmole) in freshly distilled tetrahydrofuran (100 ml), was added

dropwise a solution of tert-butyl alcohol (7.8g, 105 mmole) in tetrahydrofuran (10 ml) under a nitrogen atmosphere. After the addition was completed (ca. 30 min), a solution of 12 (5.95g, 16 mmole) in tetrahydrofuran (100 ml) was then added dropwise during a period of 5 hr, and the reaction mixture was stirred for additional 14 hr. To the cooled reaction mixture, the following were successively added dropwise: water (5 ml), 15% aqueous sodium hydroxide solution (5 ml), and water (50 ml). The inorganic residue was removed by filtration, and the residue was washed with diethyl ether. The organic layer was separated, washed with water, dried (Na_2SO_4), filtered, and concentrated to give an oily material (4.7g). The pmr spectrum of this material was similar to that of 12.

4,4-Dimethoxy-2,3,5,6-tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{5,9}$]undecane-8,11-thiocarbonate (64).-- A solution of 63 (3.7g, 10 mmole) and N,N'-thiocarbonyldiimidazole[60] (1.80g, 10.1 mmole) in dry toluene (75 ml) was refluxed with stirring under nitrogen for 2 hr.[36,44] The solvent was then removed under reduced pressure (rotary evaporator) and the yellow residue was taken up in ethyl acetate (200 ml). The resulting

solution was washed successively with 3.6N hydrochloric acid (50 ml), water (50 ml), saturated aqueous sodium bicarbonate solution (50 ml), and water (50 ml). The organic layer was then dried (Na_2SO_4), filtered, and concentrated, affording a tan solid. Recrystallization of the tan solid from benzene-hexane afforded 64 (3.74g, 89%), mp 224-227.5°. An analytical sample of 64 was obtained by sublimation of this material (130°/0.05 mm) followed by several recrystallizations of the sublimate from acetone. Pure 64 was thereby obtained as colorless prisms, mp 229-230.5°: ir (KBr, Figure 7a) 1405 (m), 1305 (s), 1267 (s), and 1232 cm^{-1} (s); pmr ($CDCl_3$, Figure 7b) δ3.43-3.72 (m, 4H, 1,7,9,10-methine protons), δ3.52 (s, 3H, $-OCH_3$), δ3.58 (s, 3H, $-OCH_3$), and δ4.95 (symmetrical multiplet, 8,11- protons); mass spectrum (Figure 7c) m/e (%) 424/422/420/418/416 (molecular ion, with the intensity profile characteristic of the Cl_4 multiplet[53]), 325(33), 323(100), 321(96), 259(36), 257(50), 183(50), 182(32), 149(48), 125(35), 113(32), 109(33), 75(55), and 63(31).

Anal. Calcd for $C_{14}H_{12}Cl_4O_4S$: C, 40.22; H, 2.89.
Found: C, 40.57; H, 2.91.

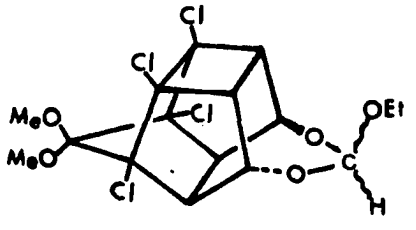
Attempted Fragmentation of Thiocarbonate 64.-- (a) A magnetically stirred solution of thiocarbonate 64 (1.28g, 3.1 mmole) in trimethylphosphite (10 ml) was refluxed under

nitrogen for 5 days. Excess trimethylphosphite was removed under reduced pressure using a rotary evaporator. The residue was poured into cold water and extracted with ethyl acetate (50 ml x 2). The combined extracts were washed successively with water (50 ml), saturated sodium bicarbonate solution (20 ml), and water (50 ml), and then dried (Na_2SO_4), filtered, and concentrated. The oily residue (ca. 1g) was chromatographed on alumina (benzene eluant), affording a material (ca. 0.6g) which resisted attempts at recrystallization. The infrared of this material displayed absorption bands at 2950 (s), 2845 (m), 1445 (m), 1370 (m), 1300-950 (complex), and 795 cm^{-1} (m). Its pmr ($CDCl_3$) exhibited multiplet (area 4H) at δ3.1, two singlets (total area 3H) at δ3.3 and 3.33, two singlet (total area 6H) at δ3.5 and 3.6, a broad singlet (area 2H) at δ4.5, and two singlets (total area 1H) at δ5.2 and 5.3. This material was tentatively assigned to be 5,14,14-trimethoxy-4,6-dioxa-1,9,10,13-tetrachlorohexacyclo[$7.4.1.0^{2,8}.0^{3,12}.0^{7,11}.0^{10,13}$]tetradecane (70) on the basis of the foregoing spectral data.

(b) Thiocarbonate 64 (1.0g) in freshly distilled trimethylphosphite (10 ml, bp 110°) was heated at reflux under nitrogen; the solution became clear when the temperature reached 80° and a white precipate formed after refluxing for about 30 min. After refluxing for a total of 72 hr, the white solids (0.92g) were collected by filtration and washed

with hexane. This material was found to be insoluble in benzene, diethyl ether, chloroform, ethyl acetate, acetone, dimethylsulfoxide, pyridine. Its infrared spectrum (KBr) showed absorption bands at 1450 (m), 1370 (m), 1300-1100 (complex), and 800 cm^{-1} (m). Its mass spectrum displayed peaks at m/e 776/774/772/770/768 (intensity profile resembling that of Cl_8 multiplet[53]), 431, 307, 305 (base peak), 184. This material is probably a dimer (71). None of the desired product (15) was obtained from the reaction of thiocarbonate 64 with trimethylphosphite.

5-Ethoxy-14,14-dimethoxy-4,6-dioxa-1,9,10,13-tetrachlorohexacyclo[7.4.1.$0^{2,8}$.$0^{3,12}$.$0^{7,11}$.$0^{10,13}$]-tetradecane (73).-- A mixture of diol 63 (2.2g, 5.85 mmole) and triethyl orthoformate (1.9g, 12.8 mmole) in the presence of catalytic amount of benzoic acid (ca. 50 mg) was heated at 135-140° for 44 hr; during this period, about o.8 ml of ethanol was distilled off. The resulting oil was cooled and dissolved in benzene (70 ml); the resulting benzene solution was washed successively with water (50 ml x 2), saturated aqueous sodium bicarbonate solution (50 ml x 2) and water (50 ml). The organic layer was then dried (Na_2SO_4), filtered, and



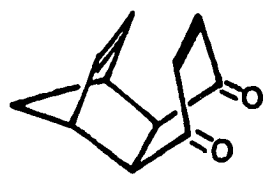
concentrated to yield a viscous oil. Recrystallization of this oil from hexane afforded crude 73 (1.88g, 74.2%), mp 100-109°. Further recrystallization of this product followed by sublimation (110°/0.02 mm) gave 73 having mp 138-144° (mixture of epimers): ir (KBr, Figure 8a) 1440 (m), 1381 (m), 1295 (s), 1238 (s), 1200-960 cm^{-1} (complex absorption pattern, s); pmr ($CDCl_3$, Figure 8b) δ1.23 (br t, 3H, $C\underline{H}_3$ of ethoxy group), δ3.71 (m, 4H, 2,8,11,12-methine protons), δ3.40-3.83 (m, containing two singlets at δ3.67 and 3.55, 8H, 2 x $-OC\underline{H}_3$ and $C\underline{H}_2$ of ethoxy group), δ4.60 (br s, 2H, 3,7- protons), δ5.33 and 5.45 (s, total 1H, 5-H, α to ethoxy group); mass spectrum (Figure 8c) m/e (%) 438/436/434/432/430 (molecular ion, with intensity profile characteristic of the Cl_4 multiplet[53]), 399(25), 397(83), 395(84), 389(50), 387(100), 385(78), 323(20), 321(19), 59(21).

Anal. Calcd for $C_{16}H_{18}Cl_4O_5$: C, 44.57; H, 3.97.
Found: C, 45.10; H, 4.09.

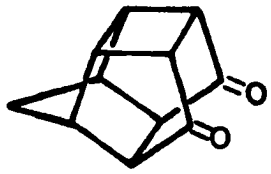
Attempted Fragmentation of 73.-- A solution of 73 (1.3g) and benzoic acid (20 mg) in dry dimethylformamide (20 ml) was refluxed for 22 hr. The solution was cooled and diluted with benzene (50 ml), washed with water (30 ml x 2), saturated sodium bicarbonate solution (50 ml), and water (50 ml), and dried (Na_2SO_4). Concentrated the benzene

solution afforded a material (ca. 1g) whose ir and pmr spectra were identical to those of the starting material (73).

1,4,4a,8a-Tetrahydro-endo-1,4-methanonaphthalene-5,8-dione (19).[66]-- To a solution of p-benzoquinone (54g, 0.5 mole) in methanol (100 ml) at -70° was added a solution of freshly cracked cyclopentadiene (35g, 0.53 mole) in cold methanol (20 ml). The solution was allowed to warm to room temperature, and the product was collected by suction filtration. Yellow crystals (75g, 86.2%) was obtained: mp 75-77° (lit., mp 76-78.5°,[66] 77-78°,[86] 75.8-76.2°[87]); ir (KBr) 1660 (conj. C=O), and 1601 cm^{-1} (conj. C=O): pmr ($CDCl_3$) δ1.48 (m, 2H, methylene bridge protons), δ3.28 (m, 2H, 4a- and 8a-H), δ3.52 (m, 2H, bridgehead protons), δ6.0 (m, 2H, ethylene bridge protons), and δ6.52 (s, 2H, enone vinyl protons).

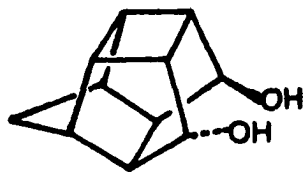


Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-8,11-dione (20).[15]-- A solution of 19 (40g, 0.23 mole) in ethyl acetate (500 ml) was irradiated for 12 hr with a Hanovia medium-pressure mecury lamp (Pyrex filter). The solution was concentrated to give 20 (30g, 75%), mp 237-240°.



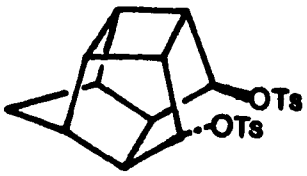
Recrystallization from ethyl acetate-hexane afforded 20g (first crop, 50%) of 20 as colorless crystals: mp 243-244° (lit.,[15] mp 245°): ir (KBr) 1742 (C=O), 1720 cm^{-1} (C=O); pmr ($CDCl_3$) δ2.5-3.3 (envelope, 8H, methine protons), AB pattern, J=12 Hz, δ_A 1.86, δ_B 2.10 (2H, methylene protons).

Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-endo,endo-8,11-diol (65).-- To a cooled (ice bath), stirred suspension of lithium aluminum hydride (4.2g, 0.11 mole) in anhydrous diethyl ether (100 ml) was added dropwise a suspension of diketone 20 (7.8g, 0.045 mole) in anhydrous diethyl ether (300 ml). After the addition was completed (ca. 3 hr), the reaction mixture was allowed to warm up to room temperature and stirring was continued for 36 hr. The reaction mixture was then cooled (ice bath) and was treated with water (20 ml) to decompose excess $LiAlH_4$. The quenched reaction mixture was filtered and the residue was stirred with chloroform (300 ml) for 30 min. in order to extract ether-insoluble product (65). The organic solutions were combined, dried (Na_2SO_4), and concentrated to



afford oily residue. Recrystallization of this material from ethyl acetate-hexane afforded 65 (5.3g, 66%): mp 271-273° (lit., mp 276-276.5°,[15] 273-276°[58]); ir (KBr) 3230 (br), 1095 (s), 1070 cm^{-1} (s); pmr ($CDCl_3$) δ6.36 (br s, 2H, hydroxyl protons), δ3.78 (br s, 2H, 8- and 11-H), δ2.1-2.8 (8H, methine protons), δ_A 1.63 and δ_B 1.03 (AB pattern, J_{AB}=10 Hz, 2H, methylene protons).

Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-endo,endo-8,11-ditosylate (76).-- Diol 65 (7.1g, 0.04 mole) and p-toluenesulfonyl chloride (19.0g, 0.1 mole) were dissolved in dry pyridine (70 ml) and the solution was refrigerated for 24 hr, during which time white needles of pyridine hydrochloride formed in the pale yellow solution. The reaction mixture was poured into ice-water (300 ml) and extracted with dichloromethane (150 ml x 3). The combined extracts were washed with cold 6N hydrochloric acid (100 ml x 2) and with cold water (100 ml x 3), then dried (Na_2SO_4), filtered, and concentrated to give crude 76 (18.6g, 95.5%). Recrystallization of this crude product from benzene-hexane afforded ditosylate 76 (16.5g, 85%), mp 143-147°. Further recrystallization from benzene gave pure 76 as colorless plates, mp 150-151°: ir



(KBr, Figure 9a) 2950 (m), 2850 (w), 1595 (s), 1355 (s), 1170 (s), 1025 (s), 985 (s), 860 (s), and 805 cm^{-1} (s); pmr ($CDCl_3$, Figure 9b) δ_A 1.02 and δ_B 1.57 (AB pattern, J_{AB}=11 Hz, 2H, methylene protons) δ2.27 (br s, 4H, methine protons), δ2.43 (s, 6H, 2 x $C\underline{H}_3$), δ2.50 (br s, 4H, methine protons), δ4.47 (br s, 2H, 8,11-protons), δ_A 7.30 and δ_B 7.78 (AA'BB' pattern, J_{AB}=8 Hz, 8H, benzene ring protons); mass spectrum (Figure 9c) m/e (%) 486(1), 315(22), 314(26), 159(44), 155(35), 144(20), 143(100), 142(16), 131(30), 91(75), 65(11).

Anal. Calcd for $C_{25}H_{26}O_2S_2$: C, 61.71; H, 5.39. Found: C, 61.82; H, 5.42.

Reaction of Ditosylate 76 with Sodium Iodide in Hexamethylphosphoramide (HMPA).-- (a) A stirred mixture of ditosylate 76 (12.1g, 0.025 mole) and sodium iodide (60g, 0.4 mole) in freshly distilled HMPA (150 ml) was heated at 125-130° for 40 hr. During the reaction, a stream of nitrogen was blown over the surface of the reaction mixture. The product, which was collected in a receiver cooled in dry ice-acetone, was taken up in pentane, washed with water, and then dried (Na_2SO_4) and filtered. Solvent was removed from the filtrate by distillation through a 12-in Vigreaux column, affording an oily residue which was sublimed at 80-90° (760 mm) to yield a white, waxy solid (415 mg, 11.6%).

Vpc analysis (column temp. 80°, flow rate 120 ml/min.) of this product indicated it contained two components in a ratio of approximately 1 to 2.5, which were separated by preparative gas chromatography (column temp. 130°, flow rate 120 ml/min.). The more volatile (minor component) of the two was identified to be tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]-undeca-2,6-diene (80), mp 141.5-142.5° (sealed tube) (lit.,[69] 143.5-144.5°): ir (CCl_4) 3055 (m), 2950 (s), 2806 (m), 1325 (m), 1018 (m), 835 cm^{-1} (m); pmr ($CDCl_3$) δ1.63 (br s, 2H, 10-methylene protons), δ2.33 (br s, 4H, 1,4,5,8-protons), δ3.17 (m, 2H, 9,11-protons), and δ5.93 (s, 4H, olefinic protons); mass spectrum m/e (%) 144(M^+, 12), 129(8), 115(9), 79(100), 78(32), 77(31), 66(15). ^{13}C nmr ($CDCl_3$) see text. The major component was characterized as hexacyclo[5.4.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$.$0^{8,10}$]undecane (81), mp 132-134° (sealed tube): ir (CCl_4, Figure 15a) 3040 (s), 2960 (s), 2850 (m), 1438 (w), 1301 (m), 1290 (m), 1198 (w), 1015 (w), 950 (w), 930 cm^{-1} (w); pmr ($CDCl_3$, Figure 15b) δ1.43 (d, J=ca. 1 Hz, 2H, 3-methylene protons), δ1.83-2.48 (complex multiplets, 4H), δ2.48-3.17

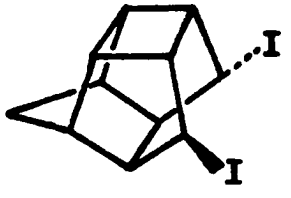
(complex multiplets, 6H); mass spectrum (figure 15c) m/e (%) 144(M^+,81), 129(45), 128(30), 116(18), 115(19), 79(100), 78(98), 77(32), 66(97), 51(18), 38(30); ^{13}C nmr (CCl_4, Figure 16a and 16b) see text.

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39.
Found: C, 91.78; H, 8.32.

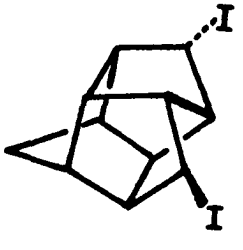
The dark mixture left in the reaction flask was poured into water and the products were extracted into hexane (100 ml x 4). The combined extracts were washed with saturated aqueous sodium bicarbonate solution (100 ml x 2), and water (100 ml x 3), and then dried (Na_2SO_4), filtered, and concentrated to afford a colorless oily material. Recrystallization of this material from hexane afforded a mixture of diiodides (4.3g, 43.4%). The pmr spectrum of this mixture displayed two broad singlets at δ3.97 and δ4.47 in ratio of 15 : 11, and complex multiplets at δ1.2-3.6. This mixture was chromatographed on silica gel (E. Merck, tlc grade, 200g, 1.5-in. o.d. column) using hexane as eluant (eluating speed ca. 15 ml/hr). Repeated recrystallization (hexane) of the first few fractions afforded a pure diiodide, mp 132-133°, and the last few fractions gave a pure diiodide, mp 122-123°. It was later found that the middle fractions contained a third diiodide which could be separated from the diiodide having mp 122-123° by additional careful elution chromatography. Recrystallization of the new material afforded the third diiodide, mp 151-

152° (hexane). Separation by this method could provide about 0.1 g of each pure diiodides from 3-4 g of the mixture of diiodides. These three diiodides were characterized based on their spectral data as followings:

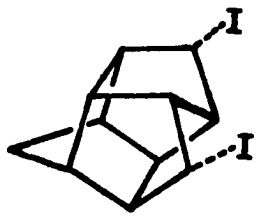
Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-exo,exo-8,11-diiodide (77), as prisms, mp 132-133°: ir (CCl_4, Figure 10a) 2990 (s), 2870 (m), 1292 (m), 1273 (m), 1165 (m), 1128 (s), 865 (m), 692 cm^{-1} (s); pmr ($CDCl_3$, Figure 10b) δ_A 1.37 (multipled doublet), δ_B 1.78 (multipled doublet) (AB pattern, J_{AB} = 12 Hz, 4-methylene protons), δ2.57 (br s, 2H, methine protons), δ2.70-3.10 (complex multiplets, 4H, methine protons), δ3.43 (m, 2H, methine protons) and δ4.47 (s, $W_{1/2}$=ca. 2 Hz, 2H, 8,11-protons); mass spectrum (Figure 10c) m/e (%) 398(M^+, 0.2), 271(37), 205(15), 193(18), 144(41), 143(18), 129(12), 128(12), 115(10), 79(100), 78(29), 77(23), 66(15); ^{13}C nmr ($CDCl_3$, Figure 13a and 13b) see text.



Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-exo,exo-4,7-diiodide (78), as needles, mp 151-152°: ir (CCl_4, Figure 11a) 2985 (s), 2870 (m), 1290 (s), 1280 (s), 1275 (s), 1238 (m), 1195 (m), 1175 (s), 1155 (s), 670 cm^{-1} (s); pmr ($CDCl_3$, Figure



11b) δ1.53 (s, $W_{1/2}$=ca. 3 Hz, 2H, 11-methylene protons), δ2.20 (br s, 4H, methine protons), δ2.73 (br s, 2H, methine protons), δ3.03 (br s, 2H, methine protons), and δ3.97 (s, $W_{1/2}$=ca.3 Hz, 2H, 4,7-protons); mass spectrum (Figure 11c) m/e (%) 398(M^+, 6), 271(65), 205(19), 193(19), 144(44), 143(37), 79(100), 78(33), 77(17), 66(15); ^{13}C nmr ($CDCl_3$, Inset Figure 14a) see text. Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-endo,exo-4,7-diiodide (79), as needles, mp 122-123°: ir (CCl_4, Figure 12a) 2985 (s), 2870 (m), 1298 (m), 1268 (s), 1172 (s), 1163 (s), 670 cm^{-1} (s); pmr ($CDCl_3$, Figure 12b) δ1.50 (d, J=ca. 1 Hz, 2H, 11-methine protons), δ1.93-2.80 (complex multiplets, 6H, methine protons), δ2.80-3.30 (complex multiplets, 2H, methine protons), and δ3.97 (br s, $W_{1/2}$=ca. 5 Hz, 2H, 4,7-protons); mass spectrum (Figure 12c) m/e (%) 398(M^+, 0.6), 271(5), 205(4), 193(4), 144(13), 143(18), 129(10), 128(13), 115(12), 79(100), 77(28), 66(23); ^{13}C nmr ($CDCl_3$, Figure 14a and 14b) see text.



Anal. Calcd for $C_{11}H_{12}I_2$: C, 33.19; H, 3.04.
Found 77: C, 33.17; H, 2.96.
78: C, 32.93; H, 3.07.
79. C, 33.04; H, 2.99.

(b) at 160°.-- A mixture of ditosylate 76 (29.1g,

0.06 mole) and sodium iodide (150g, 1 mole) in freshly distilled HMPA (250 ml) was heated at 160° under nitrogen for 23 hr. The resulting dark reaction mixture was worked up as above to give a product (15.6g) which was shown by pmr spectrum to contain, in addition to hydrocarbons 80 and 81, the diiodides 77 - 79 in ratio of 77 : (78+79) = 1 : 35.

(c) at 100-105°.-- A mixture of ditosylate 76 (4.6g, 9.4 mmole) and sodium iodide (23g, 153 mmole) in HMPA (40 ml) was heated at 100-105° under nitrogen for 42 hr. The reaction mixture was worked up as above to afford a product (3.5g) which contained the diiodides in ratio of 77 : (78+79) = 15 : 8, together with unchanged ditosylate 76 (76 : 77 = 1 : 5) and small amount of hydrocarbons 80 and 81. The yield of diiodides was 77.1% after recrystallization.

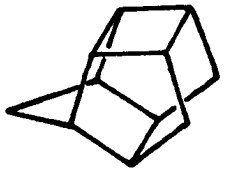
Dehalogenation of Pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-exo,exo-8,11-diiodide (77).-- (a) Using lithium-tert-butyl alcohol in tetrahydrofuran. To a solution of 77 (635 mg, 1.6 mmole, mp 131-133°) in dry tetrahydrofuran (10 ml) were added tert-butyl alcohol (1 ml, 10.6 mmole) and lithium wire (140 mg, 20 mg-atom). The reaction mixture was kept under nitrogen. After the initial reaction subsided, the mixture was refluxed for 1 hr and

then poured into ice-water. The product was extracted into pentane and the pentane solution was washed with water and then dried (Na_2SO_4). The solution was then filtered and solvent was carefully removed by fractional distillation, affording an oily residue which was sublimed at 95° (760 mm) to give a white, waxy solid (157 mg, 68.2%). Vpc (column temp. 85°, flow rate 120 ml/min.) and pmr spectral analyses indicated that this product contained only diene 80. None of the desired hydrocarbon 82 was present in detectable amount.

(b) Using lithium aluminum hydride. Diiodide 77 (520 mg, 1.3 mmole) in freshly distilled tetrahydrofuran (8 ml) was added dropwise over a 10 min period to a refluxed suspension of lithium aluminum hydride (0.38g, 10 mmole) in tetrahydrofuran (5 ml) under an atmosphere of nitrogen. After refluxing for 1 hr, the reaction mixture was cooled to 0° and water was added to destroy excess $LiAlH_4$. The product (ca. 100 mg) was isolated and analyzed in the manner described in part (a), above. Vpc and pmr spectral analyses revealed that the product contained only diene 80.

(c) Using tri-n-butyltin hydride. Diiodide 77 (200 mg, 0.5 mmole) in anhydrous diethyl ether (10 ml) was heated to reflux and to this solution was added dropwise under nitrogen an excess of freshly distilled tri-n-butyltin hydride (0.5 ml, prepared from the reaction of tri-n-butyltin

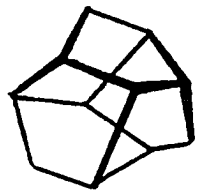
chloride with lithium aluminum hydride in diethyl ether[119]). After refluxing for 3 hr, the reaction mixture was washed with 5% aqueous sodium hydroxide solution (5 ml), water (5 ml), and then dried (Na_2SO_4), and filtered through silica gel (ca. 3 g). The solvent was removed by fractional distillation and the residue was sublimed to give solid material (ca. 40 mg). This material was purified via preparative vpc (column temp. 150°, flow rate 130 ml/min.) and was shown to consist of diene 80 and pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (82) in ratio of 80 : 82 = 9 : 7.



Hydrocarbon 82 was identified on the basis of the identities of its spectral (ir and pmr) and vpc retention time (peak enhancement method) with those of an authenic sample of 82.[66]

Dehalogenation of Pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4,7-diiodide (trishomocubyl diiodides 78 and 79).-- (a) Using zinc-acetic acid. To a stirred solution of isomeric diiodides 78 and 79 (1.02 g, 26 mmole) in glacial acetic acid (5 ml) was added zinc dust (1 g). The mixture was heated at 100° by mean of an oil bath for 2 hr, then poured into ice-water (50 ml) and extracted with pentane (30 ml x 3). The combined extracts were washed with 5%

aqueous sodium bicarbonate solution (30 ml x 3) and water (30 ml x 2), then dried (Na_2SO_4) and filtered. The solvent was removed by fractional distillation and the oily residue was sublimed (100-110°/760 mm) to yield pentacyclo[6.3.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane ("trishomocubane", 83) (0.3g, 83.4%).



Compound 83, mp 146-148° (sealed tube) (lit. 150-152°[67], 149-151°[68], 147-149°[69]) has following spectral properties (identical with those reported values in the literature[67-69]): ir (CCl_4) 2960 (s), 2875 (s), 1455 (m), 1291 (s), 1270 cm^{-1} (m); pmr ($CDCl_3$) δ1.36 (br s, 6H, methylene protons) and δ1.97 (br s, 8H, methine protons); mass spectrum m/e 146(M^+) and 80 (base peak).

(b) Using tri-n-butyltin hydride. A mixture of trishomocubyl diiodides 78 and 79 (590 mg, 1.5 mmole) in anhydrous diethyl ether (10 ml) was heated to reflux and to this solution was added dropwise under nitrogen an excess of freshly distilled tri-n-butyltin hydride (1.6 g). After refluxing for 2.5 hr, the reaction mixture was washed with 5% aqueous sodium hydroxide solution (5 ml), water (5 ml), and then dried (Na_2SO_4), filtered through silica gel (ca. 4 g). The solvent was removed by fractional distillation and the residue was sublimed to give solid material (182 mg,

83.1%). Pmr and vpc retention time (peak enhancement method, column temp. 80°, flow rate 120 ml/min.) of this material were identical to those of trishomocubane prepared by foregoing method (a).

Bromination of 81.-- Bromine was added dropwise to a solution of 81 (57 mg, 0.4 mmole) in chloroform (3 ml) at 0° until the color of bromine persisted. The solution was set aside at room temperature for 24 hr and then washed sequentially with aqueous sodium thiosulfate solution and water. The organic layer was then dried (Na_2SO_4), filtered, and concentrated to afford an oily material (ca. 100 mg). This material, which was not further purified, displayed the following spectral data: ir (film) 2970 (s), 2870 (m), 1380 (s), 1200 (s), 780 (s), and 710 cm^{-1} (s); pmr ($CDCl_3$) δ1.5 (br s) and δ1.6 (center of an AB pattern, J_{AB}=ca. 1.5 Hz, total 2H, methylene protons), δ2.0-3.2 (complex multiplet, 8H), δ4.2 (br s) and δ4.35 (br s) (total 2H, ratio ca. 2.5 : 1, respectively, CHBr); mass spectrum (10eV) m/e (%) 306/304/302, molecular ion with intensity profile characteristic of Br_2 multiplet,[53] 224(60), 223(64), 145(24), 144(28), 143(38), 79(100), 67(38). Recrystallization of this material from hexane afforded a white solid having mp 89-105°.

Reaction of Diiodides with Sodium Iodide in HMPA (Control Experiments of Diiodides).-- (a) Diiodide 77. A mixture of diiodide 77 (718 mg, mp 131-133°) and sodium iodide (4.1 g) in freshly distilled HMPA (9 ml) was heated at 125-130° under nitrogen for 41 hr. After this period, water (20 ml) and pentane (20 ml) was added through the condenser to the reaction mixture; the layers were separated and the aqueous layer was further extracted with pentane (20 ml x 3). The combined pentane extracts were washed with water (20 ml x 2), dried (Na_2SO_4), filtered, and concentrated by careful distillation through a 6-in. Vigreaux column. The residue (ca. 620 mg) was analyzed as follows: tlc displayed two spots with slow-moving one (low R_f value) corresponding to the diiodides; pmr spectrum displayed signals at δ4.47 (due to diiodide 77) and δ3.97 (due to diiodide 78 and 79) with approximately equal areas; vpc analysis (column temp. 75°, flow rate 120 ml/min.) indicated the presence of 80 and 81 in a ratio of approximately 9.5 : 1, respectively. The diiodide 77 was also gas chromatographed and was shown to be stable under the same vpc conditions.

(b) Diiodide 78. A mixture of exo,exo-trishomocubyl diiodide 78 (467 mg, mp 148-150°) and sodium iodide (3 g) in freshly distilled HMPA (8 ml) was heated at 125-130° under nitrogen for 41 hr. After this period, the

reaction mixture was worked up as above to give a product mixture (ca. 400 mg) which was analyzed as follows: tlc displayed only one spot with R_f value equal to that of 78; vpc analysis (column temp. 75°, flow rate 120 ml/min.) showed no volatile material except pentane (solvent); pmr spectrum exhibited absorption signals corresponding to those of 78 and 79 without detectable signal at δ4.47 due to diiodide 77.

(c) Diiodide 79. A mixture of endo,exo-trishomocubyl diiodide 79 (571 mg, mp 121-123°) and sodium iodide (3.3 g) in freshly distilled HMPA (8 ml) was heated at 125-130° under nitrogen for 47 hr. After this period, the crude product (ca. 540 mg) was isolated as above and was analyzed as follows: tlc showed only one spot with R_f value equal to that of 79; vpc analysis revealed absence of any volatile material; pmr spectrum displayed absorption signals corresponding to a mixture of diiodides 78 and 79 only.

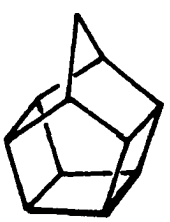
Dehalogenation of Isomeric Diiodides 77 - 79 with Zinc-Ethanol.-- A mixture of diiodides (1.2 g, 3 mmole) containing 54.5% of 77 and 45.5% of 78 and 79 (via pmr spectral analysis) was dissolved in ethanol (15 ml), and the solution was refluxed with zinc dust (1.05 g) for 90 min, and then filtered through a layer of Celite to remove insoluble materials. To the filtrate was added ice-water

(100 ml) and the solution was extracted with pentane (40 ml x 2). The combined extracts were washed with water (20 ml), dried (Na_2SO_4), filtered, and concentrated by fractional distillation to give an oily material. Sublimation of this material yielded a waxy solid (293 mg, 67.8%). Vpc (column temp. 99°, flow rate 98 ml/min.) analysis revealed that the product mixture contained at least three components. The first two peaks corresponded to diene 80 and trishomocubane 83 as evidenced by peak enhancement method. The third component had same R_f value corresponding to 81 and 82 (81 and 82 exhibited identical retention times under present vpc conditions). Pmr spectral analysis revealed this component to be 82, but not 81. No trace of homopentaprismane 53 was detected.

Tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undeca-2,6-diene (80). -- A stirred suspension of sodium (0.75 g, 33 mg-atom) in dry tetrahydrofuran (8 ml) was heated at reflux and was added dropwise a solution of a mixture of diiodides 77 - 79 (2.0 g, 5 mmole) in tetrahydrofuran (10 ml) under nitrogen. After the addition was complete (ca. 20 min), the milky reaction mixture was refluxed for additional 1.5 hr, and then filtered to remove insoluble material. The filtrate was mixed with ice-water and extracted with pentane. The pentane solution was washed with water, dried (Na_2SO_4),

filtered, and distilled through a 6-in. Vigreaux column, affording an oily material. Sublimation (125°/760 mm) of this material yielded diene 80 (0.54 g, 74.7%). The identity of this diene 80 was confirmed by comparison of pmr spectral and vpc data with that of diene obtained from the reaction of ditosylate 76 with sodium iodide.

Hexacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]undecane ("Homopentaprismane" 53).-- The apparatus (Ace Glass Inc.)



consists of a water-jacketed cylindrical pyrex vessel equipped with a ℧ 60/40 ground joint for accommodating the light source, a side arm for holding a reflux condenser, a magnetic stirring bar. A Hanovia 200 watt medium-pressure mercury lamp was used in conjunction with a Pyrex, double-walled cooling well. External cooling was provided by circulating chilled water (10-15°). The reaction vessel was charged with a solution of diene 80 (1.45g, 0.01 mole) in pentane (350 ml), and 9-xanthenone (4 g). Nitrogen was bubbled through the stirred solution for 10 minutes and the atmosphere was excluded from the reaction mixture by means of a balloon fitted on the end of the condenser. The irradiation was then started; the progress of the reaction was followed by

vpc analysis (column temperature 100°, flow rate 120 ml/min.) (Table IV). After irradiation for 18 hr, the irradiated mixture was rapidly filtered through a short column of silica gel (20 g) to remove insoluble materials. The solvent was removed by slow distillation through a 24-in. Vigreaux column, affording an oil which was sublimed at 110° (760 mm) to afford a colorless solid material (0.95 g). Vpc analysis (same conditions as above) showed the presence of an unidentified material (6.8%), unchanged diene 80 (44.3%), and homopentaprismane (53) (48.9%) in order of retention times. Pure samples of 53 (ca. 0.43 g, 30%, 42% based on uncovered diene) were obtained by preparative vpc (column temperature 135°, flow rate 120 ml/min.). Under this vpc condition, the retention times of the three components were about 10, 23, and 34 min, respectively. Further sublimation (90°/760 mm) afforded an analytical sample of 53, mp 160-162° (sealed tube): ir (CCl_4, Figure 17a) 2985 (s), 2870 (m), 1285 (m), 1245 (m), and 890 cm^{-1} (w); pmr ($CDCl_3$, Figure 17b) δ1.73 (t, J=ca. 1.5 Hz, 2H, methylene protons), δ2.67 (br s, 2H, 3,5-bridgehead protons) and δ3.03 (s, $W_{1/2}$=ca. 3 Hz, 8H, methine protons); mass spectrum (Figure 17c) m/e (%) 144(M^+, 3), 115(11), 79(100), 78(41), 77(46), 66(23), 65(12), 63(10), 51(17), 39(15).

Anal. Calcd for $C_{11}H_{12}$: C, 91.61; H, 8.39.

Found: C, 91.66; H, 8.37.
91.38 8.40.

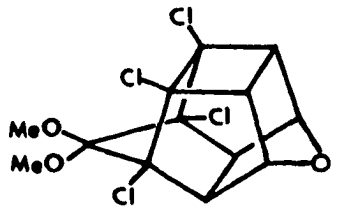
TABLE IV. Vpc Analysis[a] of Photoconversion of Diene 80 to Homopentaprismane 53.

Irradiation time (hr)	Diene 80 (mm^2)[b]	Homopentaprismane (mm^2)[b] 53	Ratio 53 : 80
2	422.5	86.8	0.21
4	235.7	92.4	0.39
6	205.7	106.4	0.52
8	178.4	119.4	0.67
10	176.6	161.3	0.91
13	177.6	182.7	1.03
16	162.1	170.9	1.01
18	131.4	168.7	1.28

a) 3% SE 30 on VarAport 100/120, 5' x 1/4", 100°, 120 ml/min. of He.

b) average area from three injection (20 µl each).

12-Oxa-4,4-dimethoxy-3,5,9,10-tetrachlorohexacyclo-[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane (68).-- A mixture of

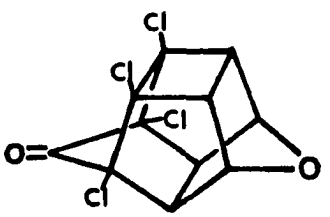


61 (64g, 0.17 mole) and p-toluenesulfonic acid (5.0g, 0.029 mole) in dry toluene (600 ml) was refluxed in a Dean-Stark apparatus for 42 hr. During this period, about 400 ml of turbid toluene was removed. Removal of the remaining solvent (rotary evaporator) afforded a tan solid which was taken up in chloroform (600 ml). The resulting solution was washed successively with water (250 ml x 2), 5% aqueous sodium bicarbonate solution (250 ml), and water (250 ml x 2). The organic layer was then dried (Na_2SO_4), filtered, and concentrated. The residue was recrystallized from ethyl acetate to afford a colorless solid (45.7g, 75%), mp 170-189°. An analytical sample of 68 was obtained via further recrystallization of the crude product from acetone. Colorless platelets, mp 189-190°, were thereby obtained. Ir (KBr, Figure 18a) 2950 (m), 2840 (w), 1435 (m), 1210 (s), 1090 (s), 1025 (s), and 780 cm^{-1} (s); pmr ($CDCl_3$, Figure 18b) δ3.03-3.23 (m, 4H, 2,6,8,11-methine protons), δ3.57 (s, 3H, $-OCH_3$), δ3.63 (s, 3H, $-OCH_3$), and δ5.18 (quintet, 2H, 1,7-methine protons); mass spectrum (Figure 18c) m/e (%) molecular ion not observable, 327(7), 325(33), 324(14), 323(97), 322(15), 321(100),

259(11), 257(16), 256(6), 190(6), 188(19), 183(6), 149(7), 125(14), 113(6), 75(6), 63(8), and 59(18).

Anal. Calcd for $C_{13}H_{12}O_3Cl_4$: C, 43.61; H, 3.38. Found: C, 43.90; H, 3.31.

12-Oxa-3,5,9,10-tetrachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane-4-one (86).-- (a) A suspension



of 68 (42g, 0.12 mole) in concentrated sulfuric acid (200 ml) was stirred at room temperature for 48 hr. The reaction mixture was then poured into ice water (1 l.) and the precipitated solid material was collected, washed with water, and then dried in vacuo. Crude 82 (32.1g, 87.7%) was thereby obtained. Recrystallization of the crude product from benzene-hexane, followed by sublimation (130°/1 mm) afforded an analytical sample of 86 as a colorless, microcrystalline solid, mp 198.5-200°: ir (KBr, Figure 19a) 1795 (s), 1260 (s), 1100 (s), 1025 (s), 1005 (s), 930 (s), and 745 cm^{-1} (s); pmr (acetone-d_6, Figure 19b) δ3.17 (br t, 4H, 2,6,8,11-methine protons) and δ5.25 (quintet, 2H, 1,7-methine protons); mass spectrum (Figure 19c) m/e (%) 318/316/314/312/310 (molecular ion, with the intensity profile characteristic of the Cl_4 multiplet[53]), 277(45), 275(44), 249(45), 247(41), 223(34),

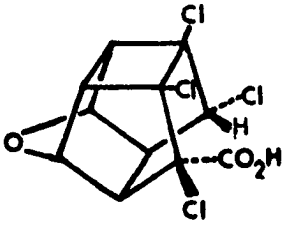
221(94), 219(94), 185(72), 183(100), 151(45), 149(91), 133(40), 85(21), and 63(34).

Anal. Calcd for $C_{11}H_6Cl_4O_2$: C, 42.34; H, 1.94. Found: C, 42.21; H, 1.98.

(b) A solution of diol 61 (2g, 5.3 mmole) in concentrated sulfuric acid (20 ml) and methylene chloride (30 ml) was stirred at room temperature for 72 hr. The organic layer was separated and the acid layer was extracted with methylene chloride (30 ml x 3). The combined organic solution was concentrated to afford crude 86 (0.7g, 36.7%). In two of other attempts under slightly different conditions, the yields were 13.2% and 32.7%.

11-Oxa-3,4,5,exo-6-tetrachloropentacyclo[6.2.1.$0^{2,7}.0^{4,10}.0^{5,9}$]undecane-endo-3-carboxylic Acid (88a).--

(a) Reaction of 86 with Sodium Hydroxide in Toluene. To a



suspension of 86 (12.5g, 40 mmole) in dry toluene (100 ml) was added crushed sodium hydroxide pellets (15g, excess). The resulting mixture was refluxed with stirring for 2 hr. The cooled reaction mixture was poured into ice water (600 ml), the layers were separated, and the aqueous layer was extracted with diethyl ether (200 ml). The aqueous solution was acidified with

excess concentrated aqueous hydrochloric acid solution, thereupon a solid material precipitated. The solid was taken up in diethyl ether (500 ml), and the resulting solution was extracted with 5% aqueous sodium bicarbonate solution (100 ml x 2). The aqueous solution was acidified and then extracted with diethyl ether (100 ml x 3). The combined extracts were washed with water, dried (Na_2SO_4), filtered, and then evaporated to afford crude 88a as a tan solid. Recrystallization of this material from diethyl ether-hexane afforded pure 88a (10.6g, 80.2%), mp 242-245° (dec.): ir (KBr) 3000 (br s) and 1725 cm^{-1} (s); pmr (acetone-d_6) δ3.03-3.47 (m, 4H, 2,7,9,10-methine protons), δ4.50 (s, 1H, 6-C<u>H</u>Cl), and δ5.27-5.60 (m, 2H, 1,8-methine protons); mass spectrum m/e (%) molecular ion not observable, 201(25), 187(47), 185(83), 151(43), 149(100), 73(33), 68(25), 60(26), 57(30), 55(27), 44(48), 43(43), 41(28), 39(25), 38(60), and 36(73). Acid 88a was further characterized *via* its methyl ester 88b. Acid 88a (1g, 3 mmole) was refluxed with thionyl chloride (10 ml, excess) for 28 hr. After this period, the excess $SOCl_2$ was removed and dry methanol (20 ml, excess) was added dropwise over a 30 min period. Refluxing was resumed and continued for an additional 12 hr. The reaction mixture was then concentrated (rotary evaporator). The residue was taken up in diethyl ether (50 ml), washed first with 5% sodium bi-

carbonate solution (20 ml) and then with water (20 ml), and then dried (Na_2SO_4). The solution was then filtered and concentrated, affording an oily material which recrystallized from benzene-hexane to afford 88b (610 mg, 59%) as a colorless needles, mp 104-107°. Sublimation (90°/1 mm) followed by recrystallization of the sublimate from hexane afforded an analytical sample of 88b as colorless platelets, mp 107-108°: ir (KBr, Figure 20a) 1745 (s), 1425 (m), 1295 (s), 1235 (s), and 1005 cm^{-1} (s); pmr ($CDCl_3$, Figure 20b) δ2.83-3.40 (m, 4H, 2,7,9,10-methine protons), δ3.88 (s, 3H, $-OCH_3$), δ4.10 (d, 1H, 6-CHCl), and δ5.22-5.60 (m, 2H, 1,7-methine protons); mass spectrum (Figure 20c) m/e (%) 350/348/346/344/342 (molecular ion, with the intensity profile characteristic of the Cl_4 multiplet[53]), 326(32), 309(45), 307(51), 291(32), 290(39), 289(35), 288(33), 207(37), 206(38), 205(48), 204(56), 185(32), 183(41), 173(31), 151(37), 149(100), 115(49), 105(33), 103(93), 75(31), 68(27), and 59(66).

Anal. Calcd for $C_{12}H_{10}Cl_4O_3$: C, 41.89; H, 2.93.
Found: C, 42.01; H, 2.94.

(b) Reaction of 86 with Sodium Hydroxide in Tetrahydrofuran. To a solution of 86 (0.56g, 1.8 mmole) in freshly distilled tetrahydrofuran (14 ml) maintained at 0-5° via external cooling (ice bath) was added crushed sodium hydroxide pellets (1 g). The resulting mixture

turned milky after ca. 20 min. The ice bath was then removed, and the reaction mixture was stirred overnight at ambient temperature. The mixture was then poured into cold 1.5N hydrochloric acid solution (30 ml), and the resulting mixture was extracted with diethyl ether (15 ml x 3). The combined ethereal extracts were washed with water and then dried (Na_2SO_4), filtered, and concentrated, affording a viscous oil (0.53 g) which solidified on standing. The ir and pmr spectra of this material were identical in all respects with those of 88a. The yield of 88a in this reaction was 89.8%.

(c) Reaction of 86 with Sodium Hydroxide in Benzene. A mixture of crushed sodium hydroxide pellets (1 g) and benzene (50 ml) was dried via azeotropic distillation (Dean-Stark apparatus). To the resulting mixture was added 86 (1.0g, 3.2 mmole), and the reaction mixture was refluxed for 20 hr. The usual workup followed by recrystallization of the product from diethyl ether-hexane afforded a colorless solid (0.74 g) which was identical in all respects with 88a. The yield of 88a in this reaction was 70%.

Reaction of 86 with Sodium Methoxide in Benzene. Methanol was dried by refluxing over magnesium turnings in the presence of a few crystals of iodine for three days.[120] To freshly-distilled dry methanol (excess) was added sodium

metal (1 g); after the reaction subsided, the excess methanol was removed under reduced pressure, and dry benzene (180 ml) was added to the residue. The resulting mixture was dried *via* azeotropic distillation (Dean-Stark apparatus). Ketone 86 (1.25g, 4.0 mmole) was then added, and the reaction mixture was refluxed with stirring for 24 hr. Workup afforded only unreacted 86 (*ca.* 1.2 g); no other product could be detected.

4,12-Dioxa-8,11-dichlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]dodecane-1-carboxylic Acid (89a). (a) Reaction of 86 with Aqueous Sodium Hydroxide. Compound 86 (630 mg, 2.0 mmole) was refluxed with 25% aqueous sodium hydroxide solution (10 ml) for 12 hr. The reaction mixture was then cooled to 0° (ice bath) and acidified *via* dropwise addition of excess concentrated hydrochloric acid. The mixture was then extracted with ethyl acetate, and the organic layer was washed with 5% aqueous sodium bicarbonate solution (15 ml x 2). The combined aqueous washings were acidified and then extracted with ethyl acetate. The organic layer was washed (H_2O), dried (Na_2SO_4), filtered, and then concentrated, affording 89a (385 mg, 66.5%). Recrystallization from ethyl acetate-

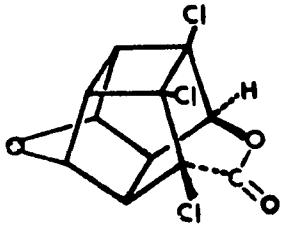
hexane afforded pure 89a (330 mg, 57.4%) as a colorless microcrystalline solid, mp 271-275° (dec.): ir (KBr) 3300-2500 (br), 1730 (sh), 1705 (s), 1450 (s), 1310 (s), 1290 (s), 1260 (s), 1200 (s), 1065 (m), 1015 (s), and 910 cm^{-1} (s); pmr (DMSO-d_6): δ3.17 (m, 4H, 2,6,9,10-methine protons) and δ4.80-5.13 (m, 3H, 3,5,7-methine protons); mass spectrum m/e (%) 278/276/274 (molecular ion, with the intensity profile characteristic of the Cl_2 multiplet[53]), 231(69), 229(100), 203(29), 201(46), 195(28), 194(28), 167(28), 165(40), 101(16), 89(17), 77(34), 75(29), 73(16), 63(25), 51(65), 50(26), 45(30), and 39(36). Acid 89a was further characterized via its methyl ester. Acid 89a (167 mg, 0.572 mmole) was treated with thionyl chloride (ca. 2 ml, excess), and the reaction mixture was refluxed for 22 hr. After this period, dry methanol (5 ml, excess) was added dropwise to the cooled reaction mixture over a 10 min period. The resulting solution was then refluxed for 5 hr. The reaction mixture was then concentrated, and the solid residue was taken up in diethyl ether (30 ml) and washed successively with water (10 ml), 5% sodium bicarbonate solution (10 ml x 2) and water (10 ml x 2). The organic layer was dried ($MgSO_4$), filtered, and concentrated, affording crude 89b (108 mg, 63%). Recrystallization from benzene-hexane afforded an analytical sample of 89b as colorless platelets, mp 138.0-138.5°: ir (KBr, Figure 21a)

3030 (w), 1752 (s), 1430 (m), 1110 (s) and 1025 cm^{-1} (s); pmr ($CDCl_3$, Figure 21b) δ3.28 (m, 4H, 2,6,9,10-methine protons), δ3.93 (s, 3H, $-OCH_3$), δ4.90 (br t, 1H, 7-methine proton), and δ4.90-5.20 (m, 2H, 3,5-methine protons); mass spectrum (Figure 21c) m/e (%) 292/290/288 (molecular ion, with the intensity profile characteristic of the Cl_2 multiplet[53]), 231(61), 229(100), 203(26), 201(42), 194(17), 165(41), 137(25), 117(27), 115(77), 102(24), 101(19), and 51(19).

Anal. Calcd for $C_{12}H_{10}Cl_2O_4$: C, 49.85; H, 3.49.
Found: C, 49.87; H, 3.14.

(b) Reaction of 88a with Aqueous Sodium Hydroxide. Compound 88a (332 mg, 1 mmole) was refluxed with 25% aqueous sodium hydroxide solution (10 ml) for 16.5 hr. Workup as above afforded a colorless solid (195 mg), mp 271-275° (dec.). The ir and pmr spectra of this solid were identical in all respects with those of 89a. The yield of 89a in this reaction was 71%.

4,13-Dioxa-1,8,11-trichlorohexacyclo[5.4.2.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]tridecane-12-one (92).-- A mixture of acid



88a (2.5g, 7.6 mmole) and barium carbonate (ca. 1 g) in 95% ethanol (50 ml) was refluxed with stirring for 44 hr. After this period,

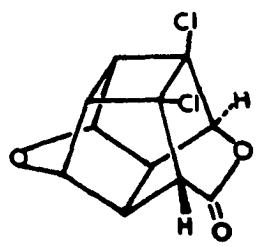
the reaction mixture was poured into ice water (100 ml), and the resulting mixture was filtered to remove insoluble material. The solid residue was then washed with ethyl acetate (50 ml). The layers in the filtrate were separated, and the aqueous layer was extracted with ethyl acetate (50 ml x 2). The combined extracts were washed (H_2O), dried ($MgSO_4$), filtered, and then concentrated, affording crude 92 (1.95g, 78.4%). Recrystallization from ethyl acetate afforded pure 92 as colorless prisms, mp 294.5-295.5°: ir (KBr, Figure 22a) 1778 (s), 1085 (s), 1025 (s), and 1000 cm^{-1} (s); pmr (DMSO-d_6, Figure 22b) δ3.07-3.53 (m, 4H, 2,6,9,10-methine protons) and δ5.10-5.53 (m, 3H, 3,5,7-methine protons); mass spectrum (Figure 22c) m/e (%) 298/296/294/292 (molecular ion, with the intensity profile characteristic of the Cl_3 multiplet[53]), 221(21), 219(21), 187(60), 185(100), 183(18), 151(51), 149(95), 115(24), and 68(17).

Anal. Calcd for $C_{11}H_7Cl_3O_3$: C, 45.01; H, 2.40.
Found: C, 44.79; H, 2.29.

Reaction of 92 with Aqueous Sodium Hydroxide Solution. Compound 92 (400 mg, 1.36 mmole) was refluxed with 25% aqueous sodium hydroxide solution (5 ml, excess) for 5 hr. Workup afforded a colorless solid (267 mg), mp 274-276° (dec.). The ir and pmr spectra of this solid were

identical in all respects with those of 89a. The yield of 89a in this reaction was 71.4%.

Reaction of 88a with Zinc in Ethanol. Formation of Carboxylic Acid 109a And Lactone 110.-- Acid 88a (5g, 15 mmole) in absolute ethanol (125 ml) was refluxed with zinc metal (5g, excess) for 40 hr; during this period, additional zinc metal (2 g) was added. The resulted milky solution was decanted into cold water (200 ml) and the mixture was stirred with 5% sodium bicarbonate solution (100 ml) and diethyl ether (200 ml) for 30 minutes and filtered to remove undissolved material. The layers were separated, and the ethereal solution was washed with water (50 ml x 2), then dried (Na_2SO_4), filtered and concentrated to afford crude 4,13-dioxa-8,11-dichlorohexacyclo[5.4.2.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.$0^{8,11}$]tridecane-12-one (110) (0.5g, 13%). This material

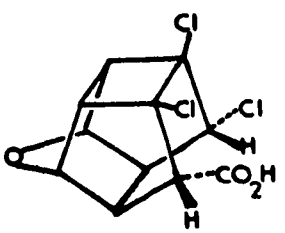


was recrystallized from ethyl acetate-hexane to give pure lactone 110 as fine colorless needles, mp 295-296°: ir (KBr, Figure 24a) 1768 (s), 1369 (m), 1181 (m), 1060 (m), 1021 cm^{-1} (s); pmr ($CDCl_3$, Figure 24b) δ2.8-3.3 (m, 5H, 1,2,6,9,10-protons) and δ4.8-5.3 (m, 3H, 3,5,7-protons); mass spectrum (Figure 24c) m/e (%) 262/260/258 (molecular ion, with the intensity

profile characteristic of the Cl_2 multiplet[53]), 153(37), 151(100), 149(23), 116(20), 115(22), 99(17), 89(16), 63(26), 51(33).

Anal. Calcd for $C_{11}H_8O_3Cl_2$: C, 50.99; H, 3.11.
Found: C, 50.79; H, 3.18.

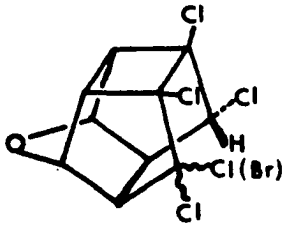
The alkaline solution was acidified with concentrated hydrochloric acid and the product was extracted with diethyl ether (100 ml x 3), yielding crude 11-oxa-4,5,exo-6-trichloropentacyclo[6.2.1.$0^{2,7}$.$0^{4,10}$.$0^{5,9}$]undecane-endo-3-carboxylic acid (109a) (3.8g, 84.8%), mp 213-223° (dec.). Recrystallization from ethyl acetate afforded 109a as colorless crystals, mp 229-231° (dec.): ir (KBr) 3200 (s), 1738 (s), 1095 cm^{-1} (s); pmr (pyridine) δ2.9-3.4 (m, 5H) and δ4.9-5.5 (m, 3H); mass spectrum m/e (%) 298/296/294 (molecular ion, with the intensity profile characteristic of the Cl_3 multiplet[53]), 153(15), 151(50), 149(29), 116(17), 115(59), 111(16), 103(24), 77(20), 75(27), 73(15), 68(100), 63(26), 51(33), 43(19), 39(28), 36(44). Acid 109a was further characterized via its methyl ester 109b. A sample of acid 109a (1g, 3.4 mmoles) was refluxed with thionyl chloride (12 ml, excess) for 20 hr to give solid acid chloride (ir (KBr) 1772 cm^{-1}), which was converted to the methyl ester 109b (570 mg, 54.3%)



by refluxing with dry methanol (30 ml) for 24 hr. Recrystallization from methanol gave 109b as colorless prisms, mp 163-164°: ir (KBr, Figure 23a) 1730 (s), 1345 (m), 1215 (s), 1040 (m), and 1010 cm^{-1} (m); pmr ($CDCl_3$, Figure 23a) δ2.83-3.13 (m, 5H, 2,3,7,9,10-protons), δ3.80 (s, 3H, OCH_3), δ4.45 (s, 1H, 6-protons), δ5.00 (m, 1H, 1- or 8-proton), and δ5.40 (m, 1H, 1- or 8-proton); mass spectrum (Figure 23c) m/e (%) 312/310/308 (molecular ion, with the intensity profile characteristic of the Cl_3 multiplet[53]), 158(20), 151(22), 150(15), 149(50), 146(17), 125(15), 116(16), 115(77), 113(15), 111(23), 103(18), 99(23), 89(16), 75(20), 69(18), 68(100), 59(46), 39(28).

Anal. Calcd for $C_{12}H_{11}O_3Cl_3$: C, 46.55; H, 3.58. Found: C, 46.68; H, 3.61.

Modified Hunsdiecker Reaction of 88a. Formation of 114.-- (a) In Carbon Tetrachloride. A mixture of acid



88a (4.4g, 13.3 mmole) and red mercuric oxide (2.2g, 10 mmole) in dry carbon tetrachloride (70 ml) was heated, with stirring, such that the rate of distillation was about one ml per minute. After 30 min. of distillation in this manner, a solution of bromine (3g, 16.7 mmole) in carbon tetrachloride (25 ml)

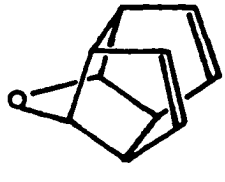
was added dropwise. Vigorous generation of carbon dioxide began in about 15 min, but the bromine color persisted during the entire period of addition (ca. 1 hr). After bromine addition had been completed, the reaction mixture was refluxed for 100 min. The cooled mixture was filtered with suction through a Celite mat to remove mercury salts. The residue was then washed with carbon tetrachloride (25 ml). The clear filtrate was washed with 5% aqueous sodium hydroxide (30 ml), and the coagulated yellow material which formed was removed from the two-phase solution by suction filtration. After the organic phase had been washed with water (30 ml x 2) and dried (Na_2SO_4), the solution was concentrated to afford a colorless oil. Recrystallization of this oil from hexane afforded white plates of 114 (3.95 g), mp 112-116°. Sublimation (95°/0.1 mm) of this material followed by several recrystallizations (hexane) raised its melting point to 117-120°. Ir (KBr, Figure 25a) 1200-1340 (complex absorption pattern, s) and 600-1090 cm^{-1} (complex absorption pattern, s); pmr ($CDCl_3$, Figure 25b) δ2.83-3.58 (complex multiplet, 4H, methine protons) and δ5.3-5.73 (complex multiplet, 3H, containing a doublet at δ5.32, 1,6,8-protons); mass spectrum (Figure 25c) m/e (%) molecular ion not observable, 287(23), 285(49), 283(37), 219(35), 183(36), 181(37), 149(58), 117(30), 115(100), 103(30), 69(40).

(b) in Bromoform. A mixture of acid 88a (1.5g, 5.1 mmole) and red mercuric oxide (1.2g, 5.5 mmole) in purified bromoform (15 ml) was maintained at 95° (oil bath temperature) and was then added dropwise a solution of bromine (1g, 6 mmole) in bromoform (8 ml). After the addition was complete (ca. 1 hr), the mixture was stirred for an additional 2 hr at 95° and then cooled. The solution was filtered and then concentrated to afford a dark oil which was taken up in diethyl ether (100 ml). The ethereal solution was washed successively with the following solutions (30 ml each): aqueous sodium thiocarbonate, water, 5% sodium bicarbonate, water, brine. The organic layer was then dried, filtered and concentrated to afford a brown oil (0.6 g). Recrystallization of this oil from hexane afforded a yellow solid (0.45g, 24.2%) which was contaminated with impurities having ir absorption bands at 1760 and 1609 cm^{-1}. Sublimation of this material at 135° (0.1 mm) gave a waxy material (ca. 0.2g, 10.8%) which exhibited infrared and pmr spectra resembling those of 114 prepared by method (a).

Dehalogenation of 114. Formation of 115 and 116.-- To a stirred solution of 114 (7.2 g) and tert-butyl alcohol (20 ml, 0.22 mole) in anhydrous tetrahydrofuran (125 ml) under nitrogen was added finely cut lithium wire (3g, 0.4 g-atom). A vigorous exothermic reaction started after a

few minutes which could be moderated by external cooling (ice bath) to maintain a gentle reflux. When the reaction subsided, the mixture was heated under reflux for an additional 3 hr and then cooled. The mixture was then poured into crushed ice (300 ml). The aqueous solution was extracted with pentane (100 ml x 3); the pentane extracts were washed with water (100 ml x 3), dried (Na_2SO_4), and filtered. The solvent was removed from the filtrate by distillation through a 6-inch Vigreux column, and the oily residue was sublimed at 80° (aspirator pressure) to afford a colorless, waxy material (2.23 g). Vpc analysis (column temperature 95°, flow rate 82 ml/min) of this product showed that it contained 10-oxatetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]-undeca-2,6-diene (115) (46%), 4-oxapentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane (116) (38%), and three unidentified products. The two major products were separated from the product mixture by preparative gas chromotography (column temperature 150°, flow rate 144 ml/min). Under these conditions, the relative retention time of 115 and 116 was 1 : 1.6.

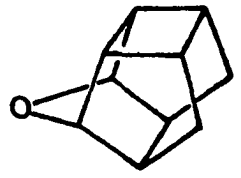
Oxa-diene 115, mp 168-169° (sealed tube) has the following spectral data: ir (KBr, Figure 26a) 3050 (m), 2960 (s), 1575 (w), 1330 (s), 1250 (m), 1055 (s), 1010 (s), 995 (s),



895 cm^{-1} (m); pmr ($CDCl_3$, Figure 26b) δ2.46 (br s, 4H, 1,4,5,8-methine protons), δ5.41 (quintet, J=ca. 3 Hz, 2H, 9,11-protons), and δ5.88 (s, $W_{1/2}$=ca. 2 Hz, 4H, olefinic protons); mass spectrum (Figure 26c) m/e (%) 146(M^+, 7), 118(17), 117(100), 115(26), 91(14), 81(32).

Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89.
Found: C, 82.26; H, 6.97.

Compound 116, mp 235-236° (sealed tube), has the following spectral data: ir (KBr, Figure 27a) 2970 (s), 2860 (m), 1330 (s), 1035 (s), 975 (s), 895 cm^{-1} (s); pmr ($CDCl_3$, Figure 27b) δ_A 1.13 (multipled doublet, 2H, exo-exo-8,11-methylene protons) and δ_B 1.50 (d, 2H, endo,endo-8,11-methylene protons) (AB pattern, J_{AB}=ca. 12 Hz), δ2.35 (m, 2H, methine protons), δ2.60 (br s, 4H, methine protons), and δ4.73 (symmetrical multiplet, 2H, 3,5-protons); mass spectrum (Figure 27c) m/e (%) 148(M^+, 31), 92(43), 91(54), 82(32), 80(40), 79(100), 77(35), 70(32), 69(34), 66(43), 41(52), 39(57).



Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16.
Found: C, 81.07; H, 8.07.

Attempts of Photocyclization of Oxa-diene 115. The light source was provided by the following lamps: (A) low-

pressure "mercury pencil" lamp (quartz filter), Ultra-Violet Products, Inc.; (B) Hanovia 200 watt medium-pressure mercury lamp; (C) Hanovia 400 watt high-pressure mercury lamp. Conditions for vpc analysis were column temperature 80° and flow rate 120 ml/min.

(a) A solution of oxa-diene 115 (78 mg) in acetone (20 ml) was irradiated with lamp (A) under nitrogen for 15 hr. The temperature of the external cooling bath was -78° (acetone-dry ice bath) at the beginning of the irradiation; it was gradually raised to 0° during the irradiation period. An aliquot was withdrawn from the solution, filtered through glasswool to remove insoluble material and analyzed by vpc. No volatile material was found except for the starting oxa-diene 115 and solvent. The irradiation on same solution was continued for 5 hr at 0-25°. Vpc analysis gave the same result as above.

(b) A solution of oxa-diene 115 (20 mg) and acetophenone (20 mg) in pentane (20 ml) was irradiated under nitrogen for 10 hr at 0-25° with lamp (A). The reaction mixture was filtered to remove insoluble material and the filtrate was analyzed by vpc and pmr spectrum. Only the starting oxa-diene 115 was detected.

(c) A solution of oxa-diene 115 (36 mg) and xanthone (75 mg) in pentane (20 ml) was irradiated as above for 10 hr. Vpc analysis of the irradiated solution indicated the

absence of any volatile material other than diene 115 and solvent.

(d) A solution of oxa-diene 115 (127 mg) in pentane (300 ml) was irradiated under nitrogen for 20 hr with lamp (C). The external cooling was provided by circulating chilled water (10-15°). An aliquot was withdrawn, filtered, and analyzed by vpc. Only oxa-diene 115 and solvent could be detected. To this solution was added xanthone (ca. 300 mg) and the irradiation was continued in the same manner for an additional 20 hr. Again, no product was detected by vpc analysis.

(e) A solution of oxa-diene 115 (250 mg) and xanthone (700 mg) in pentane (300 ml) was irradiated using lamp (B) at 10-15° for 63 hr under nitrogen. The irradiated solution was rapidly filtered through silica gel (ca. 10 g) and concentrated by distillation. No product could be detected by vpc and pmr analyses.

Transition Metal Catalyzed Rearrangements of Homopentaprismane (53).-- (a) with bis(triphenylphosphine)-rhodium carbonyl chloride. To homopentaprismane (12 mg) in chloroform-d (ca. 0.5 ml) was added few crystals of $[(C_6H_5)_3P]Rh(CO)Cl$ and the sample was degassed and sealed under vacuum in a pmr tube. After 20 hr at 70-75° (no significant rearrangement after 12 hr at 50°), a pmr spectrum

was recorded, which was identical to that of diene 80. Vpc analysis of the solution revealed only one peak corresponding to diene 80.

(b) with silver tetrafluroborate. A mixture of 53 (183 mg) and $AgBF_4$ (230 mg) in chloroform (7 ml) was sealed in a 20-ml test tube and the mixture was heated at 58-62° for 4 days. After washing with brine, the organic layer was concentrated by distillation. The single volatile material was separated from the oily residue by preparative vpc (Bentone 34-5% SE 52 on chromosorb W 60/80, 20 ft x 3/8 in, column temperature 130°, 180 ml/min. of helium, 44-min retention time). The collected material (113 mg) exhibited a melting point (160-162°) and a pmr spectrum identical to those of homopentaprismane (53).

(c) with silver perchlorate. To a solution of 53 (36 mg) in benzene-d_6 (0.5 ml) contained in a pmr tube was added $AgClO_4$ (50 mg) and the resulting solution was sealed under nitrogen. The pmr tube was washed with dilute ammonium hydroxide, distilled water and then dried (150°) prior to use. After heating at 78° for 10 days, the pmr spectrum was recorded and shown to be identical to the starting material (53). Again no rearrangement was observed when the mixture was heated at 83-110° for 24 hr.

Kinetic Measurements of Rh(I)-Catalyzed Rear-

rangement of Homopentaprismane (53). Kinetic runs were carried out with constant temperature oil bath heated with the vapor of hexane (67°) or dichloromethane (40°). The solvents were spectroscopic grade and were used without further drying. A solution of 53 and Rh(I) complex in chloroform-d or benzene-d_6 in a pmr tube was degassed and sealed under vacuum. The tube was then inserted into the oil bath, and spectra were recorded at measured time intervals. Integration of signals corresponding to the olefinic protons of diene 80 (δ6.0, 4H) and to the methylene protons of 80 and 53 (δ1.65-1.75, 2H) were performed at the same time and concentrations of homopentaprismane were then calculated by the equation shown below:

$$[53]_t = [53]_o \times \left[1 - \frac{(\text{integral of olefinic protons})/4}{(\text{integral of methylene protons})/2}\right] \quad (52)$$

(a) Catalyzed by $[(C_6H_5)_3P]_2Rh(CO)Cl$. A chloroform-d solution (0.5 ml) containing 53 (37 mg, 5.14×10^{-1} M) and Rh(I) complex (58.7 mg, 1.71×10^{-1} M) was sealed in a pmr tube. Kinetic measurements were performed at 67° for a period of 24 hr (> 2 half-life). The kinetic data are shown in Table VI and a plot of ln $[53]_o/[53]_t$ vs. time (hr) was linear (Figure 28). Least-squares treatment of the plot gave the slope = 0.07, from which a rate constant $k = 2.04 \times 10^{-1}$ M^{-1} hr^{-1} (5.7×10^{-5} M^{-1} sec^{-1}) could be calculated.

(b) with rhodium norbornadiene chloride dimer.

A benzene-d_6 solution (0.5 ml) of 53 (32.8 mg, 4.56×10^{-1} M) and $[Rh(NOR)Cl]_2$ (3.1 mg, 1.35×10^{-2} M) was sealed in a pmr tube and kinetic measurements were performed at 40° for a period of 7.5 days (ca. 1 half-life). The kinetic measurements are shown in Table VII. A plot of $\ln [53]_o/[53]_t$ vs. time (hr) was not linear (Figure 29).

TABLE VI. Kinetic Measurements of Rh(I)-Catalyzed Rearrangement of Homopentaprismane ($[(C_6H_5)_3P]_2Rh(CO)Cl$, $CDCl_3$, 67°)

Time (hr)	Integral of methylene protons[a]	Integral of olefinic protons[a]	$[53]_t$[b]	
1	16.1	1.8	0.485	
2.5	17.6	4.7	0.445	
5.5	16.0	8.8	0.373	
10	15.0	14.4	0.267	$[53]_o$=0.514 M
12	15.5	17.5	0.224	[Rh(I)]=0.171 M
13.75	15.4	18.2	0.210	$k=2.04 \times 10^{-1} M^{-1} hr^{-1}$ ($5.7 \times 10^{-5} M^{-1} sec^{-1}$)
16.5	15.3	20.8	0.163	$t_{1/2}$= 9.8 hr
19	15.4	22.6	0.123	
24	15.3	24.1	0.108	

(a) Average of five integrals. (b) Calculated using equation 52.

TABLE VII. Kinetic Measurements of Rh(I)-Catalyzed Rearrangement of Homopentaprismane (53) ($[Rh(NOR)Cl]_2$, C_6D_6, 40°)

Time (hr)	Integral of methylene protons[a]	Integral of olefinic protons[a]	$[53]_t$[b]	
0.5	16.2	1.3	0.437	
1.5	14.3	1.9	0.426	
3.0	14.6	2.5	0.417	
8.3	13.7	4.2	0.386	
14.3	13.1	5.8	0.355	$[53]_o=4.56 \times 10^{-1}$ M
22.75	13.1	6.7	0.338	$[Rh(I)]=1.35 \times 10^{-2}$ M
35	12.8	7.8	0.317	
49.3	13.6	8.9	0.305	
71.3	13.4	9.6	0.292	
95.3	12.0	10.0	0.265	
188	12.3	6.1	0.221	

(a) Average of six integrals. (b) Calculated using equation 52.

SUMMARY AND CONCLUSIONS

The extraordinary synthetic inaccessibility of pentaprismane is once again recognized. Projected synthetic routes (Scheme I) leading to pentaprismane, which key upon the semibenzylic acid rearrangement of an α-haloketone intermediate and a concerted cycloelimination of an 1,2-thiocarbonate to achieve the preparation of pentaprismane derivatives have been found to be unworkable. Attempted semibenzylic acid rearrangement on 2,3,5,6-tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-4,8,11-trione (13) resulted instead in a novel rearrangement, affording 6-chloro-*cis*-1,2-dihydrobenzocyclobutene-1,2,3-tricarboxylic acid (54a). An attempt at effecting a cycloreversion reaction on 4,4-dimethoxy-2,3,5,6-tetrachloropentacyclo[5.4.0.$0^{2,6}$.$0^{5,9}$]undecane-8,11-thiocarbonate (64) was not successful; the reaction probably afforded a dimer resulting from coupling of the corresponding carbene intermediate.

Homopentaprismane was synthesized in an overall yield of 13% *via* a six-step reaction sequence, starting with the Diels-Alder adduct of cyclopentadiene-*p*-benzoquinone. The key step (and the last) of this synthetic sequence was

the photocyclization of tetracyclo[6.3.0.$0^{4,11}$.$0^{5,9}$]undeca-2,6-diene (80). Experience has taught us that preparation of homopentaprismane (and its derivative) could not be achieved via an ionic pathway from the appropriate precursors such as pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-exo,exo-8,11-diiodide (77), since considerable strain energy must be introduced into this system (relative to its precusor) concomitant with its formation. Reaction of pentacyclo[5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$]undecane-endo,endo-8,11-ditosylate (76) with sodium iodide in hexamethylphosphoramide yielded the corresponding exo,exo-8,11-diiodide (77) and, in addition, a number of (thermodynamically favored) products: trishomocubyl diiodides (78 and 79), diene (80) and hexacyclo[5.4.0.$0^{2,6}$.$0^{4,11}$.$0^{5,9}$.$0^{8,10}$]undecane (81). The hydrocarbon 81 has been previously obtained by Underwood and Ramamoorthy via zinc-ethanol dehalogenation of the exo,exo-8,11 dibromide corresponding to 77, but was mistakenly assigned the homopentaprismane structure. Along with the knowledge that rearrangement of diradical intermediates (i.e., via decomposition of azo compounds) occur readily in this cage systems, we could conclude that a [$_{\pi}2_{s}+_{\pi}2_{s}$] photocyclization process might be the only entry to homopentaprismane and its derivatives.

Attempted semibenzilic acid rearrangements on 12-oxa-3,5,9,10-tetrachlorohexacyclo[5.4.1.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.

$O^{8,11}$]dodecane-4-one (86) resulted in the formation of 11-oxa-3,4,5-exo-6-tetrachloropentacyclo[6.2.1.$O^{2,7}$.$O^{4,10}$.$O^{5,9}$]undecane-endo-3-carboxylic acid (88a) or 4,12-dioxa-8,11-dichlorohexacyclo[5.4.1.$O^{2,6}$.$O^{3,10}$.$O^{5,9}$.$O^{8,11}$]dodecane-1-carboxylic acid (89a) depending on the solvent employed. No desired oxahomopentaprismane derivative via this base-promoted ring-contraction reaction was obtained. Attempts to synthesize oxahomopentaprismane by photocyclization of 10-oxatetracyclo[6.3.0.$O^{4,11}$.$O^{5,9}$]undeca-2,6-diene (115) were not successful, although the reasons for the failure of 115 to undergo photocyclization are not clear.

Homopentaprismane has been found to undergo Rh(I)-promoted cyclobutane-diolefin transformation, affording diene 80. However, homopentaprismane is inert to Ag(I)-induced isomerization which was expected to give hydrocarbon 81 (by analogy to the mechanism postulated previously for this type of rearrangement when carried out in the cubane system). We tentatively interpret this observation to result from insufficient relief of strain energy which would be expected upon rearrangement of homopentaprismane to 81.

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