CHROMIC ACID OXIDATION OF HYDROCARBONS AT THE BENZYLIC POSITION USING THE JONES REAGENT AND C-13 NMR STUDIES OF GEM-DIMETHYL-INDANS AND -INDANONES

By

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CHAPTER I

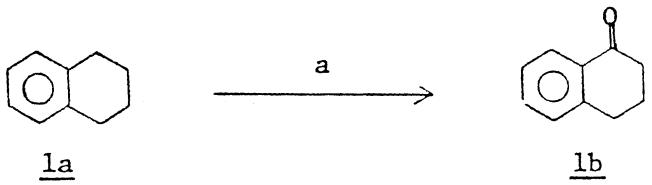
INTRODUCTION AND HISTORICAL

Chromic acid oxidation of hydrocarbons at a saturated carbon-hydrogen bond may be divided into three classes;[1] oxidation occurring α to an aromatic ring (the benzylic position); oxidation taking place to a carbon-carbon double bond (the allylic position) and those involving the oxidation of saturated aliphatics. The first type has found considerable use in the synthesis of arylketones and arylcarboxylic acids as well as for the determination of the orientation of alkyl groups attached to an aromatic nucleus.[2] The other two classes of oxidation have been of less synthetic interest and value since they generally lead to mixtures of compounds in low yields.

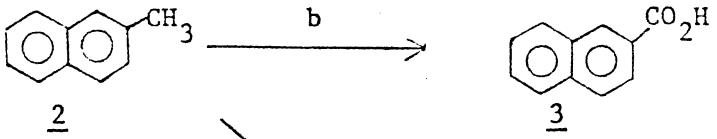
Several hexavalent-chromium reagents are available for the oxidation of hydrocarbons: chromic acid in aqueous acetic acid, aqueous sodium dichromate at high temperature, chromyl acetate in acetic anhydride, di-tertiary-butyl chromate in a variety of solvents, and chromyl chloride in an inert solvent such as carbon disulfide or carbon tetrachloride.

Chromium trioxide in aqueous acetic acid at room temperature[3] and aqueous sodium dichromate at elevated temperature[4] are widely used for oxidation of hydrocarbons at a benzylic position. Thus, oxidation of tetralin (1a) with chromium trioxide in aqueous acetic acid gives 1-tetralone (1b) in 55%[5] yield. With aqueous sodium dichromate, ring

oxidation becomes negligible and side chain oxidation predominates.[4] As applied to 2-methylnaphthalene, chromium trioxide in aqueous acetic acid gives the quinone shown below[6] and sodium dichromate forms the corresponding naphthoic acid[4] in 60% and 88% yield respectively. In general, it has been observed that the extent of aromatic ring oxidation increases with increasing acid concentration.[7] Hence in neutral Cr(VI) solutions, attack at the aromatic ring is greatly suppressed and side chains are oxidized.



1a 1b



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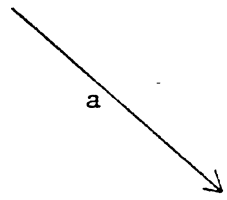
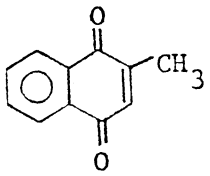




4

[a] CrO_3, aqueous acetic acid, room temperature.

[b] Aqueous sodium dichromate, 250 °C, 18 h.

Detailed mechanistic studies have been reported for Cr(VI) oxidation at the benzylic position.[3] As early at 1959, various substituted diphenylmethanes were studied by Wiberg.[8,9] His conclusions were: (1) electron-releasing groups attached para to the site of the methylene group undergoing oxidations moderately enhance the rate of oxidation to the corresponding benzophenone. (2) Rate of the reaction is proportional to the Cr(VI) concentration. However, at very high chromic acid concentrations it was found that the rate of reaction was large initially, but decreased to the normal value as the reaction progressed. Polychromate formation may be responsible for the decreased rate. (3) The rate determining step is the breaking of the carbon-hydrogen bond, since a very large kinetic isotope effect, $K_H/K_D = 6.4$ at 30 °C, was obtained during the oxidation of diphenylmethane-α,α-d_2.

The breaking of a C-H bond by a free radical mechanism and by a cation intermediate were both suggested. The former mechanism is supported by the fact that Wiberg obtained a value of -1.17 for ρ^+ in the oxidation of para-substituted diphenylmethanes. This is in good agreement with the value for hydrogen abstraction from toluene, which falls between -0.75 and -1.5. The latter mechanism was used to rationalize the poor fit of ρ^+ values in the oxidation of p,p-diphenylmethane and its p-methoxy derivative.

Rocek has shown[10] that the rates of chromic acid oxidation of hydrocarbons parallel the rates of solvolysis of the tosylates and has further concluded that steric hindrance is not important in the oxidation of alkylcyclohexanes.

The following mechanism can be considered to be general for chromic acid oxidation at the benzylic position. The initially formed species

may be a resonance hybrid of an alkyl radical-Cr(V) complex as shown in Figure 1. This hybrid possesses less energy than either one of the mesomeric forms and also accounts for the radical-like and carbonium ion-like characteristics observed during earlier investigations. The subsequent step gives the Cr(IV) ester which in turn is oxidized to the Cr(V) ester and subsequently collapses to Cr(III) and the ketone of interest.

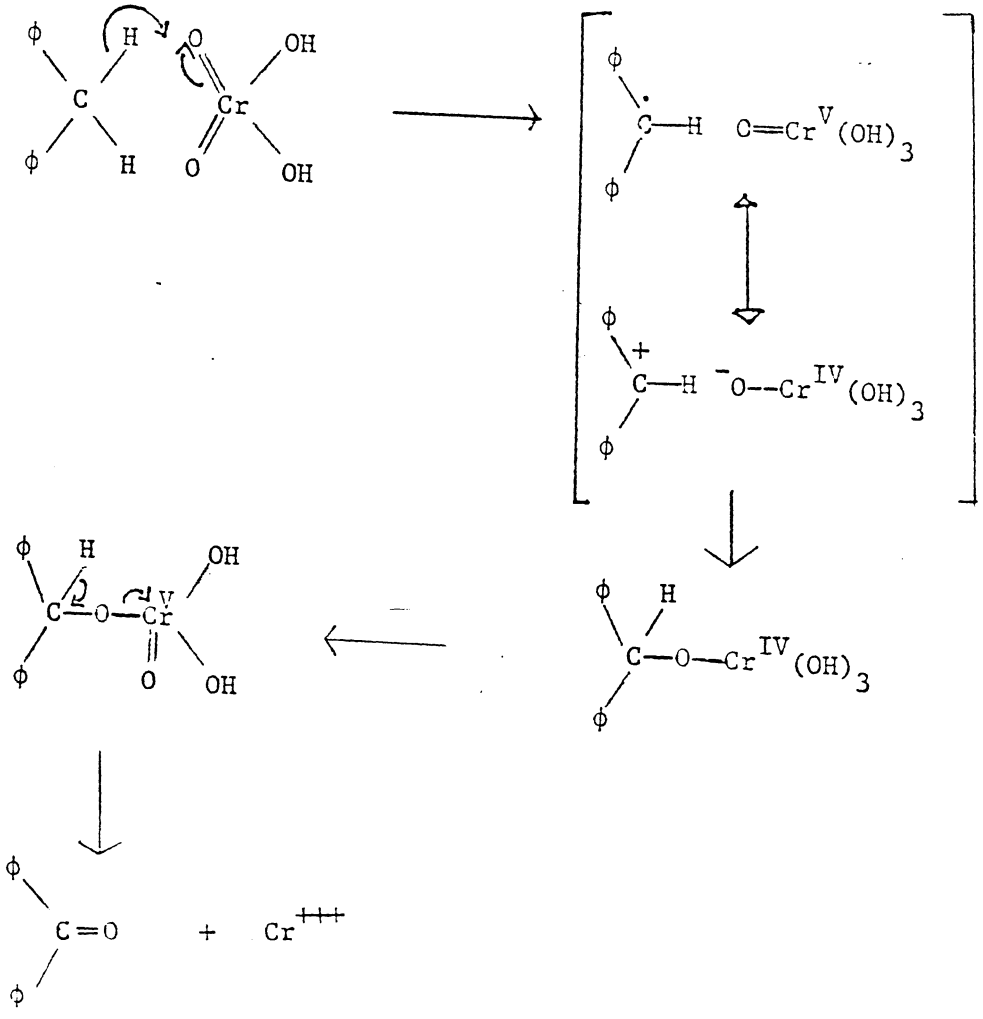
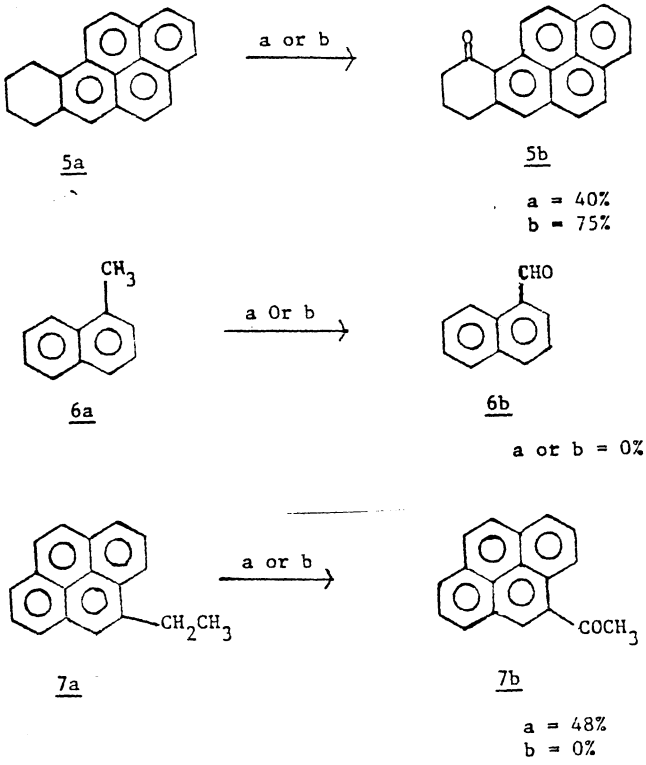


Figure 1. Mechanism for the chromic acid oxidation of hydrocarbons.

Another available oxidant, for the conversion of arylalkanes to arylketones, is 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ).[11] Though both rings and side chains are attacked by DDQ, the yield appears to be dependent upon the size of the fused ring systems as well as the solvent. Larger fused ring systems undergo oxidation more rapidly than di- or tri- nuclear aromatic hydrocarbons such as naphthalene or phenanthrene, as shown from the following examples.



a = DDQ, $CHCl_3$, H_2O, 3-16h, 65 °C.

b = DDQ, aqueous dioxane, reflux, 16 h.

Further, solvent effects were found to be unpredictable. In some cases superior yields were obtained with dioxane, while in other cases chloroform gave better results. Hence the application of DDQ has considerable limitations.

At this time, the Jones chromic acid oxidizing reagent (Jones reagent) appears to be the most effective one for oxidation at the benzylic position. Ordinarily it is used for the oxidation of secondary alcohols to ketones.[12,13] The Jones reagent is prepared by dissolving chromium trioxide in aqueous sulfuric acid.[14] Two millimoles of Jones reagent oxidizes three millimoles of a monohydric alcohol according to the following equation.

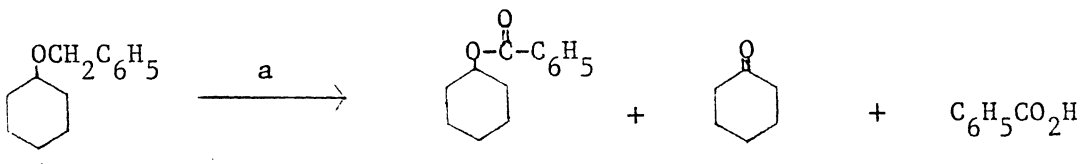
$$3R_2CHOH + 2H_2CrO_4 + 2H^+ \longrightarrow 3R_2C{=}O + 2Cr(OH)_2 + 4H_2O$$

Acetone is the usual solvent of choice for this oxidation due to its rate-enhancing properties and ease of its removal from the products. Jones oxidations of secondary alcohols are usually carried out at 0-10 °C (ice-water bath). There are literature reports of the oxidation of acetylenic carbinols with Jones reagent in satisfactory yields despite the possibility that the triple bond could be attacked by chromic acid.[12]

$$n\text{-}C_4H_9C{\equiv}C\text{-}CHOH\text{-}CH_3 \xrightarrow{\text{Jones [O]}} n\text{-}C_4H_9C{\equiv}C\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3$$

Earlier reports of chromic acid oxidation of symmetrical and unsymmetrical tetralins to 1-tetralones in high yields with considerable selectivity[5,15] was a factor in initiating this study of the Jones oxidation of hydrocarbons. There are scattered reports[16] of the use of

the Jones reagent in large-scale syntheses of alkyl quinones from alkyl phenols in moderate to high yields. This reagent also oxidizes benzyl alkyl ethers to esters.[17] Benzyl ethers are commonly used as the protected form of alcohols because they are easily formed and once formed are stable to a variety of reagents, yet there are specific methods available for regenerating the alcohol from the ether. However, in the presence of an excess of Jones reagent (4 equiv.) some benzyl ethers are oxidized as shown below.[17] Thus the utility of the benzyl group as a protecting group is diminished if oxidation is involved.



8 9 10 11

Total Yield = 72%

[a] CrO_3, aqueous H_2SO_4, acetone.

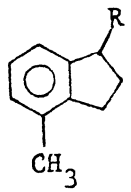
NMR Studies

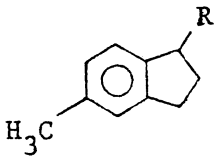
The Jones oxidation provided an interesting series of polymethylated indanones from polymethylated indans as described in chapter 2. The ^{13}C NMR investigation of these systems is the next topic of study.

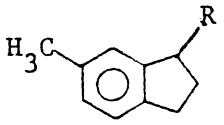
^{13}C NMR has greater potential than ^{1}H NMR for the study of organic molecules[18], especially since hydrocarbons of attached or nearby carbon atoms have a pronounced effect on ^{13}C chemical shifts.[19]

As early as 1959, Grant and Paul studied the ^{13}C chemical shifts[20,21] for 17 simple paraffins, and reported that the chemical shifts were additive and could be derived from the number of α-, β-, γ-, δ-, and ε-carbon atoms. Later several investigators[22,23] extended this work and arrived at empirical rules that predicted ^{13}C chemical shift data for about 59 paraffins.

Empirical assignments for substituted alkanes and alicyclics as well as for polymers are obtained by studying substituent shift parameters. Values so obtained are not valid in molecules having sterically crowded substituents. Earlier Palaniswamy[24] studied a series of mono- and dialkyl-substituted indans (12 through 20) and reported substituent shift parameters for monomethylated indans.







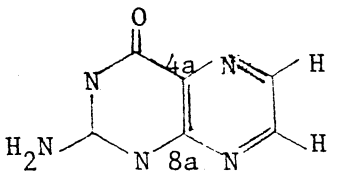
12 = R = CH_3	15 = R = CH_3	18 = R = CH_3
13 = R = C_2H_5	16 = R = C_2H_5	19 = R = C_2H_5
14 = R = i-C_3H_7	17 = R = i-C_3H_7	20 = R = i-C_3H_7

These parameters are of less value in the study of polymethylated indans. However, 300 MHz NMR studies permit assignments.

Some of the conventional experiments used in the current ^{13}C NMR study are off-resonance proton decoupling, gated-decoupling, and relaxation studies. Selective $^{13}C(^{1}H)$ decoupling (over a wide range of frequency), deuteration combined with selective $^{13}C(^{1}H)$ decoupling, and heteronuclear correlated two-dimensional spectra were used when needed. The two-dimensional experiment established direct connectivities between bonded nuclei. The two dimensions are the carbon and the proton shifts in the ^{13}C experiment. This experiment essentially expands the proton spectrum into the ^{13}C shift range.

Off-resonance proton decoupling removes all the long-range couplings and reduces the one-bond $^{13}C-^{1}H$ coupling to a fraction of its original value.[25] This indicates the multiplicity of hydrogens bonded directly to the carbon of interest. On the other hand, gated-decoupling provides information about long range C-H couplings. In aromatic rings the geminal C-H ($^{2}J_{CCH}$) as well as the four-bond coupling ($^{4}J_{CCCH}$) are found to be small (1-2 Hz) in contrast to the vicinal coupling ($^{3}J_{CCCH}$), 7-12 Hz.[25]

A one-to-one correlation between proton and ^{13}C chemical shifts can be established with the aid of selective decoupling experiments. By using this technique and removing one-bond couplings, the long range coupling in which the irradiated proton is involved is also eliminated. Hence, the assignments for quaternary carbons are simplified as is evident from the following example.[26,27]



21

$^{3}J\ C_{8a}H_{7} = 12$ Hz

$^{3}J\ C_{4a}H_{6} = 10$ Hz

In pterine (21),[28] the long range couplings of carbon 8a and 4a with protons C_7-H and C_6-H proved to be of considerable value. With the aid of low-power irradiation, the couplings as well as chemical shifts for carbons 8a and 4a were assigned, on the basis of the known proton chemical shifts.

In addition, ^{13}C relaxation studies can give sets of parameters that are useful in characterizing organic molecules.[29,30] The kind of information available from ^{13}C relaxation studies is generally unobtainable from NMR chemical shifts, spin-spin coupling and integration parameters. Further this gives a better understanding of the overall geometry of the molecules, bonded and nonbonded interactions and other factors controlling the molecular motion.[31]

Spin-lattice relaxation (T_1) is a process of energy exchange between individual nuclear spins and the surrounding liquid or solid "lattice".[32,33] This relaxation allows the lattice to act as a heat sink to establish and restore thermal equilibrium for the nuclear spins. Spin-spin relaxations (T_2) are somewhat harder to measure and are used less often.[34]

^{13}C spin-lattice relaxation occurs mainly by four mechanisms:[19] dipole-dipole relaxation (DD), spin-rotation relaxation (SR), scalar relaxation (SC), and chemical-shift anisotropy (CSA). DD relaxation

arises from local magnetic fields associated with magnetic nuclei. Relaxation of ^{13}C nuclei in organic molecules usually results from dipole-dipole interactions with protons. In fact, for protonated carbons only bonded hydrogens make major dipolar contributions to T_1^{DD}.

The SR mechanism is common in small molecules or in freely rotating molecular segments.[19] The scalar coupling mechanism is found when a ^{13}C nucleus is bound to a X (halogen atom), and can undergo spin-spin coupling if the lifetimes of their respective nuclear magnetic energy levels are sufficiently large. This is quite uncommon and is important primarily in systems where ^{13}C is bonded to one or more ^{79}Br atoms.

The last type of mechanism is the CSA relaxation. The rate of CSA depends on the square of the applied magnetic field as is evident from the following equation, unlike the other types of relaxation mechanisms. CSA is encountered in systems containing π bonds, i.e. derivatives of benzene.[35]

$$R_{CSA} = \frac{1}{T_{1\ CSA}} = \frac{2}{15} r_C^2 H_0^2 (\sigma_{11}-\sigma_1)^2 T_C$$

H_σ = applied field strength

σ_{11}, σ_1 = values of shielding tensor parallel and perpendicular to the symmetry axis respectively.

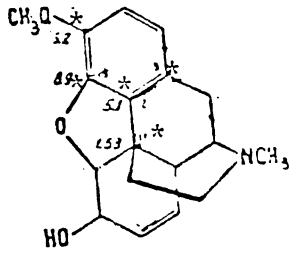
CSA contributes 50% of the relaxation of nonprotonated carbons near 68 MHz. However, T_1^{CSA} does not dominate at lower magnetic fields (25 MHz), as is evident from the equation.

Carbon atoms that have one or more directly attached hydrogens (protonated carbons) relax mainly by DD mechanism and have smaller T_1 values than nonprotonated carbons. One way of identifying individual nonprotonated carbons is from comparison of observed T_1 values. Spectral assignments are difficult for quaternary carbons in complex molecules and coupled ^{13}C spectra may not be useful.[36,37]

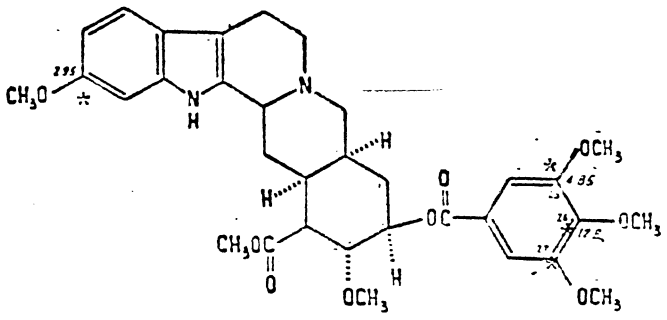
In large molecules the DD mechanism dominates, even for nonprotonated carbons (at lower magnetic fields; at high fields NOE will be reduced and T_1^{CSA} will contribute for $\underline{sp}^2$ or $\underline{sp}$ quaternary carbons.) Accurate T_1 measurements differentiate quaternary carbons from their dependence on nearby nonbonded protons for dipolar relaxation. This is illustrated in the following examples.

In codeine[38], among the four quaternary aromatic carbon signals, (as indicated in Figure 2) those at the lowest field are for chemical shift reasons assigned to the oxygen-bearing ones; since C-14 has one proton in the α-position, whereas C-13 has none, the latter should relax more slowly. Hence the signal at 146.6 ppm (T_1 = 8.9 s) belongs to C-13 and that at 141.7 ppm (T_1 = 5.2 s) to C-14. Analogous arguments can be applied to C-3 and C-12 with three and no α-protons respectively. It is also interesting to note that C-12 relaxes faster than C-13, which can be explained by the close proximity of C-12 methylene protons at C-15.

For reserpine[38](Figure 2), it is found that the four aromatic carbons that bear the methoxy groups have T_1 values related to the number of α-protons. The longest T_1 (12.8 s) is assigned to the carbon



Codeine[a]



Reserpine[a]

[a] * Carbons are Discussed in Table I.

Figure 2. Examples for ^{13}C Shift Assignments From T_1 Data.

TABLE I

Chemical Shifts and Relaxation Times of Quaternary Carbons in Codeine and Reserpine

Carbon[a]	T_1(s) Codeine	ppm[b]	T_1(s) Reserpine	ppm[b]
3	1.82	127.0	2.95	156.52
11	1.53	42.9		
12	5.1	130.9		
13	8.9	146.6		
14	5.1	130.9		
25			4.85	153.34
26			12.8	142.77
27			4.85	153.34

[a] The numbering systems refer to that used in Figure 2.

[b] In ppm relative to internal $Si(CH_3)_4$.

that has no vicinal proton (at 142.8 ppm). The indole methoxy-substituted ring carbon is assigned at 156.5 ppm, due to short T_1 (3 s). This again reflects the presence of two α hydrogens. The other two methoxy-bound ring carbons (T_1 = 4.8 s) have one α hydrogen and are assigned at 153.3 ppm. These two examples illustrate clearly that T_1 studies can be effectively used for nonprotonated carbon assignments.

CHAPTER II

RESULTS AND DISCUSSION

General

In adapting the Jones reagent for this new application, several reaction parameters were systematically examined with the intent of improving oxidation at a benzylic position. These parameters include changes in hydrocarbon structure, a search for substitutes for acetone and sulfuric acid, addition of anhydrous $MgSO_4$ or oven-dried silica gel to decrease the water content of the system as the reaction proceeds, the effect stirring has on the outcome of the reaction[39] and finally a trial of various Cr(VI) species.

This discussion is divided into four parts. The successful use of the Jones reagent in converting several different hydrocarbons to ketones is discussed in the first part. The second part is focused on the estimation of solvent oxidation, i.e. consumption of acetone, during a typical Jones oxidation reaction. The third area deals with the several tested modifications of the Jones reagent, and the final part gives a comparison of various Cr(VI) reagents available for oxidation of hydrocarbons at the benzylic position.

Table II

Jones Oxidation of Hydrocarbons at the Benzylic Position

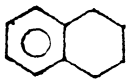
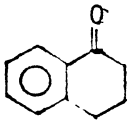
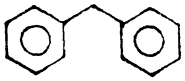
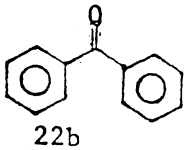
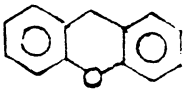
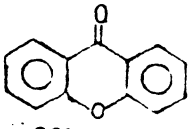
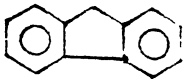
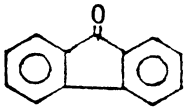
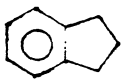
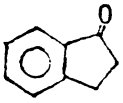
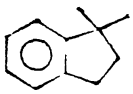
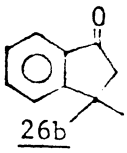
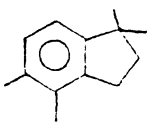
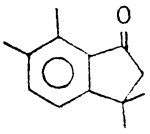
Hydrocarbons[a]	Ketones	% Yield
 1a	 1b	68
 22a	 22b	62
 23a	 23b	98
 24a	 24b	71
 25a	 25b	80
 26a	 26b	85
 27a	 27b	78

Table II (Continued)

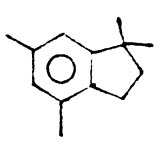
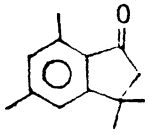
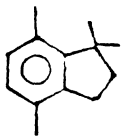
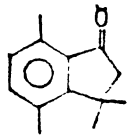
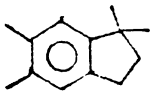
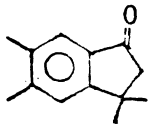
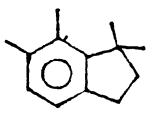
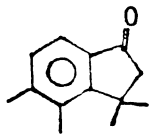
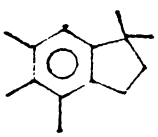
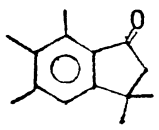
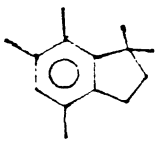
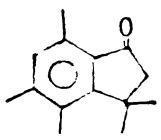
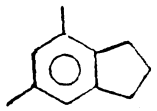
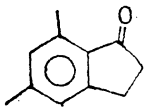
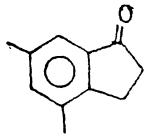
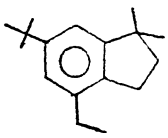
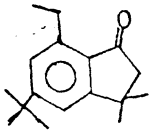
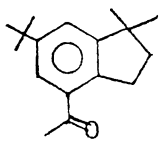
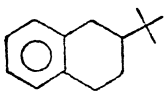
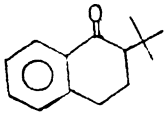
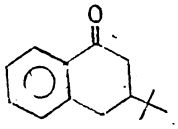
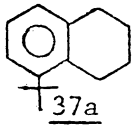
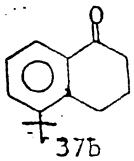
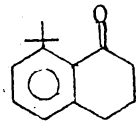
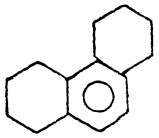
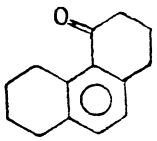
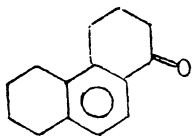
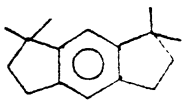
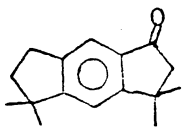
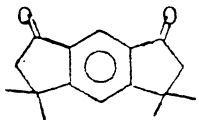
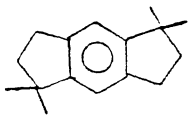
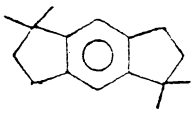
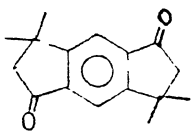
Hydrocarbons[a]	Ketones	% Yield
 28a	 28b	73
 29a	 29b	80
 30a	 30b	82
 31a	 31b	85
 32a	 32b	86
 33a	 33b	75

Table II (Continued)

Hydrocarbons[a]	Ketones[b,c]	Ratio b:c	% Yield
 34a	 34b	 34c	5:1	75
 35a	 35b	 35c	40:1	80
 36a	 36b	 36c	1:3	75
 37a	 37b	 37c	1:1	75
 38a	 38b	 38c	1:1	75
 39a	 39b	 39c	5:3	79
 40a	 40b	 40c	5:2	81

[a]Consult experimental for preparation of alkyl-substituted indans and tetralins.

[b]Ratio determined by g.l.c. A 5% Carbowax 20 M coating on 80-100 mesh Gas-Pak contained in an 0.25" x 10 copper tube was used. Peak areas for calculating ratios were obtained by triangulation of g.c. peaks.

[c]Authentic samples of 27b, 32b, 33b, 34b, 34c, 35c, 36b, 37b, 38b, 39c, and 40c were available.

Oxidation of Hydrocarbons

This study provides a convenient route to otherwise less accessible ketones, as shown in Table II. Aldol dimers have not been isolated even though they are likely to be formed. The availability of hydrocarbons 26a-40a in adequate purity[40] made this study possible. In turn, indanones 27b-33b were required for a related ^{13}C NMR study.

Table II also shows the ratio of ketones obtained when there is more than one kind of benzylic position available for oxidation. From the ratio of indanones 34b:34c (5:1), it is apparent that an electronic effect is operative in the oxidation of alkyl-substituted rings. This is also in accordance with Wiberg's observation that an electron releasing (methyl) group attached at the *para* position enhances the formation of isomer 34b over 34c. In the oxidation of 35a, attack occurs in the five-membered ring (as expected), rather than at the ethyl group.

When a bulky *tert*-butyl group is present adjacent to a potential carbonyl site (C-2), as in 36a, steric effects control the product ratio as encountered in tetralones 36b:36c (1:3).[41] However, when the bulky tert-butyl group is present at the *peri* position to a potential carbonyl site, as in 37a, the steric effect is dominated by the electron-donating effect and tetralones 37b:37c are produced in a 1:1 ratio.[41]

Oxidation of 38a also gives a 1:1 ratio of 38b:38c. Earlier,

Vuppalapaty[42] reported formation of the same isomers in 1:5 ratio by CrO_3/acetic acid oxidation of 38a. At this point we attribute this ratio difference to the more powerful oxidizing nature of the Jones reagent, which thus shows decreased selectivity.

When there is a second benzylic position available for oxidation in the same molecule, mixtures of mono- and di-ketones are produced as listed in Table II. However, the formation of a diketone is not suppressed when the benzylic-CH_2 is at the para position to an electron withdrawing carbonyl functionality. This is evidenced in the ratio of 39b:39c (5:3) as compared to 40b:40c (5:2).

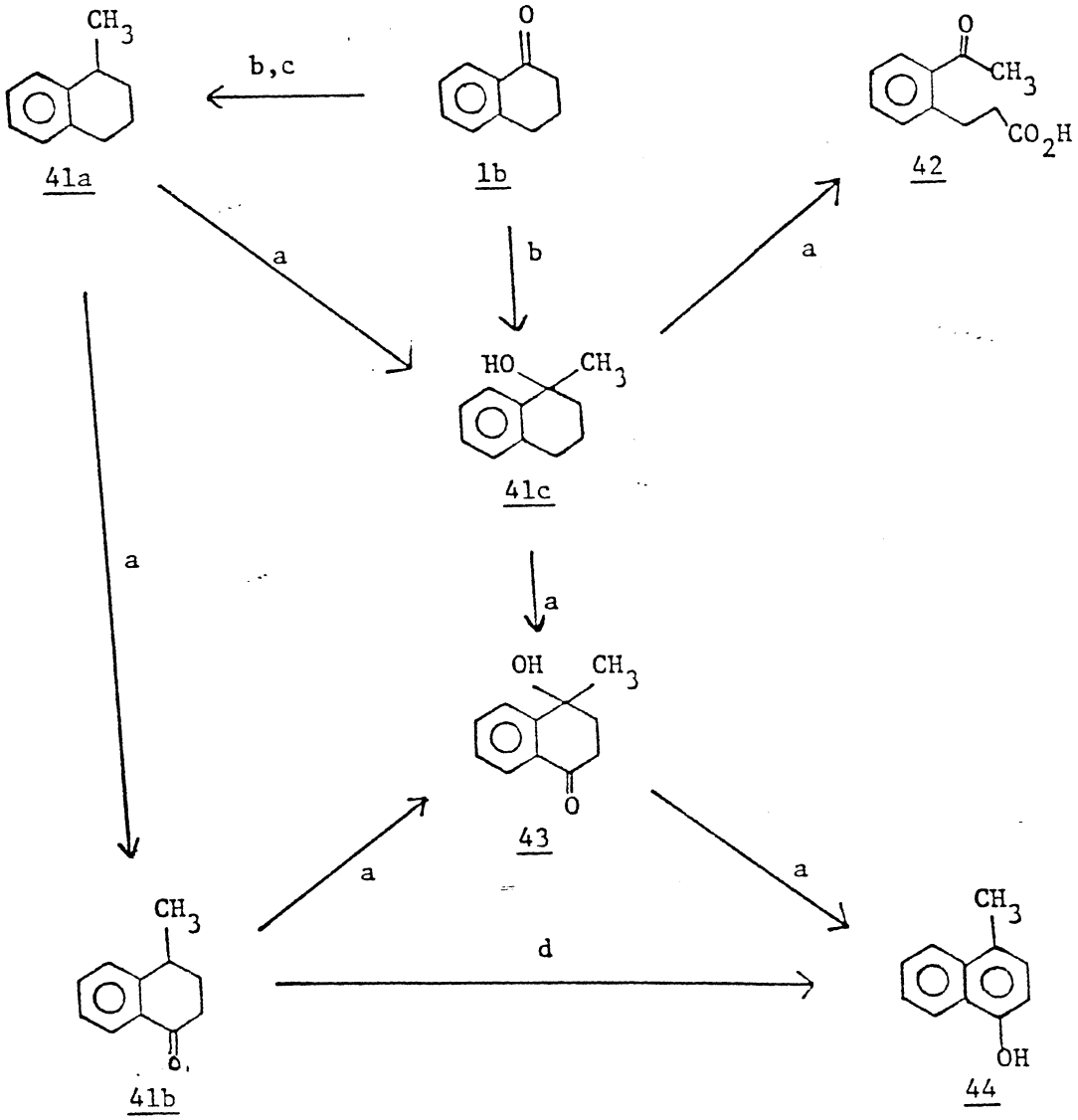
The formation of diketones in the oxidation of 39a and 40a increased with longer exposure to the oxidizing (Jones) reagent. Hence these reactions were continued until no starting material could be detected with gas chromatagraphy. The corresponding ratios of products are reported in the Table II.

1-Methyltetralin (41a), was selected as a test compound to determine whether hydrocarbons of this type would be readily oxidized to ketones in reasonable yield and whether attack of a methine (3°) hydrogen at a benzylic position would be preferred over that at a methylene position. Earlier Wiberg has shown that the rates of chromic acid oxidation of aliphatic CH bonds are in the ratio $7 \times 10^3 : 11 \times 10^2 : 1$ for 3°, 2° and 1° hydrogens respectively.[1,43]

It was expected that the Jones oxidation of 41a would provide 41b and 41c as initial products (Figure 3). Indeed, these were found in the ratio 6:1 (41b:41c), their combined yield being 36%. The bicarbonate soluble fraction provided crystalline 42 in 39% yield. However, the base-soluble fraction did not yield any 44.

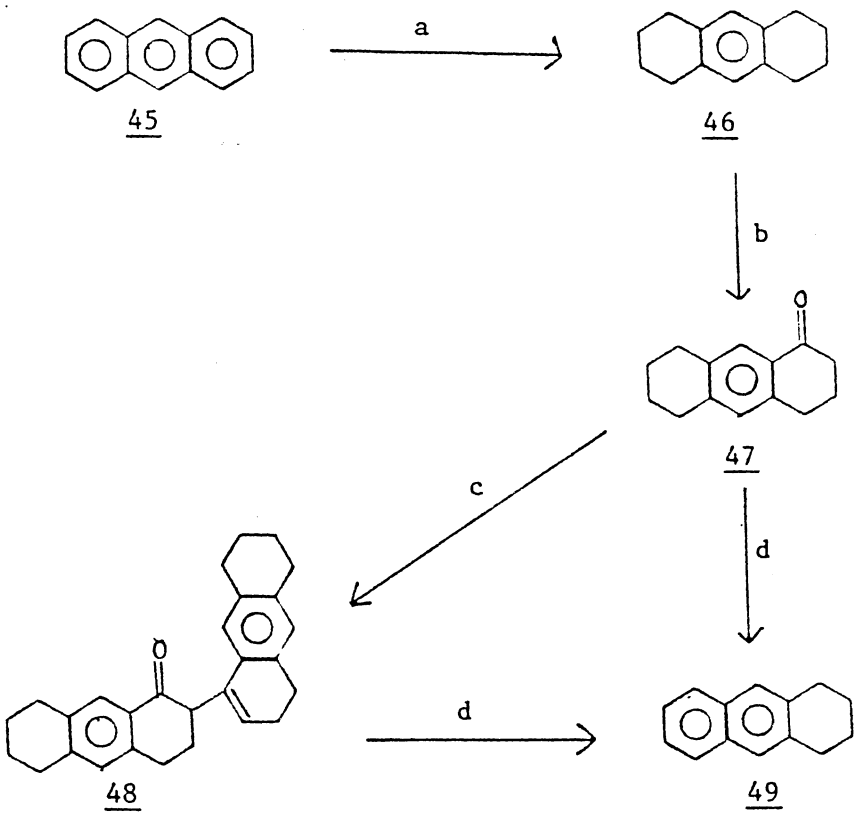
This suggested that 41c was oxidized further to 42 as to be expected from the Fieser and Szmuskovicz oxidation of 3° alcohols to keto acids.[44] To confirm this point we synthesized (Figure 3) alcohol 41c from 1b and then subjected it to Jones oxidation. This provided 42 in 60% yield. The formation of 44 (4-methyl-1-naphthol) was also anticipated to determine whether simultaneous attack at C-1 and C-4 in 41a (41b to 43 or 41c to 43) takes place, and it was not found as a product in either case. To prove the absence of 44, we also synthesized it by an independent route, as reported earlier, i.e., aromatization of 41b.[45] This study shows that extents of attack at 2° and 3° hydrogens are almost comparable in Jones oxidation, the reagent being less selective.

Jones oxidation reactions also serve as important intermediate steps in the (large-scale) conversion of 1,2,3,4,5,6,7,8-octahydroanthracene (46) to 1,2,3,4-tetrahydroanthracene (49). Hydrogenation of anthracene (45) usually provides mixtures of tetra-, octa-, and perhydroanthracenes.[46] Separation of hydrogenated products are often tedious despite the fact that procedures have been reported.[46] Also hydrogenation could be controlled to yield largely one product at times, i.e., when 45 was hydrogenated using Ni on Kieselguhr in ethyl acetate 46 was the major product (Figure 4).[47] Jones oxidation of 46 yielded 47, as expected. Earlier work done by Agranat and Shih[48] on the conversion of 3,4-dihydro-1-(2H)-anthracenone to anthracene by alkali fusion reaction and by Springer et al[49] for the conversion of various tetralones to naphthalenes prompted trial of a similar reaction on 47 to obtain 49. The aldol dimer of 47 was believed to be an intermediate in this conversion.[49] Hence 48 was synthesized and was fused with alkali to yield 49.



[a] CrO_3, H_2O, sulfuric acid, acetone. [b] CH_3MgBr, anhydrous ether. [c] H_2, Pd/C, acetic acid. [d] Pd/C, 250° C, 4 h.

Figure 3. Jones Oxidation of 1-Methyltetralin.



[a] H_2/Ni on kieselguhr, ethyl acetate. [b] CrO_3, H_2O, sulfuric acid, acetone. [c] Basic alumina, cyclohexane, ultrasonic agitation, 24 h. [d] NaOH/KOH, 220°C, 3 h.

Figure 4. Synthesis of Tetrahydroanthracene From Octahydroanthracene

Estimation of Solvent Consumption

Even though acetone appears to be a stable solvent in Jones oxidation reactions, it is to be expected that some acetone and its aldol dimer (formed as shown in the following equation) would be converted to acetic acid after prolonged exposure to chromic acid.

$$2\ CH_3COCH_3 \underset{\rightleftharpoons}{\overset{H^+}{\rightleftharpoons}} CH_3\text{-}\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}H_2COCH_3$$

Accordingly, blank studies were carried out, in which the acetic acid formed was steam distilled and estimated by titration with standardized sodium hydroxide, much as is done in a Kohn-Roth determination.[51] These results are provided in Tables III and V.

The amount of chromic acid consumed for oxidizing acetone was also estimated by repeating the blank runs under identical conditions. The chromic acid left behind was estimated by titration with standardized sodium thiosulfate; the results obtained are summarized in Tables IV and V. The results shown in Table V prove that neither the consumption of chromic acid nor the amount of acetone oxidized to acetic acid is excessive. Therefore acetone is a suitable solvent.

Attempted Modifications of the Jones Reagent

Over a number of years, Jones oxidations have been carried out with acetone as solvent.[52] This is mainly because the reaction is faster in acetone than in acetic acid and because acetone is easily removed from the product by evaporation.[52] However, we undertook a survey of substituting several common solvents for acetone. The results are listed in Table VI.

Table III

Estimation of Acetic Acid In a Jones Oxidation (blank runs[a])

distillate (100 mL)	time[b,c] 4 h	8 h	12 h
1	2.90	7.00	4.00
2	7.20	11.32	27.50
3	4.80	5.32	13.60
4	3.11	3.32	7.50
5	2.70	2.00	4.66
6	1.30	1.34	3.06
7	1.00	0.92	2.14
8	0.80	0.72	1.36
9	0.60	0.58	1.06
10	0.44	0.42	0.92
11		0.38	0.70
12		0.30	0.60
total	24.40	32.42	67.08

[a]Mean values of duplicate runs.

[b]Phenolphthalein used as indicator.

[c]Volume in mL of 0.1 N NaOH solution.

Moles of acetone used in all the cases = 0.17

% acetic acid formed after 4 h $= \frac{24.40}{0.17} \times \frac{0.1}{1} \times \frac{100}{1} = 0.2$

after 8 h $= \frac{32.42}{0.17} \times \frac{0.1}{1} \times \frac{100}{1} = 0.3$

after 12 h $= \frac{67.08}{0.17} \times \frac{0.1}{1} \times \frac{100}{1} = 0.6$

Table IV

Estimation of Chromic Acid Consumed in Blank Runs

# (50 mL each) Trial	neat	Amount of 0.1 N thiosulfate consumed after exposure to acetone (ml) 4 h	8 h	12 h
1	43.40	37.80	32.80	28.50
2	43.40	37.80	32.80	28.40
3	43.50	37.85	32.80	28.50
mean	43.43	37.82	32.80	28.47

Moles of Cr(VI) available in the neat reagent $= \frac{3.43 \times 0.1 \times 100}{3 \times 1000}$

$= 0.145$

after 4 h Cr(VI) left unconsumed $= \frac{7.82 \times 0.1 \times 100}{3 \times 1000}$

$= 0.126$

% consumed after 4 h $= (0.145 - 0.126)\ 100$

$= 1.9$

% consumed after 8 h $= 3.6$

% consumed after 12 h $= 5$

Table V

Determination of Chromium Trioxide Consumed and Acetic Acid Formed During Jones Oxidation

stirring, hours	% CrO_3 consumed	% Acetic acid formed
4	1.9	0.2
8	3.6	0.3
12	5.0	0.6

In order for a solvent to be suitable in Jones oxidation reactions, it ought to be stable to the Jones reagent over 8 hours of exposure time. As shown in Table VI, only N,N-dimethylacetamide and benzene were suitable, the others undergoing rapid oxidation. Their instability was indicated by the appearance of blue-green salt deposits. Brown[53] used ethyl ether as a solvent for chromic acid oxidation of 2° alcohols to ketones, but at a higher dilution of the oxidizing reagent. Ethyl ether, as shown in Table VI, is not a suitable solvent for Jones oxidation of tetralin.

The Jones reagent in N, N-dimethylacetamide did not cause oxidation of tetralin or diphenylmethane at ice-water bath temperatures, but rapidly effected oxidation of benzhydrol to benzophenone in quantitative yield. At room temperature, N, N-dimethylacetamide was attacked by the Jones reagent since the color changed from orange to blue-green.[54]

The Jones reagent in benzene used with prolonged stirring (24-28 h) caused oxidation of tetralin to tetralone. Several other hydrocarbons listed in Table II were also oxidized in benzene to evaluate the role of benzene as solvent in Jones oxidations.[55] However, it turned out that the yield isolated is less in most reactions in acetone and longer reaction hours were required. Hence of the solvents examined, acetone remains the best.

Substitute for Sulfuric Acid

Methanesulfonic acid,[56] trifluoroacetic acid,[56] and 85% phosphoric acid,[57] were substituted for sulfuric acid, on a molar basis, for the oxidation of tetralin. Even though color changes were observed, 1-tetralone was not obtained and most of the starting material was recovered in

Table VI

Trial of Various Solvents for the Jones Oxidation[a]

Solvent	Observation on exposure to the Jones reagent	Conclusion
Acetonitrile	Immediate hydrolysis takes place producing acetamide and acetic acid	Unsuitable
N,N-dimethylformamide	Immediate oxidation occurs	Unsuitable
N-methyl pyrrolidinone	Immediately attacked by the Jones reagent	Unsuitable
Levulinic acid	Oxidation takes place within minutes	Unsuitable
Diethyl ether	Immediate violent reaction occurs	Unsuitable
N,N-dimethyl acetamide	Stable over several hours	Suitable
Benzene	Stable over several hours	Suitable

[a]These solvents were cooled in an ice-water bath; then cold Jones reagent was added dropwise along the sides of the beaker and stirred.

all cases. Sulfuric acid remains the best acid in driving the reaction. Chromium (III) sulfate precipitates out of the reactants, as shown in the following equation.

$$3\ ArCH_2 + 4\ CrO_3 + 6\ H_2SO_4 \longrightarrow 3\ ArC{=}O + 2\ Cr_2(SO_4)_3 + 9\ H_2O$$

These results prompted a study of the effect of excess sulfuric acid on the performance of the Jones reagent. The Jones reagent does not normally use excess sulfuric acid. Examination of the CrO_3/H_2SO_4 ratios used in earlier publications show that there has been close adherence to the needed stoichiometric amount of sulfuric acid. In an attempt to minimize the need for excess Jones reagent, we decreased the equivalents from 6X to 4X, 3X and 1. At the same time sulfuric acid concentration was increased. In each case, we made runs using a two-fold and fourfold excess of sulfuric acid compared to the quantity of sulfuric acid normally present with the reagent. In all these runs, the yield of 1-tetralone from tetralin did not equal the yields in Table II. Hence we believe that an excess of concentrated sulfuric acid will not increase the yield. Possibly aldol condensation of acetone takes place and hence Jones reagent is consumed in the oxidation of these condensation products or oxidation of acetone.

Role of Anhydrous $MgSO_4$ and Silica Gel in Jones Oxidation

Water, though minimized from earlier procedures,[13,14] is necessary to dissolve chromium trioxide in the preparation of the Jones reagent. As the reaction proceeds more water is produced (3 mol/ CH_2 group) and consequently, as the Cr(III) salts appear, the reaction mixture becomes sticky. These salts cling to the sides of the flask and foul the

stirrer paddle, at times enough to cause a stirrer imbalance and thus interfere with mixing. They salts occlude starting material and product and thus cause a 15-20% yield decrease, and can prevent completion of the reaction. To minimize this problem, we added anhydrous magnesium sulfate to the reaction mixture. Presumably, the formation of magnesium sulfate hydrates decreases the water content and thus keeps the salts in suspension.

Oven-dried silica gel also is effective in preventing stickiness of the reaction mixture.[58] These drying agents are about equally effective in improving the ease of isolation of product.

We sought information about the stability of 1-tetralone toward an excess of the Jones reagent. 1-Tetralone (0.02 mol) was subjected to the same oxidation conditions as used in its preparation and 85% of 1-tetralone was found to survive the oxidation.

Trial of Various Cr(VI) Reagents for Benzylic Oxidation

A variety of chromium trioxide complexes utilizing pyridine or related structures are available for the oxidation of secondary alcohols to ketones. As early as 1968, dipyridine-chromium(VI) oxide, $(C_5H_5N)_2$-CrO_3, in dichloromethane (Collins reagent) was used for the conversion of 2° alcohols to ketones.[59] However, there are some significant difficulties associated with the Collins reagent; careful purification of the reaction mixture is required in order to remove the harmful chromium by-products from the reaction product. Further, a large excess (6-10 molar equivalence) of Collins reagent is necessary for the complete oxidation of an alcohol.[60] These problems prompted the development of other oxidizing reagents.

Among these reagents, pyridinium chlorochromate (PPC),[60] 2,2'-bipyridinium chlorochromate[61,62] and chromium(VI) oxide on graphite (200) mesh called Seloxette[63] are of considerable importance. Both PPC and 2,2'-bipyridinium chlorochromate are nonhygroscopic, air-stable and effective after months of storage at room temperature.[61] Seloxette, on the other hand, is a (60%) dispersion of chromium trioxide in graphite. Supported reagents have gained popularity in the last ten to fifteen years and have found wide application in organic, inorganic, and biochemistry.[64] They also have the following advantages: simplified reaction work-up since the reagent can usually be separated by filtration, greater selectivity than attainable in the corresponding homogeneous reaction, milder reaction conditions, and recoverability of reagents for recycling.[63,64]

Both PPC (in CH_2Cl_2) and Seloxette (in refluxing toluene) were tried as hydrocarbon oxidizing reagents and were found to be unreactive. However, 2,2'-bipyridinium chlorochromate in dichloromethane or better in acetone, causes benzylic oxidation of hydrocarbons. The usual ratio of 4:1 (oxidant to substrate) found effective for alcohols was increased to 16:1, whereupon good yields as shown in Table VII were realized. In applying these three oxidizing reagents, the original procedures reported were followed to determine the effectiveness, except that a hydrocarbon was substituted in place of an alcohol.

Comparison of Cr(VI) Oxidation Procedures

Table VII provides a study of oxidation reactions carried out on different hydrocarbons using CrO_3/HOAc, Jones reagent and 2,2'-bipyridinium chlorochromate. The data show that the Jones oxidation at the

benzylic position does not provide an overall improved yield. However, the ratio of oxidation products is significantly different from the ratios obtained through use of CrO_3/HOAc or 2,2'-bipyridinium chlorochromate.

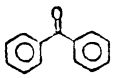
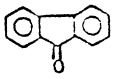
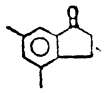
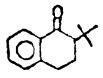
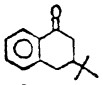
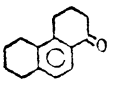
In oxidation of 36a, 37a, and 38a, where a steric effect is expected to control the product ratio, the Jones reagent causes a marked increase of the sterically hindered product at the expense of the other isomer. We attribute this ratio difference to the more powerful oxidizing nature of the Jones reagent, which thus shows decreased selectivity. Fortunately, the overall yield is not impaired.

Jones oxidation has some other advantages over the other two oxidizing reagents listed on Table VII. A practical problem associated with CrO_3/HOAc system is that a large volume of acetic acid is required as the solvent, due to the low solubility of CrO_3 in acetic acid (0.1% or less).[65] Acetic acid is unpleasant to work with and hence isolation of the reaction product becomes troublesome. On the other hand, acetone in Jones oxidations is easily removed by rotary evaporation.

2,2'-Bipyridinium chlorochromate is required in a very large excess (16 to 1 molar) for successful completion of oxidation at the benzylic position. Hence, cost of the reagent will become a limitation when large-scale reactions are considered using this reagent. On the other hand, in the preparation of Jones reagent, cost is minimized since both chromium trioxide and sulfuric acid are relatively cheap chemicals.

Table VII

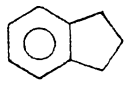
Comparison of Cr(VI) Oxidation Procedures

hydrocarbon[a]	product ketones	ratio of ketones and combined yield[b]					
		CrO_3/HOAc		Jones reagent		BiPCC/acetone	
		b:c	(%)	b:c	(%)	b:c	(%)
1a	 1b		(55)		(68)		(63)
2a	 2b		(60)		(62)		(50)
3a	 3b		(71)		(68)		(70)
34a	 34b  34c	1.0:4.4	(75)	1.0:5.0	(75)	1.0:4.8	(72)
36a	 36b  36c	1.0:5.8	(70)	1.0:3.0	(75)	1.0:6.1	(70)
37a	 37b  37c	2.9:1.0	(62)	1.0:1.0	(65)	4.0:1.0	(60)
38a	 38b  38c	1.0:5.0	(70)	1.0:1.0	(74)	1.0:4.5	(58)

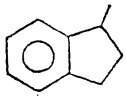
[a]Corresponding to ketones of this table. [b]Ratio determined by glc. A 5% carbowax 20 M coating on 80-100 mesh Gas Pack contained in an 0.25" x 10' copper tube was used. Two peak areas for calculating ratios were obtained by triangulation of GC peaks.

Discussion of ^{13}C NMR of Gem-Dimethylindans

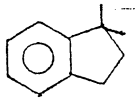
The indans 25a, 50a, 26a, 34a, 51, and 52 serve as model compounds (Table VIII) for assigning C-13 resonances in gem-dimethylindans (27a-33a).



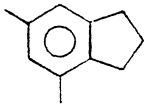
25a



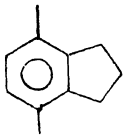
50a



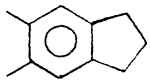
26a



34a



51



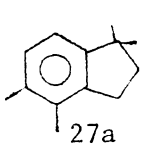
52

The ^{13}C chemical shifts for indan 25a have been reported by several other workers.[19,60] The assignments of resonance positions for the other two indans (50a and 26a) were accomplished by various techniques;[61] mainly by taking into consideration the known substituent effect of α and β carbons (deshielding) and γ carbon (shielding). Observation of a doublet in the SFORD experiment at 39.4 ppm made the C-1 assignment possible for 50a. Triplets were observed in the off-resonance spectrum for the resonance lines at 34.7 and 31.4 ppm for 50a, 41.4 and 30.1 for 26a. The lines at 34.7 are assigned to C-2 in 50a and 41.4 to C-2 in 26a since the methyl substituent(s) at C-1 should deshield the β positions in both cases while they should shield the γ positions. Hence the values 31.4 and 30.1 were assigned to C-3 for 50a and 26a respectively.

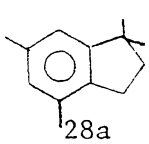
It should also be noted that C-1 and C-2 are deshielded while C-3 is shielded in 50a and 26a when compared with C-1, C-2 and C-3 of indan 25a. The assignment of signals for the six aromatic carbons were made by comparison with 25a and taking into consideration the -deshielding effect of the methyls at C-1 and γ-shielding effect on C-7. Further, assignments for aromatic carbons were aided by earlier studies done by Palaniswamy on dimethylindans 34a, 51 and 52.[24]

On the basis of the chemical shift values provided in Table VIII, ^{13}C resonances for compounds 27a-33a were assigned (Table IX). Due to the presence of gem-dimethyl groups on C-1, C-3a is more deshielded than C-7a in all the cases (being β) and C-7 is slightly more shielded (γ position) than C-4.

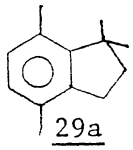
For indan 27a, HETCOR two-dimensional contour plot helped assign the resonance lines for the aromatic methyl substituents (R_4 and R_5). Of the two methyl groups, one is more shielded in both ^1H and ^{13}C spectra as evidenced from the HETCOR 2-D plot, and the other one is slightly downfield. The methyl substituent on C-4 (R_4) is surrounded on either side by a methyl group and a five-membered ring respectively. Hence the upfield value (15.8 ppm) is assigned to R_4 and the downfield signal at 19.6 is assigned to R_5.



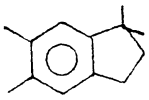
27a



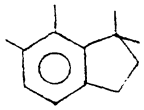
28a



29a



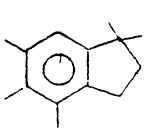
30a



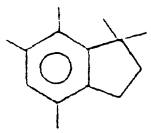
31a

Aromatic carbon assignments for indans 32a and 33a were difficult because of the presence of an extra methyl group as compared to the earlier ones and ordinary gated-decoupling experiments failed to distinguish between the quaternary aromatic carbons attached to methyl groups. Hence, selective ^{13}C [^{1}H] decoupling experiments were attempted on both 32a and 33a. All the C-H couplings due to aliphatic protons (both methyl and methylene groups) were cancelled, and only the coupling due to interaction of the single aromatic proton with all the 6 aromatic carbons were observed on the ^{13}C spectra.

This was achieved easily on the 300 MHz FT-NMR by applying enough power to the decoupler (~5dB) for both the indans. Carbons that were three bonds away from aromatic protons (C-3a, C-5 in 32a and C-4, C-7a in 33a) were split into doublets (Spectra 1 and 2), while the quaternary carbons that are two and four bonds away from the aromatic proton remain unsplit. $^{3}J_{C-H}$ Coupling constant were also measured in these cases. Table X comprises the coupling constants for 32a and 33a. The protonated aromatic carbon gives a doublet with a very large J value, which is obvious due to its upfield nature. Assignments for methyl groups on the aromatic ring for 32a and 33a were done based on the values from 27a-31a.



32a



33a

Table VIII

^{13}Chemical Shifts of Model Indans[a]

Compound	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	CH_3
25a	32.8	25.4	32.8	143.6	124.1	125.8	125.8	124.1	143.6	
50a	39.4	34.7	31.4	143.3	124.0	125.9	125.9	122.8	148.2	19.8
26a	43.8	41.4	30.1	142.1	124.2	126.0	126.0	121.3	152.0	22.6
34a	33.0	42.0	30.9	139.4	132.8	127.5	135.3	122.2	143.5	R_4=18.9; R_6=21.0
51	31.6	24.2	31.6	142.0	130.4	126.9	126.9	130.4	142.0	R_4,R_7=18.8
52	32.6	25.7	32.6	141.3	125.4	133.6	133.6	125.4	141.3	R_5,R_6=19.6

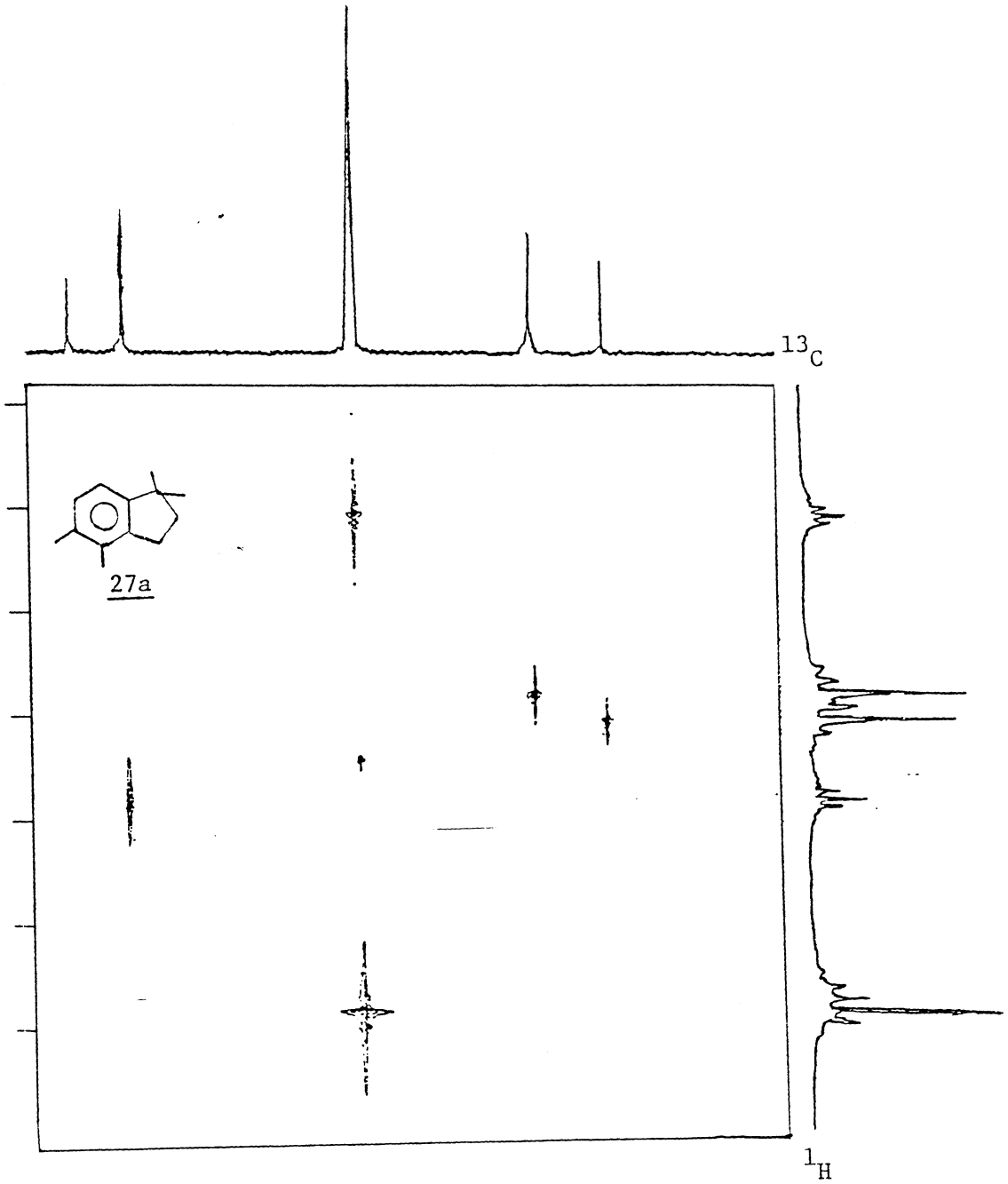
[a]In ppm from internal Me_4Si in 2 M solution.

Table IX

^{13}C Chemical Shifts of gem-Dimethylindans[a,b]

Compound	C-1[c]	C-2[d]	C-3[d]	C-3a[c]	C-4[e]	C-5[e]	C-6[e]	C-7[e]	C-7a[c]	C-8[f] C-9	R[f]
27a	44.0	41.2	28.9	141.7	132.2[c]	134.2[c]	128.1	119.0	149.9	28.9	R_4=15.8 R_5=19.6
28a	44.0	41.3	28.2	138.3	133.3[c]	127.9	135.9[c]	119.8	152.3	28.8	R_4=18.9 R_6=18.6
29a	45.0	42.4	28.4	141.6	130.7[c]	127.2	129.2	130.0[c]	148.0	27.4	R_4=18.9 R_7=18.9
30a	43.6	41.7	29.6	140.1	125.6	134.1[c]	134.1[c]	123.0	149.9	28.6	R_5=19.6[g] R_6=19.8[g]
31a	45.3	43.5	29.5	141.2	121.8	128.3	135.1[c]	123.3[c]	148.9	27.6	R_6=20.1 R_7=15.2
32a	44.1	41.1	29.8	139.3	132.0[c]	132.6[c]	134.5[c]	120.8	149.3	28.8	R_4=16.4 R_5=15.2 R_6=21.0
33a	45.5	43.1	27.8	139.8	130.3[c]	129.4	135.1[c]	129.3[c]	148.6	27.7	R_4=18.6 R_6=19.4 R_7=14.8

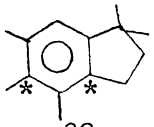
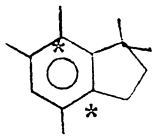
[a] ($CDCl_3$) in ppm from internal $MeSi_4$. [b] Numbering system provided as in 25a. [c] Singlet observed in off-resonance decoupled spectrum (ORDS). [d] Triplet observed (ORDS). [e] Doublet observed (ORDS) unless otherwise specified. [f] Quartet observed (RDS). [g] Assignments may be interchanged.



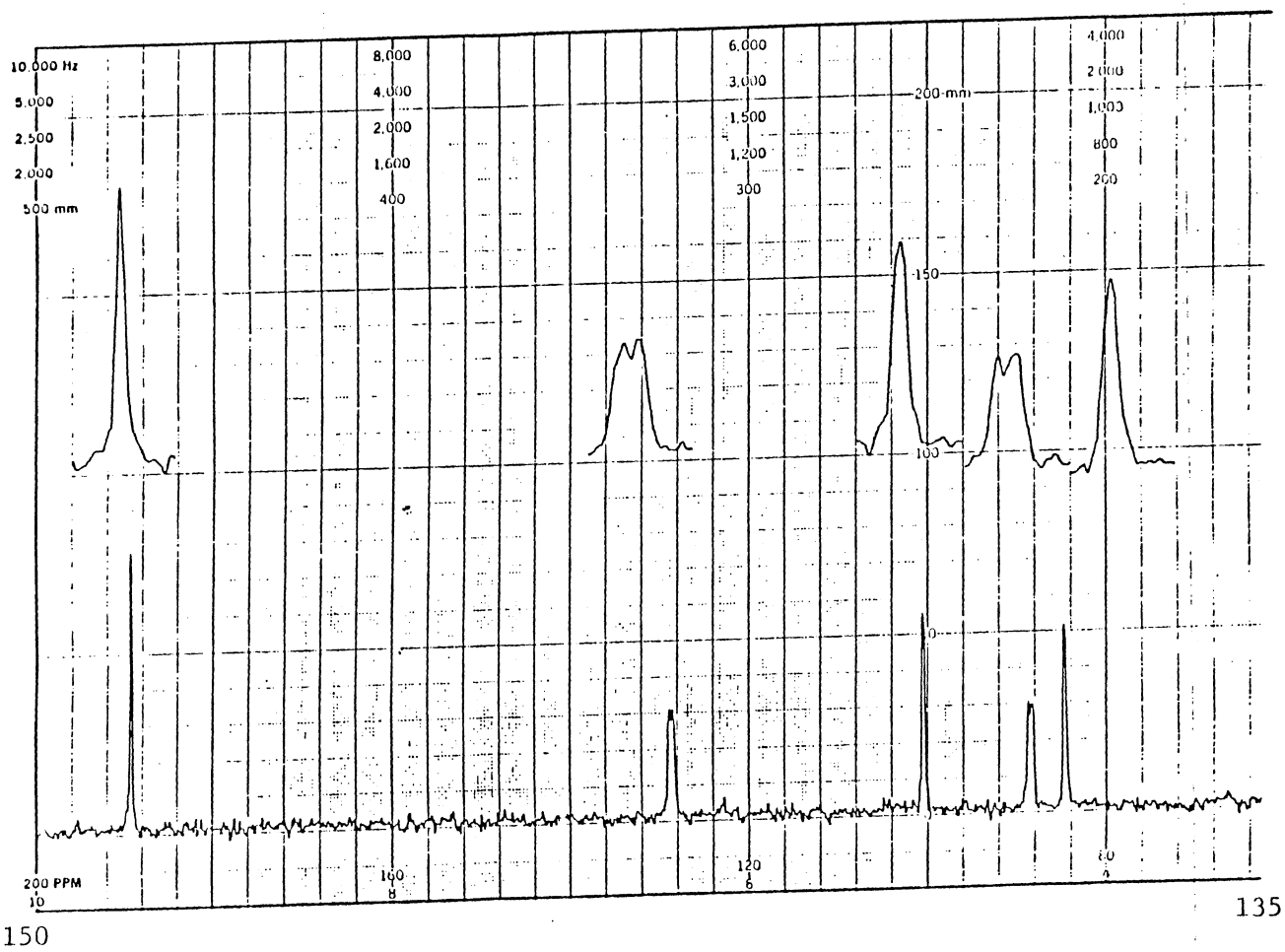
Spectrum 1. HETCOR-Two Dimensional Plot for the Aliphtic Region of 27a.

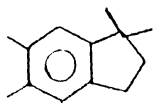
Table X

Long-range Aromatic Carbon-proton Coupling Data[a]

Compound	Carbon	coupling[a] with protons on C-3a	C-4	C-5	C-6	C-7	C-7a
 32a	C-3a					4.0	
	C-4						
	C-5					5.8	
	C-6						
	C-7						
	C-7a						
 33a	C-3a			7.0			
	C-4						
	C-5						
	C-6						
	C-7			6.6			
	C-7a						

[a]($CDCl_3$) in hertz. *Aromatic carbons three bonds away from aromatic proton.



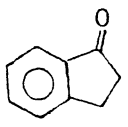


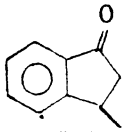
32a

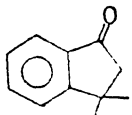
Spectrum 2. The Aromatic Region of 32a Selectively Decoupled ($^{13}C[^{1}H]$).

^{13}C NMR Assignments for Gem-Dimethylindanones

Indanones 25b, 50b and 26b served as models for assigning ^{13}C chemical shifts for all the 3,3-dimethyl-1-indanones.

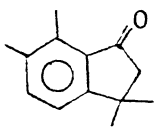

25b

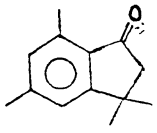

50b

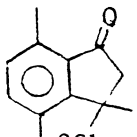

26b

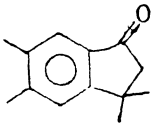
Chemical shifts for 25b[62] and 26b[61] have been reported by several workers. Careful examination of the data on Table XI, makes it evident that in all the indanones C-3a (ortho carbon) is considerably deshielded compared to C-7a (ipso carbon to the carbonyl group). This deshielding effect gets more pronounced as more methyl groups are added to C-3. Further, C-5, which is para to the carbonyl group is more deshielded than any other aromatic carbon other than for C-3a. Also, C-4 is seen farther downfield as compared to C-7 as methyl groups are added on C-3.

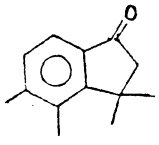
The C-13 chemical shift values for the seven gem-dimethylindanones shown below are summarized in Table XII.

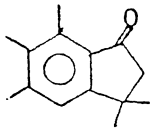

27b


28b


29b


30b


31b


32b

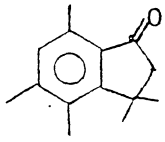

33b

Table XI

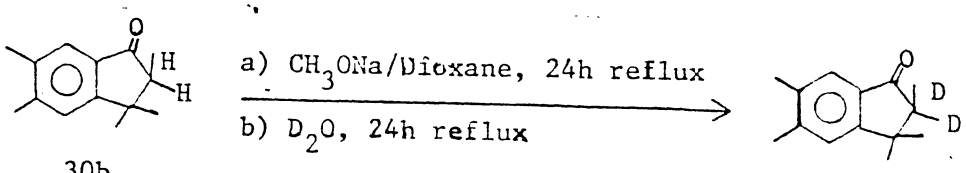
^{13}C Chemical Shifts of Model Indanones[a]

Indanone	C-1	C-2	C-3	C-3a	C-4	C-5	C-6	C-7	C-7a	C-8 C-9
25b	206.2	36.0	25.6	154.9	127.0	134.3	126.6	123.3	136.9	
50b	205.6	45.1	32.6	159.7	125.2	134.6	127.2	123.1	136.3	21.2
26b	204.9	52.7	38.3	163.3	122.9	134.6	127.1	123.3	136.9	29.8

[a]In ppm ($CDCl_3$) from internal TMS.

For indanone 28b, ^{13}C resonance lines were assigned with the help of T_1 values. T_1^{DD} values depend on the number of α hydrogens present and in 29b, both C-3a and C-7 have one α hydrogen, C-5 has two and C-7a has none. Hence at 25.2 MHz, C-5 relaxes faster (indicated by small T_1 value) than C-7 or C-3a. C-7a has a very large T_1 value (from Table XIII), indicating the absence of α hydrogens.

In all the indanones studied, whenever there is a methyl group present on C-5 (as in 30b), that carbon appears farther downfield from C-7a. However, in order to make unequivocal assignments for C-5 and C-7a (for 31b), the $-CH_2$ group adjacent to carbonyl functionality was deuterated, followed by a selective decoupling ^{13}C [^1H] experiment where the aromatic protons on C-4 and C-7 were both decoupled.



30b 30c

C-7a can couple with hydrogens on C-2 and C-4 and C-5 can couple with the methyl protons on C-6 as well as with the aromatic proton on C-7. Incorporation of deuterium atoms on C-2 prevents C-7a from coupling with C-2 hydrogens and decoupling the aromatic protons make it appear as a sharp singlet (133.3 ppm), while the signal at 144.7 ppm (C-5) was split into a multiplet. This is illustrated in Spectrum 4.

Table XII

^{13}C Chemical Shift Assignments for gem-Dimethylindanones[a]

Indanone	C-1	C-2[c]	C-3[c]	C-3a[c]	C-4[d]	C-5[d]	C-6[d]	C-7[d]	C-7a[c]	C-8[f] C-9	R[f]
27b	207.1	53.9	36.8	162.6	120.2	135.9	136.1[c]	132.1[c]	136.1	30.2	R_6=20.9 R_7=15.7
28b	206.3	53.6	37.5	165.2	121.3	145.2[c]	130.4	138.2[c]	130.6	30.1	R_5=21.9 R_7=18.9
29b	206.2	54.9	38.3	159.9	131.8[c]	136.6	129.3	133.0[c]	135.8	27.6	R_4=17.9[g] R_7=18.9[g]
30b	204.2	52.8	37.8	161.7	123.7	144.7[c]	135.9[c]	123.9	133.3	29.6	R_5=20.5 R_6=19.3
31b	205.6	55.4	39.7	159.9	133.8[c]	145.5[c]	129.8	120.8	134.5	28.4	R_4=15.7 R_5=20.9
32b	206.2	53.8	36.6	162.1	121.9	143.9[c]	134.9[c]	136.5[c]	130.7	29.9	R_5=21.9 R_6=14.9 R_7=15.7
33b	206.2	56.0	38.7	160.5	131.8[c]	144.6[c]	131.9	135.5[c]	130.8	28.5	R_4=15.4 R_5=20.6 R_7=18.2

[a]($CDCl_3$) in ppm from internal $MeSi_4$. [b]Numbering systems provided with structures. [c]Singlet observed in off-resonance decoupled spectra. [d]Doublet obsrved in ORDS. [e]Triplet observed on ORDS. [f]Quartet observed in ORDS. [g]Assignments may be interchanged.

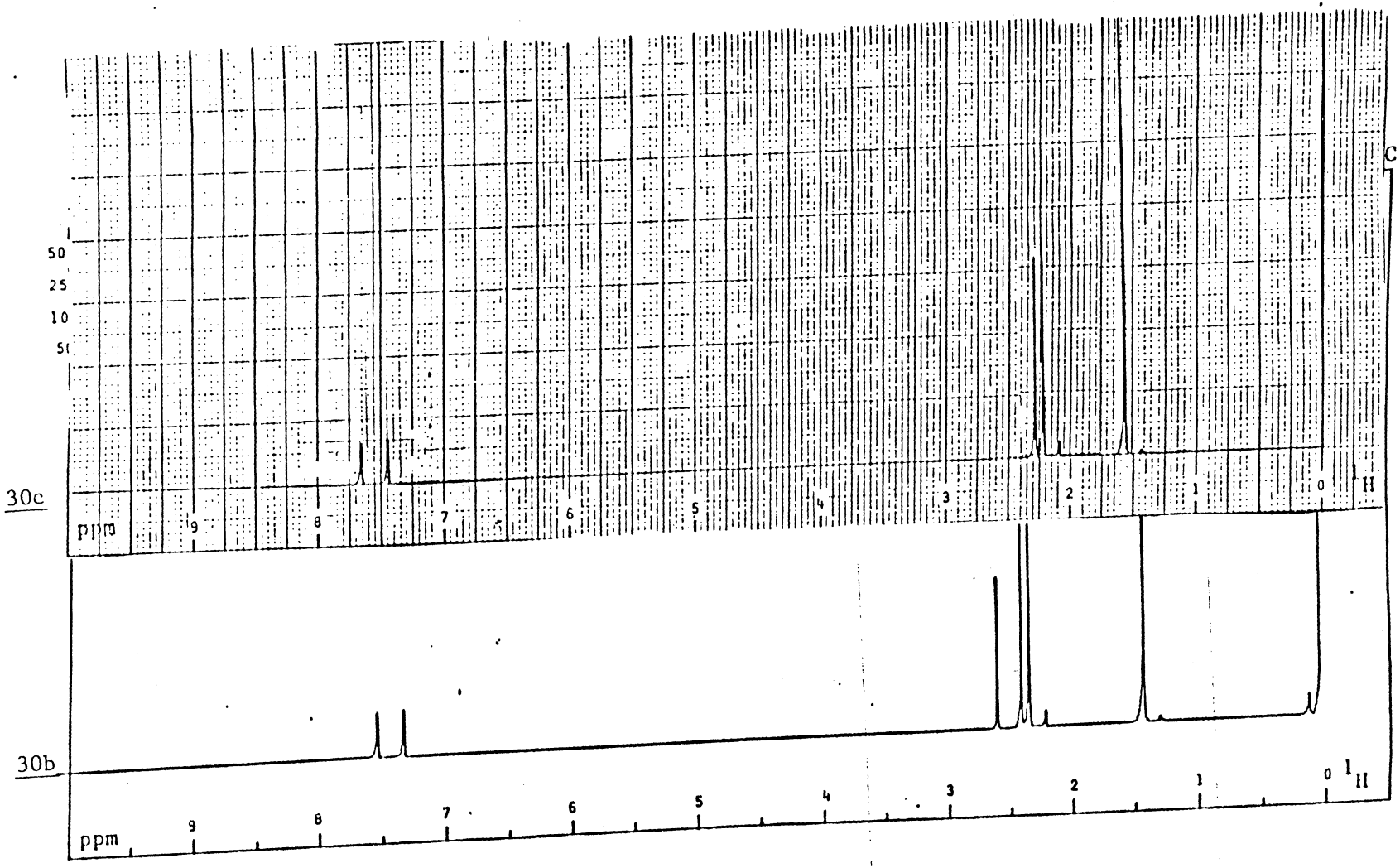
Table XIII

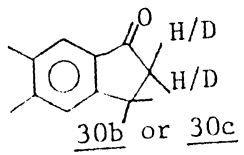
Relaxation Times and Chemical Shift Assignments for Indanone 28b[a]

T_1(s)	ppm	C-Assignment
26	165.2	C-3a
20	145.2	C-5
28	138.2	C-7
39	130.6	C-7a
1.8	121.3	C-4
1.9	130.4	C-6

[a] In ppm from Me_4Si in $CDCl_3$.

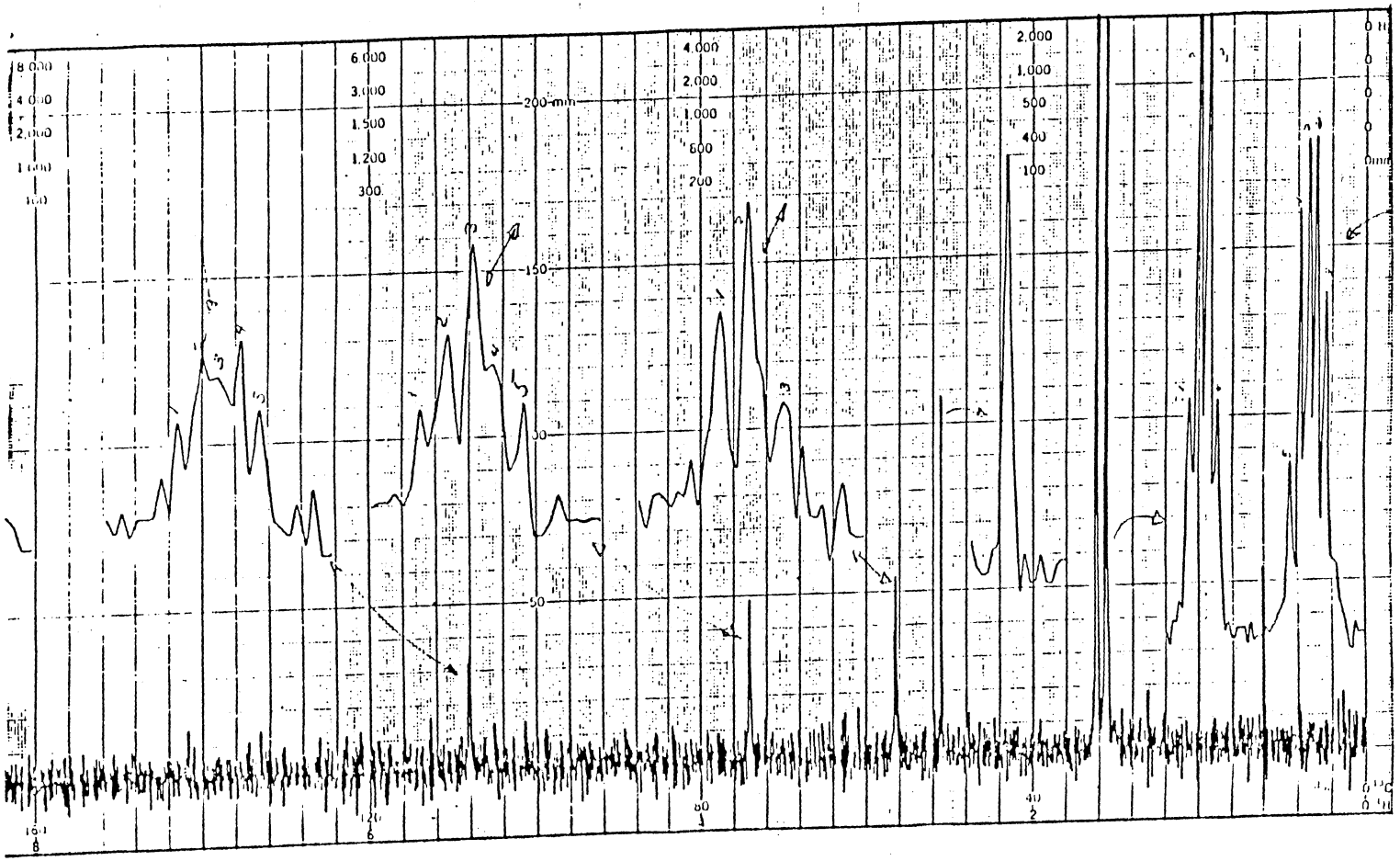
Aromatic carbons in 32b and 33b were assigned, again, by using selective $^{13}C[^1H]$ decoupling experiments as shown in Spectrum 5. The coupling constants on Table XIV allow assignments for carbons that are three bonds away from an aromatic proton. The splittings can be easily seen on Spectra 5 and 6.

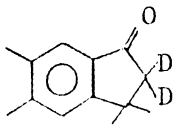




30b or 30c

Spectrum 3 ^{1}H NMR of 30b and 30c



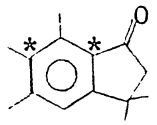
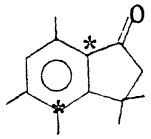


30c

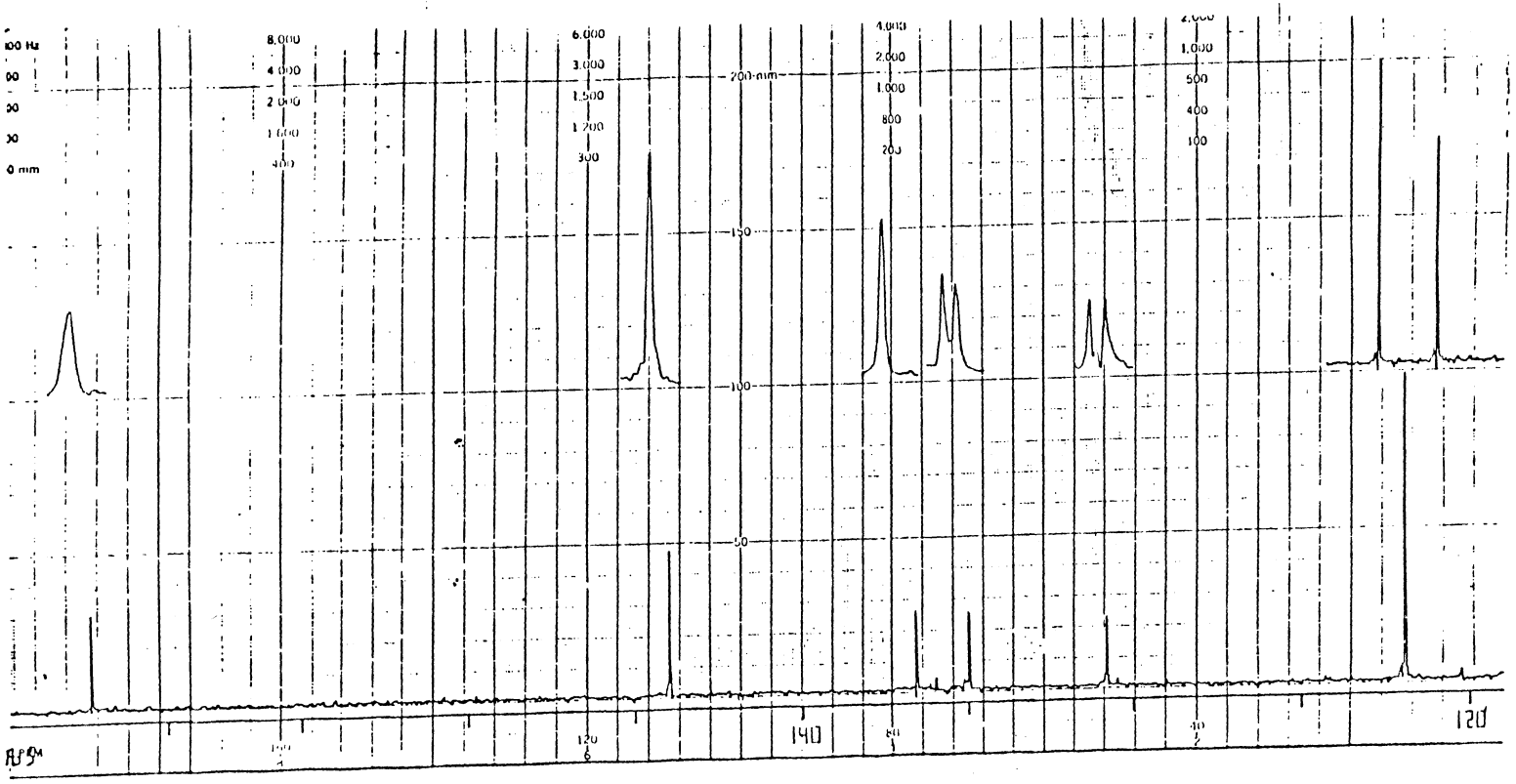
Spectrum 4. Aromatic Region of 30c Selectively Decoupled ($^{13}C[^{1}H]$).

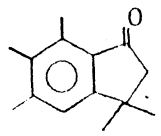
Table XIV

Long-Range Aromatic Carbon-Proton Coupling Data

Compound	Carbon	Coupling[a] with Protons on C-4	C-5	C-6	C-7
 32b	C-3a				
	C-4				
	C-5				
	C-6	5.2			
	C-7				
	C-7a	5.2			
 33b	C-3a				
	C-4			4.9	
	C-5				
	C-6				
	C-7				
	C-7a			4.5	

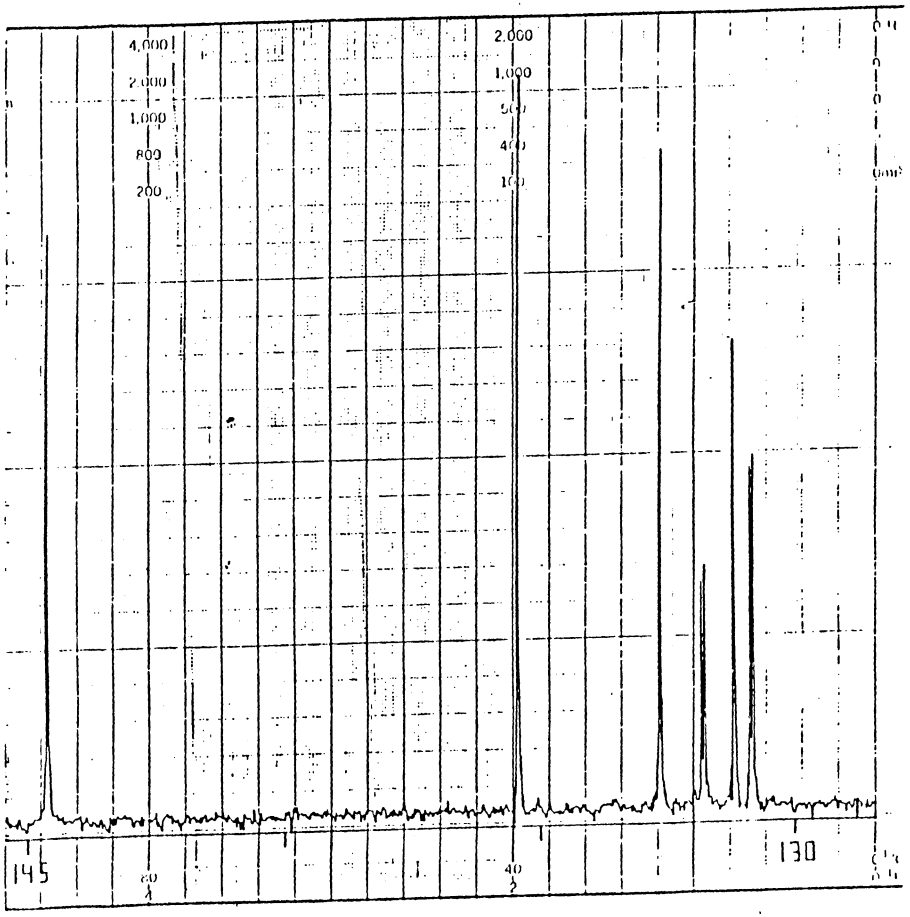
[a] ($CDCl_3$) in hertz. *Carbons 3 bonds away from aromatic proton.

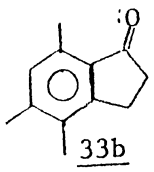




32b

Spectrum 5. The Aromatic Region of 32b Selectively Decoupled (^{13}C ^{1}H).





33b

Spectrum 6. The Aromatic Region of 33b Selectively Decoupled ($^{13}C\{^{1}H\}$)

Summary of Significance of the Research

Although conversion of aromatic hydrocarbons to aryl ketones is a well known reaction, a comparative study of different available reagents has not been done before. This study also brings out a new application for the Jones reagent, which is ordinarily used for the conversion of 2° alcohols to ketones.

The ^{13}C chemical shift assignments as reported in this thesis for the gem-dimethylindans and -indanones have been successfully achieved. Even though mono- and dimethylindans have been studied before,[42] this is the first case where polymethylated indans and indanones have been investigated.

CHAPTER III

EXPERIMENTAL

General Information

Proton NMR spectra were recorded at 300 MHz on a Varian XL-300 NMR spectrometer. The ^{13}C NMR spectra (fully decoupled, selectively decoupled ($^{13}C[^{1}H]$), off-resonance proton decoupled and two-dimensional) were recorded at 75.4 MHz in the FT mode on a Varian XL-300 spectrometer. Chemical shifts are reported in ppm downfield from internal $SiMe_4$ as standard. T_1 studies were done at 25.2 MHz in the FT mode on a Varian XL 100A spectrometer interfaced with a 12K Nicolet 1080 computer system. Infrared spectral data were collected with a Perkin-Elmer 681 spectrometer. Mass spectra were recorded with a CEC 21-110B high resolution mass spectrometer with Data General DS-50s data system at 70 ev. Melting points were determined with a Thomas-Hoover capillary melting point apparatus. Melting and boiling points are uncorrected. Gas chromatographic analyses were obtained with a Varian Model 3700 Capillary gas chromatograph, and a Varian Aerograph model 550 instrument. Analytical and preparative high-pressure LC were conducted on a Waters Associates Micro-porosil (silica gel) column with a Waters Associates analytical or preparative LC system 500 liquid chromatograph, equipped with UV and index of refraction detectors. Acetone, used in all Jones oxidation reactions, was distilled (once) from commercially available grade.

Jones Reagent Preparation

The Jones reagent was made up in 1.00 mol batches by dissolving 100 g of CrO_3 in a minimum of distilled water. Sulfuric acid (86.5 mL) was added and more water (about 194 mL total) was then added to effect solution of precipitated salts.[14] The final volume was 336 mL (3.36 molar with respect to CrO_3).

General Oxidation Procedure Using the Jones Reagent

To a two-necked 300-mL flask fitted with a high-speed mechanical stirrer and immersed in an ice-bath was added 0.2 mol of the hydrocarbon in 50 mL of acetone. The cooled mixture was stirred vigorously during the addition of 46 mL of Jones reagent over a period of 30 min.[12] The ice-bath temperature was maintained at 5-15 °C throughout the reaction. As the green $Cr_2(SO_4)_3$ began appearing, 8.4 g (0.07 mol) of anhydrous $MgSO_4$ was added. This treatment minimized stirrer imbalance resulting from adhering salts. The use of 50 g of oven-dried (120-130 °C) silica (50 mol/mol hydrocarbon) as a substitute for anhydrous magnesium sulfate proved equally effective.[58]

Samples were withdrawn at intervals and analyzed by gas chromatography to determine the completeness of reaction. In most cases, 6-8 h of reaction time was adequate for complete oxidation. Additional Jones reagent was added to those hydrocarbons which oxidize slowly and stirring was continued for a total of 10 h.

On disappearance of starting material (as evidenced by gc) excess Jones reagent was destroyed by adding isopropyl alcohol.[14] The contents of the flask were filtered through Dicalite to remove suspended chromium

salts. The filter cake was washed as needed with acetone and ether. The filtrate was rotary-evaporated, the reaction product was dissolved in ether and the ether solution was extracted with sodium bicarbonate solution to remove any remaining sulfuric acid and acetic acid formed through the oxidation of acetone.[50] The ether extract was dried ($MgSO_4$), filtered and concentrated to obtain the ketone of interest.

Yield Optimization in Converting Tetralin to 1-Tetralone

A series of five experiments in which the molar ratio of CrO_3:tetralin ranged from 4:1 to 10:1 were carried out. The maximum yield of 1-tetralone was obtained with a ratio of 6:1. The theoretical chromium trioxide/tetralin ratio is 4:3.

Stability of 1-Tetralone During Jones Oxidation

1-Tetralone (2.92 g, 0.02 mol) and 46.0 mL of Jones reagent in 50 mL of acetone were stirred together for 4 h at ice-bath temperature. The isolation was carried out as described in the general procedure. The product showed a single glc peak (1-tetralone) and the recovered yield (85%) of 1-tetralone was determined by GC analysis using added tetralin as an internal standard.

Preparation of Hydrocarbons

The hydrocarbons used in this study were obtained in part from the API hydrocarbon synthesis project. They were synthesized as outlined below and their purity established by glc and spectral data.

Hydrocarbons 1a, 22a, 25a and 38a. These were commercially available and were oxidized without further purification.

Indans 26a, 39a and 40a. These were available from earlier acid-catalyzed reaction (cyclialkylation) of benzene with isoprene.[69]

Indans 27a, 30a and 31a. These were available as a mixture from acid catalyzed cyclization of o-xylene with isoprene.[70] They were separated and characterized by earlier workers.[70]

Indans 38a and 29a were obtained by the acid-catalyzed reaction between m-xylene and p-xylene with isoprene independently.[70]

Indans 32a and 33a were obtained as a mixture by the acid-catalyzed cyclization of isoprene with 1,2,4-trimethylbenzene (pseudocumene).[71] Their structures were also established by independent synthetic routes.

Indan 34a was synthesized by the Wolf-Kishner reduction of 34b itself.

Tetralin 36a was prepared by the hydrogenation of 2-tert-butyl-naphthalene.[72]

Tetralin 37a was synthesized from ethyl-5,6,7,8-tetrahydro-1-naphthoate as described earlier.[72]

26b: bp 107 °C (4.7mm); IR (film) 1709 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.59-7.05 (m,4,ArH), 2.44 (s,2,$ArCOCH_2$), 1.40 (s,6,gem-CH_3); mass spectrum m/e, M^+ 160(85), 145(60), 130(60), 127(48).

27b: mp 66-68 °C; IR (KBr) 1708 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38, 7.22 (2d,2,ArH), 2.60 (2s,6,$ArCH_3$), 2.40 (s,2,$ArCOCH_2$), 1.39 (s,6,gem-CH_3); mass spectrum m/e, M^+ 188(40, 173(100), 148(40), 133(20), 69(100).

2,4-DNP mp 215-216 °C.

28b: mp 57-58 °C; IR (KBr) 1708 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.10, 6.90 (2s,2,ArH), 2.60-2.50 (s,6,$ArCH_3$), 2.40 (s,2,$ArCOCH_2$), 1.39 (s,6,gem-CH_3); mass spectrum m/e, M^+ 188(25), 173(100), 155(10), 128(30), 69(100).

2,4-DNP mp 238.5-239.5 °C.

29b: mp 60-61 °C; IR (KBr) 1715 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.18, 7.00 (d,2,ArH), 2.56, 2.26 (s,3,$ArCH_3$), 2.46 (s,2,$ArCOCH_2$), 1.42 (s,6,gem-CH_3); mass spectrum m/e, M^+ 188(30), 173 (100), 145(20), 115(20), 69(100).

2,4-DNP mp 236-238 °C.

30b: mp 78-80 °C; IR (KBr) 1715 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.46, 7.28 (s,2,ArH), 2.56 (s,2,$ArCOCH_2$), 2.38, 2.30 (s,3,$ArCH_3$), 1.40 (s,6,gem-CH_3); mass spectrum m/e, M^+ 188(20), 173(100), 155(20), 128(10), 69(100).

2,4-DNP mp 261-262 °C.

31b: mp 55-56 °C; IR (KBr) 1712 (CO)cm^{-1}; ^1H NMR ($CDCL_3$) δ 7.50, 7.20 (d,2,ArH), 2.60 (s,2,$ArCOCH_2$), 2.40, 2.38 (s,6,$ArCH_3$), 1.54 (s,6,gem-CH_3); mass spectrum m/e, M^+ 188(30), 173(100), 145(50), 128(30), 69(100).

2,4-DNP mp 219-221 °C.

32b: mp 95-96 °C; IR (KBr) 1700 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (s,1,ArH), 2.62, 2.58, 2.20 (s,9,$ArCH_3$), 2.40 (s,2,$ArCOCH_2$), 1.40 (s,6,gem-CH_3); mass spectrum m/e, M^+ 202(40), 187(100).

2,4-DNP mp 249-251 °C.

33b: mp 52-53 °C; IR (KBr) 1705 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.83 (s,1,ArH), 2.51, 2.35, 2.30 (s,9,$ArCH_3$), 2.46 (s,2,$ArCOCH_2$) 1.38 (s,6,gem-CH_3); mass spectrum m/e, M^+ 202(30), 187(100), 128(40), 115(35).

2,4-DNP mp 236-238 °C.

36b: bp 109 °C (0.1mm); IR (KBr) 1680 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.94-7.80 (m,1,ArH peri to carbonyl), 7.40-7.01 (m,3,ArH), 3.02-2.84

(m,2,$ArCH_2$), 2.38-1.69 (m,3,$ArCOCH\underline{CH_2}$), 1.08 (s,9,tert-butyl); mass spectrum m/e, M^+ 202(2), 147(37), 146(100), 145(27), 131(19), 118(19).

2,4-DNP mp 228-230 °C.

36c: mp 68-70 °C; IR(KBr) 1675 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.98-7.83 (m,1,ArH peri to carbonyl), 7.48-7.07 (m,3,ArH), 3.08-2.45 (m,3,$ArCH_2$ and ArCOCH), 2.38-1.66 (m,2,ArCOCH and $ArCH_2\underline{CH}$), 0.98 (s,9,tert-butyl); mass spectrum m/e, M^+ 202(24), 146(100), 145(37), 117(21), 115(22), 57(47).

2,4-DNP mp 223-224 °C.

37b: bp 96-98 °C; IR (film) 1675 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.90, 7.82 (d of d,1,ArH peri to carbonyl), 7.50, 7.42 (d of d, 1, ArH), 7.13 (t,1,ArH), 3.14 (t,2,$ArCH_2$), 2.54 (t,2,$ArCH_2CH_2\underline{CH_2}$), 2.06 (p,2,ArCH $\underline{CH_2}$), 1.42 (s,9,tert-butyl); mass spectrum m/e, M^+ 202(28), 188(15), 187(100), 117(13), 115(19), 41(11).

37c: bp 93-95 °C; IR (film) 1700 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.40-6.86 (m,3,ArH), 2.84-2.54 (overlapping m,4,$ArCH_2CH_2\underline{CH_2}$), 2.17-1.90 (p,2,$ArCH_2\underline{CH_2}$), 1.38 (s,9,tert-butyl); mass spectrum m/e, M^+ 202(85), 187(94), 174(100), 159(96), 115(49), 43(35).

38b and 38c: A 1:1 mixture of 38b and 38c was subjected to Kugelrohr distillation followed by recrystallization using iso-hexane, to give 38c mostly. Column chromatography of the mother liquor of neutral alumina using isohexane afforded 38b.

38b: mp 40.5-41 °C; IR(KBr) 1675 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.02 (q,2,ArH), 3.15 (s,2,CH_2 at C-5), 2.80 (q,4,CH_2 at C_1 and C_3), 2.58 (t,2,CH_2 at C-8), 2.00 (q,2,CH_2 at C-2), 1.71 (m,4,CH_2 at C-6 and C-7); mass spectrum m/e, M^+ 200(100), 185(62), 175(33), 129(34), 119(32).

38c: mp 81-82 °C; IR (KBr) 1670 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.82

(d,1,ArH at C-10), 7.01 (d,1,ArH at C-9), 2.78 (t,4,Hs at CO2 and C-4), 2.58 (t,4,CH_2 at C-5 and C-8), 2.10 (q,2,CH_2 at C-3), 1.96-1.68 (m,4,CH_2 at C-6 and C-7); mass spectrum m/e, M^+ 200(100), 172(82), 144(60), 129(44), 114(31).

Synthesis of 41c from 1-tetralone (1b): Commercially available methylmagnesium bromide (175 ml, 3.1 in ether) was stirred in a three-necked flask fitted with a dropping funnel, condenser and a nitrogen inlet. 1-Tetralone (0.5 molar, 75 g) was dissolved in 250 ml of anhydrous ether and added dropwise to the Grignard reagent. Formation of pale yellow salts indicated that the reaction was progressing. Stirring was continued for 5 h. The contents of the flask were then poured into saturated ammonium chloride and the mixture was extracted with ether three times. The combined ether extract was dried ($MgSO_4$), filtered, concentrated and was distilled to yield 69 g (85%) of colorless 1-methyl-1,2,3,4-tetrahydro-1-naphthol (41b): mp 85-87 °C; ^{1}H NMR ($CDCl_3$) δ 8.02 (d,1,ArH at C-8), 7.60 (d,1,ArH at C-4) 7.50 and 7.30 (2t,2,$ArCH_2$), 2.60 (t,2,$ArCCH_2$), 2.10 (p,$ArCH_2\underline{CH_2}$), 3.5 (s,1,OH); mass spectrum m/e, M^+ 162(24), 146(100), 131(30), 91(25).

Hydrogenation of 41c to 1-methyl-1,2,3,4-tetrahydronaphthalene (41a): A 65 g (0.4 mol) sample of 41b in 600 ml acetic acid was hydrogenated for 20 h with 2 g of 10% Pd/C catalyst. At the end, product was filtered to remove the catalyst and the acetic acid was evaporated. The resulting concentrate was added to ether, extracted with water and sodium bicarbonate solution respectively. The organic layer was then dried ($MgSO_4$), filtered, concentrated and distilled to give 50 g (85%) of 41a: bp 40 °C at 0.3 mm of Hg; ^{1}H NMR ($CDCl_3$) 8.10 (d,1,ArH at C-5), 7.50 (a,1,ArH at C-5), 7.3 (2,m,ArH at C-6 and C-7), 2.90 (t,2,$ArCH_2$),

2.80 (m,1,H at C-1), 1.78 (m,4,CH_2 at C-2 and C-3) 1.40 (d,3,CH_3); mass spectrum m/e, M^+ 146(100), 131(100), 119(100), 115(70), 91(85), 69(100).

41b: bp 95 °C (1 mm Hg); IR (film) 1690 (CO)cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.00 (d,1,ArH at C-8), 7.45 (d,1,ArH at C-4), 2.65 (m,2,$ArCOCH_2$), 2.20 (m,2,$ArCOCH_2\underline{CH_2}$), 1.40 (d,3,CH_3); mass spectrum m/e, M^+ 169(100), 145(70), 132(100), 118(60), 105(90), 69(100).

2,4-DNP mp 204-206 °C.

Aromatization of 41b to 4-methyl-1-naphthol (44): A 25-mL, three-necked, round-bottomed flask fitted with gas inlet and outlet and a reflux condenser served as the reaction vessel. A 5-g sample of 4-methyl-1-tetralone (41c) and 0.5 g of Pd/C were poured into the reaction vessel. A fast flow of helium was used initially to sweep air from the system. The helium flow was then reduced to maintain a slight positive pressure. The flask was lowered into a Wood's metal bath preheated to 70 °C and the bath temperature (by thermocouple probe as a safety measure) was raised rapidly (15-20 °/min) to 260 °C and was held stationary. After being heated for 4 h, the reaction mixture was allowed to cool under helium atmosphere. Severe bumping due to water formed in the reaction was lessened by submerging the reaction flask into the bath far enough that the level of the molten metal was approximately 0.5" above that of the liquid in the flask.

The cooled reaction mixture was extracted successively with ether and chloroform and the solution was filtered through Dicalite. The filtrate was washed thoroughly with 10% NaOH solution. The alkaline solution was acidified with conc. HCl acid and extracted with ether. The extract was washed with water, dried ($MgSO_4$), filtered and concentrated to give crystals of 4-methyl-1-naphthol (44). This was purified

by sublimation. mp 75-78 °C; ^{1}H NMR ($CDCl_3$) δ 8.21 (d,1,ArH at C-8), 7.98 (d,1,ArH on C-4), 7.58 (m,2,ArH at C-2 and C-3), 7.25 (m,2,ArH at C-6 and C-7), 5.2 (s,1,ArOH), mass spectrum m/e, M^+ 158(100), 157(46), 144(35), 115(40), 128(30).

4-Methyl-1-tetralone (41b): bp 95 °C (1 mm of Hg); IR (film) 1690 (CO)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.00 (d,1,Ar-H at C-8); 7.45 (d,1,Ar-H at C-4), 7.25 (m,2,Ar-H at C-6 and C-7), 3.18 (m,1,H at C-4), 2.65 (m,2,$ArCOCH_2$), 2.20 (m,2,$ArCOCH_2CH_2$), 1.40 (d,3,CH_3); mass spectrum m/e, M^+ 160(100), 145(70), 132(100), 118(60), 105(90), 69(100).

2,4-DNP mp 204-206 °C.

3-(2-Acetylphenyl)propionic acid (42): This was isolated from the reaction mixture produced by Jones oxidation of 41a by extraction with sodium bicarbonate solution, followed by acidification and extraction with ether to give: mp 68-69.5 °C; IR (KBr) 1720 (CO)cm^{-1}, 1680 (CO of CO_2H)cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 12.01 (s,1,CO_2H), 7.9 (d,1,ArH at C-8), 7.42-7.38 (m,3,ArH), 2.60 (s,3,CH_3), 2.08 (t,4,$2CH_2$); mass spectrum m/e, M^+ 192(15), 174(20), 146(100), 132(60).

2,4-DNP mp 140-142 °C.

Hydrogenation of 34 to 1,2,3,4,5,6,7,8-octahydroanthracene (46): Commercially available anthracene (45), (1.5 moles, 267 g), was dissolved in 1 L of ethyl acetate, and was hydrogenated in the presence of 10 g of 10% Ni on Kieselguhr at 160 °C for 3.5 h at 1600 psi. At the end, the catalyst was filtered out with Dicalite and ethyl acetate was evaporated to obtain crystalline 46 in 80% yield. This was recrystallized from ethyl acetate to give: mp 69-71 °C; ^{1}H NMR ($CDCl_3$) δ 6.90 (s,2,Ar-H), 2.65 (t,8,$ArCH_2$), 1.78 (t,8,$ArCH_2CH_2$); mass spectrum m/e, M^+ 186(100), 158(70), 128(30), 115(20), 69(100).

3,4,5,6,7,8-Hexahydroanthracene(2H)-1-one (47): This was synthesized by Jones oxidation of 46: mp 43-44 °C; ^{1}H NMR ($CDCl_3$) δ 7.80 and 7.00 (s,2,ArH), 2.90 (t,2,$ArCOCH_2$), 2.80 (s,4,$ArCH_2$), 2.64 (t,2,$ArCH_2$), 2.16 (m,2,$ArCOCH_2CH_2$), 1.80 (m,4,$ArCH_2CH_2CH_2$); mass spectrum m/e, M^+ 200(100), 172(90), 144(90), 132(60), 128(40), 115(40).

Aldol Condensation of 47 to 48 Using Basic Alumina: 10 g (0.05 mol) of 47, and 50 g of basic alumina were suspended in 35 ml of cyclo hexane in a two-necked flask fitted with a nitrogen inlet, condenser and an outlet. This was placed in an ultrasonic tank (251 x 15w x 10h cm) fitted with deionized water, and agitation was applied for 26 h along with heat (80 °C). At the end, the reaction product was loaded on a soxhlet column containing basic alumina and extracted with hexane for 8 h followed by ether for 8 more h. Hexane removed all the unreacted starting material, while ether brought down the aldol dimer. Removal of ether by evaporation gave 22% of 48: mp 158-160 °C; ^{1}H NMR ($CDCl_3$) δ 7.80-7.90 (s,2,ArH), 7.10-6.90 (d,2,ArH), 5.5 (t,1,ArCOCH), 3.8 (t,1, vinylic proton), 2.70-2.80 (m,12,$ArCH_2$), 1.80 (m,10,$ArCH_2CH_2$); mass spectrum m/e, M^+ 382(100), 354(45), 267(30), 200(100).

Conversion of 47 or 48 to 1,2,3,4-Tetrahydroanthracene (49) with KOH/NaOH.

Apparatus: The reaction vessel was a 25-ml, one-necked, flat-bottomed, stainless steel flask surmounted by a water-cooled, straight-bore glass condenser. One end of the condenser was a ball joint fitted with a Teflon O ring that provides a seal with the flask. The other end is threaded and fitted with a screw cap bearing a 1.25"-o.d., thin-walled stainless steel tube which extends ca. one-third the way into the flask. The tube, which provided a helium inlet, was sealed to the screw

cap with a silicone rubber gasket. An extra side arm of the condenser located above the water jacket acted as the helium outlet. The inlet and the outlet were fitted with Tygon tubing. The end of the latter tube was immersed in water so that gas flow could be observed. Heating is accomplished with a heating mantle held at 220 °C (measured with a thermocouple probe).

Procedure: A 10-g sample (0.05 mol) of 47, 1.6 g of KOH pellets and 1.6 g of NaOH pellets were added to the flask and the assembled system was purged for several minutes with a fast flow of helium. The flow was lessened to maintain a slight positive pressure and the flask is lowered into a preheated heating mantle. After 3 h of heating (220 °C), the reaction mixture is allowed to cool under helium. Then the reaction mixture was dissolved in ether and extracted with $NaHCO_3$ solution, dried ($MgSO_4$), filtered and rotary-evaporated. The solid residue obtained was loaded on a soxhlet column with basic alumina and was extracted with n-hexane to obtain white, crystalline 49 in 75% yield: mp 103-105 °C. ^{1}H NMR ($CDCl_3$) δ 7.65 (m,2,ArH), 7.48 (s,2,ArH), 7.38 (m,2,ArH), 3.0 (t,4,ArCH_2), 1.84 (t,4,ArCH_2CH_2); mass spectrum m/e M^+ 182(100), 181(30), 154(45), 141(40), 101(30).

Chromium Trioxide Consumed and Acetic Acid Formed During Blank Runs. Samples of acetone (50 mL, 1.17 mol) were stirred with 10 mL of Jones reagent for 4, 8, and 12 h, under conditions typical of those used to oxidize hydrocarbons. At the end, the excess Jones reagent was destroyed by adding isopropyl alcohol and steam was passed through the mixture. Several 100-mL distillation fractions were collected and titrated with 0.1N NaOH to the phenolphthalein end point. These data are found in Table III.

The amount of chromium trioxide consumed for the same oxidation was also determined by repeating the reaction for 4, 8, and 12 h under identical experimental conditions and rotary-evaporating the remaining acetone. The residue was diluted to 1000 mL and several 50-mL portions were titrated with standardized sodium thiosulfate solution after the addition of potassium iodide and 1% starch solution for end point determination.[51] Again, the results are shown in Table IV and V.

Deuteration of 3,3,5,6-Tetramethyl-1-indanone (30b). Indanone 30b (2 g, 10.6 mmol) was dissolved in 20 mL of dioxane, and was refluxed for 24 h with 0.3 g of anhydrous sodium methoxide under nitrogen atmosphere. 17 mL of deuterium oxide was added and reflux was continued for an additional 24 h under nitrogen atmosphere. After this, the solution was cooled to room temperature and poured into slightly acidified water and the organic material extracted with water. The ethereal solution was washed with saturated NaCl, dried ($MgSO_4$) and the solvent evaporated. The residue was purified by recrystallization from n-hexane to give 1.80 g (90%) of 3,3,5,6-Tetramethyl-2,2-d_2-1-indanone. ^1H and ^{13}C spectra confirmed complete deuteration at the expected position.

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39. A high-speed mechanical stirrer with a multi-blade paddle was found to be adequate. Stirring with a Teflon-covered magnetic stirring bar gave approximately the same yields. However, it was necessary to use a powerful magnetic stirrer. This application required a heavy-wall flask since the stirring magnet is capable of breaking the wall of a conventional flask.

40. The author thanks Drs. R. C. Bansal, J. R. Mattox and C. F. Browne for providing these hydrocarbons.

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55. Percent yield was estimated on the amount of starting material recovered.

56. Methanesulfonic acid and trifluoroacetic acid were substituted, 2 moles for one mole of sulfuric acid. Otherwise, the oxidation procedure remained the same.

57. Phosphoric acid, 85% was substituted (2 moles for 3 moles of sulfuric acid). The oxidation procedure remained the same except that water was omitted during preparation of the reagent.

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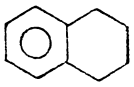
APPENDIX A

GLOSSARY OF STRUCTURES



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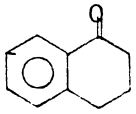

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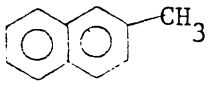

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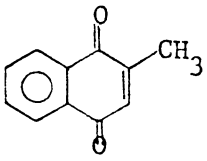

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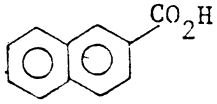

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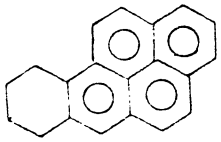

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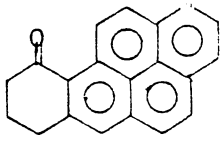

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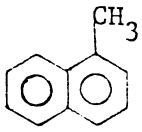

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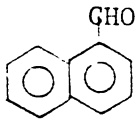

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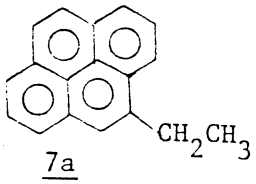

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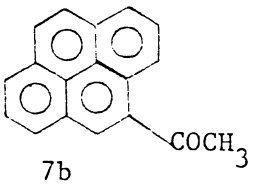

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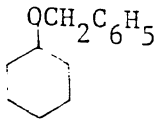

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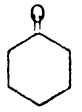

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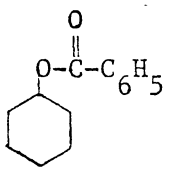

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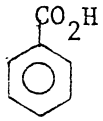

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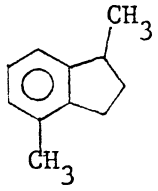

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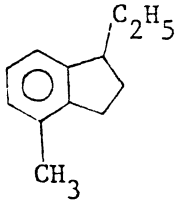

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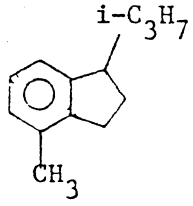

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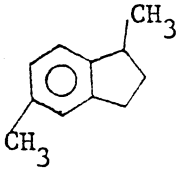

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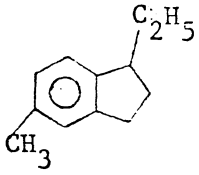

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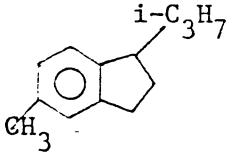

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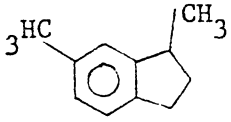

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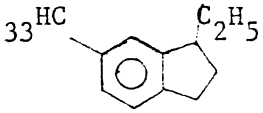

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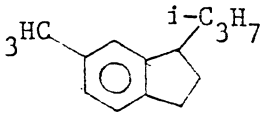

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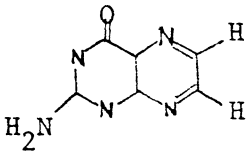

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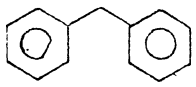

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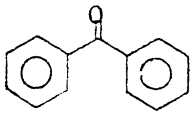

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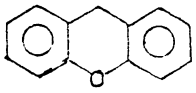

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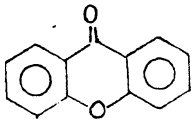

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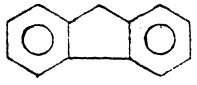

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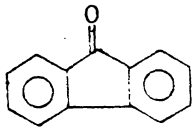

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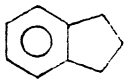

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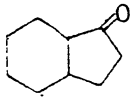

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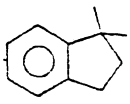

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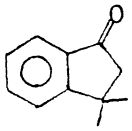

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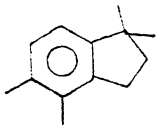

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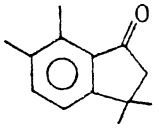

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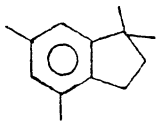

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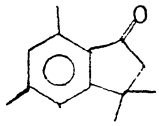

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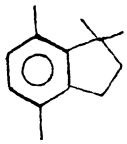

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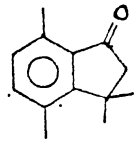

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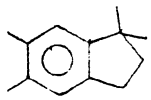

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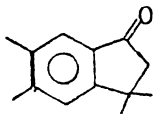

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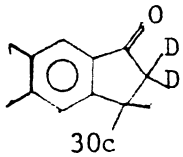

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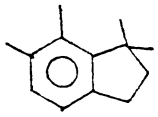

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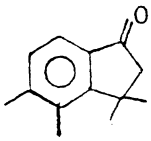

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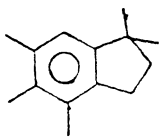

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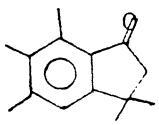

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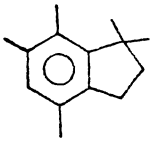

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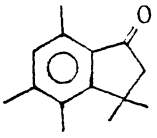

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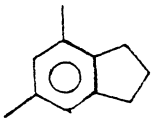

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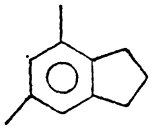

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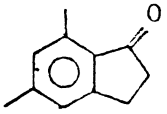

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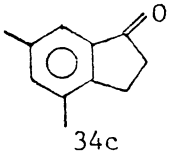

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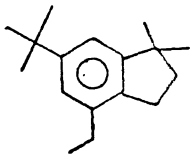

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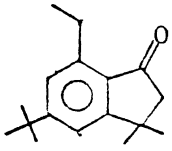

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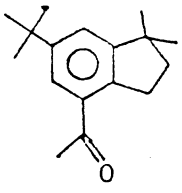

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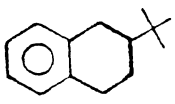

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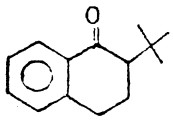

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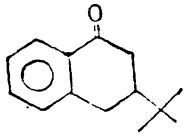

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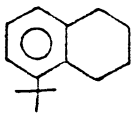

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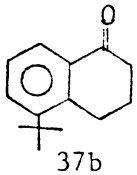

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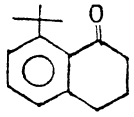

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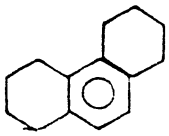

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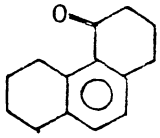

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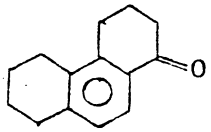

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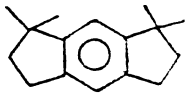

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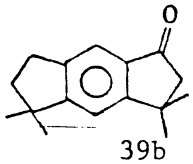

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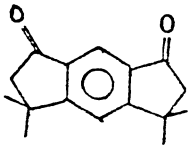

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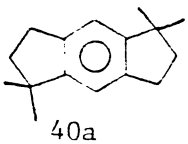

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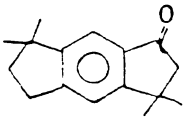

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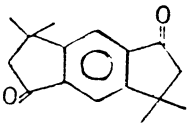

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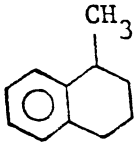

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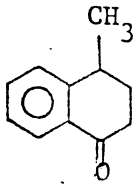
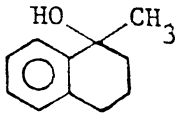


41b



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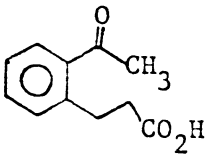

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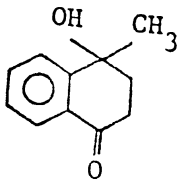

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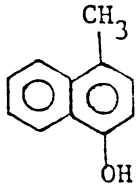

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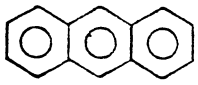

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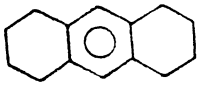

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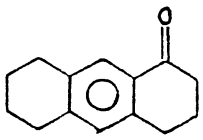

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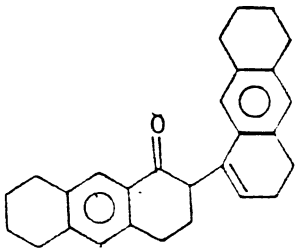

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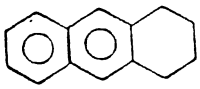

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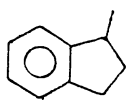

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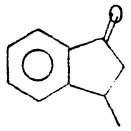
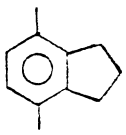


50b



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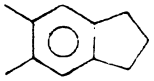

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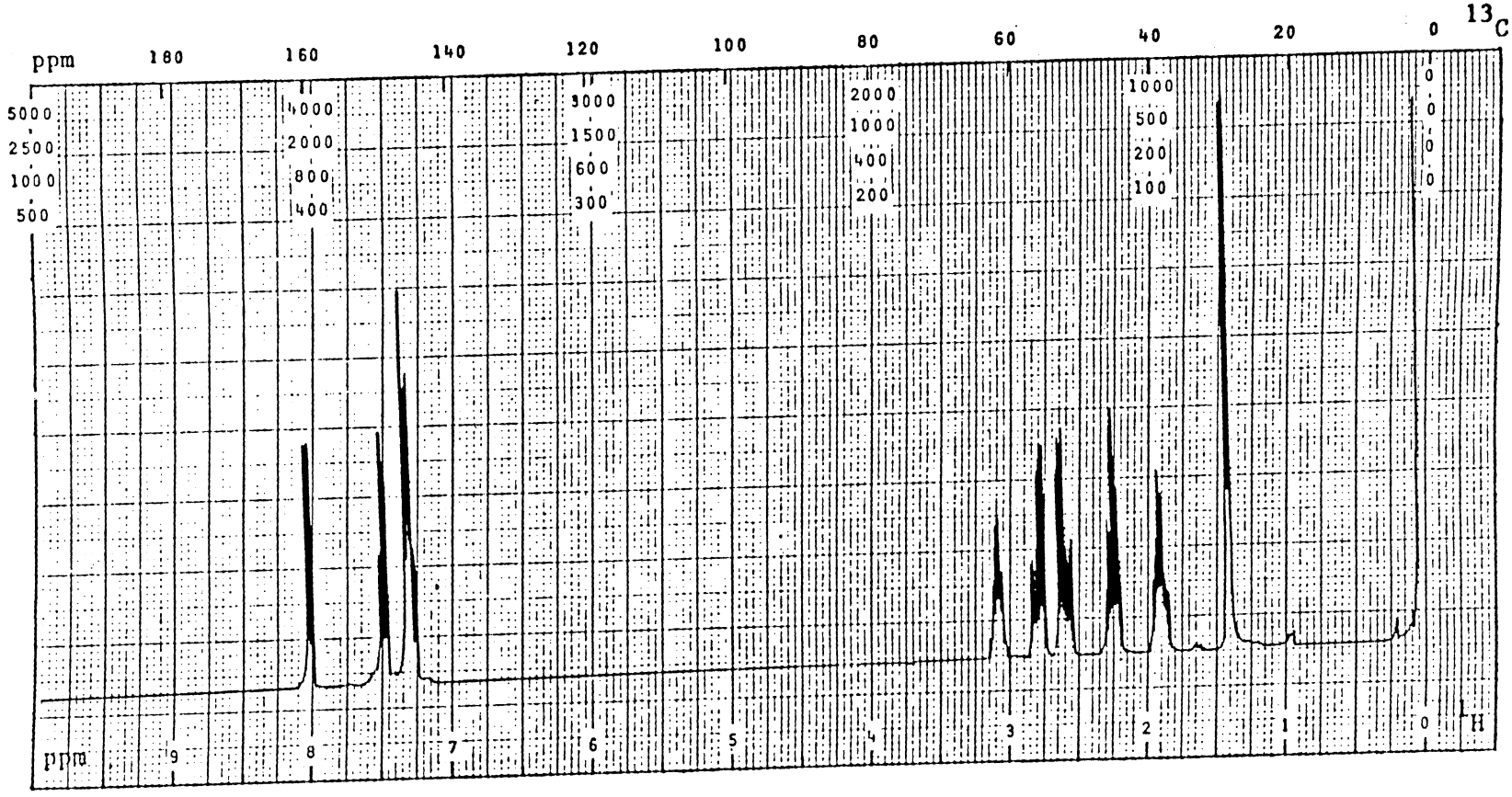
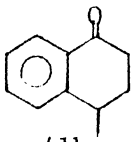
APPENDIX B

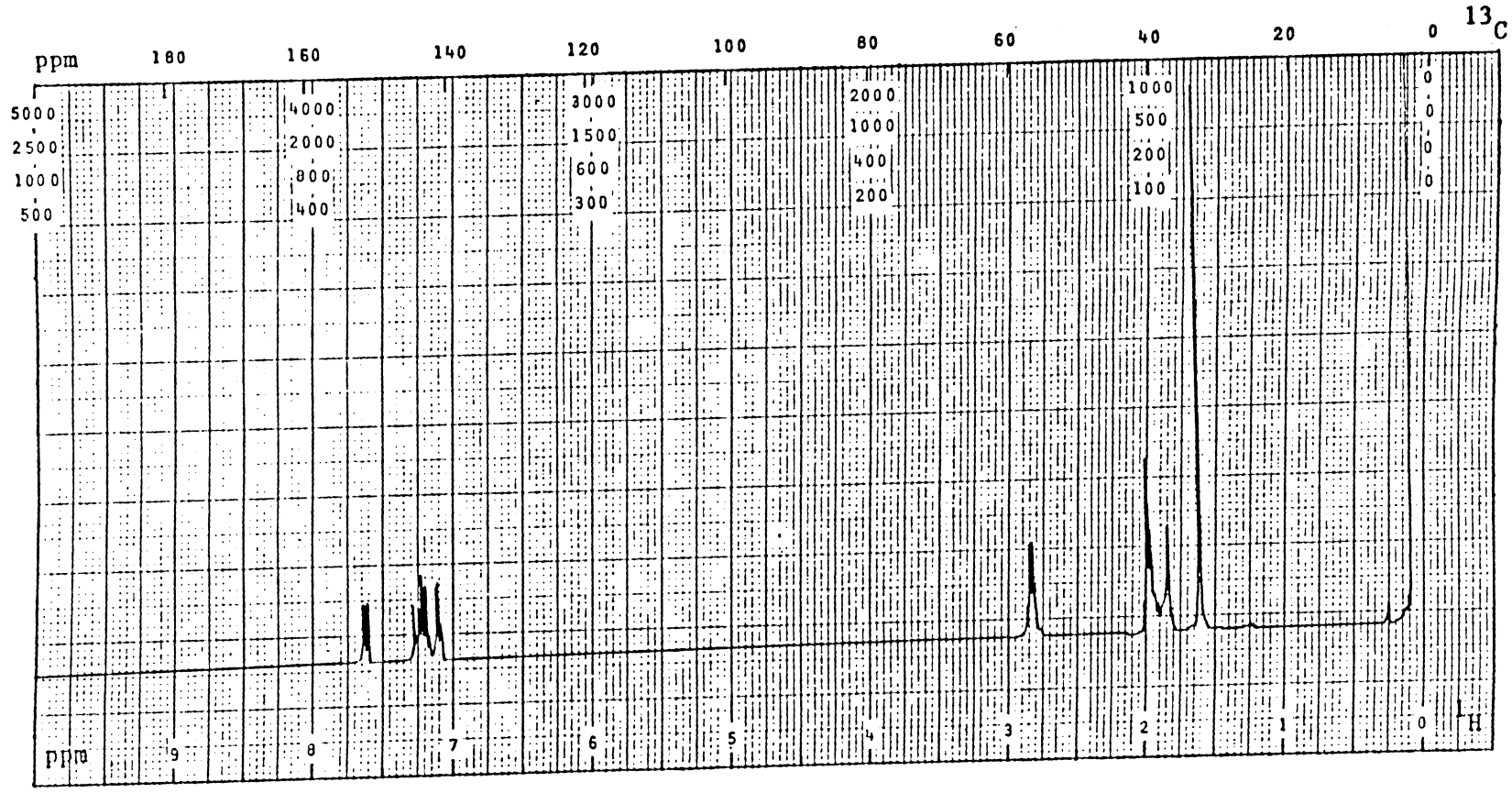
SELECTED SPECTRA

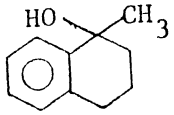




41b

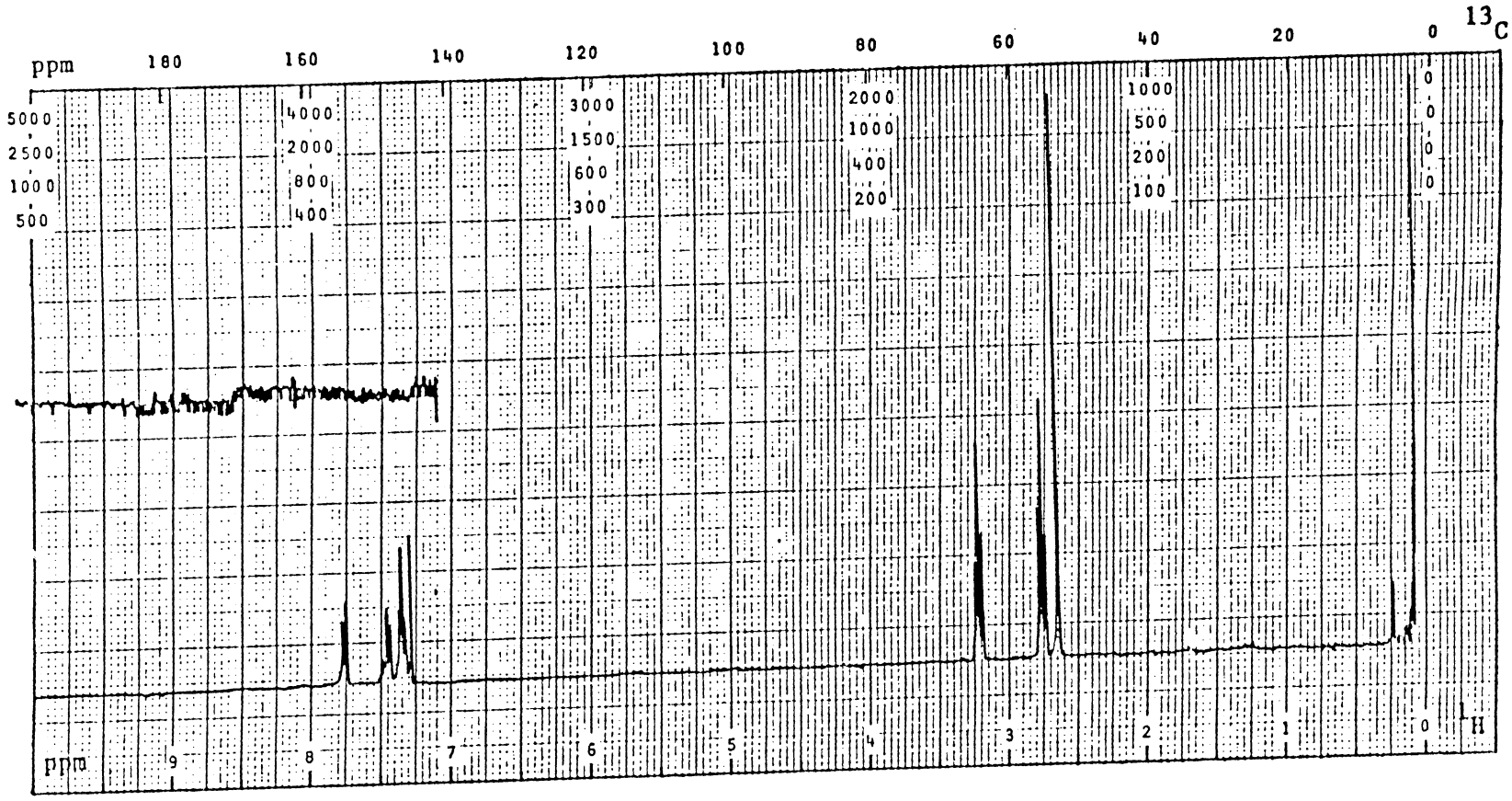
Spectrum 7. ^{1}H NMR of 4-Methyl-1-tetralone (41b)



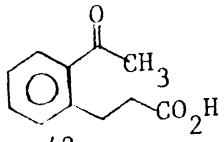


41c

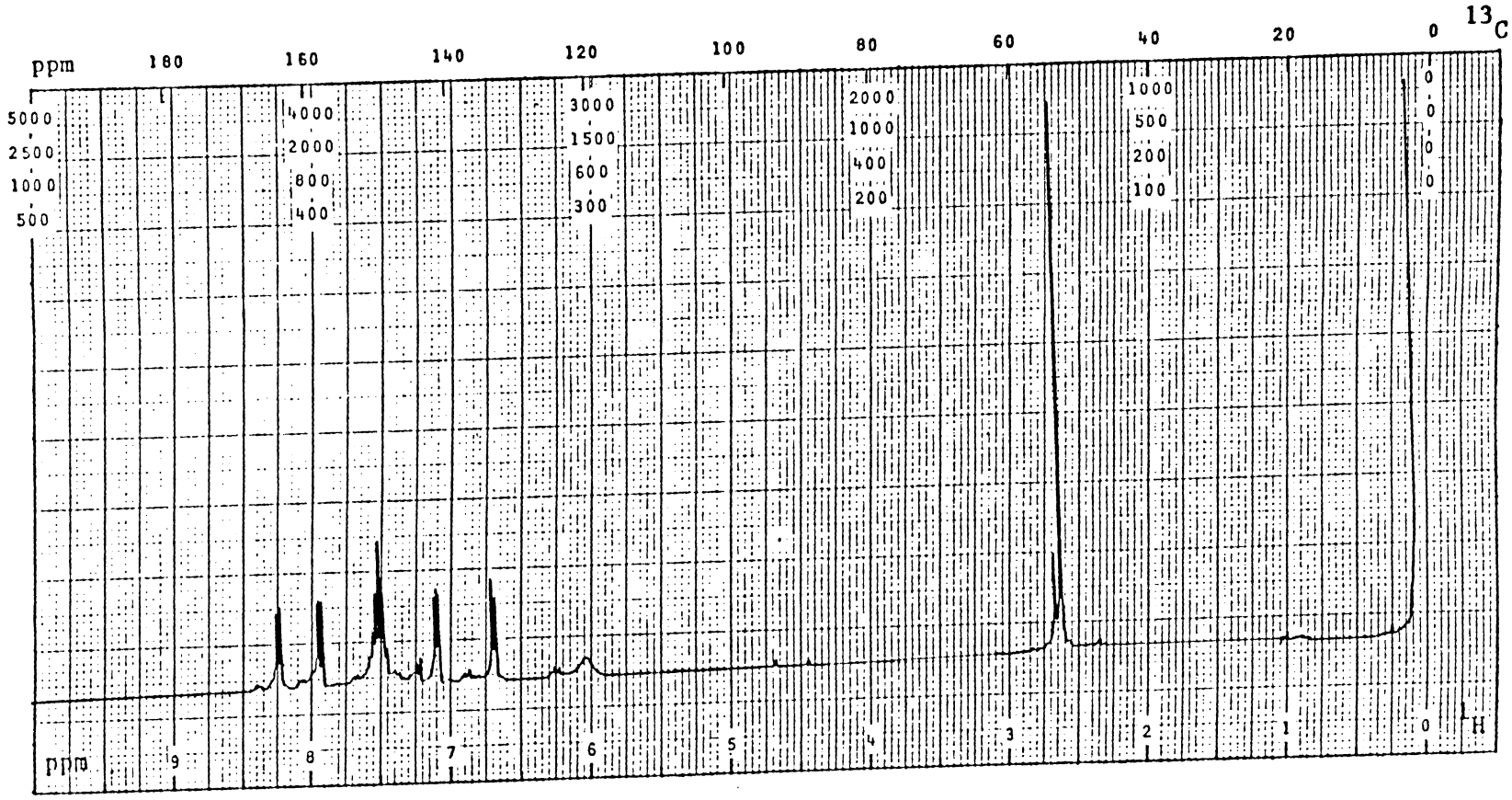
Spectrum 8. ^{1}H NMR of 1-Methyl-1,2,3,4-tetrahydro-1-naphthol (41c)

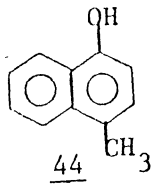


Spectrum 9. ^{1}H NMR of 3-(2-Acetylphenyl) propionic acid (42)



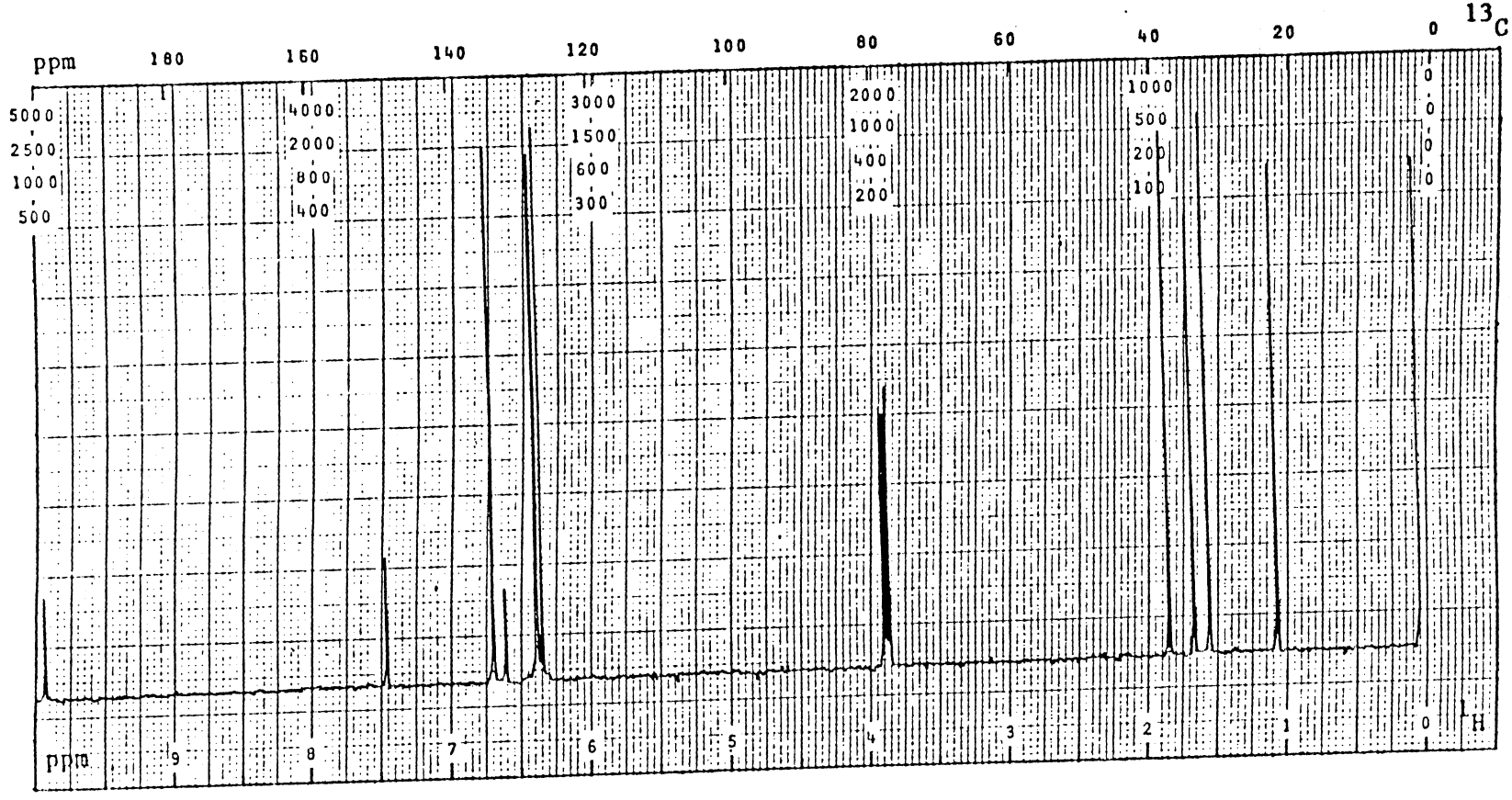
42

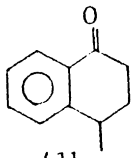




44

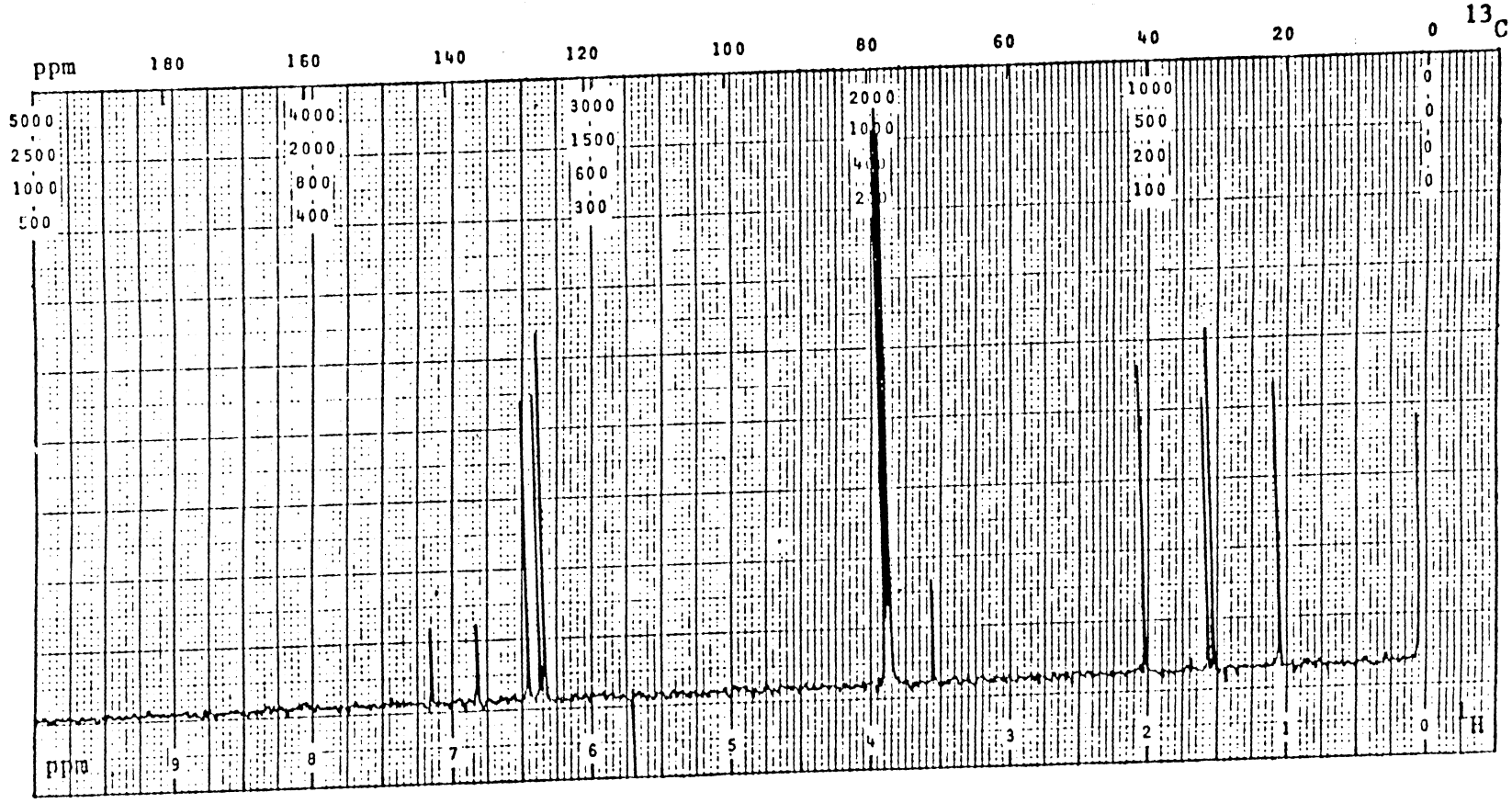
Spectrum 10. ^{1}H NMR of 4-Methyl-1-naphthol (44)

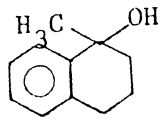




41b

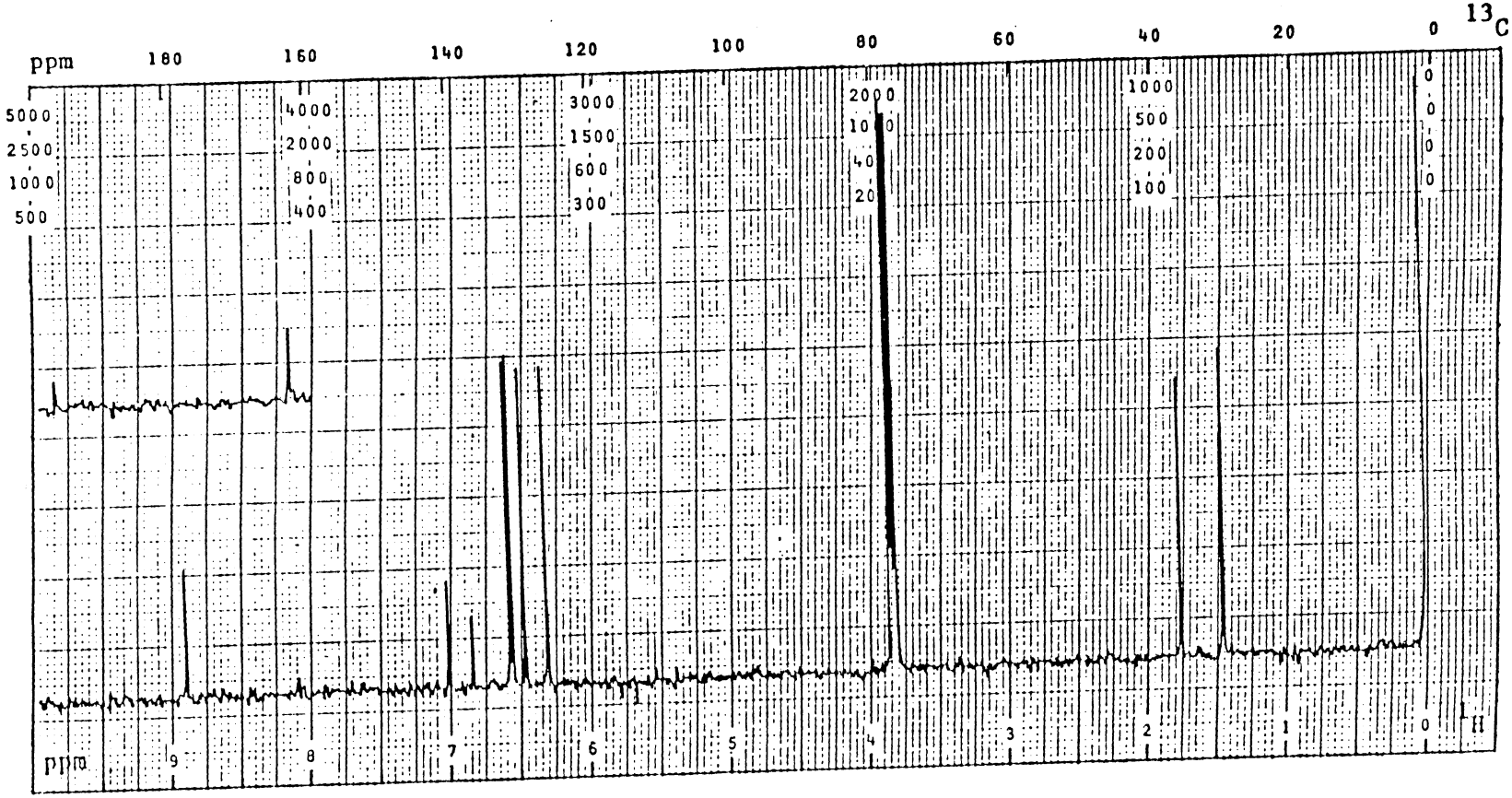
Spectrum 11. ^{13}C NMR of 4-Methyl-1-tetralone (41b)

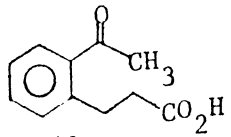




41c

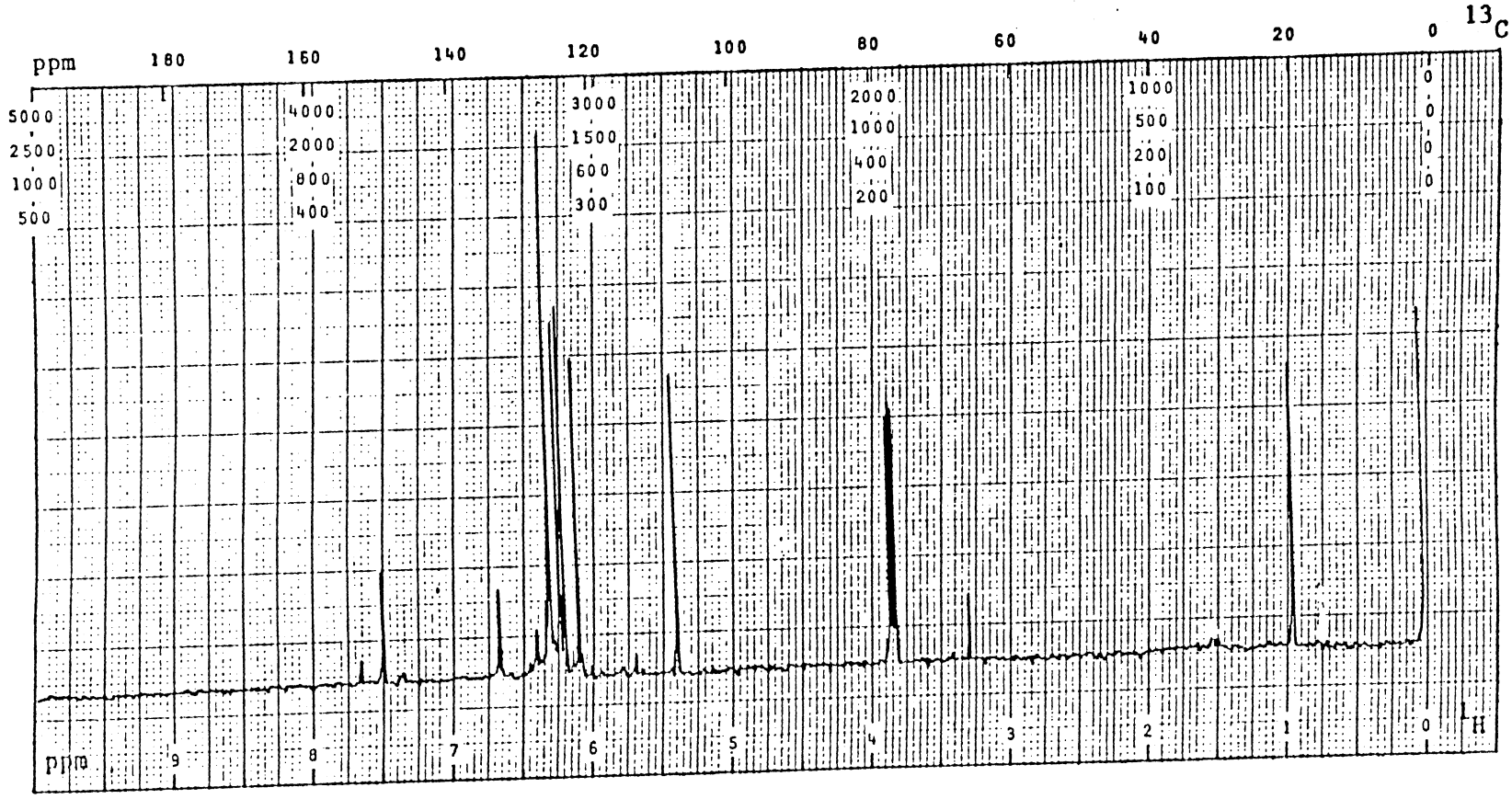
Spectrum 12. ^{13}C NMR of 1-Methyl-1,2,3,4-tetrahydro-1-naphthol (41c)



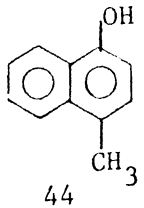


42

Spectrum 13. ^{13}C NMR of 3-(2-Acetylphenyl)propionic acid (42).



Spectrum 14. ^{13}C NMR of 4-Methyl-1-naphthol (44)



44

VITA 2

Radhika Rangarajan

Candidate for the Degree of

Doctor of Philosophy

Thesis: CHROMIC ACID OXIDATION OF HYDROCARBONS AT THE BENZYLIC POSITION USING THE JONES REAGENT AND C-13 NMR STUDY OF GEM-DIMETHYL-INDANS AND -INDANONES

Major Field: Chemistry

Biographical:

Personal Data: The author was born in Chidambaram, India on January 29, 1959, to Seshadhri Rangarajan and Shantha Rangarajan.

Education: The author graduated from the Government Girls' High School, Chidambaram, India, in 1975; received the Bachelor of Science Degree in Chemistry from Annamalai University, Annamalai Nagar, India, in 1979; completed requirements for the Doctor of Philosophy Degree in Chemistry at Oklahoma State University, Stillwater, Oklahoma, in December, 1984.

Professional Experience: Graduate Teaching Assistant in the Department of Chemistry, Oklahoma State University, Stillwater, September, 1980 - May, 1983; Graduate Research Assistant, Department of Energy, Oklahoma State University, Stillwater, Summer, 1983; Graduate Teaching Assistant, Department of Chemistry, Oklahoma State University, Stillwater, September, 1983 - May, 1984; Graduate Research Assistant, Dow Chemical Company and Department of Energy, Summer, 1984; Graduate Teaching Assistant, Chemistry Department, Oklahoma State University, September, 1984 - December, 1984.