

I. PHOTOLYSIS AND PYROLYSIS OF SILVER BENZOATE
IN CYCLOHEXENE

II. STEREOCHEMISTRY OF ADDITION OF HYDROGEN
BROMIDE AND HYDROGEN CHLORIDE TO 4-TERT-
BUTYL-1-PHENYLCYCLOHEXENE

By

DON ELDON GIBBS

Bachelor of Science

Oklahoma State University

Stillwater, Oklahoma

1964

Submitted to the faculty of the Graduate College
of the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
May, 1969

SEP 29 1989

I. PHOTOLYSIS AND PYROLYSIS OF SILVER BENZOATE
IN CYCLOHEXENE

II. STEREOCHEMISTRY OF ADDITION OF HYDROGEN
BROMIDE AND HYDROGEN CHLORIDE TO 4-TERT-
BUTYL-1-PHENYLCYCLOHEXENE

Thesis Approved:

K. A. Berlin

Thesis Adviser

E. J. Ciombro

Tom E. Moore

Theodore L. Agnew

D. N. Anham

Dean of the Graduate College

724846

to my wife

ACKNOWLEDGMENTS

The author expresses gratitude for the guidance and encouragement provided by his adviser, Dr. K. Darrell Berlin, during these investigations. Gratitude is also expressed to Dr. O. C. Dermer who read the manuscript and offered helpful suggestions.

Indebtedness is acknowledged to the Department of Health, Education and Welfare and to the Department of Chemistry of the Oklahoma State University for financial aids in the form of research and teaching assistantships, respectively.

Gratitude is expressed to Dr. J. Paul Devlin for determining the Raman spectra.

TABLE OF CONTENTS

	Page
INTRODUCTION	ix
Part	
I. PHOTOLYSIS AND PYROLYSIS OF SILVER BENZOATE IN CYCLOHEXENE	1
II. STEREOCHEMISTRY OF ADDITION OF HYDROGEN BROMIDE AND HYDROGEN CHLORIDE TO 4- <u>TERT</u> -BUTYL-1- PHENYLCYCLOHEXENE	34

PART I

PHOTOLYSIS AND PYROLYSIS OF SILVER

BENZOATE IN CYCLOHEXENE

TABLE OF CONTENTS

Chapter	Page
PART I	
I. HISTORICAL.	7
Photochemistry of Silver Salts of Carboxylic Acids	7
Pyrolysis of Silver Salts of Carboxylic Acids.	2
Decomposition of Benzoyl Peroxide in Cyclohexene	5
II. DISCUSSION OF RESULTS AND CONCLUSIONS	9
III. EXPERIMENTAL.	14
Preparation of Silver Benzoate (III)	14
Photolysis of Silver Benzoate (III) in Cyclohexene (XXI).	14
Pyrolysis of Silver Benzoate (III) in Cyclohexene (XXI).	16
Preparation of Cyclohexyl Benzoate (XXXIV)	16
Preparation of 3-Bromocyclohexene (LII).	17
Preparation of 3-Cyclohexenyl Benzoate (XXXV). Method 1	17
Preparation of 3-Cyclohexenyl Benzoate (XXXV). Method 2	18
Preparation of 2-(3-Cyclohexenyl)cyclohexyl Benzoate (XXXVI)	19
Preparation of 1-Phenylcyclohexene (L). Method 1.	20
Preparation of 1-Phenylcyclohexene (L). Method 2.	21
Preparation of Bicyclohexyl (XXXVIII).	22
Preparation of 3-Cyclohexylcyclohexene (XLIII)	22
BIBLIOGRAPHY	31

LIST OF ILLUSTRATIONS

Plate		Page
	Infrared Spectra	
I.	Silver Benzoate (III), KBr Pellet.	24
II.	Cyclohexyl Benzoate (XXXIV), Film on NaCl Plates	25
III.	3-Cyclohexenyl Benzoate (XXXV), Film on NaCl Plates.	26
IV.	2-(3-Cyclohexenyl)cyclohexyl Benzoate (XXXVI), Film on NaCl Plates.	27
V.	1-Phenylcyclohexene (L), Film on NaCl Plates	28
VI.	3-Cyclohexylcyclohexene (XLIIII), Film on NaCl Plates	29
	Gas-Liquid Chromatograph (GLC) Spectrum	
VII.	Photolyzate of Silver Benzoate (III) in Cyclohexene (XXI).	30

INTRODUCTION

Part I describes an investigation of silver benzoate as a source of phenyl and benzoyloxy radicals. Advantages envisioned for silver benzoate over other radical sources include use over a wider temperature range, convenient preparation in high purity, and freedom from hazards in handling and reaction work-up. Salient features of the present work are analysis of products by gas liquid chromatography (GLC) and structure confirmation by unequivocal syntheses.

Part II describes the isolation and characterization as separate entities of the stereomers resulting from electrophilic addition of hydrogen halides to a cyclic alkene, 4-tert-butyl-1-phenylcyclohexene. Isolation and rigorous characterization of the products from this type of reaction do not appear to have been reported previously. A striking example of the influence of the tert-butyl group on chemical reactivity is presented. Also, one of the few known unambiguous examples of possible S_Ni -type reaction between an alcohol and hydrogen halide is discussed.

CHAPTER I

HISTORICAL

Photochemistry of Silver Salts of Carboxylic Acids

A wide variety of silver salts of carboxylic acids have been shown to be light-sensitive.⁴¹ Variations in photosensitivity of different salts may be due to absorption maxima, degree of optical rotation, and cis-trans isomerism.⁴³ Colorless silver salts exhibit the greatest absorption in the 5490-5700 Å region. Chemical constitution appears to affect sensitivity only as structure influences color of the silver compounds.⁴⁵ The long-wavelength limit of photosensitivity of aliphatic salts was observed to increase with the number of carbon atoms.²⁸

Photographic emulsions prepared with silver salts of aromatic acids were one hundred times less sensitive than those with silver chloride,²⁹ while emulsions containing aliphatic salts were only two to three times less sensitive.²⁸ Silver oxalate (I) has been studied far more extensively than any other salt. The impossibility of generating hydrocarbon species from the oxalate limits analogies with other salts, but mechanistic studies on the oxalate may be generally useful. In an investigation of the kinetics and mechanism of the photolysis of I, prolonged irradiation of 2537Å wavelength resulted in 90% decomposition.¹⁷ Carbon dioxide and silver were formed in stoichiometric

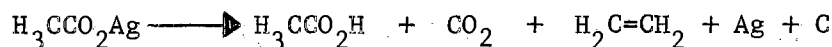
amounts. The activation energy was determined to be 950 cal./mole.

Electron paramagnetic resonance spectroscopy indicated the presence of a radical ion in UV-irradiated I.⁴⁰ The effect of impurities on rate of photolysis was measured by observing silver nuclei formation via electron microscopy.⁸ Cupric ions (3×10^{-3} mole %) markedly increased the rate, presumably because of the facility for accepting electrons.

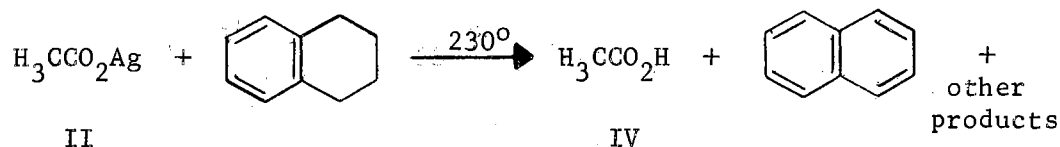
Applications for silver salts as radical sources have been found. For example, vinyl polymers were effectively photopolymerized in the presence of silver acetate (II) and silver benzoate (III).¹⁹

Pyrolysis of Silver Salts of Carboxylic Acids

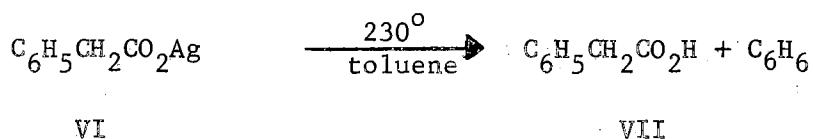
From the dry distillation of silver acetate (II), Chenevix reported acetic acid (IV), carbon dioxide, and a residue of silver and carbon.¹⁰ In repeating this experiment, Twig and Hecht failed to



observe any ethylene.²⁵ When II was heated with toluene in a sealed tube for 14 hr. at 230° , only silver and IV were observed; no acetic anhydride (V) or carbon dioxide was detected.³⁶ Silver acetate (II) dehydrogenated tetralin to naphthalene at 230° .³⁶

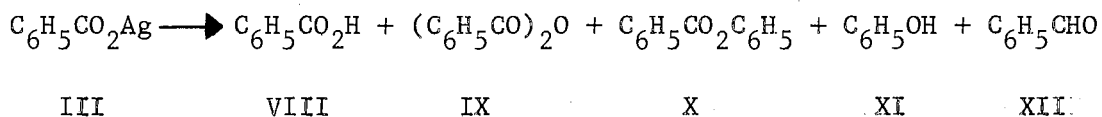


Liquid media may affect the reaction path. From silver phenylacetate (VI) in toluene at 230° , only benzene and phenylacetic acid



(VII) could be isolated.³⁶ Dry pyrolysis of VI at the same temperature gave benzene, benzoic acid (VIII) and two unidentified organic products, neither of which could be VII or its anhydride.³⁶

Evidence for the intermediacy of anhydrides was provided by Kamevs-kaya and co-workers. Since formation of anhydride and metal oxide are exothermic and decomposition to products is endothermic, intermediates may be isolated by quenching partially pyrolyzed silver salts.²⁷ Some acetic anhydride (V) was obtained with the acid IV from silver acetate (II). The major products from silver benzoate (III) were benzoic anhydride (IX), benzoic acid (VIII), phenyl benzoate (X), and small amounts of phenol (XI) and benzaldehyde (XII).²⁶ The ester X was sup-

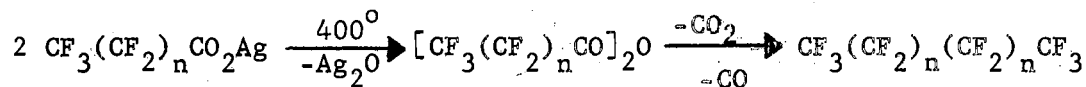


posed to have resulted from reaction of XI and IX. Pyrolysis of silver benzoate (III) in XI also gives X.³⁶ Further work showed that the silver, copper, and calcium salts of a variety of carboxylic acids give anhydrides on pyrolysis.⁴²

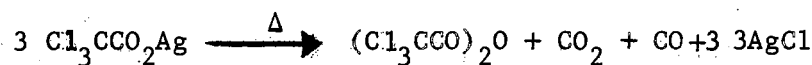
Decomposition of silver carboxylates to the corresponding anhydrides and the metal oxide are thermodynamically allowed. The salts of many other metals cannot decompose by this route.⁴⁶

Extension of carbon chains predominates in the pyrolysis of fluorinated salts.³¹ Thus, silver trifluoroacetate (XIII) at 400° gives hexafluoroethane (XIV) in good yield. Similarly, the perfluoropropionate (XV) gives perfluorobutane (XVI); the perfluorobutyrate (XVII) gives perfluorohexane (XVIII). Anhydrides were postulated as intermediates because carbon monoxide was evolved. Under conditions of the

reaction, silver oxide decomposes to the free metal.

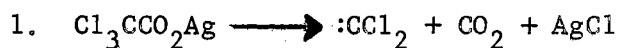


Dichlorocarbene (XIX) apparently results from the pyrolysis of silver trichloroacetate (XX).²⁴ The stoichiometry was found to be



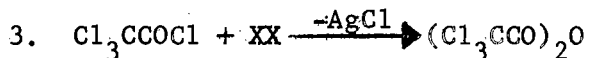
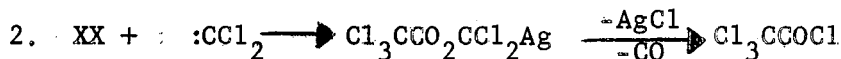
XX

The following mechanism was proposed:

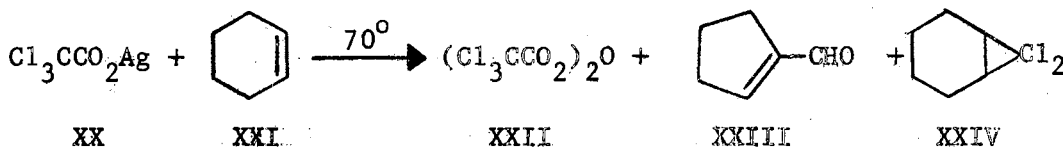


XX

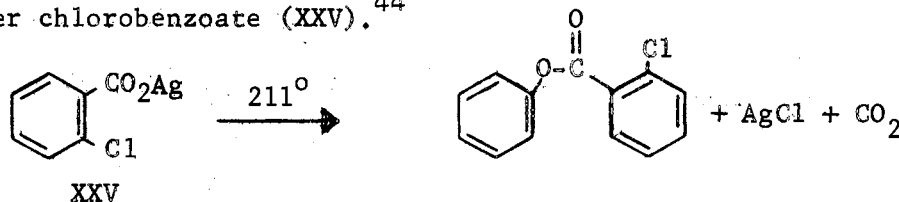
XIX



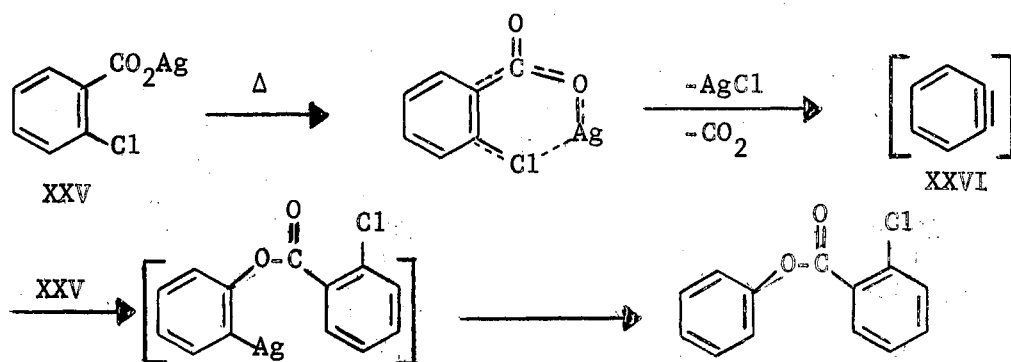
More direct evidence for the carbene XIX was furnished by heating XX in cyclohexene (XXI) at 70°. In addition to trichloroacetic anhydride (XXII), significant quantities of 1-formyl-cyclopentene (XXIII) and dichloronorcaradiene (XXIV) were obtained.²⁴



Neighboring group participation was observed for the pyrolysis of silver chlorobenzoate (XXV).⁴⁴



Benzynes (XXVI) was proposed as an intermediate. No organic products

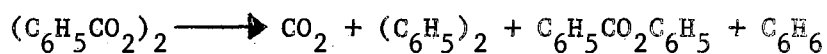


other than benzoic acid (VIII) were detected in an unexplained pyrolysis of XXV in furan at 250°. The same materials at 175° gave chlorobenzoic acid (XXVII).⁴⁴

The pyrolysis of previously irradiated silver oxalate (I) was shown to be autocatalyzed by silver.⁴ Surprisingly, decomposition did not appear to be influenced by foreign silver. Sulfur compounds greatly accelerated the reaction while oxygen retarded it.

Decomposition of Benzoyl Peroxide in Cyclohexene

Benzoyl peroxide (XXVIII) on being heated alone gave CO₂ and biphenyl (XXIX) plus small amounts of phenyl benzoate (X) and benzene.¹³ Initial formation of benzoyloxy radicals was demonstrated by decomposi-

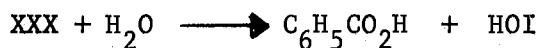


tion of XXVIII in CCl₄ containing traces of water and iodine.²¹ Quantitative conversion to benzoic acid (VIII), presumably via benzoyl hypoiodite (XXX), was realized. A similar reaction in cyclohexene



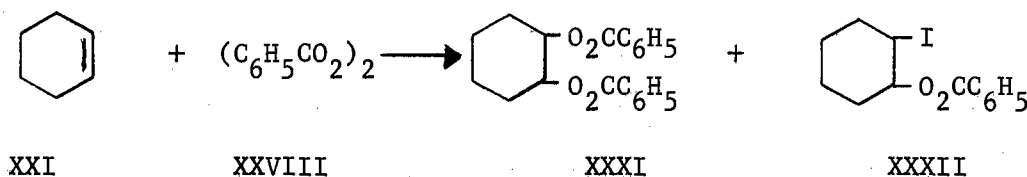
XXVIII

XXX



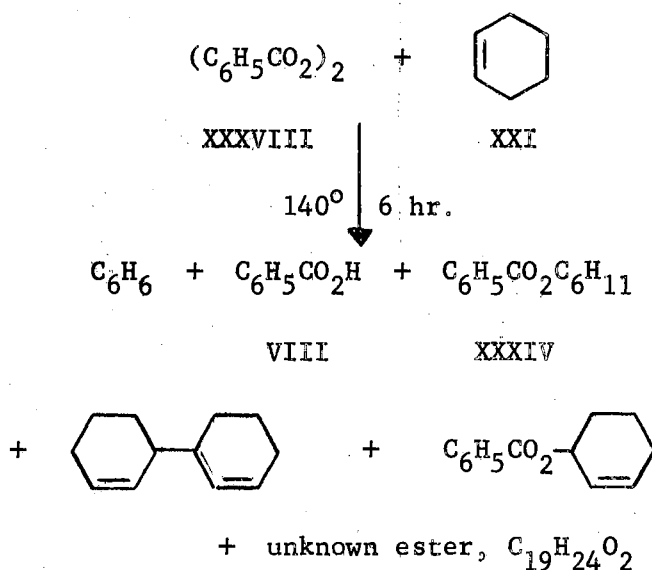
VIII

(XXI) gave cyclohexylene 1,2-dibenzoate (XXXI) and 2-iodocyclohexyl benzoate (XXXII).³⁹

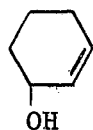


In general, when XXVIII is decomposed in alkenes, the quantity of benzoic acid (VIII) formed accounts for about half of the reacted peroxide XXVIII. The remainder of XXVIII mostly gives rise to benzoates through solvent attack by benzoyloxy radicals. Little carbon dioxide is evolved and phenylation products can be isolated only in low yield. Since CO_2 evolution increases with temperature, the activation energy for formation of benzoyloxy radicals appears to be higher than for attack of many solvents.²

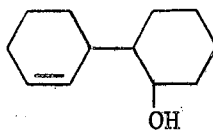
Apparently the first attempt to identify products resulting from pyrolysis of XXVIII in XXI was that of Farmer and Michael.¹⁵ Reaction at 140° for 6 hr. gave a complex mixture which was partially separated by repeated fractional distillations. The products positively identified were benzene, benzoic acid (VIII), 3,3'-bicyclohexenyl (XXXIII), and cyclohexyl benzoate (XXXIV). Tentative evidence for the production of 3-cyclohexenyl benzoate (XXXV) was obtained. A tricyclic olefinic ester (XXXVI) was also isolated. No evidence was found for the presence of cyclohexane (XXXVII), bicyclohexyl (XXXVIII), or phenylcyclohexane (XXXIX).



Distillation fractions, none of which were pure compounds, were analyzed by carbon-hydrogen determination, iodine number, and degradation. Esters XXXV and XXXVI could not be separated by distillation. Saponification of the C_{13} -ester fraction gave cyclohexanol (XL) and 3-cyclohexenol (XLI). From the occurrence of the latter alcohol, XXXV was assumed to be 3-cyclohexenyl benzoate. Esters XXXV and XXXVI were obtained in a ratio of 3:10 based on iodine and benzoyl values. Saponification of a C_{19} -ester fraction yielded a compound $\text{C}_{12}\text{H}_{20}\text{O}$, from elemental analysis and molecular weight determination. This product was assumed to be 2-(3-cyclohexenyl)cyclohexanol (XLII) and XXXVI, the corresponding benzoate, without further justification.



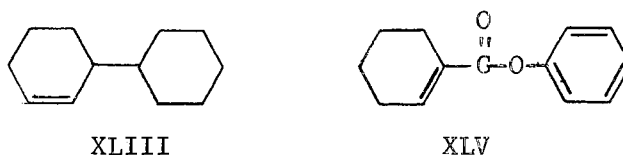
XLI



XLII

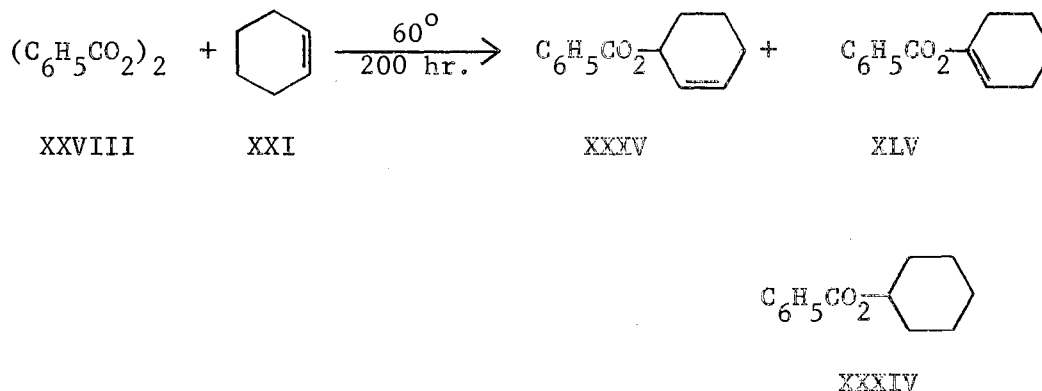
A more quantitative study of the decomposition of XXVIII in XXI has been made by Hermans and Van Eyk.²³ The average number of chain steps was 2-3. Benzoyloxy radicals preferentially attacked the double

bond. The resulting secondary radicals tended to attack the allylic position. To judge by the yield of CO_2 , one mole of XXXVIII gave 1.7 mole benzoyloxy radicals and only 0.3 mole phenyl radicals. The fate of the latter was not determined. Of the benzoyloxy radicals, 0.31 mole appeared as benzoic acid (VIII); the remainder, as benzoates. In addition to the products of Farmer and Michael, evidence was obtained for the presence of a hydrocarbon assumed to be 3-cyclohexylcyclohexene (XLIII) and a cyclohexylcyclohexyl benzoate (XLIV). 1-Cyclohexenyl



benzoate (XLV) was shown to be absent. No further evidence was acquired on the structure of XXXVI.

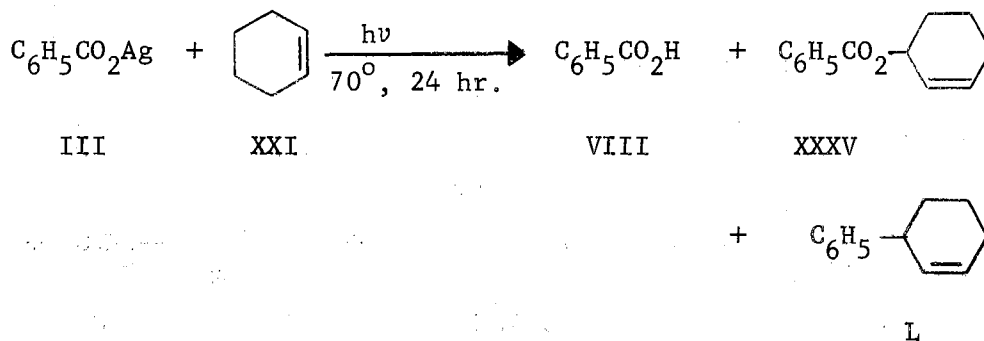
Noma and Tsuchida studied the decomposition of XXVIII in XXI at 60° for 200 hr.³⁷ The major product reported was 3-cyclohexenyl benzoate (XXXV) with less of the 1-isomer XLV and a trace of cyclohexyl benzoate (XXXIV). Small amounts of benzoyloxycyclohexane polymers were also reported with tentative structures.



CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

In the photolysis of silver benzoate (III) in cyclohexene (XXI) at 70°, significant products are benzoic acid (VIII) and 3-cyclohexenyl benzoate (XXXV).⁶ About 5% of the cyclohexene undergoes reaction in 24-26 hr. at 70°. Phenylation is a minor reaction. Several major

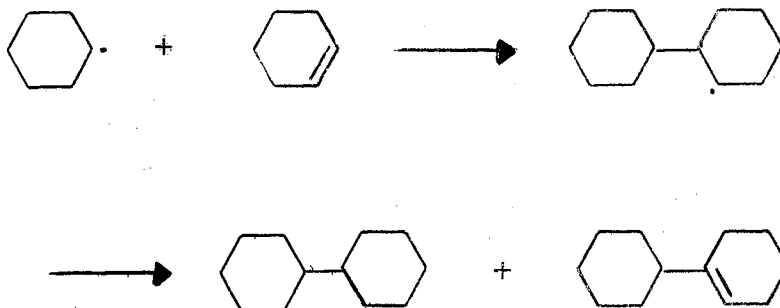


products remain unidentified. Either heat or irradiation alone promotes little decomposition of III. The reaction is accelerated by cuprous ion.

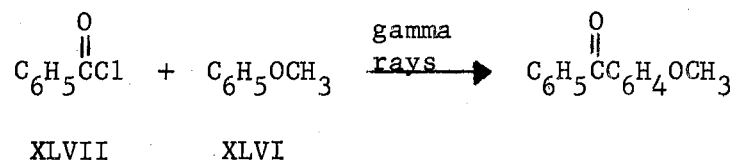
Positive identification of cyclohexyl benzoate (XXXIV) is lacking. This ester and XXXV were not cleanly separated by any of the three GLC columns employed. A component of the reaction mixture had a retention time comparable to that of XXXIV, but peak reinforcement did not appear to take place with mixed injections. If XXXIV is present, the amount is considerably less than that of XXXV.

No bicyclohexyl (XXXVIII) was found, suggesting that the participation of cyclohexyl radicals is negligible. Attack of cyclohexene by

cyclohexyl radical would be expected a priori to give XXXVIII.

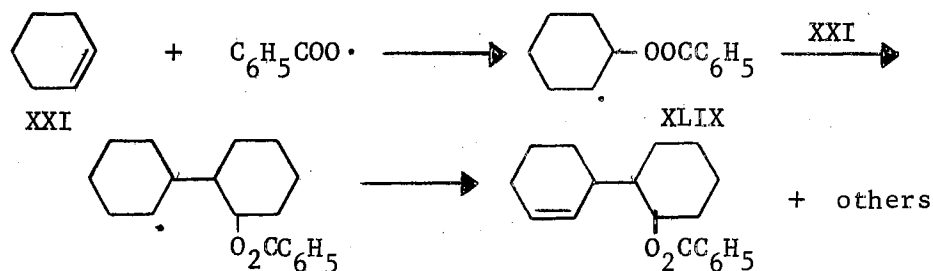


The generation of benzoyl radicals in the photolysis of silver benzoate (III) in cyclohexene (XXI) has been discounted by inference from the photolysis of III in anisole (XLVI).⁵ The possibility was raised by the discovery that benzoyl chloride (XLVII) in XLVI subjected to gamma radiation gave methoxybenzophenones.¹⁴ If the

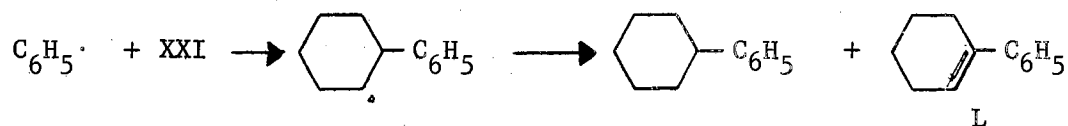


energy of activation for nuclear substitution were too high to occur under photolytic conditions, benzaldehyde (XII) or benzil (XLVIII) would be expected. However, none of the possible products was observed.

Structure XXXVI proposed by previous workers¹⁵ for one photolysis product has been disproven by an independent synthesis. A likely path for the formation of XXXVI involves attack of the secondary radical XLIX on the readily available cyclohexene (XXI). That no XXXVI was found suggests that hydrogen abstraction and/or disproportionation are more likely than addition of XLIX to cyclohexene.

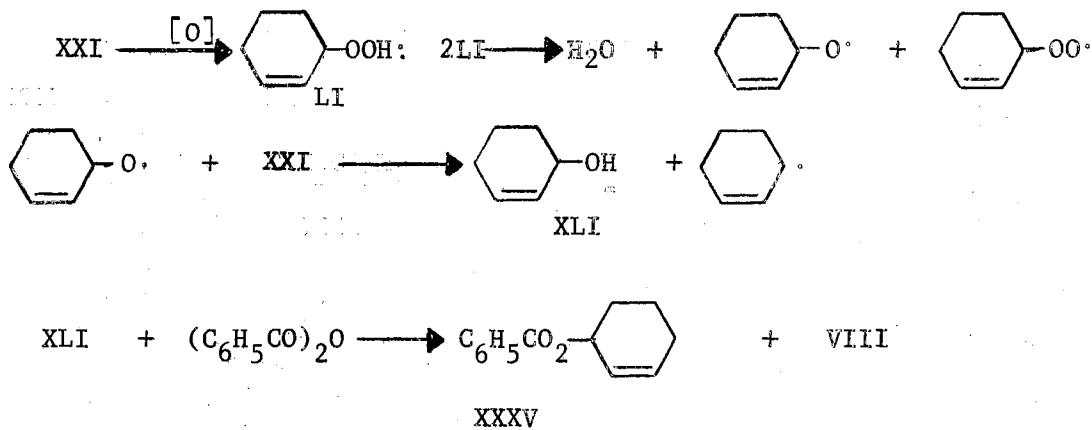


Phenylation accounts for a very small portion of the identified products. Since the phenyl radical has been shown to add readily to olefin bonds, 1-phenylcyclohexene (L) would be expected. The production of L in only trace amounts in benzoate photolysis seems to preclude



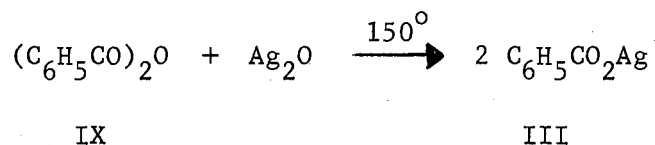
phenylation as being significant.

Benzoic anhydride (IX) was examined as a possible intermediate in silver benzoate (III) photolysis, since IX has been shown to form upon pyrolysis of III.^{26,27,42} Neither heat nor UV irradiation gave reaction mixtures comparable to photolyzates of III in cyclohexene (XXI) or anisole (XLVI). Cyclohexene and IX did give 3-cyclohexenyl benzoate (XXXV), but this product was shown to arise from cyclohexyl hydroperoxide (LI).⁷



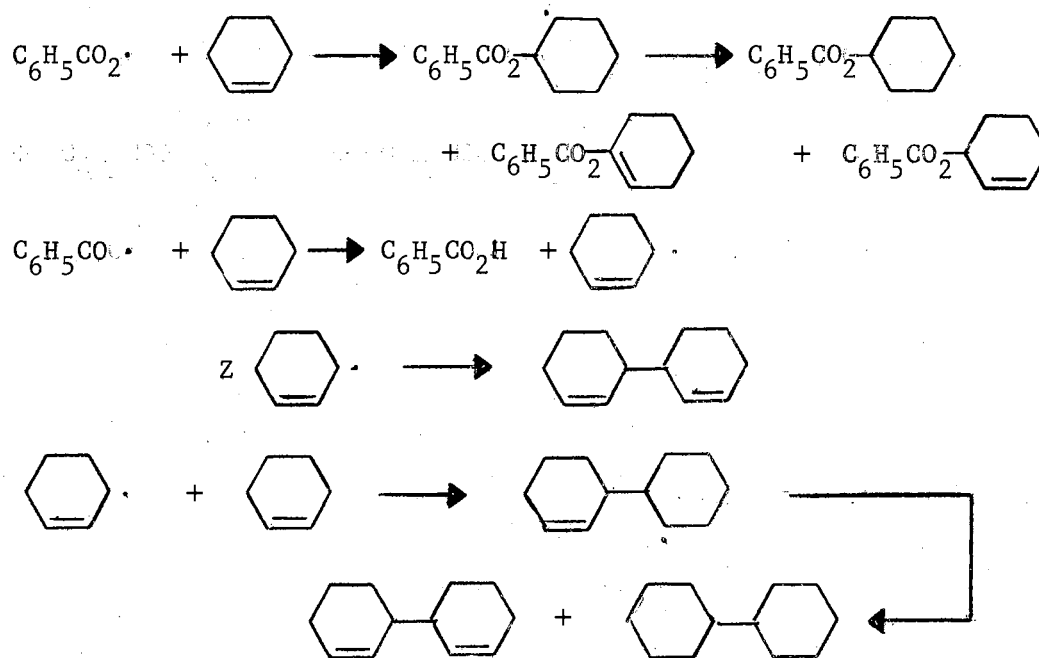
Carefully purified IX under conditions designed to promote radical reactions gave none of ester XXXV. No benzoic anhydride (IX) could be detected by GLC under a variety of conditions.

Added silver oxide was without significant effect on the photolysis of III in anisole (XLVI). Silver oxide and IX were found to give III in almost quantitative yield when heated together at 150° for 1 hr; the same starting materials gave no visible reaction at 70-80° (2 hr.).⁵



Hence, if IX were a crucial intermediate, a large excess of silver oxide should suppress product formation. Such an effect for the yield of benzoic acid (VIII) was not observed.⁵ Therefore, IX does not appear to be an intermediate.

A composite of peroxide and benzoate decompositions may be rationalized by the following reactions:



Other reactions could well give rise to the above products, but those cited seem most reasonable in view of the concentrations of reactive species.

There is fair correlation among products of the pyrolysis of benzoyl peroxide (XXVIII) in cyclohexene (XXI) and the photolysis of silver benzoate (III) in XXI. Pronounced differences exist, however, concerning the relative amounts of certain products. Ratios of 3-cyclohexenyl benzoate (XXXV) to cyclohexyl benzoate (XXXIV) in the mixtures have been determined as 23 (60°, 200 hr.);³⁷ 0.2 (70°, 24 hr.);²³ and 0.3 (140°, 6 hr.).¹⁶ If ester XXXIV is produced by photolysis of III in XXI, its concentration is much less than that of ester XXXV. Ester XXXV would almost certainly undergo radical attack more readily than would XXXIV. Thus, there is presently no simple explanation for the variation in the ratio of XXXIV to XXXV reported in the present work as well as from other studies.^{16,23,37}

CHAPTER III

EXPERIMENTAL^{a-c}

Preparation of Silver Benzoate (III). To a suspension of 31.0 g. (0.250 mole) benzoic acid (VIII) in 100 ml. water was added 40 ml. of concentrated ammonium hydroxide. After the solution was neutralized with benzoic acid (about 1.0 g.), 38.5 g. (0.250 mole) of silver nitrate in 100 ml. of water was added with rapid stirring. The white precipitate was removed by suction filtration and washed successively with 500 ml. of water, methanol, and ether.

Since the salt III is partially decomposed by heat, it was dried over phosphorus pentoxide at 1 mm. for 8 hr; yield was quantitative. To ensure complete removal of moisture, the product was recrystallized from hot pyridine which had been distilled from barium oxide. Because this precaution had no observed effect on photolyzate analyses, silver benzoate (III) was ordinarily used without purification.

Photolysis of Silver Benzoate (III) in Cyclohexene (XXI). Photolysis

^aChromatographic analyses were made on an Aerograph A-550 apparatus (Wilkins Instruments, Inc.) with a hydrogen flame ionization detector. Three columns were used: 10% silicone rubber (1/8 in. by 8 ft.), 20% SE-30 (1/8 in. by 8 ft.), and 4% UCON non-polar (1/8 in. by 4 ft.). All substrates were on acid-washed Chromosorb W.

^bInfrared spectra were determined on a Beckman IR-5A spectrophotometer. Liquids were examined as films on sodium chloride plates, and solids, as potassium bromide pellets.

^cMicroanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

was conducted in a 100-ml. quartz flask equipped with a reflux condenser. The ultraviolet source was a Hanovia mercury lamp which emitted radiation of wavelength 1849 to 4000 Å. The intensity of 3130 Å radiation at 40 cm. was 250 microwatts. The reaction mixture was held 10 cm. from the source. In a typical experiment, 1.30 g. (0.00560 mole) of silver benzoate (III) suspended in 20 ml. of cyclohexene (XXI) (dried over MgSO_4 and redistilled) was irradiated 26 hr. while being stirred magnetically. The resulting deposit of silver on the reaction vessel was mechanically removed as necessary.

In some runs the apparatus was flushed with dry nitrogen and protected by a calcium chloride tube. These precautions appeared to have no influence on the reaction.

Heating of the irradiated mixture was necessary for any significant reaction. When the UV source was fitted with a quartz heat filter, only trace amounts of products were detected. Without this filter, the reaction mixture was heated under reflux (70°) by the UV source alone.

The reaction mixture was filtered and the filtrate concentrated on a water bath under aspirator pressure. The IR spectrum of the resulting yellow oil was similar to a composite of the spectra of VII and XXXV.

The photolyzate, dissolved in ether, was shaken with aqueous sodium bicarbonate solution, dried (MgSO_4), and analyzed by GLC. Analysis of the photolyzate prior to bicarbonate treatment showed this step affected none of the products except benzoic acid.

The influence of cuprous ion was studied under the same conditions as described by adding 0.50 g. of anhydrous cuprous chloride. Work-up in the same way gave a green oil. The color indicated the presence of

organic copper compounds as cuprous chloride is not noticeably soluble in the starting materials.

Control experiments performed by irradiating cyclohexene neat showed that none of the high-boiling photolysis products were formed.

Pyrolysis of Silver Benzoate (III) in Cyclohexene (XXI). Reaction conditions were the same as outlined previously for photolysis except that electrical heating of the mixture in a flask protected from light by aluminum foil was employed. Silver benzoate (III) was only slightly darkened. The pyrolyzate contained components corresponding in retention times to those from photolysis. Amounts were near the detection limits of the instrument.

Preparation of Cyclohexyl Benzoate (XXXIV). While a solution of 10 ml. (0.10 mole) of cyclohexanol, 20 ml. (0.25 mole) of pyridine, and 30 ml. of benzene was stirred vigorously, 14 ml. (0.12 mole) of benzoyl chloride was added in several portions over a period of 14 minutes. Precipitation began within 3 minutes. Stirring was continued 1 hr. The reaction mixture was filtered by suction, and the residue was washed with benzene. After solvent was removed from the combined filtrate and washings, the product was distilled to give three fractions: (1) b.p. 112-124/10 mm, (2) b.p. 133-137/10 mm, and (3) b.p. 140-143/7 mm; (lit.,³³ b.p. for XXXIV, 132-3°/15 mm). The last fraction had a refractive index of 1.5175_D³⁵ and was pure cyclohexyl benzoate (XXXIV) by gas chromatography; yield 19 g. (93%). Absorption maxima were observed for C=O (1700 cm.⁻¹) and C₆H₅ (710 cm.⁻¹); see Plate II.

Anal. Calcd. for C₁₃H₁₆O₂: C, 76.44; H, 7.90.

Found: C, 75.95; H, 7.64.

Attempted preparation of XXXIV from cyclohexanol and benzoyl

chloride in aqueous sodium hydroxide gave only benzoic acid. Virtually none of ester XXXIV resulted when the sodium salt of cyclohexanol was treated with benzoyl chloride in dry benzene.

Preparation of 3-Bromocyclohexene (LII). A mixture of 89.0 g. (0.500 mole) of N-bromosuccinimide and 2.0 g (0.0083 mole) of benzoyl peroxide (XXVIII) was added over a period of 20 minutes to a boiling solution of 100 ml. (1.10 mole) of cyclohexene (XXI), 2.0 g. (0.0083 mole) of benzoyl peroxide, and 350 ml. of CCl_4 .^{16,22,47} During 30 minutes of heating, the yellow solid was replaced by the white, less dense succinimide. After the reaction mixture was cooled with an ice bath, it was filtered by suction. The filtrate was concentrated to 180 ml, on a steam bath under aspirator pressure and stored over marble chips in a refrigerator. This solution was used directly for synthetic purposes; characteristic absorption²¹ was observed at 731 cm.^{-1} .

Further concentration of the above solution always resulted in decomposition, as evidenced by gas evolution and pronounced discoloration. Samples shaken with aqueous ferrous ammonium sulfate to remove peroxides decomposed similarly upon concentration.

Preparation of 3-Cyclohexenyl Benzoate (XXXV). Method I. To a suspension of 20.0 g. (0.0830 mole) of silver benzoate (III) in 50 ml. of benzene was added 42 ml. (0.12 mole maximum) of a solution of 3-bromocyclohexene (LII) in CCl_4 , with vigorous swirling after addition of each portion. Removal of silver bromide by filtration and concentration of the filtrate under reduced pressure gave a light yellow oil. Fractionation of this oil afforded, after a forerun b.p. $59-84^{\circ}/1 \text{ mm.}$, a colorless liquid, pure XXXV by GLC, b.p. $84^{\circ}/1 \text{ mm.}$, n_D^{25} 1.5382; yield 7.05 g. (42%). Peaks for H-C=C (2560 cm.^{-1}), C=O (1710 cm.^{-1}), C=C

(1670 cm.^{-1}), and C_6H_5 (705 cm.^{-1}) were observed for XXXV.

Anal. Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2$: C, 77.20; H, 6.98.

Found: C, 76.82; H, 6.99.

The forerun of the distillation deposited solid upon cooling which, after recrystallization from hexane, was shown to be benzoic acid.

Preparation of 3-Cyclohexenyl Benzoate (XXXV). Method 2. Following the procedure of Miles and Surgenor,³⁴ tert-butyl perbenzoate was made by simultaneous addition of 14.05 g. (0.1000 mole) of benzoyl chloride and 7.20 g. (0.130 mole) of potassium hydroxide in 17 ml. of water to a rapidly stirred mixture of 12.8 ml. (0.110 mole) of tert-butyl hydroperoxide and 7.0 ml. of water at 8-12° over a period of 45 minutes. After the mixture had been stirred 11 hr., the upper layer was washed with 5% aqueous sodium bicarbonate and dried (MgSO_4). Distillation gave three fractions: (1) b.p. 88-89.5°/3 mm., (2) b.p. 89.5-91°/3 mm., and (3) b.p. 91-100°/3 mm. The third fraction was light yellow. The center cut, pure tert-butyl perbenzoate n_D^{34} 1.4982 (lit.,³⁴ n_D^{20} 1.5007, b.p. 75-77°/2 mm.), was used in the following synthesis.

A general procedure for preparation of XXXV has been given by Kharasch and Sosnovsky,^{30,11} although no physical properties for this ester were reported. To a solution of 0.82 g. (0.0040 mole) of tert-butyl perbenzoate in 0.53 g. (0.0060 mole) of cyclohexene (XXI) (dried over CaCl_2 , b.p. 82.5-83.5°/740 mm.) cooled by an ice bath was added 0.104 g. (0.000350 mole) of anhydrous, freshly prepared cuprous bromide. The ensuing exothermic reaction gave a dark blue-green mixture, which was heated under reflux for 30 minutes and then extracted with benzene. Evaporation of the benzene left a green oil, which was

chromatographed on a 25 x 2.5 cm. column of acid-washed alumina with benzene-ether mixtures as eluent. The product, obtained in 5% yield (40 mg.), had an IR spectrum identical to that of 3-cyclohexenyl benzoate (XXXV) obtained by method 1 (Plate III).

Preparation of 2-(3-Cyclohexenyl)cyclohexyl Benzoate (XXXVI).

Using the procedure of Pelton,³⁸ XLII was made by adding 40 ml. (0.50 mole) of cyclohexanone in small portions with hand stirring to a gel made from 50 ml. (0.50 mole) of cyclohexanol, 27 g. of sodium hydroxide, and 6.0 ml. of water. After being heated under vigorous reflux for 2.5 hr., the yellow semi-solid was stirred while being extracted with 200 ml. each of benzene and ether. Removal of solvent on a rotary evaporator and distillation of the residue gave, after a forerun of b.p. 42-110°/3 mm., a colorless liquid, b.p. 110-13/3 mm. (lit.,³⁸ 135-45/20 mm.) n_D^{36} 1.5010; yield 36.0 g. (40%). The product, 2-(3-cyclohexenyl)cyclohexanol (XLII), contained some cyclohexanone by GLC analysis.

To a stirred solution of 27.3 g. (0.135 mole) of XXXV, 20 ml. of pyridine, and 15 ml. of benzene was added dropwise 19 ml. (0.15 mole) of benzoyl chloride. After being stirred 1 hr., pyridine hydrochloride was removed by filtration and the filtrate was concentrated on a steam bath under reduced pressure. Distillation gave a slightly yellow product which solidified near room temperature, b.p. 168-70/2 mm., n_D^{25} 1.5375, yield 33.0 g. (86% based on XLII). Absorption maxima were observed at 1710 (C=O), 1650 (C=C), and 710 (C₆H₅) cm.⁻¹ for 2-(3-cyclohexenyl)cyclohexyl benzoate (XXXVI); see Plate IV.

Anal. Calcd. for C₁₉H₂₄O₂: C, 80.28; H, 8.45.

Found: C, 80.08; H, 8.38.

Preparation of 1-Phenylcyclohexene (L). Method 1. A 500-ml.

pre-marked Morton stirring flask flushed with N_2 was charged with 8.51 g. (0.350 g.-atom) of magnesium turnings. After the metal was covered with 30 ml. anhydrous ether, 4.0 ml. of bromobenzene (dried over Linde 4-A molecular sieve) was added, and the reaction was initiated by vigorous stirring (required 10 minutes). To the rapidly boiling mixture, 25 ml. ether was added. When the liquid became dark brown, the remainder of the bromobenzene in 100 ml. of ether was added dropwise during 35 minutes. Heating under reflux with rapid stirring was continued for 2 hr; yield of Grignard reagent, 95%, as determined by the standard titration technique.

A solution of 26.3 g. (0.267 mole) of cyclohexanone in 70 ml. ether was added to the phenylmagnesium bromide at such a rate as to maintain vigorous reflux (20 minutes). After being kept under nitrogen for 12 hr., the suspension was poured into 1 liter of ice-water mixture containing 100 ml. of 6N HCl which was extracted with 600 then 100 ml. of ether. The extracts were combined, washed with 250 ml. of 5% aqueous sodium chloride, and dried ($MgSO_4$). Concentration and, finally, air-drying gave 44.0 g. of crude 1-phenylcyclohexanol.

The 1-phenylcyclohexanol thus prepared was dehydrated by the method of Garbisch¹⁸ for tertiary benzylic alcohols. Powdered, crude alcohol (44 g., 0.25 mole) was shaken 5 minutes with a freshly prepared (warm) solution of 12 ml. concentrated sulfuric acid and 48 ml. of glacial acetic acid. The resulting orange emulsion was poured into a mixture of 200 ml. of ether and 300 ml. of water. The separated aqueous phase was extracted with 100 ml. of ether. To the ether solution was added 200 ml. of water followed by sufficient sodium carbonate

monohydrate to neutralize the acid (required 23.0 g.). The organic layer, after washing with 200 ml. of 5% aqueous NaCl, was dried (MgSO_4) and concentrated, first by a rotary evaporator, then under high vacuum (2 mm.). The yield of crude 1-phenylcyclohexene (L) was 34.8 g., 88% based on cyclohexanone.

By distillation of the crude alkene, three fractions, in addition to forerun, were obtained: (1) b.p. 59-63°/0.6-0.8 mm., n_D^{25} 1.5674, 8.1 g.; (2) b.p. 63.5-4.5°/0.7 mm., n_D^{24} 1.5684, 19.9 g.; and (3) b.p. 64.5-65°/0.7 mm., n_D^{24} 1.5664, 0.60 g. of 1-phenylcyclohexene (L) (lit.,⁹ b.p. 82°/1 mm., n_D^{25} 1.5660). The yield of fractions 1, 2, and 3 combined was 24.8 g., or 62% based on ketone. The IR spectrum of fraction three (Plate V) corresponded to the tabulated maxima³⁴ of L, with characteristic absorption³ occurring at 1310 ($\text{R}_1\text{R}_2\text{C}=\text{CHR}_3$), 1650 (C=C), 1600 (conjugated C=C), and 793 ($\text{R}_1\text{R}_2\overset{\text{H}}{\text{C}}=\text{CR}_3$) cm.^{-1} . The NMR spectrum (20% in CCl_4) exhibited multiplets at δ 1.6, δ 2.2, δ 5.95, and δ 7.1.

Preparation of 1-Phenylcyclohexene (L). Method 2. 1-Phenylcyclohexanol was recrystallized from hexane as large rhombic crystals, m.p. 56.5-57°. A second recrystallization (hexane) gave a colorless solid, m.p. 60° (lit.,²⁰ 62°). Alcohol of m.p. 60° (21.8 g., 0.120 mole) was heated in a sand bath with 30.0 g. (0.220 mole) of powdered, freshly fused potassium hydrogen sulfate at 110-140° for 1.5 hr. The dark product was ground with ether until the liquid was no longer colored. Distillation of the combined washings gave a colorless liquid, b.p. 67.5-72/0.3 mm.; yield of 1-phenylcyclohexene (L) was 16.3 g., 86% based on the alcohol. The chromatographically pure fraction used as an analytical standard had a b.p. 69-70/0.3 mm., n_D^{25} 1.5665. NMR and IR spectra were identical to those for the product of method 1. Use of

purified alcohol does not appear to be necessary for the preparation of L.

When 2-phenylcyclohexanol (LIII) (cis-trans-mixture) was subjected to the procedure of method 1, a complex mixture free of alcohol was obtained from which L could not be isolated easily. Likewise, complex mixtures were invariably realized when LIII was heated with 85% phosphoric acid. Extensive rearrangement with the trans isomer and phosphoric acid has been reported.¹²

Preparation of Bicyclohexyl (XXXVIII). Zinc dust (35.0 g., 0.540 g. atom) was quickly sifted into a solution of 3 g. of mercuric chloride in 200 ml. of water. After the mixture had been stirred vigorously for 30 minutes, the liquid was decanted. To the residue was added 40 ml. of water followed by 90 ml. of conc. hydrochloric acid. The ensuing exothermic reaction subsided within 1 minute. 2-Cyclohexylcyclohexanone (18 g., 0.10 mole) was introduced followed by 50 ml. of benzene. The mixture was heated under reflux for 9 hrs. During this time, three 20-ml. portions of conc. hydrochloric acid were added with the reaction flask being cooled prior to each addition. Heating was finally discontinued when only a few granules of amalgam remained and no gas was being evolved. The organic layer was washed with water and dried (CaCl_2). Distillation gave a colorless liquid, bicyclohexyl (XXXVIII) b.p. 81-81.5°/2.6 mm., n_D^{26} 1.4830 (lit.,³² b.p. 76-8/2 mm., n_D^{20} 1.4801), which by GLC analysis at 188°, contained a small amount of starting material (retention time 8 minutes) in addition to the single product (retention time 4.3 minutes). IR absorption corresponded to reported values.³²

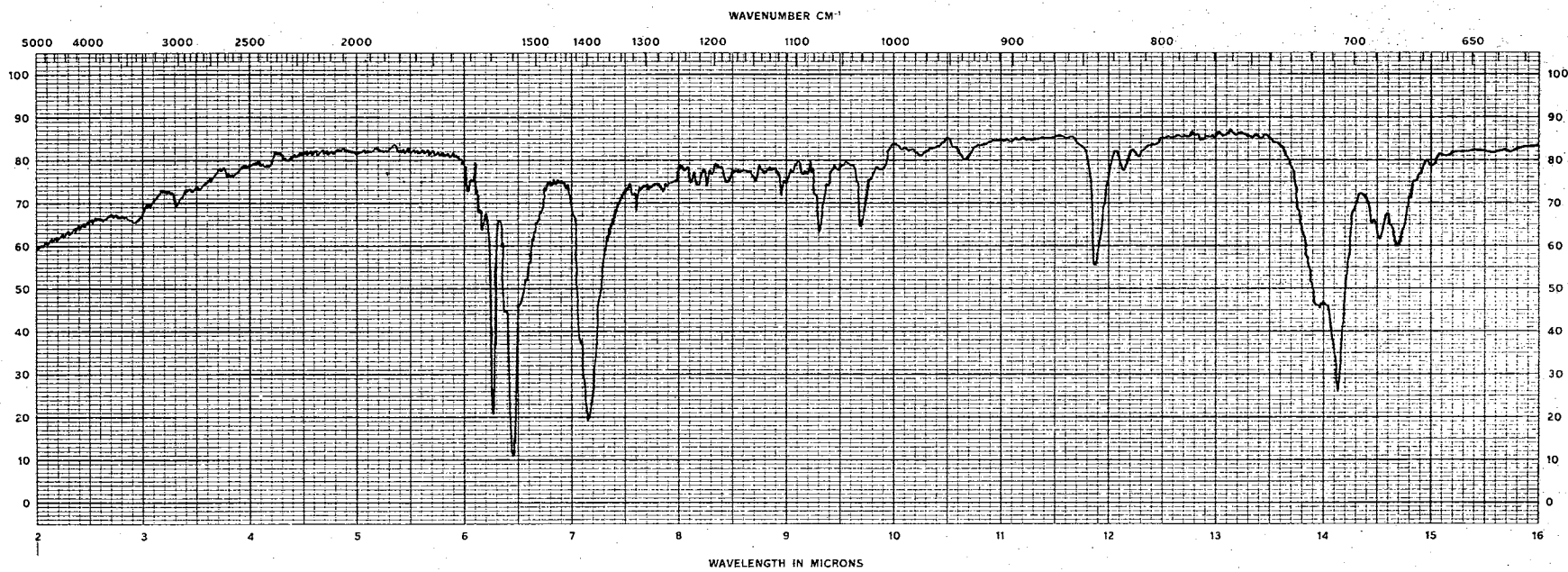
Preparation of 3-Cyclohexylcyclohexene (XLII). All liquid reagents were dried with Linde 4-A molecular sieve. Glassware was dried

at 110° and flushed with dry nitrogen while still warm.

A 200-ml. flask was charged with 2.0 g. (0.083 g.-atom) of magnesium turnings. The metal was covered with 10 ml. of ether; 1.0 ml. of chlorocyclohexane (LIV) was added followed by a crystal of iodine. The mixture was heated until the iodine color had disappeared (required 5 min.); heating was continued 5 min. longer. After 13 ml. of ether had been added, stirring was begun. The remainder of a total of 9.0 g. (0.075 mole) of chlorocyclohexane (LIV) in 23 ml. of ether was added dropwise over a period of 30 min. The resulting dark brown suspension was then heated under reflux for 20 min. and filtered through glass wool into a 250-ml. Morton flask. The light brown solution of cyclohexylmagnesium chloride (LV) was diluted with 80 ml. of ether and treated dropwise with a mixture prepared from 20 ml. of a solution of 3-bromocyclohexene (LII) in CCl_4 (density 1.237 g./ml.) and 30 ml. of ether. The solution of LII was added until no more white precipitate formed. An ice-bath maintained the reaction temperature at 10-15°. Over a period of 1 hr., 13 ml. of the solution containing LII was used. The white suspension was stirred 5 hr. at 25° and filtered by suction. The yellow filtrate was concentrated then distilled to give 3.0 g. (25%) of 3-cyclohexylcyclohexene (XLIII), a colorless, mobile liquid; b.p. 57-60°/0.4 mm., n_D^{28} 1.4930. Absorption (Plate VI) was observed at 3000 (HC=C), 1640 (C=C), and 723 cm.^{-1} (HC=C); these maxima are characteristic of cyclohexene derivatives.¹

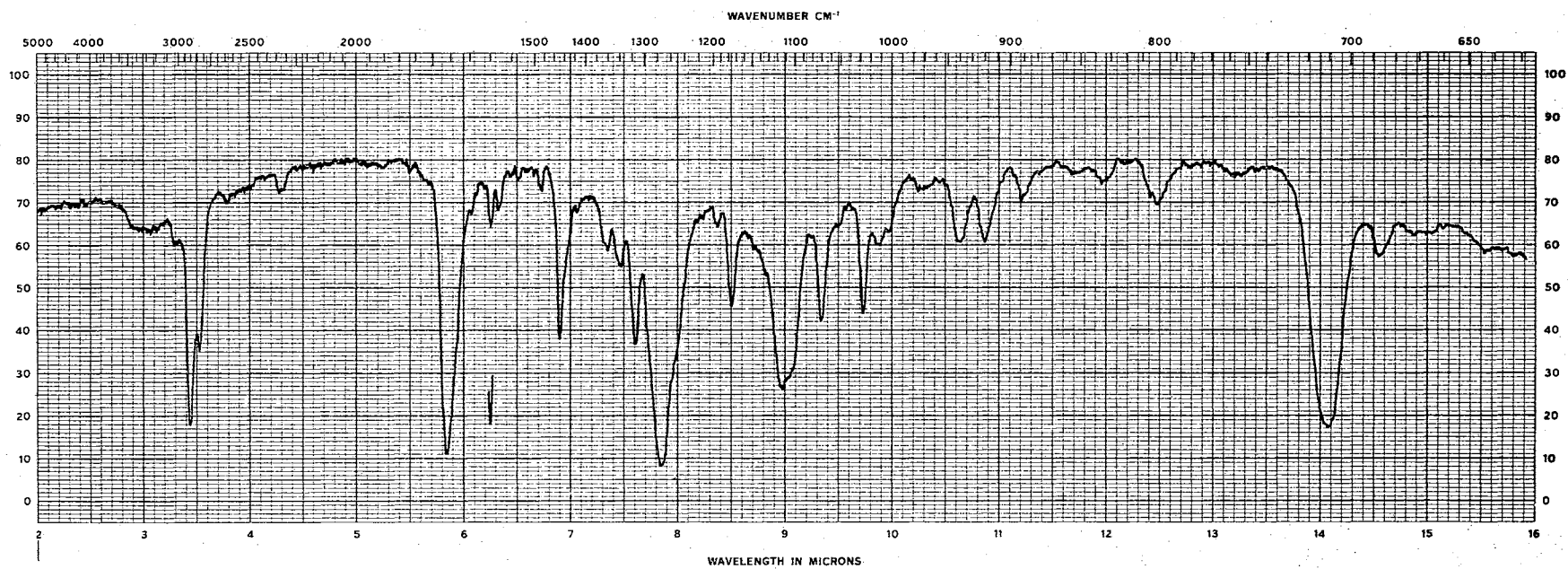
Hydrocarbon XLIII was shown by mixed injections to be absent from the photolyzate of silver benzoate (III) in cyclohexene (XXI).

Plate I



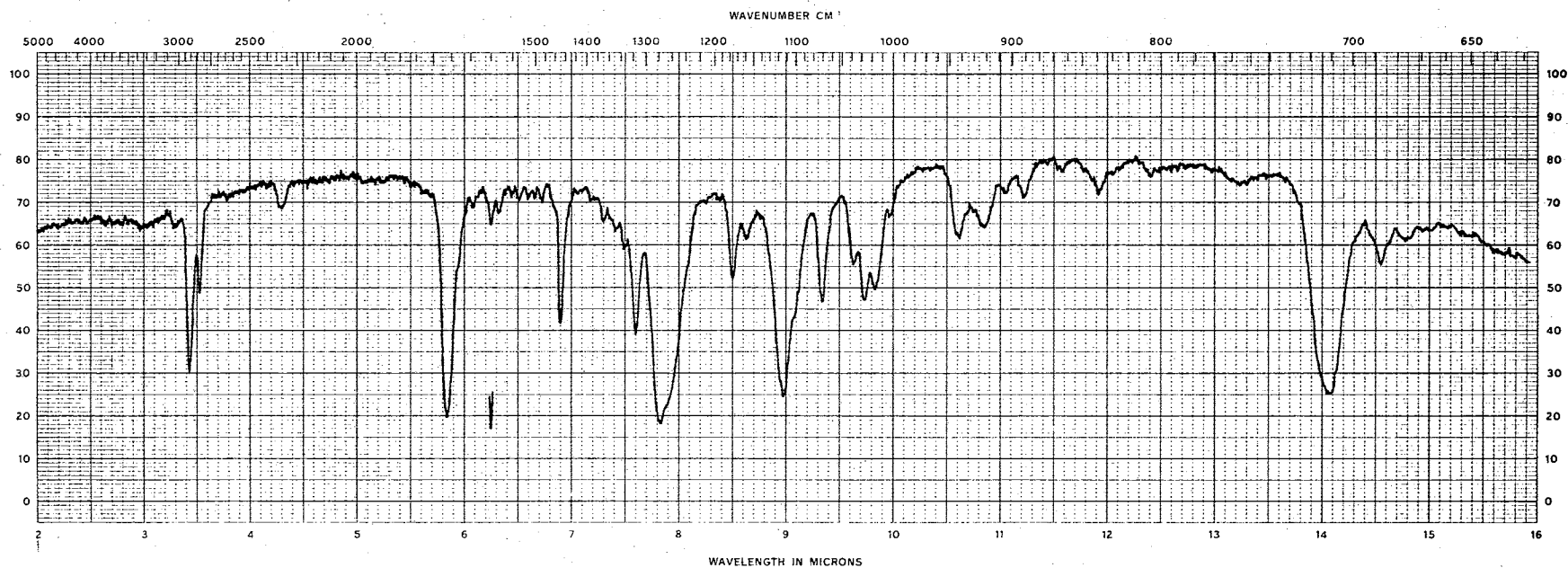
Silver Benzoate (III), KBr Pellet

Plate II



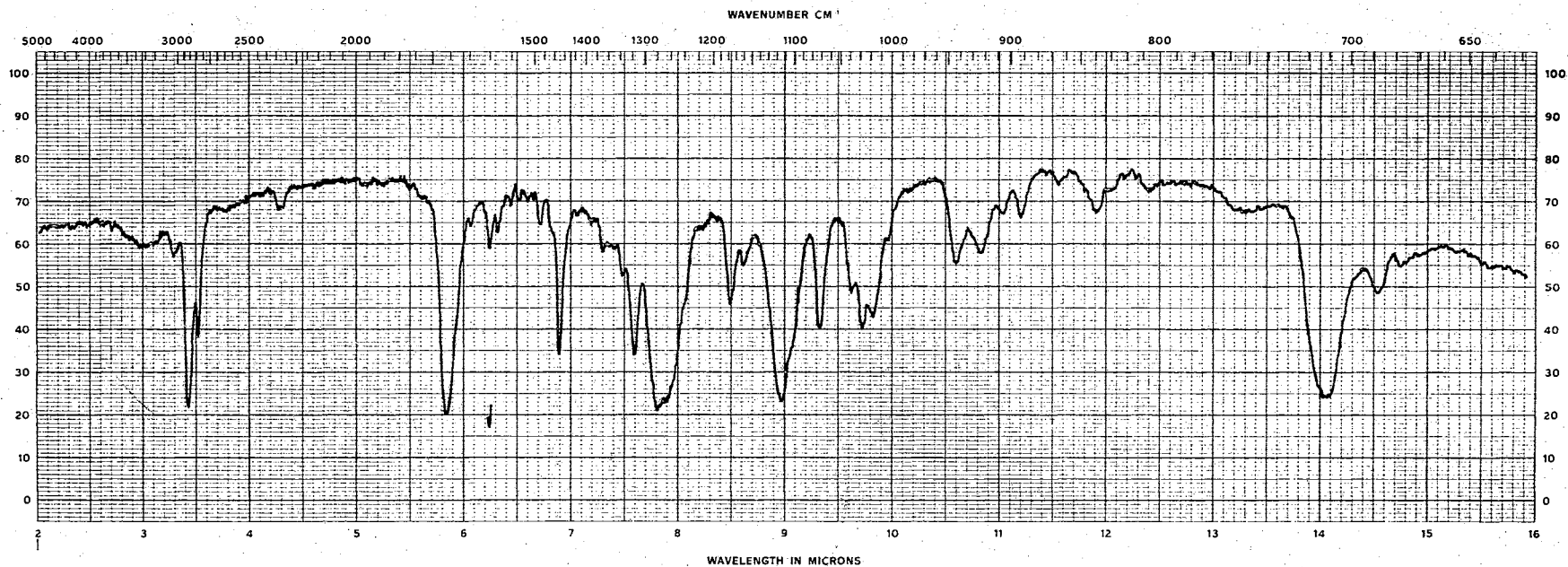
Cyclohexyl Benzoate (XXXIV), Film on NaCl Plates

Plate III



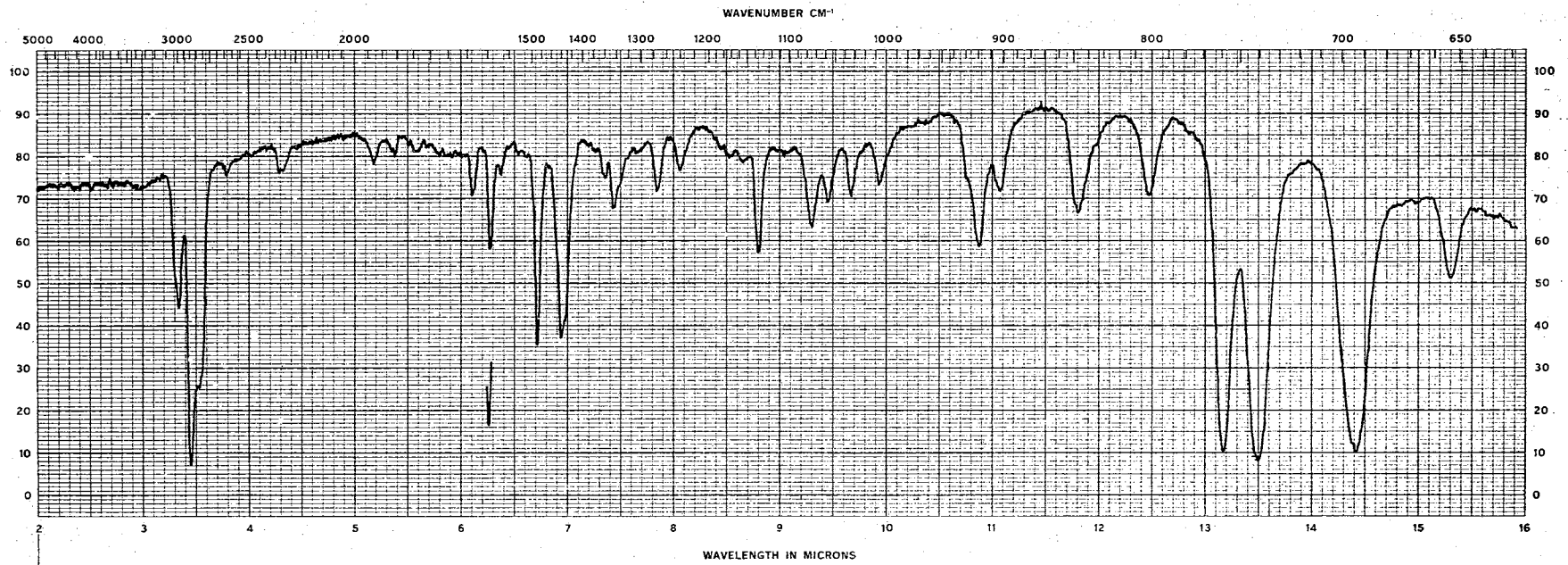
3-Cyclohexenyl Benzoate (XXXV), Film on NaCl Plates

Plate IV



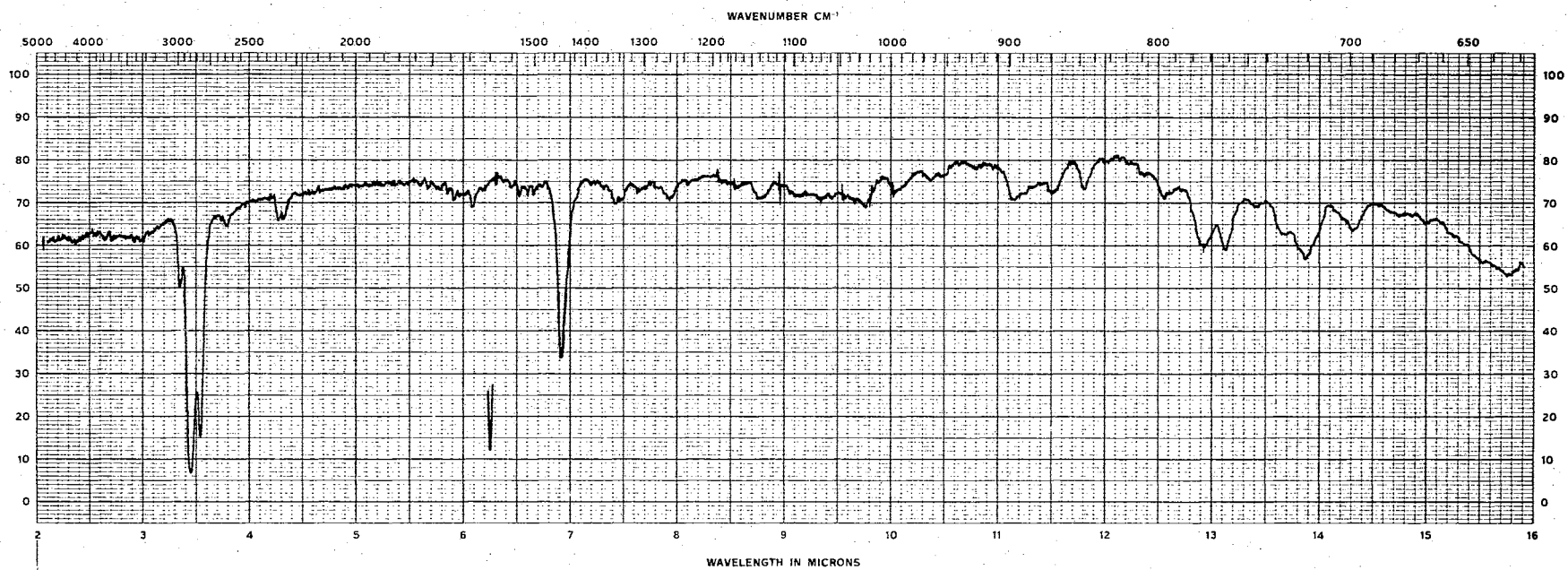
2(3-Cyclohexenyl)cyclohexyl Benzoate (XXXVI), Film on NaCl Plates

Plate V



l-Phenylcyclohexene (L), Film on NaCl Plates

Plate VI



3-Cyclohexylcyclohexene (XLIII), Film on NaCl Plates

Plate VII



Photolyzate of Silver Benzoate (III) in Cyclohexene (XXI).
10% Silicone Rubber, 188°. 1 cm. = 1 min.

- A Benzoic Acid (VIII)
- B 1-Phenylcyclohexene (L)
- C 3-Cyclohexenyl Benzoate (XXXV)

BIBLIOGRAPHY

1. Aude, G., and de Gaudemaris, G., *Compt. rend.*, 254, 113 (1962).
2. Bartlett, P. D., and Cohen, S. G., *J. Am. Chem. Soc.*, 65, 543 (1943).
3. Bellamy, L. J., "The Infra-red Spectra of Complex Molecules," J. Wiley and Sons, New York, N. Y., 1956.
4. Benton, A., and Cunningham, G., *J. Am. Chem. Soc.*, 57, 2227 (1935).
5. Berlin, K. D., and Gibbs, D. E., Unpublished results.
6. Berlin, K. D., and Gibbs, D. E., *Proc. Okla. Acad. Sci.*, 44, 89 (1964).
7. Berlin, K. D., Hopper, D., and Gibbs, D. E., *Proc. Okla. Acad. Sci.*, 45, 108 (1965).
8. Boldyrev, V. V., Eroshkin, V. I., Ryzhak, I. A., and Kefeli, L. M., *Dokl. Akad. Nauk SSSR*, 173, 117 (1967); *Chem. Abstr.*, 67, 59568 (1967).
9. Carlin, R. C., and Landerl, H. P., *J. Am. Chem. Soc.*, 75, 3969 (1953).
10. Chenevix, *Gilbert's Ann.*, 32, 179 (1809).
11. Denney, D. B., Denney, D. G., and Feig, G., *Tetrahedron Lett.* 19 (1959).
12. Eliel, E. L., McCoy, J. W., and Price, C. C., *J. Org. Chem.*, 22, 1533 (1959).
13. Erlenmeyer, H., and Schoenaur, W., *Helv. Chim. Acta*, 19, 338 (1936).
14. Everard, A. F., and Swan, G. A., *J. Chem. Soc.*, 914 (1962).
15. Farmer, E. H., and Michael, S. E., *J. Chem. Soc.*, 513 (1942).
16. Farmer, E. H., and Shipley, F. W., *J. Chem. Soc.*, 1519 (1947).
17. Finch, A., Jacobs, P. W. M., and Tompkins, F. C., *J. Chem. Soc.*, 2053 (1954).

18. Garbisch, E. W., *J. Org. Chem.*, 26, 4165 (1961).
19. General Aniline & Film Corp., *Brit.* 858,037 (Jan. 4, 1961); *Chem. Abstr.*, 55, 16015 (1961).
20. Govindachari, T. R., Nagarajan, K., Pai, B. R., and Arumugam, N., *J. Chem. Soc.*, 4280 (1956).
21. Hammond, G. S., and Soffer, L. M., *J. Am. Chem. Soc.*, 72, 4711 (1950).
22. Henbest, H. B., Meakins, G. D., Nicholls, B., and Wilson, R. A. L., *J. Chem. Soc.*, 997 (1957).
23. Hermans, P. H., and Van Eyk, J., *J. Polymer Sci.*, 1, 407 (1946).
24. Ioan, V., Badea, F., Cioranescu, E., and Nenitzescu, C. D., *Angew. Chem.*, 72, 416 (1960).
25. Iwig, F., and Hecht, O., *Ber.*, 19, 238 (1886).
26. Kamevskaya, S. Y., and Shemyakin, M. M., *Ber.*, 69, 2152 (1936).
27. Kamevskaya, S. Y., Shemyakin, M. M., and Bamdas-Shemyakima, E. M., *Ber.*, 69, 257 (1936).
28. Kawasaki, M., *Nippon Shashin Gakkai Kaishi*, 23, 161 (1960); *Chem. Abstr.*, 56, 1089 (1962).
29. Kawasaki, M., *Nippon Shashin Gakkai Kaishi*, 25, 82 (1962); *Chem. Abstr.*, 58, 6369 (1963).
30. Kharasch, M. S., and Sosnovsky, G., *J. Am. Chem. Soc.*, 80, 756 (1958).
31. Kirshenbaum, A. D., Streng, A. G., and Hauptschein, M., *J. Am. Chem. Soc.*, 75, 3141 (1953).
32. Laber, G., *Ann.*, 588, 79 (1954).
33. Mangelberg, M., *Ber.*, 87, 1425 (1954).
34. Miles, N. A., and Surgenor, D. M., *J. Am. Chem. Soc.*, 68, 642 (1946).
35. Mixer, R. Y., and Young, W. G., *J. Am. Chem. Soc.*, 78, 3379 (1956).
36. Murakami, M., and Fukoumoto, T., *Mem. Inst. Sci. Ind. Research Osaka Univ.*, 10, 186 (1953); *Chem. Abstr.* 49, 6864 (1955).
37. Noma, K., and Tsuchida, T., *Chem. High Polymers (Japan)*, 5, 166 (1948); *Chem. Abstr.*, 46, 4492 (1952).

38. Pelton, E. L., U. S. 2,576,078, (Nov. 20, 1951); Chem. Abstr., 46, 50826 (1952).
39. Perret, A., and Perrot, A., Helv. Chim. Acta., 28, 558 (1945).
40. Potapovich, A. K., Sviridov, V. V., Branitskii, G., and Makatum, V. N., Teor. Eksp. Khim., 3, 375 (1967); Chem. Abstr., 67, 103893 (1967).
41. Schaum, K., and Scheld, O., Z. wiss. Phot., 36, 121 (1937); Chem. Abstr., 32, 2801 (1938).
42. Shemyakin, M. M., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1515 (1961); Chem. Abstr. 56, 1323 (1962).
43. Silveira Ramos, A. de, Anais assoc. quim Brazil, 1, 55 (1942); Chem. Abstr., 37, 868 (1943).
44. Simmons, H., J. Org. Chem., 25, 691 (1960).
45. Unger, G., Radiologica, 2, 49 (1938); Chem. Abstr., 35, 6197 (1941).
46. Yakerson, V. I., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1003 (1963); Chem. Abstr., 59, 12395 (1963).
47. Ziegler, K., Spath., Schaaf, E., Schumann, W., and Winklemann, E., Ann., 80, 550 (1942).

PART II

STEREOCHEMISTRY OF THE ADDITION OF HYDROGEN
BROMIDE AND HYDROGEN CHLORIDE TO
4-TERT-BUTYL-1-PHENYLCYCLOHEXENE

TABLE OF CONTENTS

Chapter	Page
I. HISTORICAL	39
II. DISCUSSION OF RESULTS AND CONCLUSIONS	48
III. EXPERIMENTAL	78
Preparation of 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII)	78
Preparation of <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Bromides: (XXXIX and XL)	81
Preparation of <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chlorides: (XLI and XLII)	83
Addition of Hydrogen Bromide to 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII)	86
Addition of Hydrogen Chloride to 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII)	88
Reaction of Hydrogen Bromide with <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanols: (XLIII and XLIV)	89
Reaction of Hydrogen Chloride with <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanols: (XLIII and XLIV)	89
Preparation of <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanes: (LXXX and LXXXI)	91
Preparation of 1-Chloro-1-phenylcyclohexane (XLV)	92
IV. BIBLIOGRAPHY	121

LIST OF ILLUSTRATIONS

Plate	Page
Raman Spectra	
I. <u>cis</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chloride (XLI), Solution in <u>n</u> -Heptane	94
II. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chloride (XLII), Solution in <u>n</u> -Heptane	95
III. 1-Chloro-1-Phenylcyclohexane (XLV), Neat	96
IV. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexane (LXXXI), Solution in <u>n</u> -Heptane	97
Infrared Spectra	
V. 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII), Film on NaCl Plates	98
VI. <u>cis</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Bromide (XXXIX), KBr Pellet	99
VII. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Bromide (XL), KBr Pellet	100
VIII. <u>cis</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chloride (XLI), Nujol Mull on NaCl Plates	101
IX. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chloride (XLII), KBr Pellet	102
X. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanol (XLIV), KBr Pellet	103
XI. 1-Chloro-1-phenylcyclohexane (XLV), Film on NaCl Plates	104
XII. 1-Phenylcyclohexanol (LIX), KBr Pellet	105
XIII. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexane (LXXXI), KBr Pellet	106

Plate	Page
Nuclear Magnetic Resonance Spectra	
XIV. 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII)	107
XV. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Bromide (XL)	108
XVI. <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Bromides: (XXXIX and XL)	109
XVII. <u>cis</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chloride (XLI)	110
XVIII. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chloride (XLII)	111
XIX. <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chlorides: (XLI and XLII)	112
XX. <u>cis</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanol (XLIII)	113
XXI. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanol (XLIV)	114
XXII. <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanols: (XLIII and XLIV)	115
XXIII. 1-Chloro-1-phenylcyclohexane (XLV)	116
XXIV. 1-Phenylcyclohexanol (LIX)	117
XXV. 1-Phenylcyclohexene (LX)	118
XXVI. <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexane (LXXXI)	119
XXVII. <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexanes: (LXXX and LXXXI)	120

LIST OF TABLES

Table		Page
I.	Raman Spectra of Substituted Cyclohexanes in the 600-800 cm^{-1} Region	74
II.	<u>tert</u> -Butyl Proton NMR Data for Substituted Cyclohexanes	75
III.	Addition of Hydrogen Bromide to 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII) in <u>n</u> -Pentane	76
IV.	Addition of Hydrogen Chloride to 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII) in <u>n</u> -Pentane	77
V.	Fractional Recrystallization of <u>cis</u> - and <u>trans</u> -4- <u>tert</u> -Butyl-1-phenylcyclohexyl Chlorides: (XLI and XLII)	84

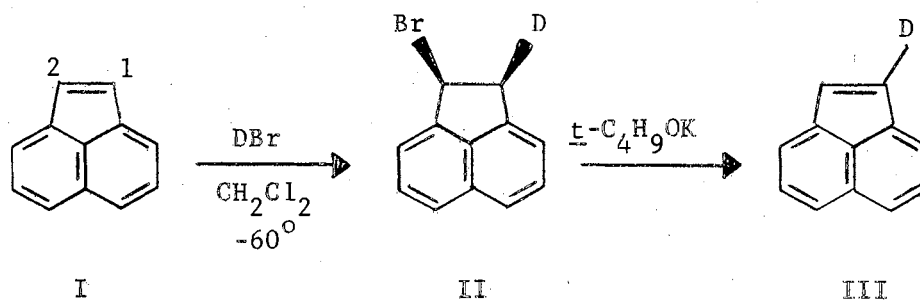
LIST OF FIGURES

Figure		Page
1.	<u>cis</u> Addition of Hydrogen Halide to 4- <u>tert</u> -Butyl-1-phenylcyclohexene (XXXVIII)	60
2.	<u>cis</u> Addition of Hydrogen Halide to 1,2-Dimethylcyclopentene (XVIII)	61
3.	Reaction of Alcohols with Hydrogen Halide	72

CHAPTER I

HISTORICAL

Dewar and co-workers have proposed that cis addition is the normal mode of electrophilic reaction of alkenes with hydrogen halides.⁹ Addition of deuterium bromide to acenaphthalene (I) gave the cis adduct II, assuming that dehydrohalogenation of the adduct was a trans elimination.⁹ Excellent agreement was achieved between two different



methods of product analysis. One method was determination of deuterium orientation in the adducts using the coupling constants of vicinal protons, which will be discussed in detail later. The other method consisted of measuring the deuterium content of the elimination products from treatment of the adduct mixtures with base.

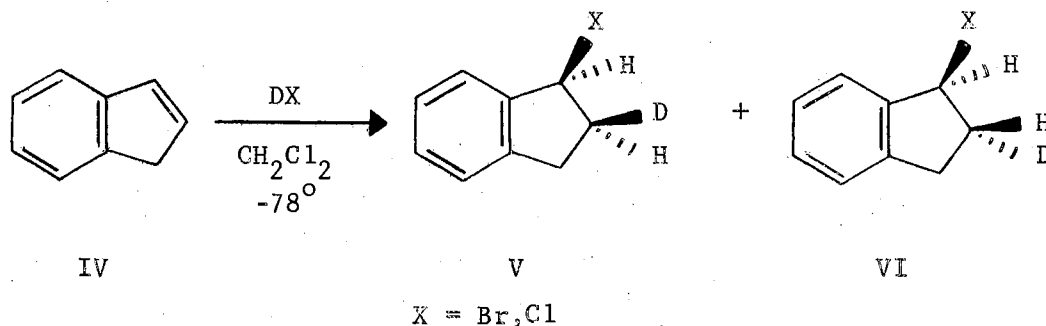
Mass spectral and NMR detection of 1-deuterioacenaphthalene (III) indicated that the cis adduct II comprised 74-90% of the product, the remainder being trans adduct.¹⁰ The latter compound was shown by controls to be a primary product of polar addition rather than a product

of isomerization or radical addition.

The stereochemistry of addition of deuterium bromide to I was independent of temperature (-78 to 25°) and DBr concentration (0.2 to 2M).¹⁰ At high DBr concentration (11M) equal amounts of cis and trans adducts resulted. Increasing solvent polarity also increased the yield of trans adduct.

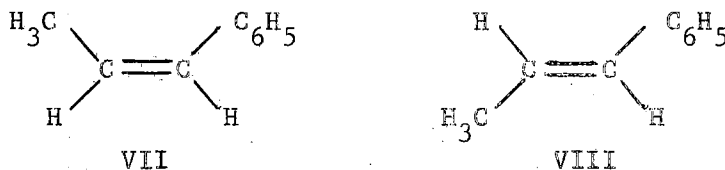
Addition of deuterium chloride to I was slower than addition of DBr. Significant isomerization of the chlorides was observed.

Addition of deuterium bromide and chloride to indene (IV) gave 80% of the cis adduct (V) and 20% of trans adduct (VI).¹¹ Ratios of



V and VI were obtained from NMR peak heights. The magnitude of vicinal coupling constants depends on the dihedral angle involved.¹ With the aid of molecular models, the $J_{1,2}$ value for V was predicted to be 7 c.p.s., and for VI, 2 c.p.s. Observed values were 6.8 and 2.7 c.p.s., respectively. Attempted elimination of V and VI gave very little indene (IV).

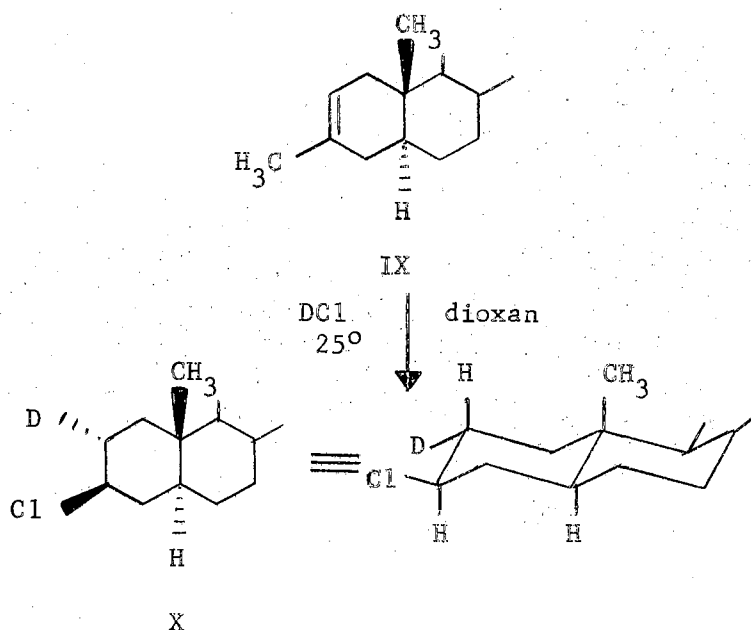
Predominance of cis addition of DBr to cis- and trans-1-phenylpropene (VII and VIII) has also been observed.¹²



The reactions presented thus far progressively provided conditions favorable to participation of π complexes. An extreme is found in acenaphthalene (I) for which steric effects would not favor one mode of attack over another. Furthermore, a classical ion would be resonance stabilized while a π complex would be destabilized by the strain of the five-membered ring in I. The preponderance of cis addition in all of the preceding examples led Dewar to reject the intermediacy of π complexes in favor of classical ions or ion pairs.¹¹ Where steric hindrance prevented immediate collapse of the ion pair, rearrangement could occur to give trans adducts.

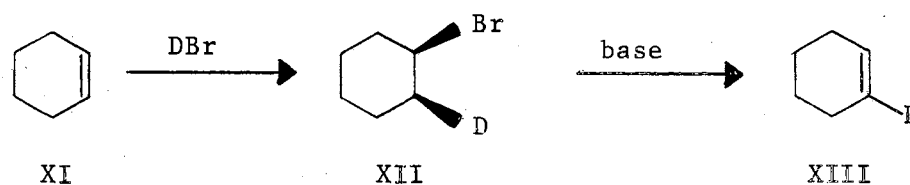
The reply has been well made that electrophilic additions have never been completely described in terms of π complexes.³⁰ By only slight changes in geometry, initial π complexes could form cis adducts provided the halide ion were still associated with the proton in an ion pair.

A proton bridge (π complex) has been proposed to explain the trans addition of DCl to 3-methylcholest-2-ene (IX).³ Configurational



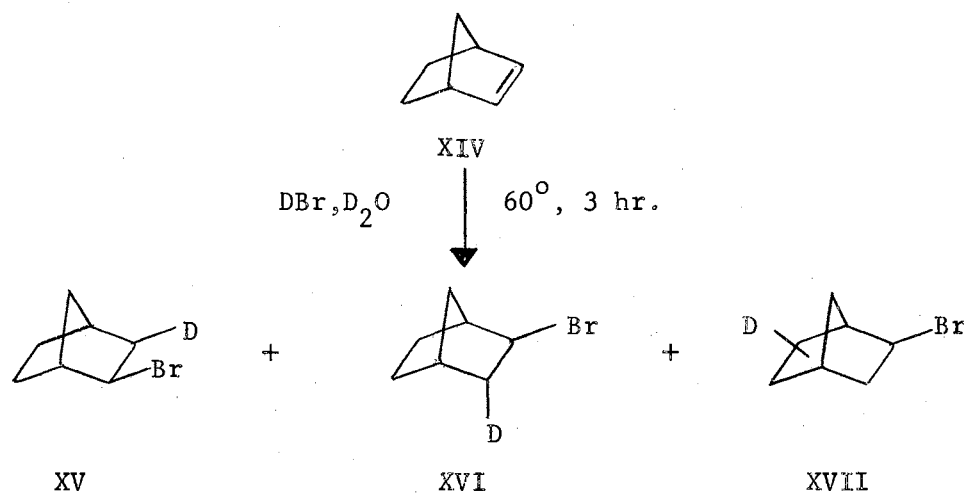
assignments for X were based on well-founded IR (absorption associated with C-Cl stretch at 782 cm^{-1}) and elimination data.

Addition of DBr to cyclohexene (XI) has been studied.³⁷ The yield of cis-2-d-bromocyclohexane (XII) increased from 26% at 10° to 74% at 60° . This trend, which is opposite the temperature effect found by Dewar and coworkers,¹⁰ should be investigated further. No consideration



seems to have been given to the possibility of isomerization or to the effect of temperature on ionization of DBr.

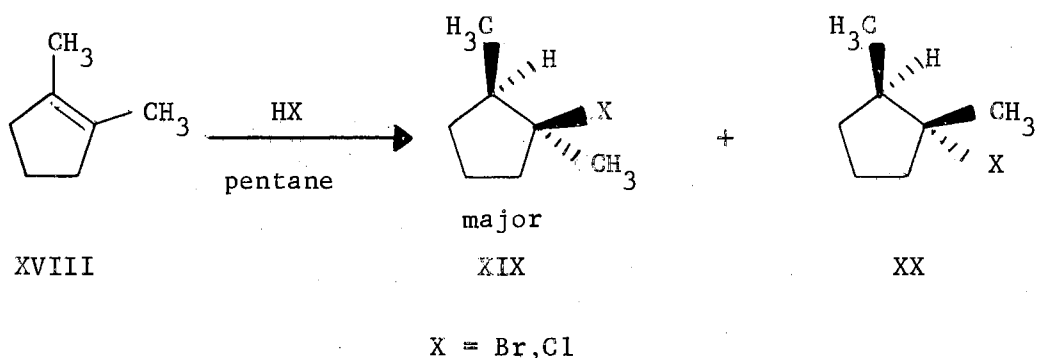
For the polar reaction of DBr with norbornene (XIV) cis addition has been reported.²⁷ As shown by deuterium distribution in degradation



products (cis elimination), 46% of the original reaction mixture was the cis-exo product XV.

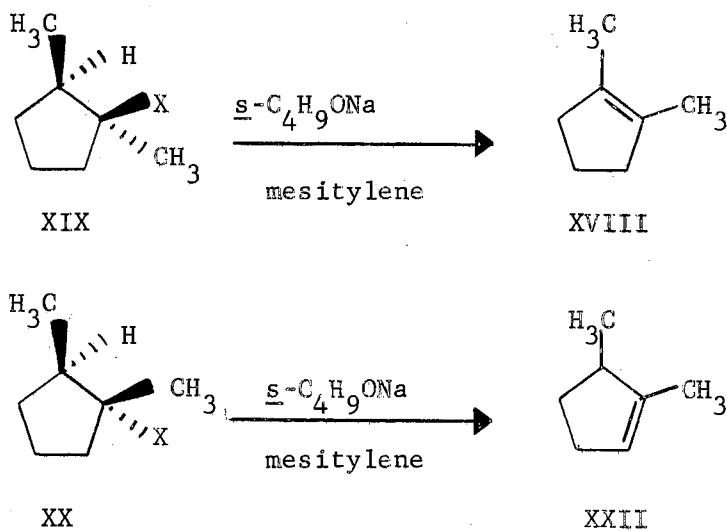
The reaction of hydrogen halide with 1,2-dimethylcyclopentene (XVIII) at 0° and -78° can be explained most readily in terms of trans

addition.¹⁹ For addition of HBr, the product of both kinetic and



thermodynamic control was the trans adduct XIX (X=Br). However, the cis adduct XX (X=Cl) from HCl appeared more stable than the trans adduct XIX (X=Cl).

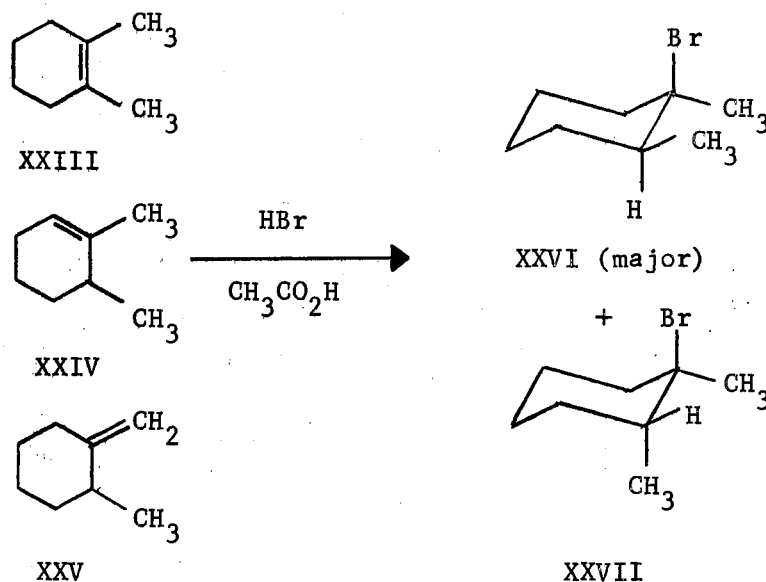
The addition products XIX and XX were not isolated; their relative amounts were deduced from the assumption that each halide would give primarily a different alkene upon base-catalyzed elimination. It was



assumed that E1 elimination was insignificant, although no information was available on this point.

A high degree of trans addition of HBr to 1,2-dimethylcyclohexene (XXIII), 2,3-dimethylcyclohexene (XXIV), and 2-methylmethylenecyclohexane

(XXV) has been reported.²⁰ It was claimed that bromide XXVI was



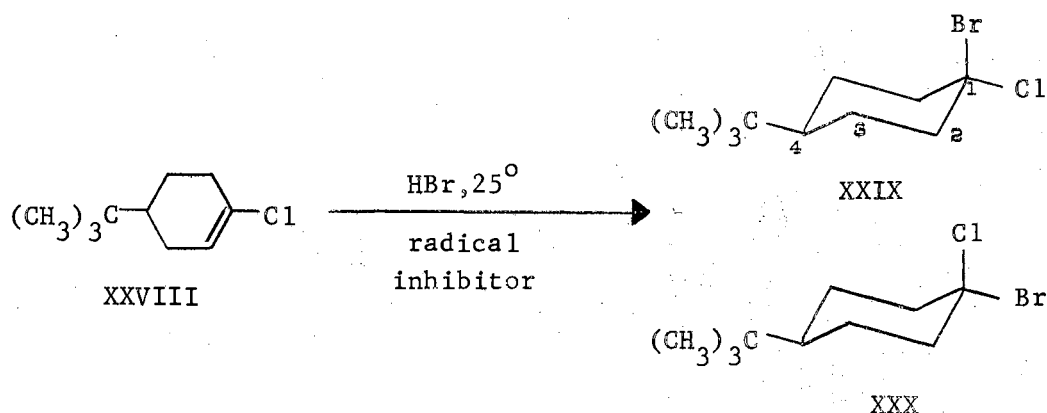
isolated free from the isomeric XXVII, but the only justification seems to be the uniform rate of solvolysis of the isolated material. Unfortunately, NMR analysis of the products has not been reported. Reaction mixtures were analyzed by a kinetic method involving elimination catalyzed by 0.3N NaOH in 98% ethanol.³² After the time interval calculated as necessary for reaction of 99% of the trans bromide XXVI, the rate of elimination was followed by titration. The second-order plot for this phase was extrapolated to zero time to give to initial concentration of cis bromide XXVII.

No investigation was made of the importance of radical addition of HBr to any of the alkenes XXIII, XXIV, or XXV. The rate of addition at -78° was so rapid that it was assumed that the polar addition was the exclusive reaction.

A significant feature was the finding that alkenes XXIII, XXIV, and XXV did not give the same ratios of bromides XVI and XVII under

comparable conditions. These variations, considerably beyond the range of experimental error, require that the additions proceed in some way other than through a common carbonium ion of classical planar configuration.

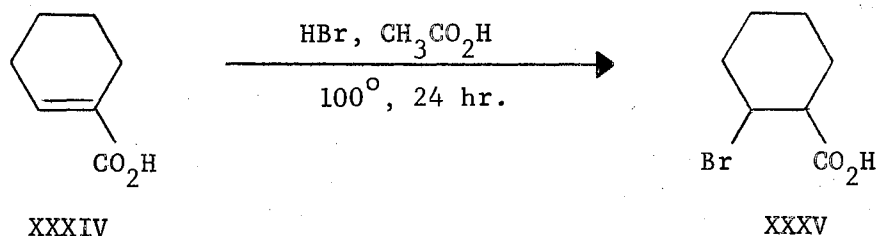
Tentative structural evidence has been presented for the products from ionic addition of HBr to 4-tert-butyl-1-chlorocyclohexene (XXVIII).³³ At low HBr concentration the radical process competed with



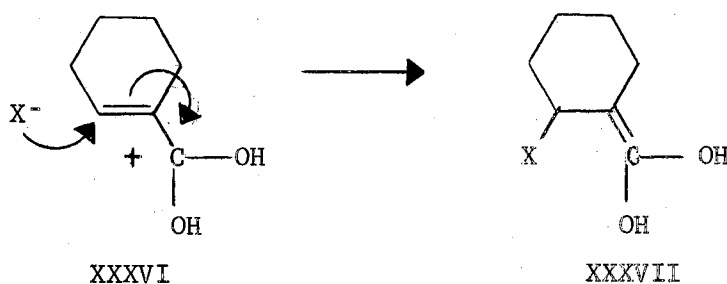
ionic addition. Radical addition appeared insignificant in the presence of ferric chloride or a radical inhibitor [4,4'-bis(2,5-di-tert-butylphenol) (XXXI)]. With either of these compounds present, the only products detected by IR and NMR were those of ionic addition, the C-1 geminal dihalides XXIX and XXX. In the presence of inhibitor XXXI, reaction in a sealed tube without solvent (25° , 8.5 hr.) gave cis-1-bromo-4-tert-butyl-1-chlorocyclohexane (XXIX) and trans-1-bromo-4-tert-butyl-1-chlorocyclohexane (XXX) in a ratio of 9:1 (estimated by IR). When the radical inhibitor XXXI was replaced with ferric chloride (25° , 4 hr.), the ratio of XXIX to XXX was 7:3. Neither of the addition products was isolated. However, product XXIX could be removed with ethanolic NaOH. The second-order rate constant for this dehydrohalogenation was in good agreement with rates for model compounds,

1,1-dibromocyclohexane (XXXII) and 1-bromo-1-chlorocyclohexane (XXXIII).

Addition of HBr to α,β -unsaturated acids was found to occur in a trans fashion, as shown in the example of cyclohexencarboxylic acid (XXXIV).³⁸ It has been argued that protonation of XXXIV would give



carbonium ion XXXVI.¹² The rate-determining step would be attack on



XXXVI by halide ion to form enol XXXVII. Thus, the reaction would be a nucleophilic addition not directly related to the electrophilic addition of hydrogen halide to other alkenes.

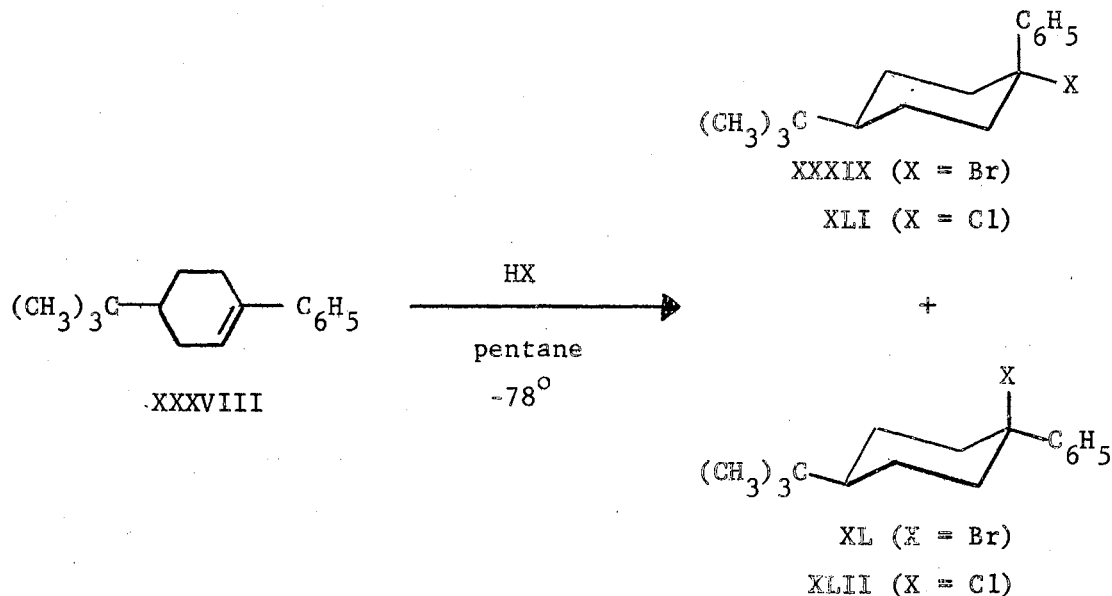
In reply to the preceding view, it has been maintained that an enol could not be involved.³⁸ The addition product XXV was isomerized to the more stable trans isomer with HBr in acetic acid (100°, 24 hr.); much less of the trans isomer resulted with potassium bromide in acetic acid. Consequently, enol formation was thereby implicated in the rearrangement but was rendered unlikely for the addition reaction. These results are open to question since reaction mixture compositions were

determined only by phase diagrams. More evidence is needed before the results with these unsaturated acids can be related with electrophilic additions to alkenes in general.

CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

Addition of hydrogen bromide to 4-tert-butyl-1-phenylcyclohexene (XXXVIII), under the appropriate conditions, gives cis-4-tert-butyl-1-phenylcyclohexyl bromide (XXXIX) and trans-4-tert-butyl-1-phenylcyclohexyl bromide (XL). Likewise, hydrogen chloride gives the corresponding chlorides XLI and XLII. The cis chloride is the product of kinetic



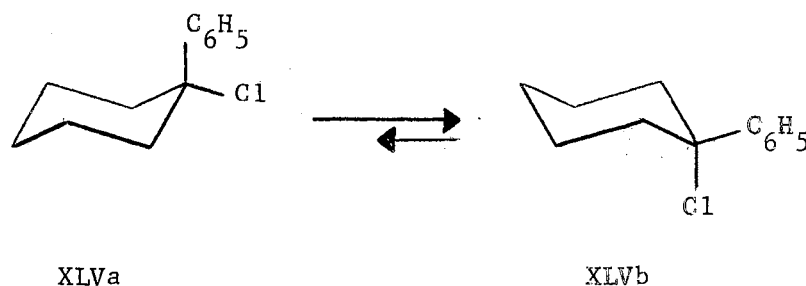
control, and the trans chloride, the product of thermodynamic control.

All four of the halides were isolated. Structures were elucidated, in part, by Raman and NMR spectroscopy. The trans chloride XLII was also obtained by a stereospecific synthesis.

Raman spectra clearly distinguish the cis and trans chlorides

hence the frequency of this motion is higher.

For the compound 1-chloro-1-phenylcyclohexane (XLV), maxima for both chlorine orientations should be observed. This is the case as Table I shows. Further confirmation of these assignments comes from the relative intensities of these bands for XLV (see Plate III). That conformation XLVb will predominate is most probable from the large



difference in the conformational free energies of the two groups in the monosubstituted compounds: $\Delta G_{Cl}^{\circ} = 0.4$ kcal./mole, $\Delta G_{C_6H_5}^{\circ} = 3.0$ kcal./mole.¹³

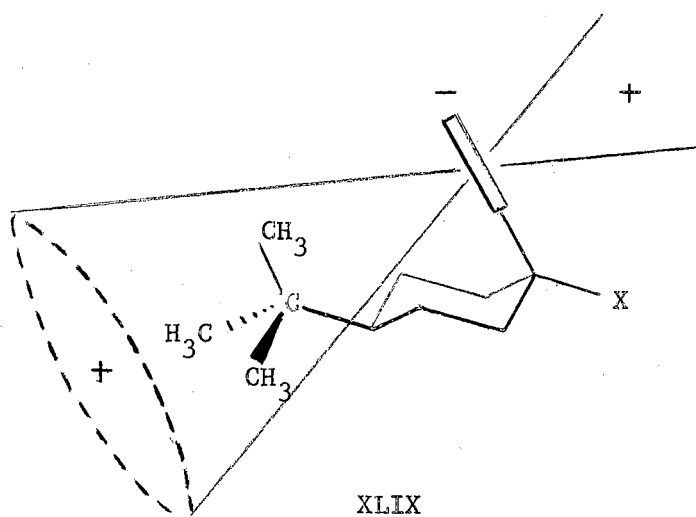
A rough approximation of the expected frequencies for chlorides XLI and XLII may be made on the basis of simpler molecules. The influence of the phenyl group on the C-Cl frequency in the Raman spectra may be estimated from the C-Cl frequency of 712 cm^{-1} for chloromethane (XLVI) and 679 cm^{-1} for α -chlorotoluene (XLVII).³⁶ The phenyl group is seen to cause a hypsochromic shift of 33 cm^{-1} . For chlorocyclohexane (XLVIII) the axial and equatorial maxima have been identified as 684.5 and 731 cm^{-1} , respectively.²⁶ Phenyl substitution, then, might be expected to shift the frequencies associated with the C-Cl stretch to 652 and 698 cm^{-1} for the cis isomer XLI and the trans isomer XLII, respectively. This prediction is in fair agreement with the observed values of 647 and 689 cm^{-1} .

IR absorption occurs at 685 cm^{-1} for the cis chloride XLI (equatorial Cl) and at 643 cm^{-1} for the trans chloride XLII (axial Cl). While these maxima are near those observed in the Raman spectra, it cannot be stated with any certainty that the IR absorption arises solely from C-Cl stretching. One reason is that the bromides XXXIX and XL absorb at 678 and 638 cm^{-1} , respectively. It is unlikely that the C-Br and C-Cl stretching frequencies should be so similar. Furthermore, the band at 638 cm^{-1} is Raman active, but the intensity is much less than would be expected if this absorption arose purely from a C-Br stretch. The Raman spectrum of bromide XXXIX was not determined. Presently, it can only be concluded that the IR frequencies discussed can distinguish these isomeric halides, but their origin cannot be specified.

Proton NMR spectra also clearly distinguish chlorides XLI and XLII. Evidence is provided by the field positions for both the tert-butyl protons and the equatorial protons on C-2 and C-6. When the phenyl substituent is axial, the 4-tert-butyl protons resonate at a higher field than when the phenyl group is equatorial. These frequencies are compared in Table II.

Regions of magnetic shielding exist above and below the plane of aromatic rings.²³ The tert-butyl protons apparently may fall within this region when the phenyl group is axial; thus, the protons of the tert-butyl group of XLI may thereby be shielded more than in XLII as a result of the magnetic anisotropy of the aromatic ring. This situation is depicted by structure XLIX. The tert-butyl protons thus shielded resonate at a higher field than they would otherwise.

From Table II it is seen that the magnitude of the shielding effect



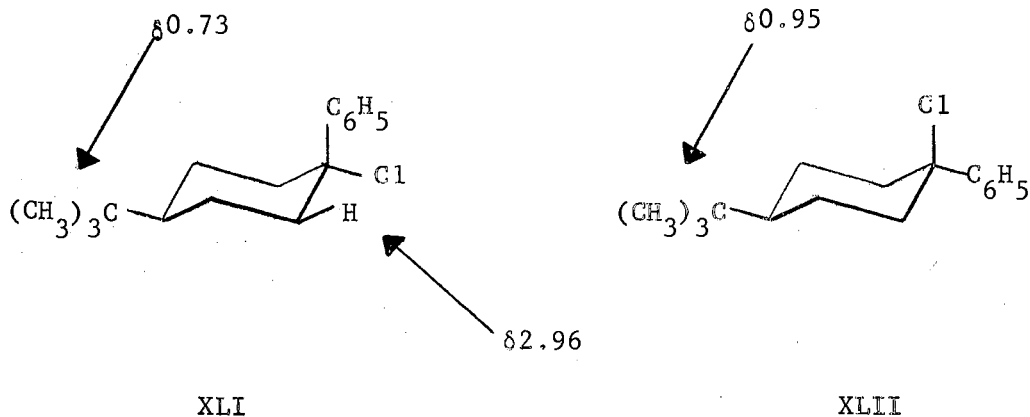
appears to be related to the size of the X substituent in structure XLIX. The order of increasing covalent atomic radii, parallels the

	H	<	O	<	Cl	<	Br
covalent radius, Å ¹⁸	0.28		0.74		0.99		1.14
$-\Delta G_X^\circ$ kcal./mole ¹³		(OH)	1.0		0.4		0.5

postulated shielding effect. The observed trend does not correspond to that of the conformational free energies ΔG_X° . Indeed, it is not reasonable that such a correlation should exist. The steric interaction of the phenyl group with X is probably so severe that factors other than atomic size which influence ΔG_X° may be much less significant.⁵

Another distinguishing feature in the NMR spectra of chlorides XLI and XLII is a doublet centered at $\delta 2.96$ in the spectrum of the cis isomer XLI. Apparently, a comparable distinction exists between the spectra of alcohols XLIII and XLIV. Since the latter compounds have been studied in detail along with their 2,2,6,6-tetradeuterio derivatives, they will be considered first.¹⁶

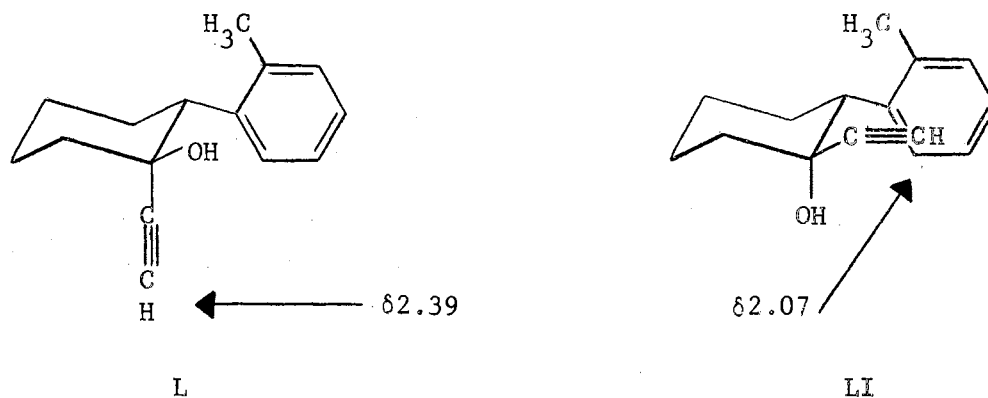
The NMR spectrum of the cis alcohol XLIII exhibits a doublet centered at $\delta 2.52$. The spectrum of the 2,2,6,6-tetradeuterio derivative of XLIII shows this doublet to be the low field half of an AB spectrum and that it arises from the protons on C-2 and C-6, in particular, the equatorial protons. The observed coupling constant of 11.5 c.p.s. corresponding to coupling between $H_{2,6e}$ and $H_{2,6a}$ is consistent with known couplings of this type.¹ The chemical shift difference between axial and equatorial protons for many cyclohexane derivatives is 0.5 to 0.6 p.p.m. with equatorial absorption occurring at lower field.¹ The greater difference between $H_{2,6e}$ and $H_{2,6a}$ of 0.82 p.p.m. may arise from the magnetic anisotropy of the benzene ring. Calculations show that the C-2 and C-6 equatorial protons will be deshielded about 0.25 p.p.m. more than the C-2 and C-6 axial protons.¹⁶ As expected, no methylene absorption for the trans alcohol XLIV is observed above $\delta 1.65$.



The spectra of chlorides XLI and XLIII are readily understood in view of the preceding discussion. The doublet at $\delta 2.96$ for the cis chloride XLI has a width at half-height of 7 c.p.s. and $J = 12$ c.p.s. This signal is, therefore, attributed to the C-2 and C-6 equatorial

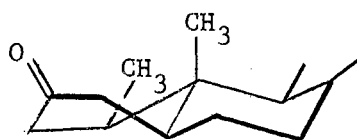
protons in the compound having the axial phenyl group, that is, the cis chloride XLI. For the trans chloride XLII no absorption occurs above $\delta 2.7$, except, of course, for the aromatic protons at $\delta 7.5$.

Very few examples of the stereochemical implications of NMR spectra of alkyl substituents have been reported. The acetylenic protons of the cis- and trans-1-ethynyl-2-o-tolylcyclohexanols (L and LI) resonate at $\delta 2.39$ and $\delta 2.07$, respectively.²³ The equatorial ethynyl

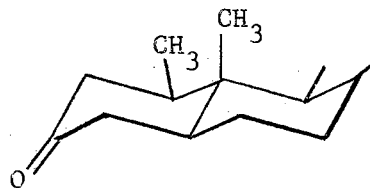


group of alcohol LI hinders rotation of the tolyl group causing the aromatic ring to approach a position perpendicular to the cyclohexane ring. The acetylenic hydrogen is thus subjected to a region of shielding.

A second example is provided by 3-keto-steroids.⁴⁰ If the A ring is forced into a twist conformation by interaction of a β -1-methyl group with the α -11-hydrogen, the C-19 angular methyl group moves into the diamagnetic anisotropy cone of the carbonyl function as shown by structure LII. Thus, the C-19 protons will resonate at a higher field than if the molecule were in the all-chair conformation LIII. It should be pointed out here that the preceding explanation has been opened to question. Karabatsos and coworkers have presented some evidence that the regions of shielding and deshielding associated

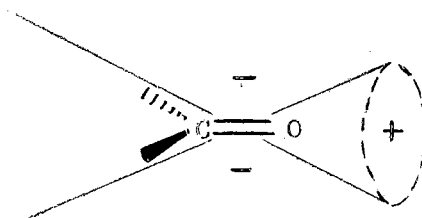


LIII



LIIII

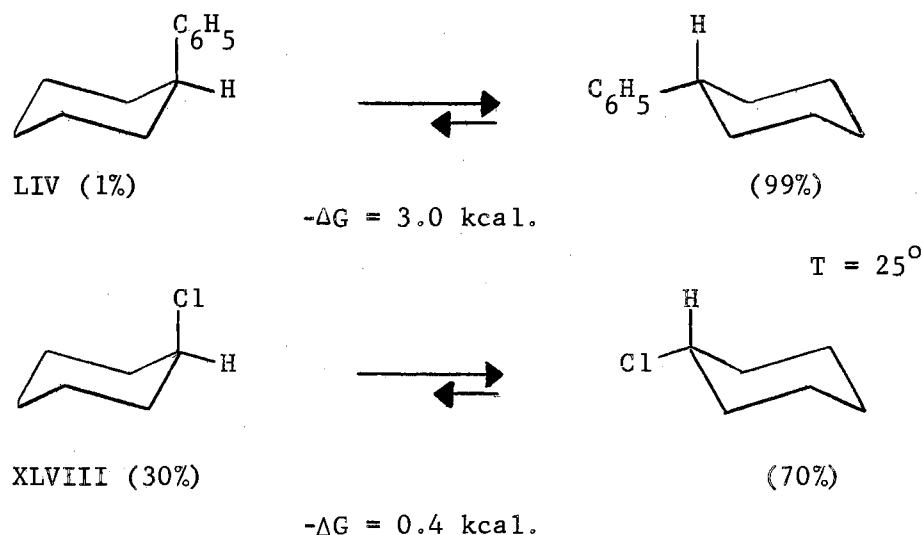
with the carbonyl function may be as shown below.²⁴



In addition to spectral evidence, the proposed structures for the addition products are supported by reasonable elemental analyses for the trans bromide XL and the trans chloride XLII. The cis halides XXXIX and XLI lose hydrogen halide so readily that satisfactory analyses could not be obtained.

Such instability is in itself structural evidence. By operation of "steric assistance" for reactants proceeding through a common transition state, generally the structure with the greater ground state energy will react more readily.⁶ The cis halides, being the less stable thermodynamically, would be expected to undergo elimination by an E1 process with greater ease than the trans isomer.

From the ΔG_X^0 values for the following equilibria, the equatorial conformers are favored in each case, but the equatorial:axial ratio is different for each system.¹³ On the basis of the marked preference of the phenyl group for the equatorial position in phenylcyclohexane (LIV), the instability of chloride XLI is perhaps the result of



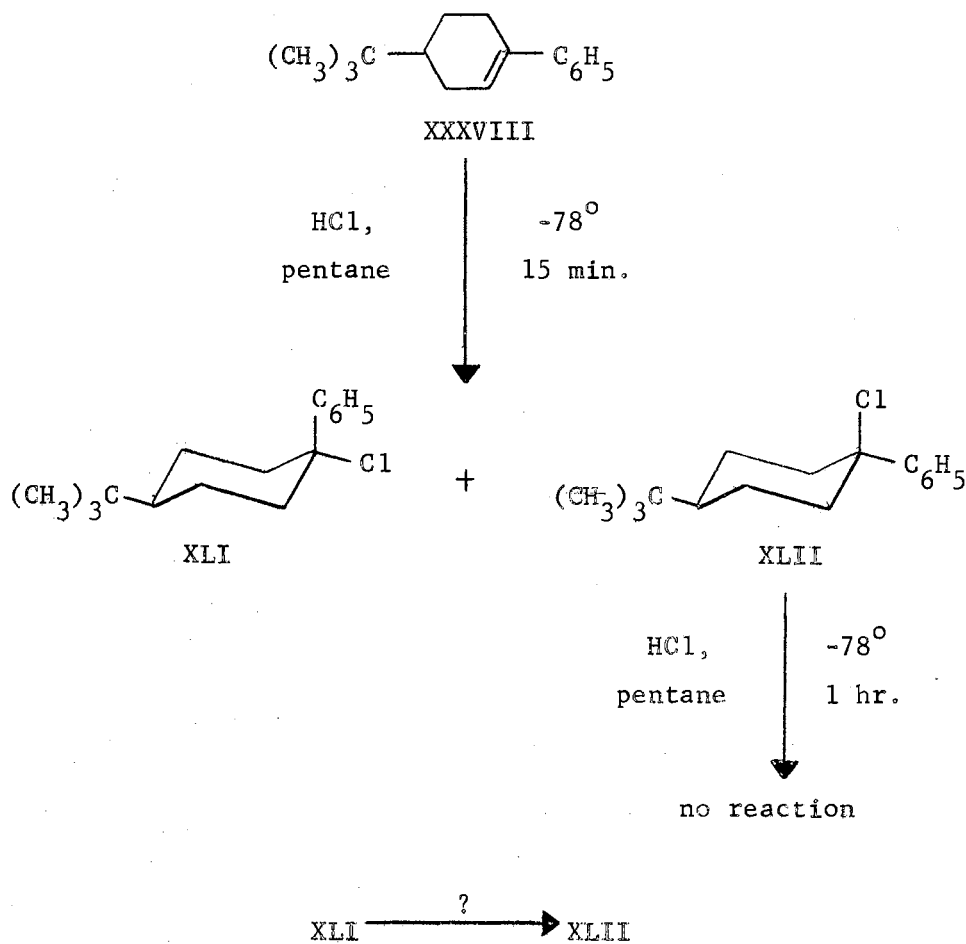
considerable 1,3-interaction, thereby facilitating an E1 process for XLI as compared to XLII.

Experimental evidence for the relative stabilities of XLI and XLII is provided by heating chloride XLI at its melting point. The product consists almost entirely of trans chloride XLII and the alkene XXXVIII.

The kinetic and thermodynamic products of addition may be identified from the results at different temperatures (Table IV).

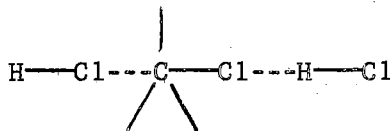
For less than complete addition of HCl (Table IV, reaction 2), the cis chloride XLI is formed in decidedly greater amount than trans chloride XLII. Since thermal equilibration favors XLII rather than XLI, the higher yield of XLI in the addition reaction may result from XLI being formed more readily (in other words, it is the kinetic product). At -78° (reaction 1) the yield of XLI remains high. It may be objected that such a high yield results from the equilibrium between XLI and XLII being altered by the lower temperature. However,

the trans chloride XLII experienced no rearrangement under these reaction conditions. The results can be explained by assuming that at -78° , XLI is definitely the major initial product, being the result of kinetic control and is partially isomerized to the more stable XLII. Since the

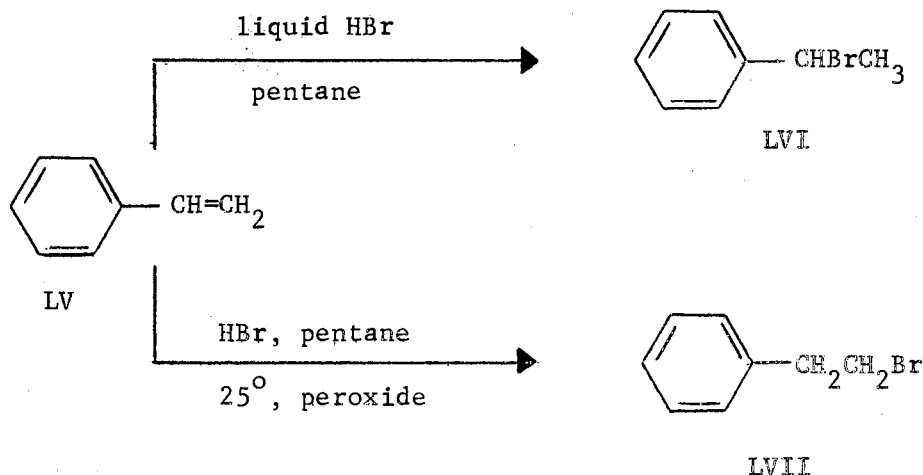


cis chloride XLI is stable in CCl_4 at 25° for at least a day, it is improbable that isomerization results from simple elimination and subsequent addition of HCl. It is also difficult to imagine chloride ion (from HCl) being present in pentane at -78° in sufficiently high concentration to effect extensive isomerization. From these considerations arises the possibility that nucleophilic substitution is involved as

shown below. The heavy lines indicate original bonds.



The results with HBr are inconclusive but at least appear to coincide with HCl addition (Table III). Only traces of a suspected radical addition product could be detected (see Experimental, page 87). Either the rate of ionic addition far exceeds that of radical addition or the initially formed radical products are readily rearranged. The latter possibility was invoked to explain, for example, why styrene (LV) gave almost entirely either 1-bromo-1-phenylethane (LVI) or 2-bromo-1-phenylethane (LVII), depending on reaction conditions.³⁹



With identification of the kinetic product as chloride XLI, it is now possible to consider the mechanism of addition of HCl to alkene XXXVIII. Without deuterium labeling a definite conclusion concerning the mode of addition is not possible, but cis addition of hydrogen halide to alkene XXXVIII appears as reasonable as does trans addition.

The reasoning involved may be explained with the following examples.

A possible mechanism for cis addition to XXXVIII, involving ion pairs as suggested by Dewar, is outlined in Figure 1.¹¹ The termolecular association of hydrogen halide is proposed to agree with the finding that additions are near third order in HX.³¹ There appears to be no significant steric hindrance to immediate collapse of the ion pair LVIII to the twist form of the product. Form LVIII may actually be nearer the configuration of the initial conformer produced than is the chair form of the product.³⁵

For the ion pairs resulting initially from attack either cis or trans to the tert-butyl group there appears to be the same degree of interaction between the phenyl group and the C-2 hydrogens. The only other apparently significant interaction arises from the tert-butyl group. Thus, it would be expected that the kinetic product would arise from the approach for which this interaction between the tert-butyl group and the incoming HX complex would be minimized. Thus, the predicted initial product is the cis chloride XLI, which is in agreement with experimental result.

It is true that for addition of HCl to 1,2-dimethylcyclopentene (XVIII) the kinetic product incorporates the elements of HCl in a trans arrangement (see Historical, p. 43).¹⁹ Care is taken here not to ascribe this result to trans addition of HCl by a concerted process or by way of a protonium ion for such need not be the case. The rate determining protonation of the double bond in XVIII could give ion pair XVIIIa, collapse of which would form the cis adduct (Figure 2). In so doing, however, form XVIIIa must pass through a state in which the methyl groups are eclipsed. Consequently, rearrangement to ion pair XVIIIb occurs, from which the product XIX is formed.

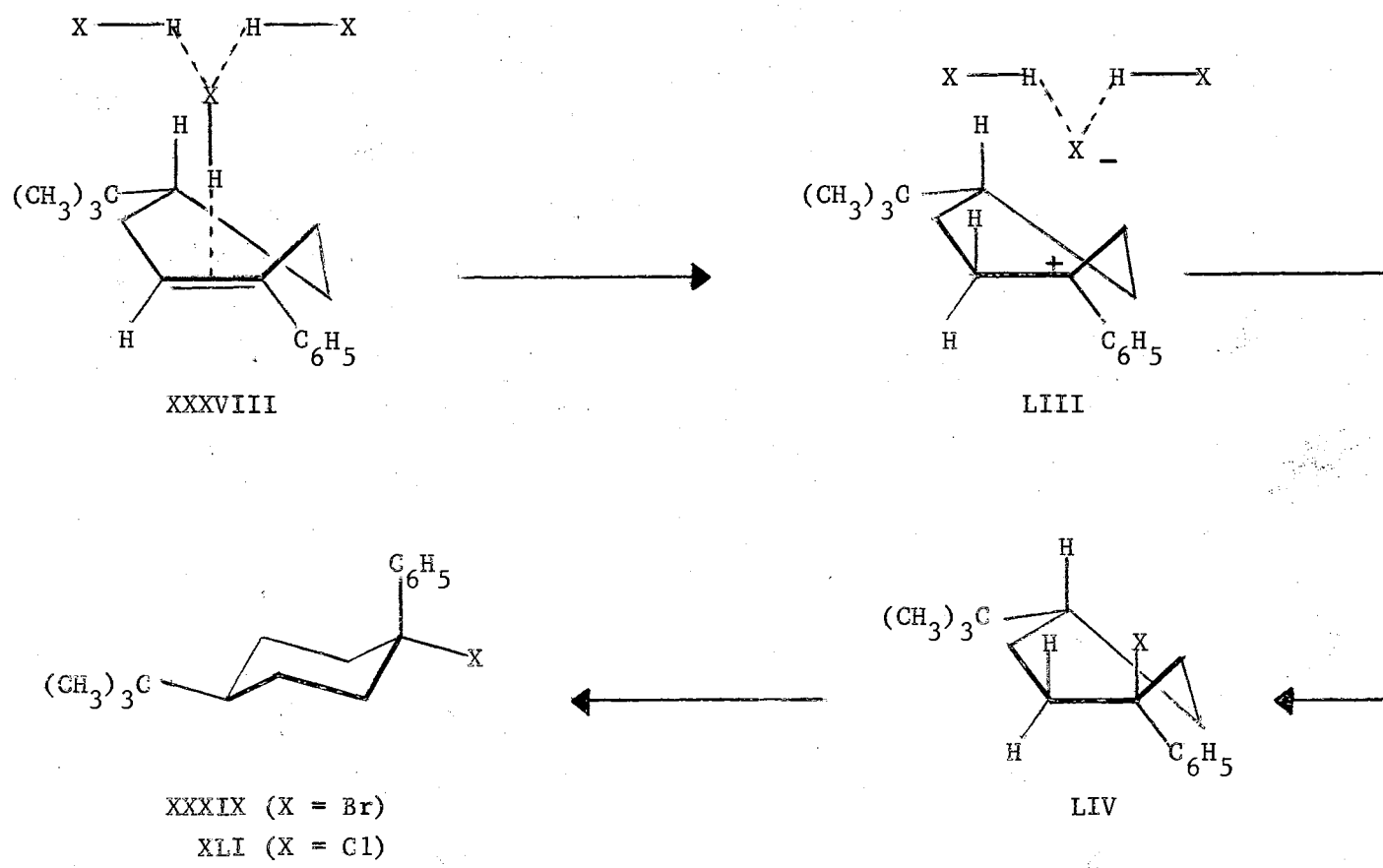


Figure 1. cis Addition of Hydrogen Halide to 4-tert-Butyl-1-phenylcyclohexene (XXXVIII)

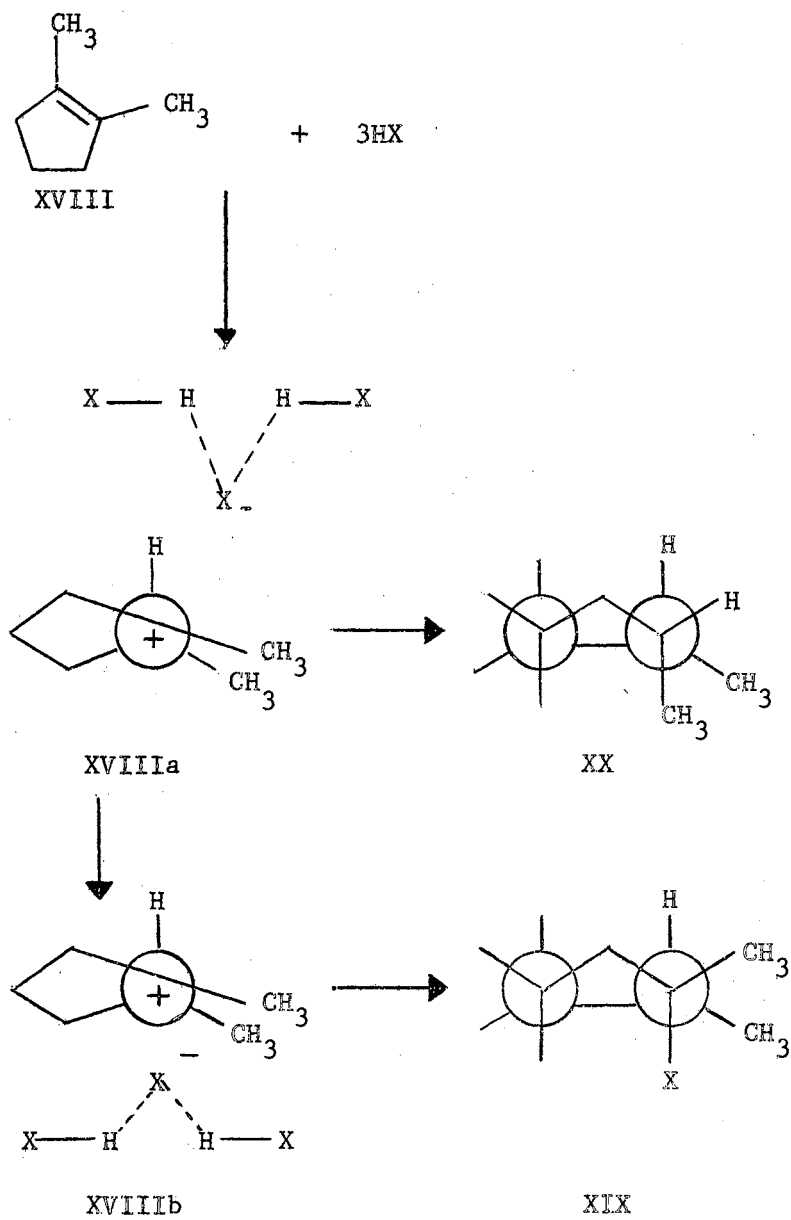
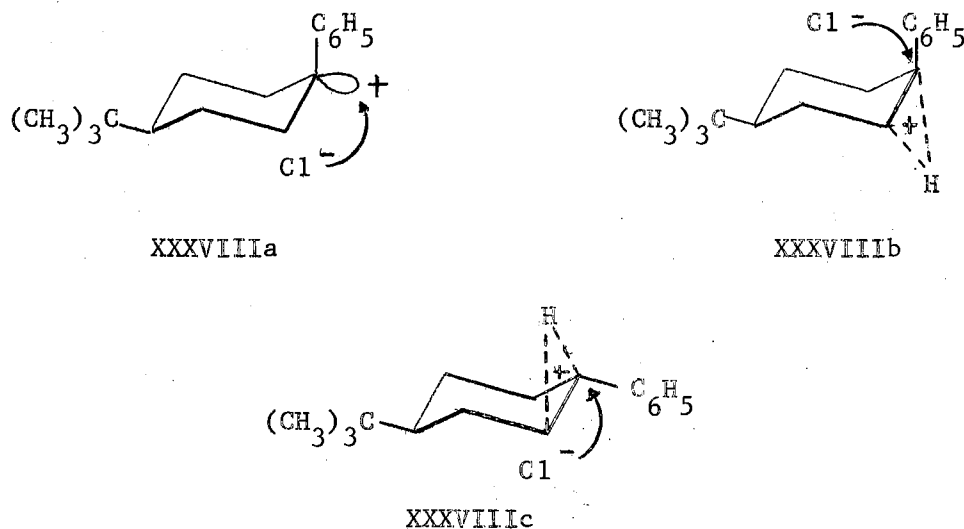


Figure 2. cis Addition of Hydrogen Halide to 1,2-Dimethylcyclopentene (XVIII)

As already discussed, the type of interaction which favors ion pair XVIIIb over XVIIIa does not exist for addition to alkene XXXVIII. A pronounced preference is observed for cis addition to other systems (see Historical, p. 41) for which steric effects do not favor rearrangement of the initial ion pair. There appears, then, no reason why cis addition to XXXVIII should not occur.

It is possible, however, to account for the initial product of the reaction of HCl with XXXVIII by a trans addition. Since addition is rapid at -78° it is likely that the transition state formed by attack of a proton or HCl on XXXVIII more closely resembles product than starting material. In this light, three intermediates with approximate chair conformations may be deemed candidates for consideration. On the basis of the strong preference of the phenyl group for

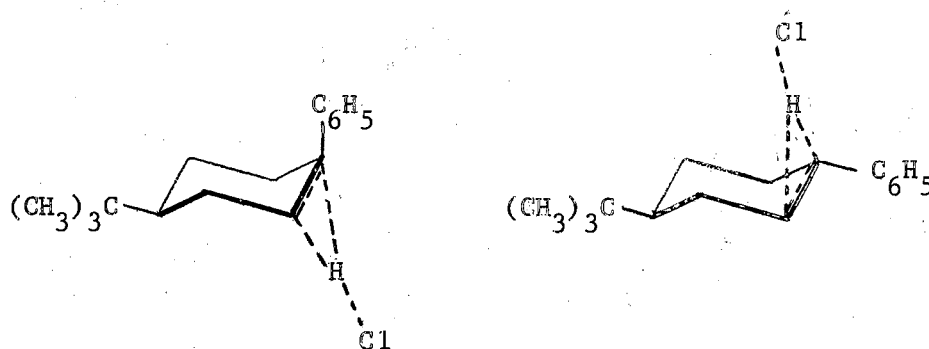


the equatorial position, the open carbonium ion XXXVIIIa with the phenyl group axial is the least attractive candidate for the intermediate precursor of the kinetic product XLI. This argument assumes the vacant

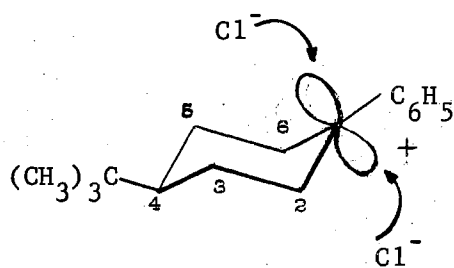
orbital occupies less space than the phenyl group which seems reasonable.

In the bridged ion XXXVIIIb, with the tert-butyl group trans to the bridge, it is observed that 1,3-interaction of protons at C-3 and C-5 would create an increased energy requirement for chloride ion attack at C-1. This factor might explain the lower yield of XLII compared to XLI.

Thus, intermediate XXXVIIIc seems to afford the best compromise with regard to ease of attack by chloride ion to give the kinetic product XLI. Since the reaction of HCl with XXXVIII at -78° is fast, the resemblance of intermediate XXXVIIIc, or the transition state resulting therefrom, to product seems reasonable. This is also in keeping with the known ability of the tert-butyl group to impart a high degree of conformational homogeneity to cyclohexane systems so that chair forms are preferred to minimize internal torsional strain.⁴² Similar arguments could be applied to alkene-hydrogen chloride complexes as shown below.



There is also the possibility of an intermediate ion XXXVIIIId, the structure of which is somewhat between that of starting material and product. The binodal orbital (with the phenyl group, C-1, C-2, and C-6 coplanar or nearly so) could be attacked from either side. However, attack from above would encounter interference from axial protons at



XXXVIIIId

C-3 and C-5. Consequently, attack from below could be favored to give XLI more readily as is observed. Ion XXXVIIIId cannot be entirely discounted as the intermediate from the evidence available.

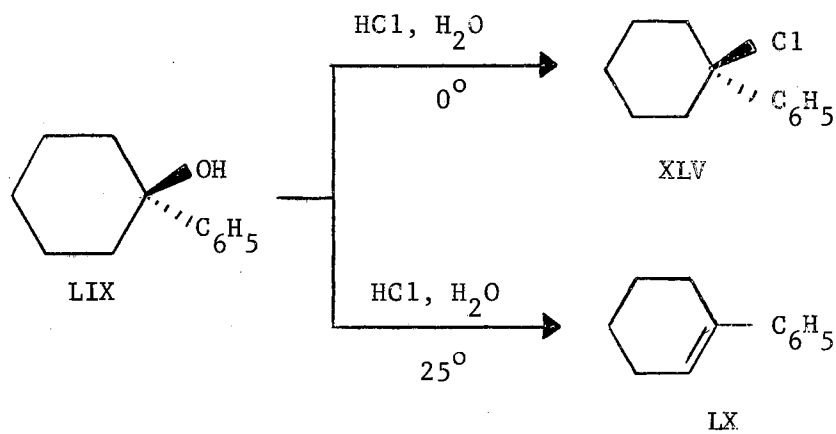
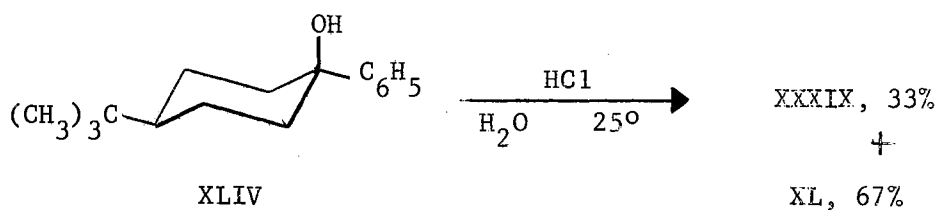
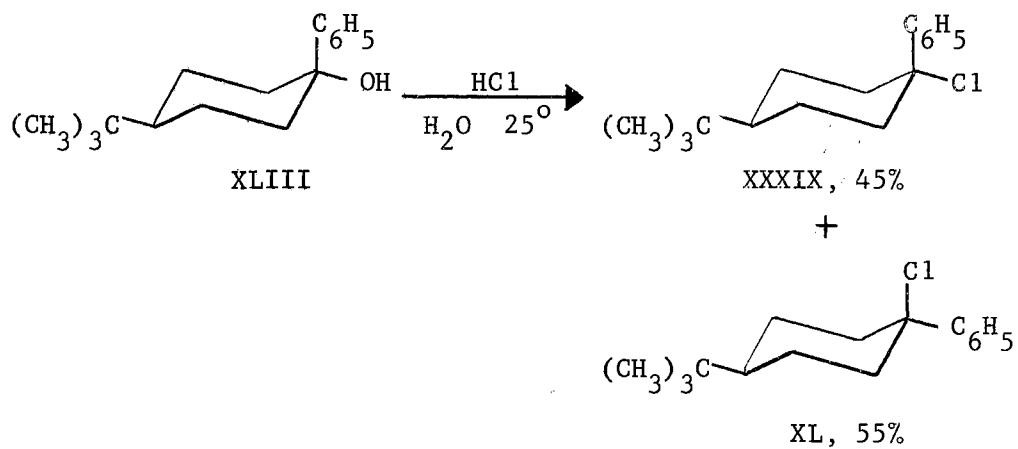
The addition of HCl to XXXVIII is accelerated by decreasing the temperature. Negative temperature coefficients have also been observed for other hydrogen halide additions.²¹ These results are consistent with formation of an alkene-hydrogen halide complex which is less stable at higher temperatures.³⁰

As reported for many other examples, HBr adds more readily than HCl to alkene XXXVIII.³⁰ This trend is probably a consequence of bromine being more easily polarized than chlorine.

Interestingly, addition of HBr to a solution of alkene XXXVIII in CS₂ in the presence of ferric chloride gives exclusively the trans bromide. The role of ferric chloride in this case cannot be evaluated, however, until addition in CS₂ without ferric chloride has been investigated. Also, a detailed study of addition in the presence of ferric chloride in pentane, the solvent used for the other reactions, is needed.

Rather surprisingly, substitution rather than elimination predominates in the reaction of cis- and trans-4-tert-butyl-1-phenyl-

cyclohexanols (XLIII and XLIV) with aqueous hydrogen halide. Under the same conditions, 1-phenylcyclohexanol (LIX) gives only the expected alkene LX, while at a lower temperature the halide XLV is the major product.



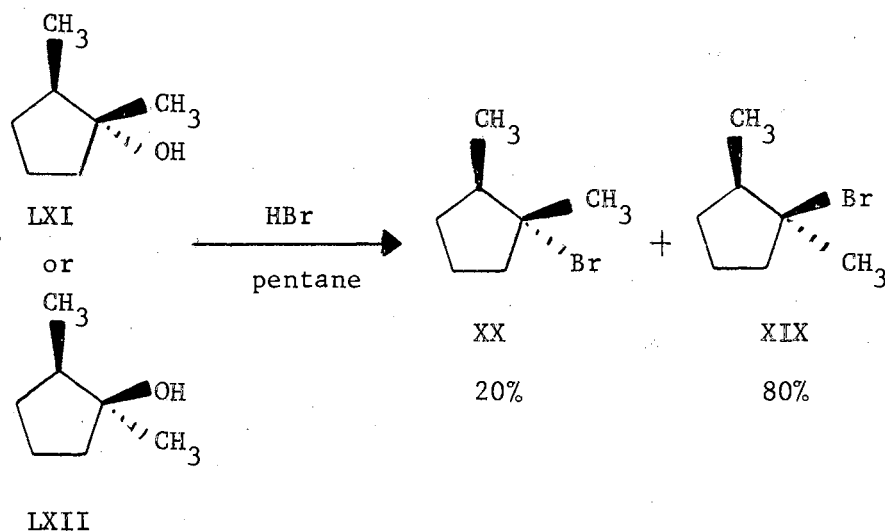
The difference in reactivity of alcohol LIX as compared with XLIII and XLIV does not arise from differences in stability of the products since chloride XLV is unaltered under the reaction conditions at 25°. Also, the alkenes XXXVIII and LX are not precursors for the respective halides in the reactions with the alcohols since both alkenes are recovered quantitatively when subjected to the reaction conditions used for the alcohols. The conclusion, then, is that the tert-butyl group alters an intermediate in the reaction with HX. An intermediate approximating an open carbonium ion is proposed and will be discussed in detail shortly.

It appears unlikely that addition of HX in pentane to alkene XXXVIII and reaction of aqueous HX with alcohols XLIII and XLIV proceed through a common intermediate. The reason is that the ratio of cis halide to trans halide for the two reactions is not the same.

The evidence available indicates that the ratio of halides observed from reaction of alcohols and HX approximates initial ratios of products. In other words, isomerization of one or both halides is probably minimal. Prolonged contact of HBr in pentane with alkene XXXVIII affords the trans bromide XXXIX exclusively (Table III). On the other hand, no change, within experimental error, is observed in the ratio of halides from alcohols XLIII and XLIV. In other words, the halide ratio for reaction of HX with the alcohols does not represent an equilibrated mixture.

An example of the reaction of HX with alcohols and alkene giving different ratios of the cis and trans halides has already been reported. Reaction of either cis- or trans-1,2-dimethylcyclopentanol (LXI and LXII) with hydrogen bromide in pentane gave the same mixture of cis

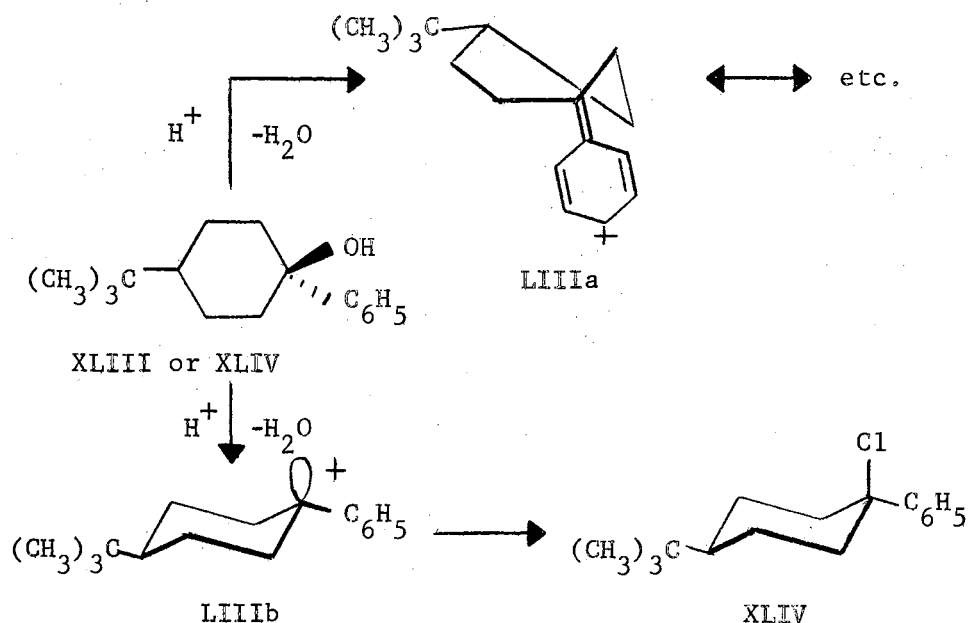
and trans bromides XX and XIX (X = Br) over the temperature range of -78° to 25° .¹⁹ The bromide mixtures from the alcohols were richer in



the trans bromide XIX (X = Br) which is in keeping with the proposed greater thermodynamic stability of this isomer. Similar results were obtained for reaction of HCl with alcohols LXI and LXII, except that the chloride mixture from the alcohols contained less of the trans chloride XIX (X = Cl) than did the alkene reaction mixture. Again, this relation is consistent with the cis chloride being the more stable isomer. The comparison between reactions with alkene XVIII and alcohols LXI and LXII is especially appropriate since the same reaction conditions were used for both types of compounds.

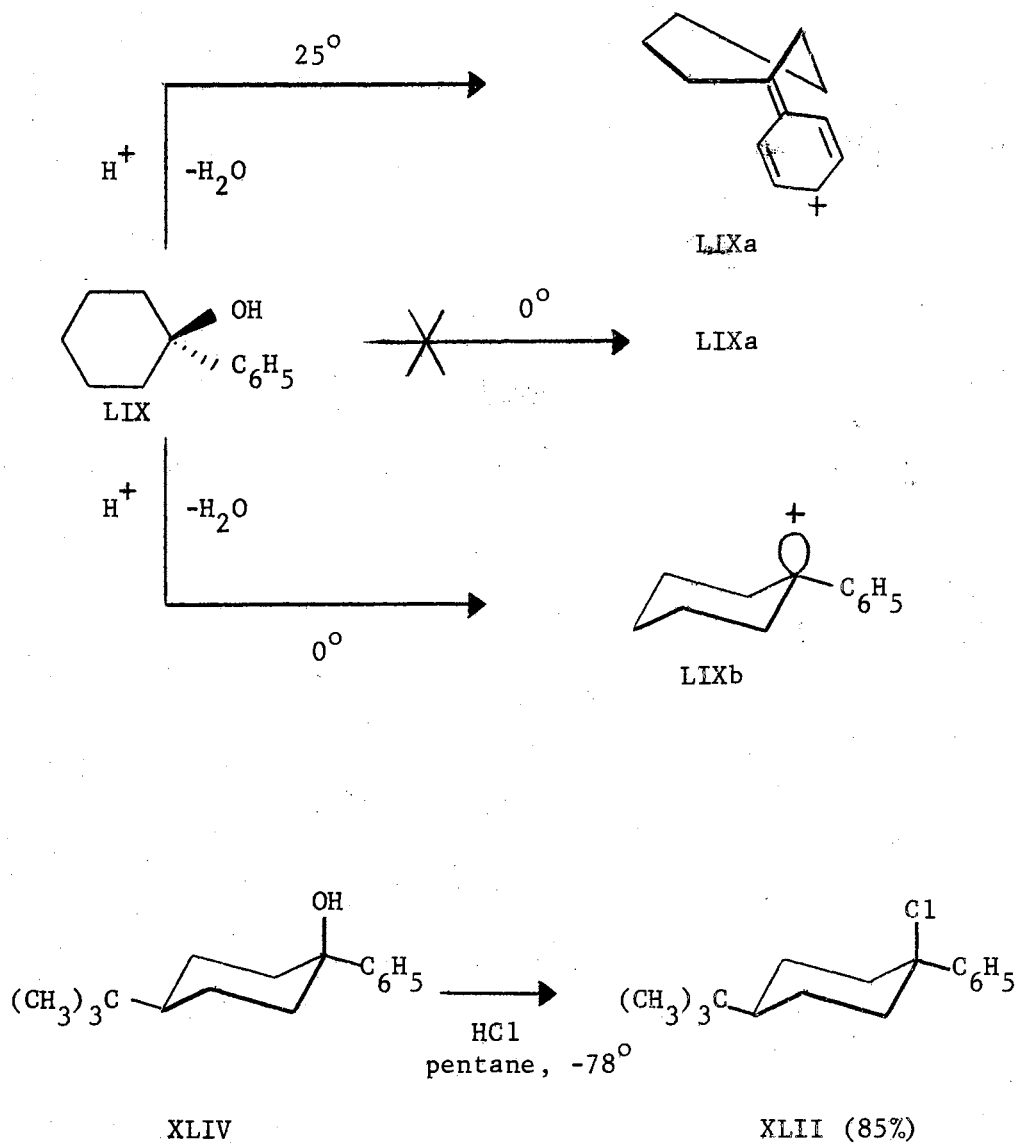
A possible reason for the course of substitution versus elimination for alcohols LXIII, LXIV, and LIX may now be considered. To the extent that an incipient carbonium ion is stabilized by benzylic resonance, sp^2 hybridization at C-1 is involved. The change from sp^3 hybridization of C-1 in the ground state to something approximating sp^2 hybridization in the transition state or intermediate may involve considerable ring

deformation. Such deformation will be rendered more difficult by strain imposed from the tert-butyl substituent. The intermediate of lower energy, LXIIIb could possibly exist in preference to LXIIIa and, hence, would be product determining.



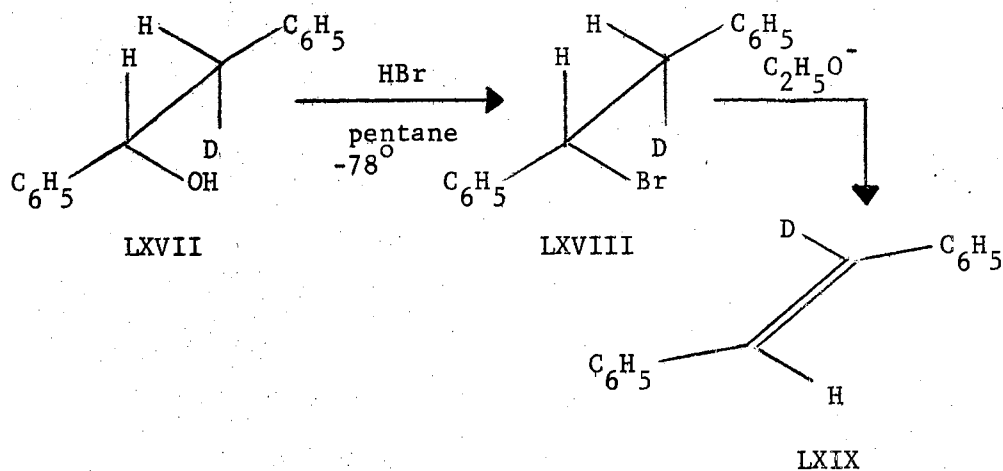
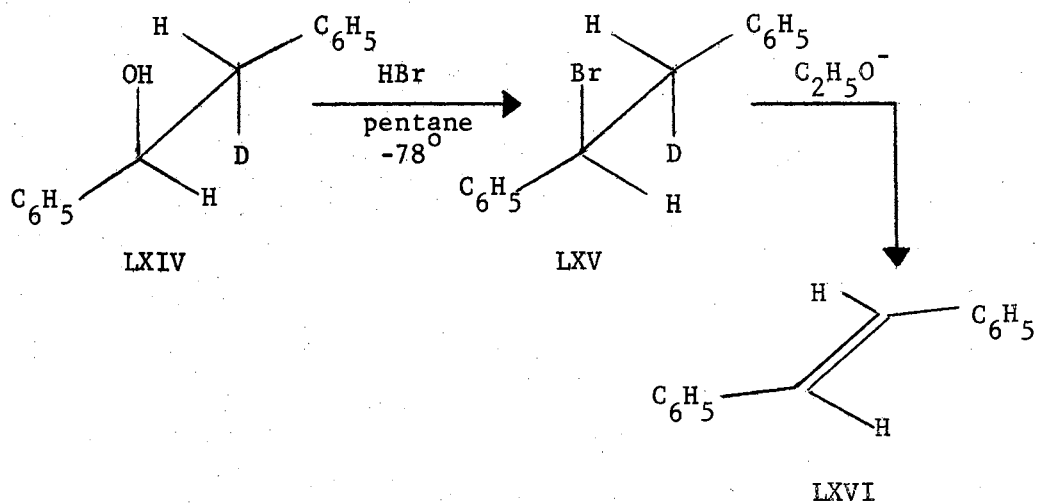
In the case of 1-phenylcyclohexanol (LIX) sufficient energy is available at 25° to give the twist-boat intermediate LIXa necessary for alkene formation. However, the activation energy is apparently too great for LIXa to form at 0° . Instead, a hybrid approximated by LIXb may result from ionization of the hydroxyl group from LIX. Substitution, then, occurs on cation LIXb.

Surprisingly, reaction of trans-4-tert-butyl-1-phenylcyclohexanol (XLIV) with HCl in pentane at -78° occurs with at least 85% retention of configuration. This finding is one of the few unambiguous examples available of what appears to be an $\text{S}_{\text{N}}1$ -type reaction with hydrogen chloride. Addition of HCl to alkene XXXVI under these conditions gives cis chloride XLI as the major product.



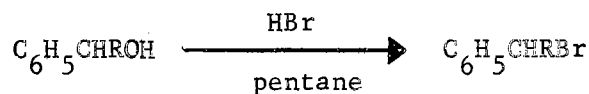
A model example is also provided by the reaction of the erythro and threo forms of 1,2-diphenylethanol (LXIV and LXVII).⁸ For reaction of either isomer in pentane at -78° , 85-90% retention was found.

The use of optically active alcohols for reaction with HX is generally complicated by the difficulty of determining the optical purity of the resulting halide. The reaction of phenylcarbinols of the type LXX had been reported to proceed with essentially complete



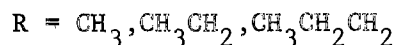
retention of configuration.²⁹ Later, the bromides were prepared having optical rotations of twice the values assumed for pure XLLI in the earlier work.¹⁷

The study of the phenylcarbinols is valuable in that the optical activity of products as a function of temperature was carefully investigated. Three mechanisms were indicated over the temperature



LXX

LXXI

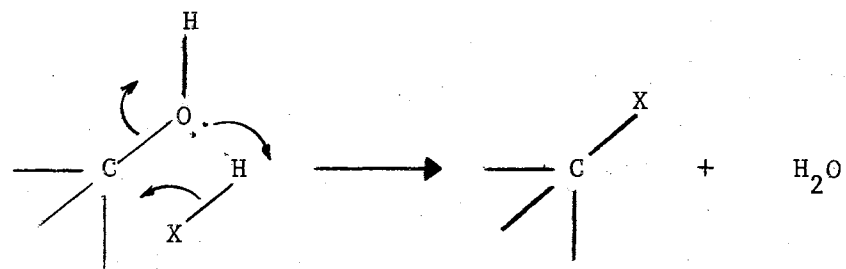


range studied (-80° to 25°); these are represented in Figure 3.

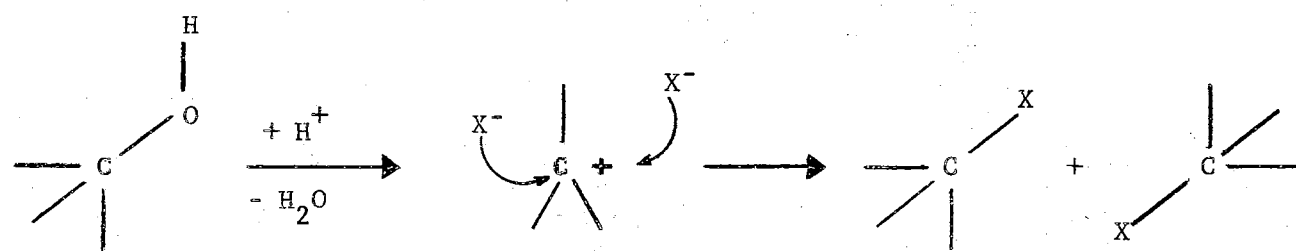
In summary, structural assignments for chlorides XLI and XLII are based on the following evidence. One of the compounds XLII, m.p. $56.5-58^\circ$, dec., analyzes for $\text{C}_{16}\text{H}_{23}\text{Cl}$. Passage of this compound through a column of neutral alumina gives 4-tert-butyl-1-phenylcyclohexene (XXXVIII) as the only isolable product. For this chloride, a Raman maximum occurs at 647 cm^{-1} , which is consistent with axial chlorine. NMR absorption for the tert-butyl group (9 protons by integration) occurs at $\delta 0.95$. The reduced shielding, as compared with the other chloride XLI, is in agreement with an equatorial orientation for the phenyl group. Therefore, the preceding compound described is proposed to be trans-4-tert-butyl-1-phenylcyclohexyl chloride (XLII).

The other chloride XLI, m.p. $77.5-78^\circ$, dec., exhibits a Raman maximum at 689 cm^{-1} , which is consistent with equatorial chlorine. NMR absorption for the tert-butyl protons occurs at $\delta 0.73$, which is in keeping with shielding by an axial phenyl group. Also, a doublet at $\delta 2.96$ is observed, corresponding to two protons. By its field position and coupling constant this signal is assigned to the equatorial protons on C-2 and C-6. The deshielding of these two protons is in keeping with the phenyl group being axial. Upon being heated at its melting point, this chloride is converted to the trans chloride XLII plus

A. S_N1



B. S_N1



C. S_N2

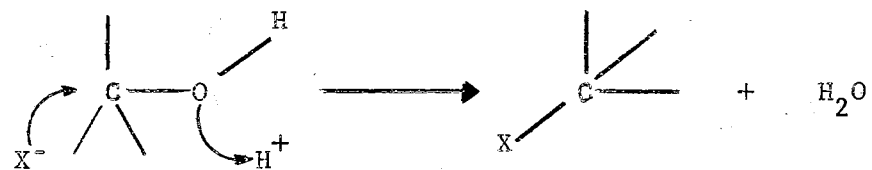
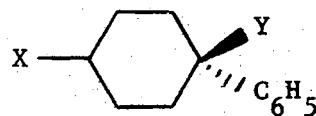


Figure 3. Reaction of Alcohols with Hydrogen Halide

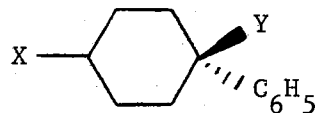
TABLE I

RAMAN SPECTRA OF SUBSTITUTED CYCLOHEXANES IN THE 600-800 CM^{-1} REGION

LXXXI	(trans) ^a	XLII	(trans) ^a	XLI	(cis) ^a	XLV	^b	LIV	^{b,c}
X = (CH ₃) ₃ C, Y = H		X = (CH ₃) ₃ C, Y = Cl		X = (CH ₃) ₃ C, Y = Cl		X = H, Y = Cl		X = H, Y = H	
	623		622		623		623		621
			647				642		
					689		686		
	748		748		740-760		745		741
	792		779		782		786		773

^a n-Heptane solution.^b Neat liquid.^c Reference 14.

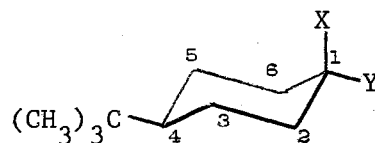
TABLE I

RAMAN SPECTRA OF SUBSTITUTED CYCLOHEXANES IN THE 600-800 CM^{-1} REGION

LXXXI	(trans) ^a	XLII	(trans) ^a	XLI	(cis) ^a	XLV	^b	LIV	^{b,c}
X = (CH ₃) ₃ C, Y = H		X = (CH ₃) ₃ C, Y = Cl		X = (CH ₃) ₃ C, Y = Cl		X = H, Y = Cl		X = H, Y = H	
	623		622		623		623		621
			647				642		
					689		686		
	748		748		740-760		745		741
	792		779		782		786		773

^a n-Heptane solution.^b Neat liquid.^c Reference 14.

TABLE II

TERT-BUTYL PROTON NMR DATA FOR SUBSTITUTED CYCLOHEXANES

Cpd.	X	Y	Plate	δ (p.p.m.) ^a
XLIII	C_6H_5	OH	XX	0.77 ^b
XL	C_6H_5	Br	XVI	0.70 ^b
XLI	C_6H_5	Cl	XVII	0.73
LXXXI	C_6H_5	H	XXVII	0.80 ^b
XLIV	OH	C_6H_5	XXI	0.89
XXXIX	Br	C_6H_5	XV	0.90
XLII	Cl	C_6H_5	XVIII	0.95
LXXX	H	C_6H_5	XXVI	0.88

^a CCl_4 solution.

^bDetermined from a mixture of cis and trans isomers.

TABLE III

ADDITION OF HYDROGEN BROMIDE TO 4-TERT-BUTYL-1-PHENYLCYCLOHEXENE (XXXVIII) IN n-PENTANE

Reaction	Alkene, moles/50 ml.	Additives 5 mole %	Temp. $\pm 1^\circ\text{C}$	Time, min.	Product Composition %		
					XL	XXXIX	XXXVIII
1	0.0023	none	-54	15	60	40	0
2	0.0023	none	-78	15	60	40	0
3	0.0023	none	25	15	70	30	0
4	0.0250	$\text{FeCl}_3(\text{CS}_2)^a$	25	60	100	0	0
5	0.0250	FeCl_3	25	60	70	30	0
6	0.0390	$(\text{C}_6\text{H}_5)_2\text{NH}$	25	480	major ^b		
7	0.0250	AIBN, UV ^c	25	480	major ^b		
8	0.0023	H_2O , 0.50 g.	-54	15			$\sim 100^b$

^aCarbon disulfide as solvent.^bEstimated by IR.^c α, α' -Azobisisobutyronitrile, ultraviolet irradiation.

TABLE IV

ADDITION OF HYDROGEN CHLORIDE TO 4-TERT-BUTYL-1-PHENYLCYCLOHEXENE (XXXVIII) IN n-PENTANE

Reaction	Alkene moles/50 ml.	Temp., $\pm 1^{\circ}\text{C}$	Time, min.	Product Composition, %		
				XLII	XLI	XXXVIII
1	0.0023	-78	15	46	54	0
2	0.0023	-54	15	11	48	41
3	0.0023	-15	15	0	0	100
4	0.0023	25	180	0	0	100
5	0.0100	-78	15	40	60	0
6	0.0100	-78	45	33	67	0

CHAPTER III

EXPERIMENTAL^{a-g}

Preparation of 4-*tert*-Butyl-1-phenylcyclohexene (XXXVIII). For the preparation of phenylmagnesium bromide (LXXII) all liquid reagents were dried with Linde 4-A molecular sieve. Reaction vessels were dried at 110° and flushed with nitrogen while they were still warm.

A 500-ml. Morton flask was equipped with a mechanical stirrer,

^aThe infrared spectra were determined with a Beckman IR-5A spectrophotometer as films on sodium chloride plates or as potassium bromide pellets.

^bThe Raman spectra were determined using a helium-neon laser Raman spectrophotometer with a Jerrall-Ash double monochromator. Liquid samples were measured neat and solids as solutions in *n*-heptane.

^cThe proton nuclear magnetic resonance spectra were measured on a Varian A-60 high resolution spectrometer. Tetramethylsilane was used as an internal standard. The solvent was carbon tetrachloride unless otherwise indicated.

^dGas-liquid chromatographic analyses were made with a Varian-Aerograph 1520 apparatus using a thermal conductivity bridge. Columns used were 5% silicone rubber (with dimethyldichlorosilane) on acid-washed Chromosorb G (1/8 in. by 8 ft.), 2% fluorosilicone (QF-1) with hexamethyldisilane on Chromosorb W (1/8 in. by 6 ft.), and 5% nitrile gum (XE-60) on Chromosorb W (1/8 in. by 6 ft.).

^eAreas on spectrograms were measured with a Keuffel and Esser compensating polar planimeter.

^fMicroanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

^gMelting points were determined on a Fisher-Johns heating stage and are uncorrected.

addition funnel with nitrogen inlet, and a Friederich condenser. To the flask was added 8.41 g. (0.350 g.-atom) of magnesium turnings and 20 ml. of ether followed by 3.0 ml. of bromobenzene (LXXIII). Reaction was initiated by rapid stirring for 1-2 min. When the mixture was boiling vigorously and had become dark brown, 25 ml. of ether was introduced. The remainder of a total of 50.0 g. (0.318 mole) of bromobenzene (LXXIII) in 100 ml. of ether was added during 30 min. with rapid stirring. The mixture was heated under reflux for 1.5 hr. and then brought up to 200 ml. with additional ether. Three 1.00 ml. aliquots were added to 50.00 ml. of 0.04855N HCl, heated almost to boiling, cooled, and titrated to a phenolphthalein end point with 0.04671N NaOH. The yield was 0.312 mole (98%).

While being stirred, the solution of phenylmagnesium bromide (LXXII), containing some unreacted magnesium, was treated dropwise under nitrogen with 43.3 g. (0.281 mole) of 4-tert-butylcyclohexanone (LXXIV) [Dow Chemical Co., m.p. 39-40° (lit.,²² m.p. 47.8-48.7°)] dissolved in 100 ml. of ether. Addition at a rate which maintained vigorous reflux required 30 min. Solid was deposited within 15-20 min. after addition of LXXIV had begun.

The thick mixture was stirred 2 hr. and then poured into 300 ml. of ice water; 300 ml. of 3N HCl was added followed by 600 ml. of ether. Stirring for 15-20 min. was necessary to dissolve the solid. The organic phase was dried ($MgSO_4$) and concentrated under aspirator pressure. The tan solid thus obtained was pulverized and air-dried. The yield was 61.6 g. (95%) of a mixture of cis-4-tert-butyl-1-phenylcyclohexanol (XLIII) and trans-4-tert-butyl-1-phenylcyclohexanol (XLIV). NMR analysis indicated equal amounts of each isomer to be

present.

The product was always contaminated with ketone LXXIV. Heating the reaction mixture under reflux for 2 hr. and stirring for up to 18 hr. at 25° did not result in complete reaction of the ketone. Using 30% in excess of the theoretical amount of Grignard reagent was also ineffective.

An unsuccessful attempt was made to extract the impurities from the Grignard-ketone complex prior to hydrolysis. The complex was easily filtered by suction, but washing with a total of 800 ml. of anhydrous ether left ketone in the product as shown by infrared absorption at 1720 cm^{-1} .

However, ketone LXXIV was removed by derivation. Crude product (alcohols XLIII and XLIV) (10.0 g.) with 2.5 g. of Girard's reagent T [(carboxymethyl) trimethylammonium chloride, hydrazide (LXXV)] in 50 ml. of methanol and 5 ml. of acetic acid was heated under reflux 4 hr. The cooled solution was poured into a mixture of ether-water (250 ml:250 ml). The ether layer was washed (100 ml. of water) and dried (MgSO_4). The concentrated product exhibited no carbonyl absorption.

Since ketone LXXIV could be removed from the compounds derived from the crude mixture of alcohols either by distillation or crystallization; the purification just described was not usually employed.

The mixture of alcohols XLIII and XLIV was dehydrated by the procedure of Garbisch.¹⁵ Crude alcohol (61.6 g.) was shaken 5 min. with a freshly prepared solution of 20 ml. of concentrated sulfuric acid and 30 ml. of acetic acid. The resulting red, opaque suspension was poured into a mixture of ether-water (150 ml:250 ml). The organic

phase was washed with 100 ml. of water and 100 ml. of 10% aqueous potassium carbonate solution then dried ($MgSO_4$). Removal of solvent gave a brown oil weighing 54.5 g. (91% yield of crude alkene based on ketone). Distillation yielded the following fractions: (1) b.p. 42-85°/0.05 mm., 1.96 g.; (2) b.p. 90-95°/0.05 mm., 8.02 g., η_D^{23} 1.5436; and (3) b.p. 95-99°/0.05-0.08 mm., 36.45 g. (61% based on ketone), η_D^{23} 1.5432, of 4-tert-butyl-1-phenylcyclohexene (XXXVIII) (lit., η_D^{15} b.p. 106-107°/0.4 mm., η_D^{20} 1.5437).

The first two fractions contained biphenyl (LXXVI) and 4-tert-butylcyclohexanone (LXXIV) in addition to XXXVIII. The third fraction was pure alkene XXXVIII. Analysis was performed by TLC (Silica G with chloroform) and GLC (5% silicone rubber on Chromosorb G).

Alkene XXXVIII showed an ultraviolet absorption maximum at 248 $m\mu$ (ϵ_{max} 11,300). Characteristic infrared absorption (Plate V) occurred at 1650, 1260, and 655 cm^{-1} . Absorption at 1650 cm^{-1} was also observed in saturated derivatives of XXXVIII but at reduced intensity.

NMR spectroscopy was the most convenient means of detecting 4-tert-butyl-1-phenylcyclohexene (XXXVIII). Absorption was observed (Plate XIV) at δ 0.88[(CH_3)₃C], δ 5.95(vinyl H), and δ 7.15(Ar-H).

Preparation of *cis*- and *trans*-4-tert-Butyl-1-phenylcyclohexyl Bromides: (XXXIX) and (XL). Hydrogen bromide was bubbled for 1 hr. into a solution of 21.4 g. (0.100 mole) of 4-tert butyl-1-phenylcyclohexene (XXXVIII) in 100 ml. of hexane. The solution rapidly turned orange and deposited a few drops of brown oil, which adhered to the flask wall when the solution was poured out. After being concentrated under aspirator pressure, the product was taken up in 50 ml. of hexane and clarified by swirling 2 min. with 200 mg. of activated

charcoal (Darco G-60). Gravity filtration and removal of solvent (aspirator at 25°) gave a white crystalline mass, which after three recrystallizations over a 12-hr. period from hexane at -15°, afforded 8.8 g. (30%) of trans-4-tert-butyl-1-phenylcyclohexyl bromide (XL), m.p. 73-75°, dec.

Anal. Calcd for C₁₆H₂₃Br: C, 65.09; H, 7.85; Br, 27.06.

Found: C, 64.90; H, 7.64; Br, 26.84.

The crude bromide, free of alcohol by infrared measurement, exhibited maxima at 678 and 638 cm⁻¹, whereas only the latter absorption was observed for XL (Plate VII). In the 400-600 cm⁻¹ region, only two maxima were seen, at 495 and 546 cm⁻¹. The Raman spectrum (powder) of XL displayed an intense maximum at 555 cm⁻¹.

In the NMR spectrum (Plate XV) of bromide XL absorption for the tert-butyl protons occurred at δ 0.90. A doublet at δ 2.6 corresponded to two protons for equatorial hydrogens on C-2 and C-6.

Crude bromide was prepared as described above but was recrystallized twice from isopropyl ether within 1 hr. One gram (0.0034 mole) of this product was immediately dissolved in 30 ml. of tetrahydrofuran, which had been heated under reflux with sodium ribbon for 20 hr. and distilled from LiAlH₄ just prior to use. Under an atmosphere of dry N₂, 0.049g, (0.0070 g-atom) of lithium cut in small pieces was quickly added. The mixture was stirred 12 hr. during which time a white precipitate formed. Titration of a 3 ml. aliquot showed no basic compounds to be present. The reaction mixture was rapidly filtered and concentrated. The precipitate mentioned above appeared by solubility and flame tests to be LiBr.

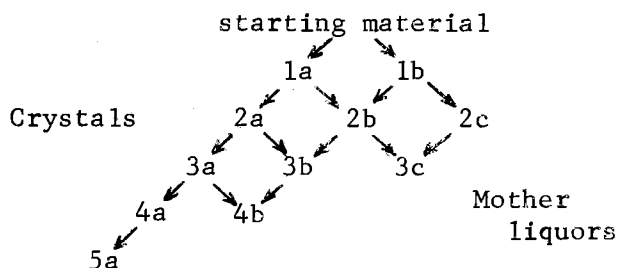
The organic residue was recrystallized from isopropyl ether (30

min. at -15°), m.p. $84-84.5^{\circ}$, dec., for cis-4-tert-butyl-1-phenylcyclohexyl bromide (XXXIX). The infrared spectrum (Plate VI) showed absorption at 678 but not at 638 cm^{-1} . A composite of the spectra of XXXIX and XL was identical to that of crude bromide.

Rapid deterioration of XXXIX prevented further investigations. Recrystallization of crude bromide provided enrichment of the crystals in the cis bromide (XXXIX) as evidenced by the ratio of NMR signals at $\delta 0.90$ (trans) and at $\delta 0.70$ (cis) for the respective tert-butyl groups. However, after 3-4 recrystallizations (hexane or isopropyl ether) the amount of the cis-bromide in the solid began to decrease.

Preparation of cis- and trans-4-tert-Butyl-1-phenylcyclohexyl Chlorides: (XLI) and (XLII). The crude mixture of alcohols XLIII and XLIV (42.2 g., 0.182 mole) suspended in 120 ml. of hexane was shaken with 100 ml. of concentrated HCl (1.16 moles) at 26° until all solid had disappeared (10 min.). The yellow mixture was separated and the aqueous layer extracted with two 25-ml. portions of hexane. The hexane solution was stirred in a stoppered flask for 1.5 hr. with 14.0 g. of MgSO_4 . The filtered solution was concentrated on a rotary evaporator at $26-30^{\circ}$ to a constant weight of 36.4 g.; the yield of crude XLI and XLII was 80%.

The mixture of chlorides XLI and XLII was subjected to the "diamond" fractional recrystallization scheme described by Richards and Hall.³⁴ The scheme is outlined below.



All crystallizations were performed at -15° using hexane as solvent. Details are summarized in Table V. For example, 14.9 g. of solid 1a was obtained by dissolving the starting material (36.4 g.) in 25 ml. of hexane and keeping the solution at -15° for 40 min.

TABLE V
FRACTIONAL RECRYSTALLIZATION OF CIS- AND TRANS-4-TERT-BUTYL-
1-PHENYLCYCLOHEXYL CHLORIDES (XLI AND XLII)

Product	Volume, ml.	Time, min.	Weight, g.	M.P., $^{\circ}\text{C}$
1a	25	40	14.9	
2a	25	75	4.3	
3a	20	210	2.9	72-6 d.
4a	20	600	1.9	74-7 d.
5a	10	120	0.9	75-7 d.
2b	10	75	3.7	
3b	7	45	4.5	
4b	20	20	2.6	
1a'	10	240	5.5	
2a'	8	210	2.2	
3a'	5	60	0.8	53-6 d.
4a'	5	120	0.3	56.5-8 d.

Mother liquors (2c) and (3c) were concentrated to 21.6 g. of orange solid. This solid, dissolved in 35 ml. of hexane, was stirred 3 hr. with a solution of 5.2 g. (0.13 mole) of NaOH in 25 ml. of water.

The organic layer was washed (5% aqueous sodium chloride solution) until the washings were neutral (required three 100-ml. portions). The dried (MgSO_4) product was concentrated and recrystallized (products 1a'-4a') according to the aforementioned scheme.

Product (4a') was trans-4-tert-butyl-1-phenylcyclohexyl chloride (XLII). Characteristic maxima occurred in the Raman spectrum (Plate II) at 647 cm^{-1} and in the infrared (Plate IX) at 643 and 848 cm^{-1} . NMR absorption (Plate XV) for the tert-butyl protons was measured at $\delta 0.95$ plus $\delta 0.5-2.6$ (cyclohexyl H), and $\delta 7.5$ (Ar H).

Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{Cl}$: C, 76.60; H, 9.26; Cl, 14.14.

Found: C, 76.56; H, 9.17; Cl, 14.02.

Product (5a) was cis-4-tert-butyl-1-phenylcyclohexyl chloride (XLI) shown by elemental and NMR analysis to contain 10% of trans-4-tert-butyl-1-phenylcyclohexanol (XLIV). Identifying maxima were observed in the Raman spectrum (Plate I) at 689 cm^{-1} and in the infrared (Plate VII) at 685 and 837 cm^{-1} . NMR absorption (Plate XVI) of the tert-butyl protons occurred at $\delta 0.73$.

Chloride XLI, free from the alcohol XLIV and the isomeric chloride XLII (NMR analysis), was prepared by bubbling hydrogen chloride into a solution of 3.0 g. of 4-tert-butyl-1-phenylcyclohexene (XXXVIII) in 50 ml. of hexane at -78° for 1 hr. Concentration and three recrystallizations of the product from hexane at -15° gave 0.30 g. of cis-4-tert-butyl-1-phenylcyclohexyl chloride (XLI), m.p. $77.5-78^\circ$, dec. The compound decomposes rapidly and a good analysis could not be obtained.

Anal. Calcd for $\text{C}_{16}\text{H}_{23}\text{Cl}$: C, 76.60; H, 9.26; Cl, 14.14.

Found: C, 77.25; H, 9.49; Cl, 13.20.

When chloride XLI was kept at 75-80° for 10 min. and then quickly cooled, essentially complete conversion to alkene XXXVIII and chloride XLII was realized as determined by infrared analysis.

Addition of Hydrogen Bromide to 4-*tert*-Butyl-1-phenylcyclohexene (XXXVIII). Hydrogen bromide gas (99.8% minimum) was passed from a cylinder through a 4 x 20 cm. column of anhydrous calcium chloride and then through a fritted glass inlet into a flask covered with aluminum foil and fitted with a thermometer. The effluent gas passed through a 7 x 7 cm. column of calcium chloride, over a 30% solution of potassium hydroxide, and finally through a U-tube partially filled with concentrated hydrobromic acid. Reaction mixtures were stirred magnetically except at low temperatures where shaking was used. Glass components were connected with Tygon tubing, which had to be replaced frequently because it was readily attacked by the gas.

Reaction temperatures could be maintained within $\pm 1^{\circ}\text{C}$. For studies at -78° and -54° , Dry Ice-acetone baths were employed, and for -15° an ethanol-ice mixture was used. These baths were contained in Dewar flasks. Repeated experiments showed that expansion of hydrogen bromide had no measurable affect on the temperature of the reaction mixture.

Product compositions were determined by NMR analysis. The signals used were those at $\delta 7.15$ (aromatic), $\delta 5.95$ (vinyl H), $\delta 0.90$ (*tert*-butyl H for *trans*-bromide XL), and $\delta 0.70$ (*tert*-butyl H for *cis*-bromide XXXIX). Since absorption for the *tert*-butyl protons of alkene XXXVIII, occurring at $\delta 0.88$, overlapped with the $\delta 0.90$ absorption (in XL), correction for alkene content had to be made to determine the amount of *trans*-bromide XXXIX present. Experimental results varied $\pm 3\%$.

Thus, composition values differing by as much as 6% cannot be considered significant.

Reactions were performed in n-pentane (spectroquality); samples were made up to a total volume of 50.0 ml. At the end of the reaction time, solvent was removed under aspirator pressure (10 min.); the residue was kept at 0.10 mm. at 25° for 30 min. Analytical samples were dissolved in CCl₄ containing tetramethylsilane for NMR analysis. Results are summarized in Table I.

Rigorous purification of solvents did not appear to be necessary. Petroleum ether (bp 35-50°) was stirred 20 hr. with 10% alkaline potassium permanganate and then for another 20 hr. with concentrated sulfuric acid, and distilled. Solvent thus prepared gave the same results as did reagent grade hexane or petroleum ether (b.p. 35-54°). However, water in more than trace amounts did inhibit a reaction (Table III, reaction 8).

The formation of products of radical addition was investigated under a variety of conditions. From reaction 7 (Table III) three components were isolated by preparative TLC (Silica G with pentane) with R_f values of 0.00, 0.17, and 0.32. The latter fraction was identified by IR and NMR spectra as pure 4-tert-butyl-1-phenylcyclohexene (XXXVIII). The fraction with R_f = 0.17 was a colorless oil, which eventually formed a solid giving a positive halogen test (ethanolic AgNO₃); it was tentatively identified as 3-bromo-tert-butyl-4-phenylcyclohexane (LXXVII) on spectroscopic evidence. The NMR spectrum (CCl₄) showed absorption at δ 0.8-2.8 (aliphatic ring protons), δ 0.91 [(CH₃)₃C], δ 4.65 (1 HCB_r), and δ 7.13 (aromatic protons). Assignment for the absorption at δ 4.65 was based on the values of δ 4.60- δ 3.80

reported for 4-bromo-tert-butylcyclohexane (LXXVIII).⁴¹ All of the infrared absorption maxima of LXXVII (neat) occurred in the spectra of either trans bromide XL or cis bromide XXXIX with variations in relative intensities.

When addition of hydrogen bromide was performed in the dark (Table III, reaction 3), a lesser amount of LXXVII was obtained than in reaction (7). With diphenylamine (LXXIX), and again with exclusion of light, none of bromide LXXVII was detected. Yields of LXXVII were visually estimated from TLC spot areas. Recrystallized trans bromide XL was judged free from the secondary bromide LXXVII by TLC analysis.

All attempts at column chromatography (neutral alumina and silica) and gas-liquid chromatography (5% silicone rubber on Chromosorb G) of mixtures of cis and trans bromides XXXIX and XL resulted only in formation of 4-tert-butyl-1-phenylcyclohexene (XXXVIII).

Addition of Hydrogen Chloride to 4-tert-Butyl-1-phenylcyclohexene (XXXVIII). The procedure was the same as that described for the addition of hydrogen bromide except that light was not excluded from the reaction mixture.

NMR analysis for the reactants and products was based on absorption at δ 7.15 (aromatic H), δ 5.95 (vinyl H), δ 0.95 (tert-butyl H for trans chloride XLII), and δ 0.73 (tert-butyl H for cis chloride XLI). Semi-quantitative determination of products was possible with IR analysis.

Addition did not appear to occur when an aqueous solution of hydrogen chloride was used. 4-tert-Butyl-1-phenylcyclohexene (XXXVIII) (4.60 g. 0.0430 mole) in 8.0 ml. of hexane was shaken for 15 min. with 25.0 ml. of concentrated hydrochloric acid. Drying

(MgSO₄) and concentration of the hexane solution gave a liquid which was shown by IR and NMR to be identical to starting material.

Reaction of Hydrogen Bromide with *cis*- and *trans*-4-*tert*-Butyl-1-phenylcyclohexanols: (XLIII and XLIV). A mixture of bromides XXXIX and XL was also obtained from the corresponding alcohols. A suspension of 16.34 g. (approximately 0.07 mole) of a 50:50 mixture of the *cis* and *trans* alcohols XLIII and XLIV in 65 ml. of hexane was shaken 5 min. with 80 ml. of fuming hydrobromic acid. Work-up and treatment at 25° with activated charcoal (hexane solution) gave 19.2 g. (92%) of light yellow solid consisting of 63% *trans* bromide XL, 24% *cis* bromide XXXIX, and 13% 4-*tert*-butyl-1-phenylcyclohexene (XXXVIII). For a reaction time of 30 min., the respective percentages were 62, 21, and 17. No hydroxyl absorption was observed in the IR spectrum.

Isolation of *trans*-4-*tert*-butyl-1-phenylcyclohexanol (XLIV) was realized in preparing bromides XXXIX and XL. The solid reaction mixture from 23 g. of alcohols XLIII and XLIV, 150 ml. of hexane, and 100 ml. of fuming hydrobromic acid (shaken 15 min. at 25°) was treated with 60 ml. of hexane. Most of the solid dissolved leaving a white crystalline solid. Recrystallization of this residue from hexane gave 1.3 g. of colorless needles, m.p. 110.5-111.5°, having an IR spectrum identical to that of *trans*-4-*tert*-butyl-1-phenylcyclohexanol (XLIV).

Reaction of Hydrogen Chloride with *cis*- and *trans*-4-*tert*-Butyl-1-phenylcyclohexanols: (XLIII and XLIV). An equimolar mixture of *cis*- and *trans*-4-*tert*-butyl-1-phenylcyclohexanols (XLIII and XLIV) (5.0 g., 0.022 mole) suspended in 15 ml. of hexane was shaken 15 min. at 25° with 50 ml. of concentrated hydrochloric acid. The layers were

separated, and the aqueous layer was extracted with two 10-ml. portions of hexane. Drying (MgSO_4) and removal of the hexane gave a pale yellow oil which solidified after being kept at -15° for 12 hr; yield 4.7 g. (85%), IR absorption maxima corresponded exactly to those of the cis and trans chlorides XLI and XLII plus weak absorption at 3330 (hydroxyl) and 1720 cm^{-1} (carbonyl). The NMR spectrum exhibited tert-butyl proton absorption at $\delta 0.90$ and $\delta 0.70$ in a ratio of 2:1. 4-tert-Butyl-1-phenylcyclohexene (XXXVIII) was present but in amounts too small to be measured. TLC (alumina with pentane) showed two components, $R_f = 0.0$ and $R_f = 0.4$, the latter corresponding to alkene XXXVIII.

trans-4-tert-Butyl-1-phenylcyclohexanol (XLIV) was isolated by column chromatography. An equimolar mixture of cis and trans alcohols XLIII and XLIV (2.0 g.) dissolved in 20 ml. of ether was put onto 80 g. of alumina (Merck acid-washed) in a 3 x 23 cm. column packed in hexane. Every 20 min., 100-ml. fractions were collected. Following 700 ml. of hexane which gave some alkene and 200 ml. of hexane:ether (9:1), 300 ml. of ether gave a solid, which after recrystallization from hexane afforded 40 mg. of trans alcohol XLIV, m.p. $109.8-110^\circ$ (lit.,¹⁶ $117-118^\circ$). NMR absorption (Plate XXI) occurred at $\delta 0.90$ (tert-butyl H), $\delta 1-2$ (aliphatic ring H), $\delta 1.59$ (OH), and $\delta 7.3$ (aromatic H) in agreement with reported values.¹⁶ IR absorption (Plate X) useful for distinguishing XLIV from the cis isomer XLIII occurred at 825 and 755 cm^{-1} .

The trans alcohol XLIV thus prepared (30 mg., 0.0013 mole) in 5 ml. of hexane was shaken 5 min. with 5 ml. of concentrated hydrochloric acid and worked up in the usual way. Assuming the amount of

alcohols XLIII and XLIV to be negligible (as indicated by IR) the product was 76% trans chloride XLII and 33% cis chloride XLI. No alkene XXXVIII could be detected by NMR as evidence by absence of a signal at δ 5.95.

A suspension of trans alcohol [0.30 g., 0.013 mole, m.p. 110.5-111.5° (hexane), 98% by GLC (5% silicone rubber on Chromosorb G)] in 50 ml. of pentane was cooled to -78°. Hydrogen chloride was bubbled in for 1 hr. By NMR analysis the product was 85% trans chloride XLII and 15% cis chloride XLI.

cis-4-tert-Butyl-1-phenylcyclohexanol (XLIII) was isolated by chromatography of the cis-trans mixture (50:50) on silicic acid (2.0 g. on a 3 x 23 cm. column). Development was with hexane using 100-ml. fractions. Fractions 10-11 contained 50 mg. of cis alcohol XLIII, m.p. 138-142° (methanol-water) (lit.,¹⁶ 158-159°). NMR absorption (Plate XX) was observed at δ 0.77 [$(\text{CH}_3)_3\text{C}$], δ 1.82 (OH), and δ 7.3 (aromatic H). A doublet centered at δ 2.50, corresponding to two protons, was cleanly separated from the remaining absorption (δ 0.7-2.0) and tentatively assigned to protons on C-2 and C-6.

Reaction of cis alcohol XLIII with hydrochloric acid at 25° was performed as described for the trans isomer XLIV. The product was 55% trans (XLII) and 45% cis chloride XLI (again assuming the alcohol content to be negligible as evidenced by IR absorption for the hydroxyl group).

Preparation of cis- and trans-4-tert-Butyl-1-phenylcyclohexane: (LXXX) and (LXXXI). A mixture of 6.0 g. (0.028 mole) of 4-tert-butyl-1-phenylcyclohexene (XXXVIII), 10 g. of W-6 Raney nickel, and 50 ml. of absolute ethanol was stirred 30 min., gravity filtered, and the

filtrate concentrated to 3.5 g. (59%) of the cis and trans alkanes LXXX and LXXXI. Complete reduction of XXXVIII was indicated by TLC (alumina with pentane) and GLC analysis (5% SE-30 on Chromosorb W).

Equilibration of the alkane mixture was accomplished by the method of Garbisch.¹⁶ A mixture of 2.8 g. of cis-trans alkane mixture, 100 mg. of 10% palladium on charcoal, and 10 ml. of glacial acetic acid was heated under reflux 1.5 hr. then filtered into 25 ml. of water. Crystalline trans-4-tert-butyl-1-phenylcyclohexane (LXXXI) appeared immediately. Recrystallization from ethanol gave XLLLI m.p. 38° (lit.,¹⁶ 41-2°).

The NMR spectrum of LXXXI (Plate XXVI) showed absorption at δ 0.88 [$(\text{CH}_3)_3\text{C}$], δ 7.07 (aromatic H), and in a range of δ 1.0-2.8 (aliphatic ring H) and indicated the product was free of the cis isomer LXXX. Absorption occurring at δ 0.80 and δ 2.97 in the mixture of cis and trans alkanes LXXX and LXXXI was attributed to the tert-butyl and C-1 protons, respectively, of the cis alkane LXXX (Plate XXVII).

Preparation of 1-chloro-1-phenylcyclohexane (XLV): Hydrogen chloride was bubbled for 1 hr. into a solution of 3.0 g. (0.019 mole) 1-phenylcyclohexene (LX) (See Part I) in 50 ml. of pentane at -78°. The colorless liquid remaining after removal of solvent was kept at 0.1 mm. (25°) until a constant index of refraction was achieved, n_D^{27} 1.5524. Characteristic IR absorption (Plate XI) was observed at 835 and 638 cm^{-1} with weak shoulders at 823 and 680 cm^{-1} . The NMR spectrum (Plate XXIII) showed only multiplets at δ 1.8 and δ 7.3.

Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{Cl}$: C, 74.01; H, 7.77; Cl, 18.22.

Found: C, 74.86; H, 7.51; Cl, 17.52.

A portion of the material used for analysis showed evidence of decom-

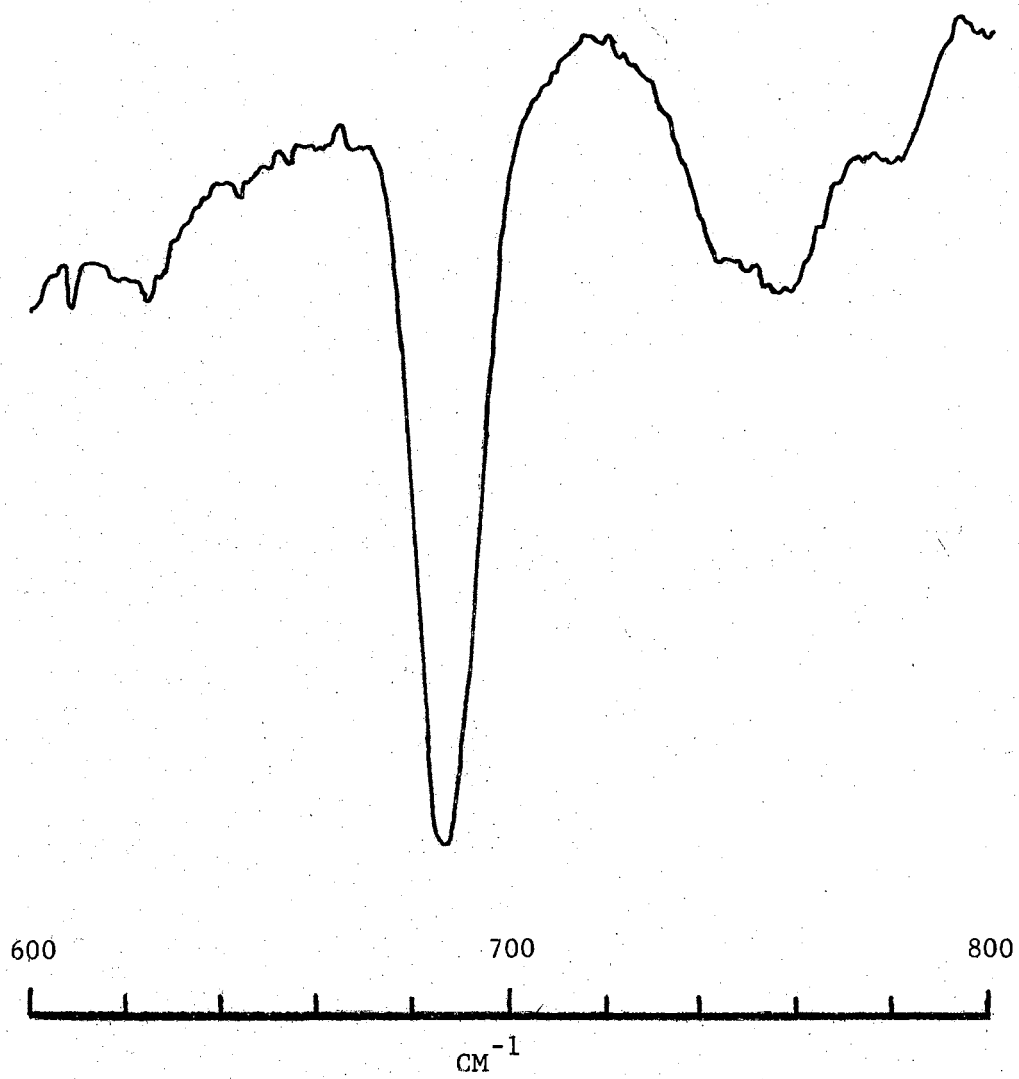
position within a day (discoloration and evolution of HCl).

1-Phenylcyclohexanol (LIX) (Part I, 3.77 g., 0.0215 mole) suspended in 15 ml. of hexane was shaken 5 min. with 50 ml. of concentrated hydrochloric acid. The usual work-up gave a liquid identified by its IR (Part I, Plate V) and NMR (Plate XXV) spectra as LX.

With the same procedure at -10 to 0° the product was 93% 1-chloro-1-phenylcyclohexane (XLV).

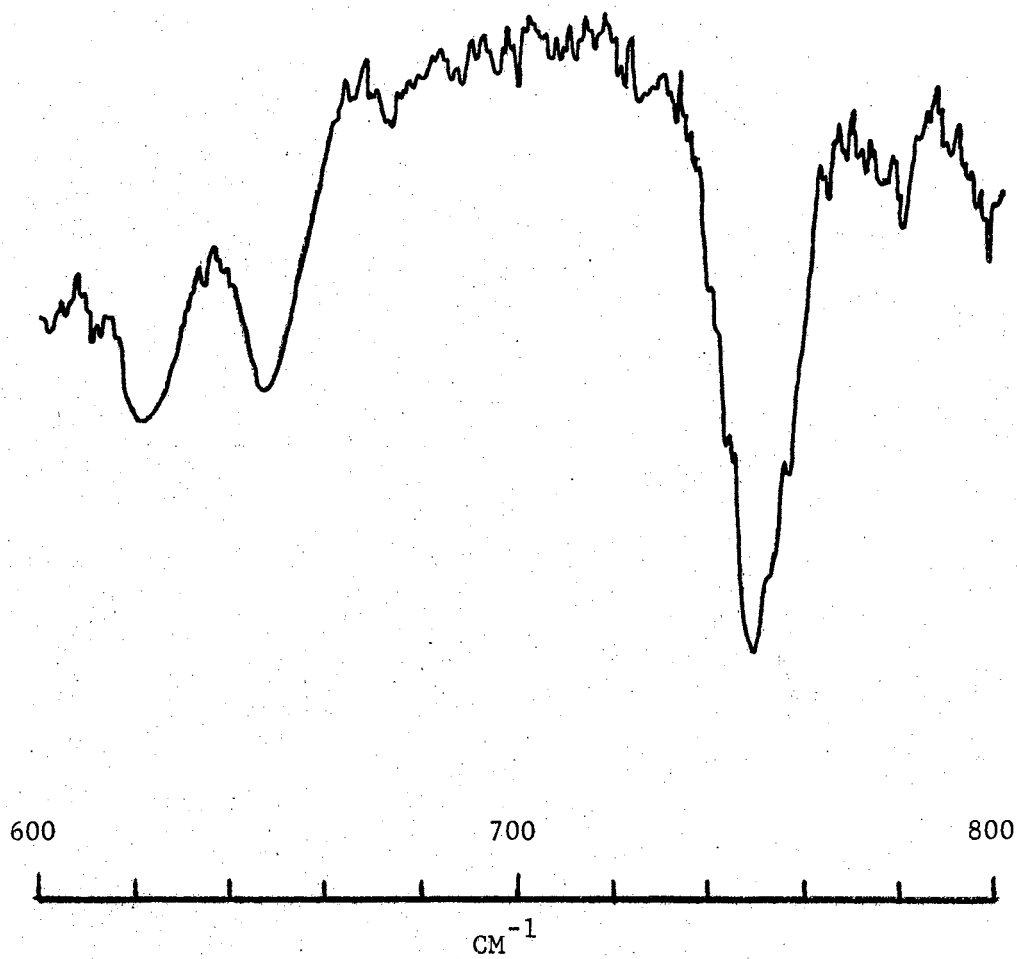
When XLV (η_D^{27} 1.5515) was subjected to the procedure at 25° , chloride XLV was recovered unaffected (η_D^{26} 1.5520).

Plate I



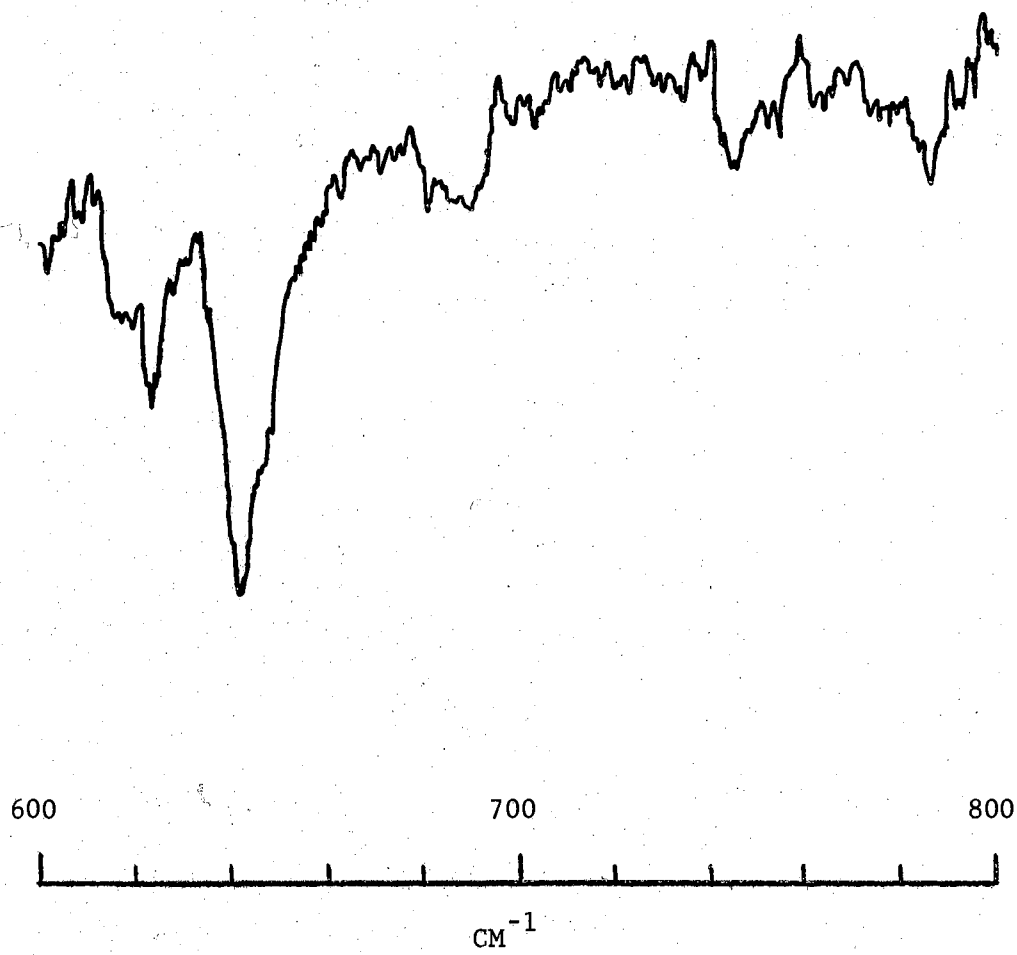
cis-4-tert-Butyl-1-phenylcyclohexyl Chloride (XLI),
Solution in n-Heptane

Plate II



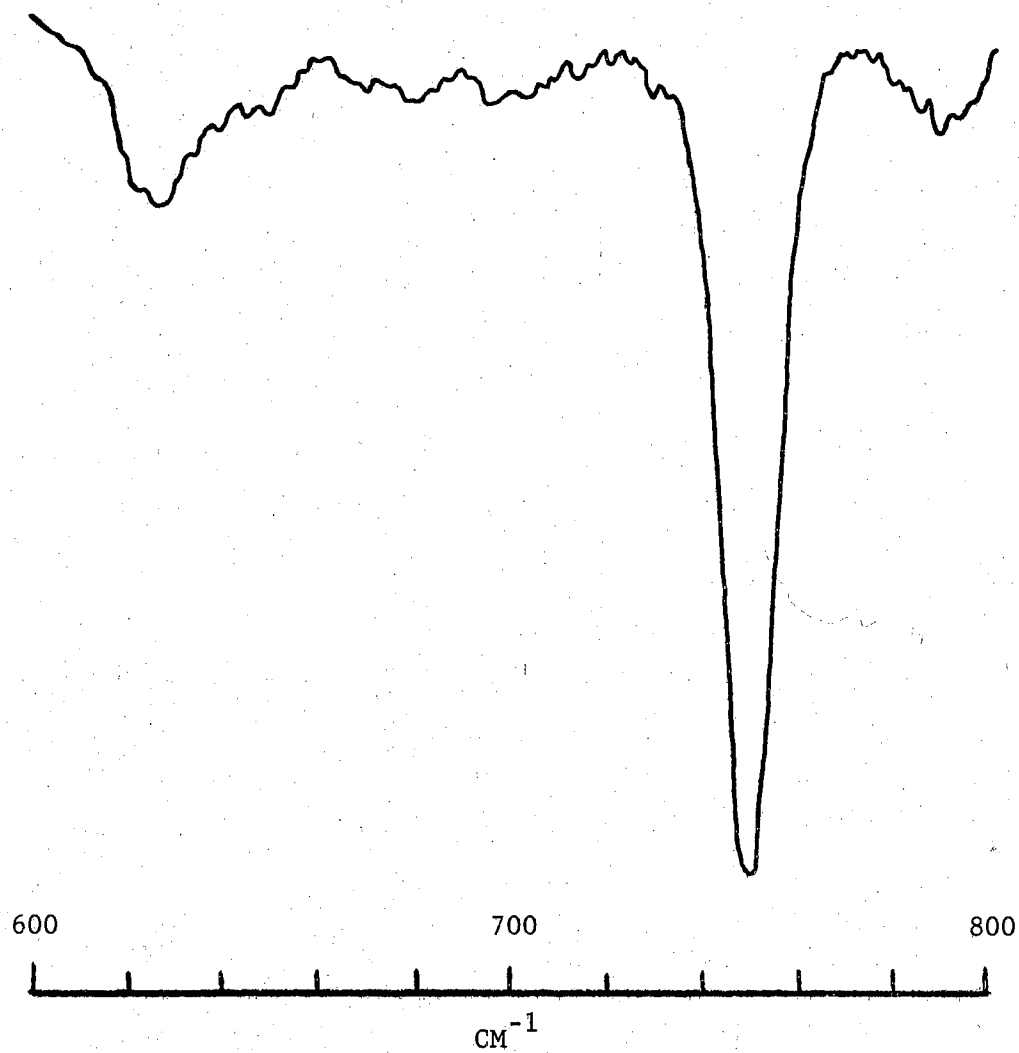
trans-4-tert-Butyl-1-phenylcyclohexyl Chloride (XLII),
Solution in n-Heptane

Plate III



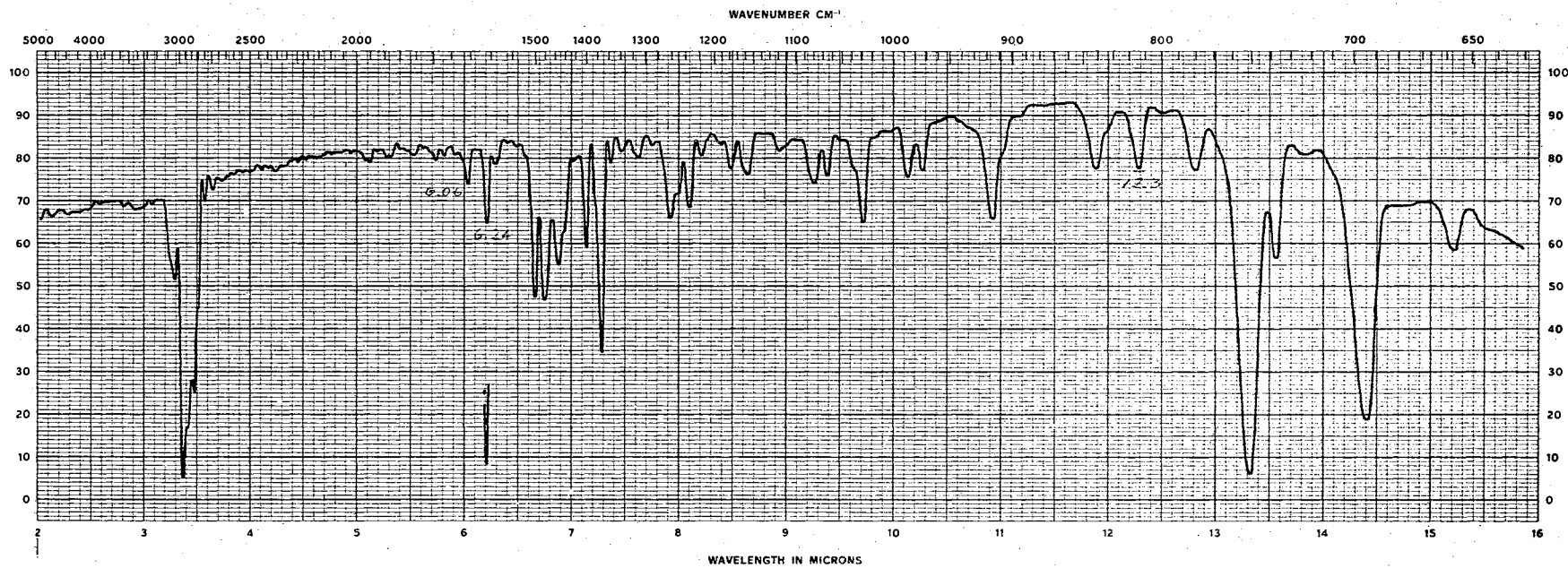
1-Chloro-1-phenylcyclohexane (XLV),
Neat Liquid

Plate IV



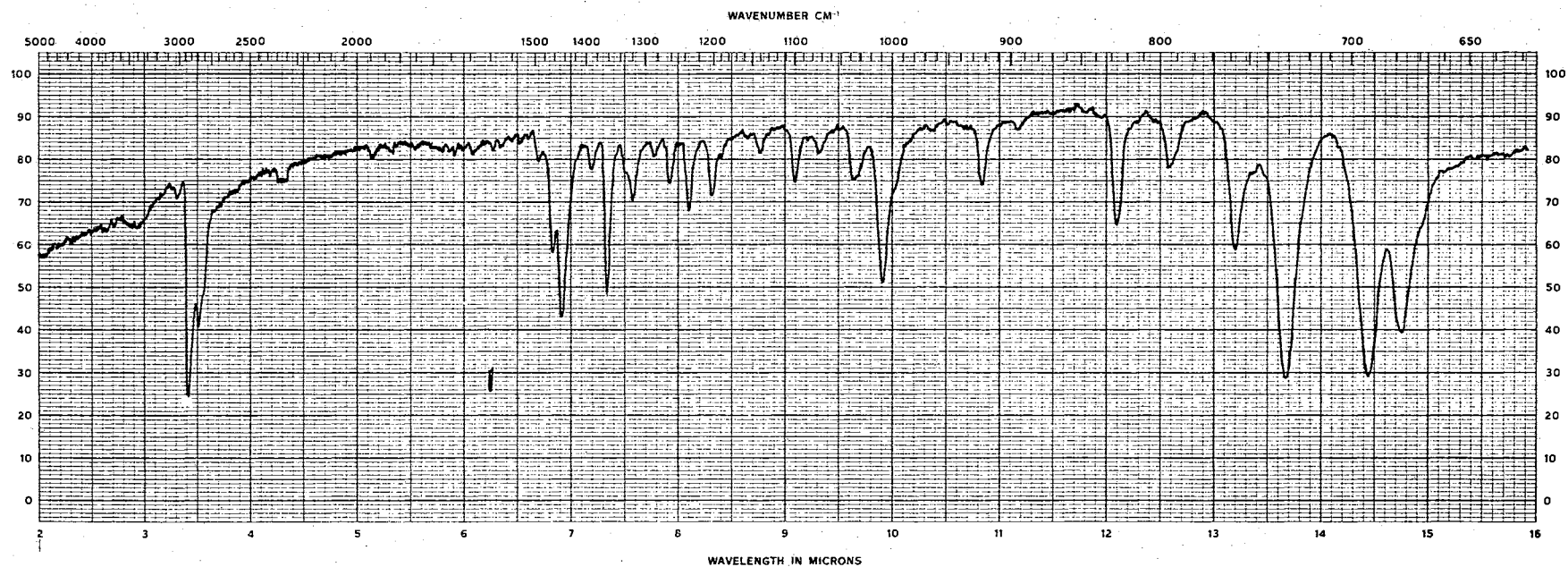
trans-4-tert-Butyl-1-phenylcyclohexane (LXXXI),
Solution in n-Heptane

Plate V



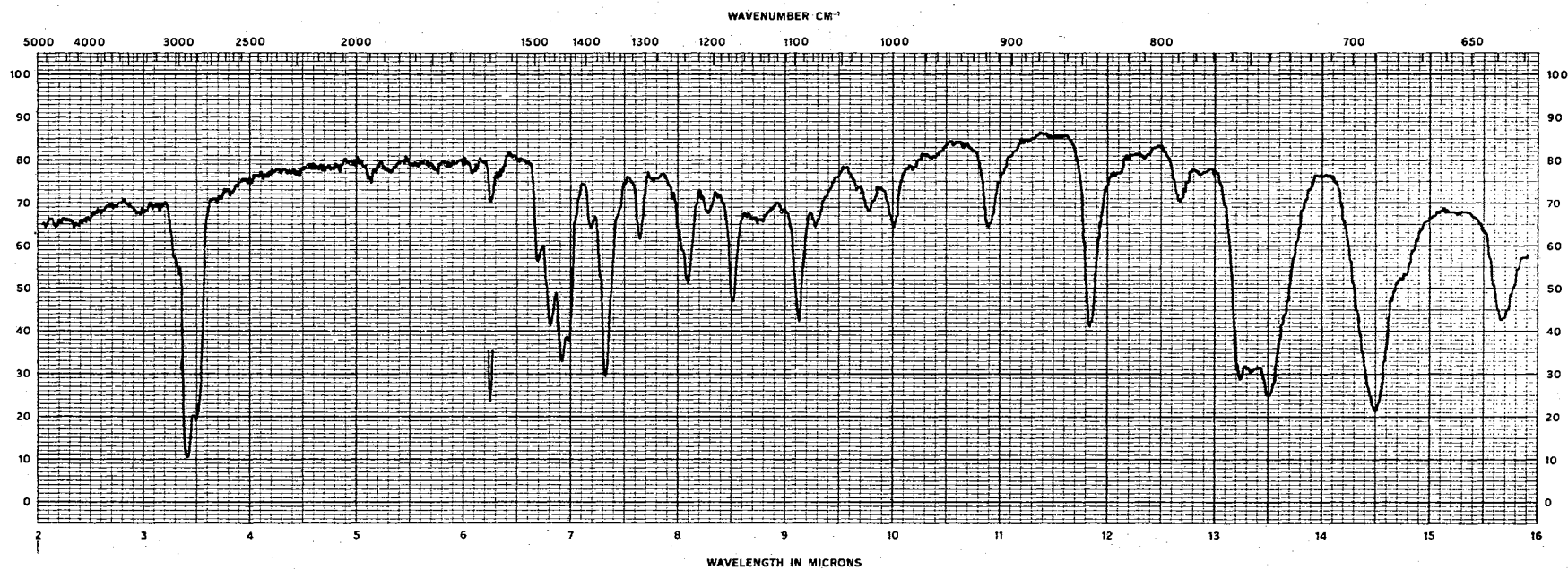
4-tert-Butyl-1-phenylcyclohexene (XXXVIII), Film on NaCl Plates

Plate VI



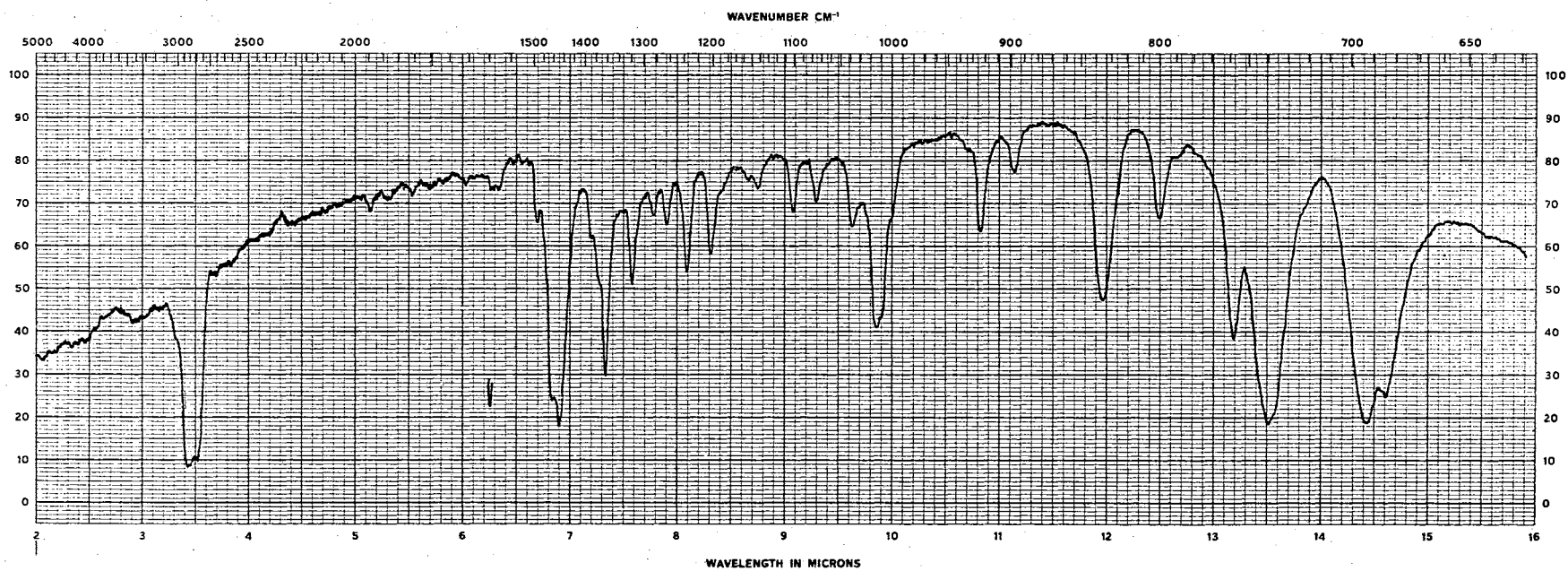
cis-4-tert-Butyl-1-phenylcyclohexyl Bromide (XXXIX), KBr Pellet

Plate VII



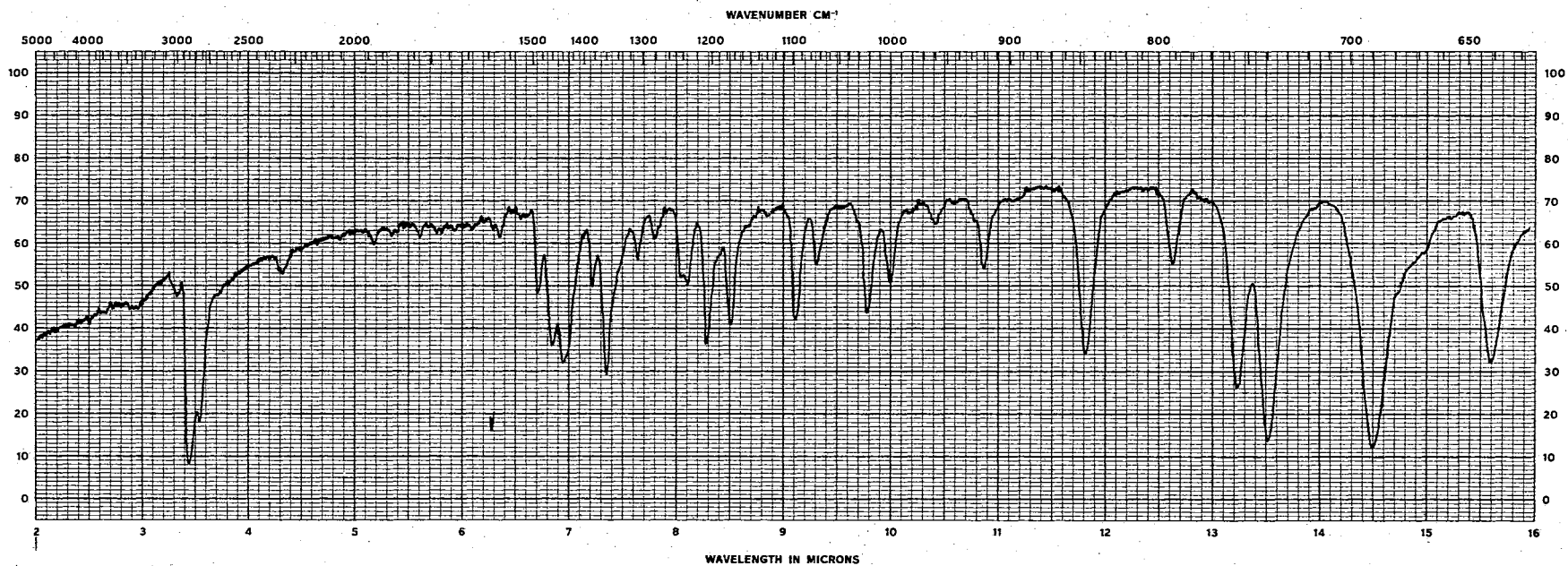
trans-4-tert-Butyl-1-phenylcyclohexyl Bromide (XL), KBr Pellet

Plate VIII



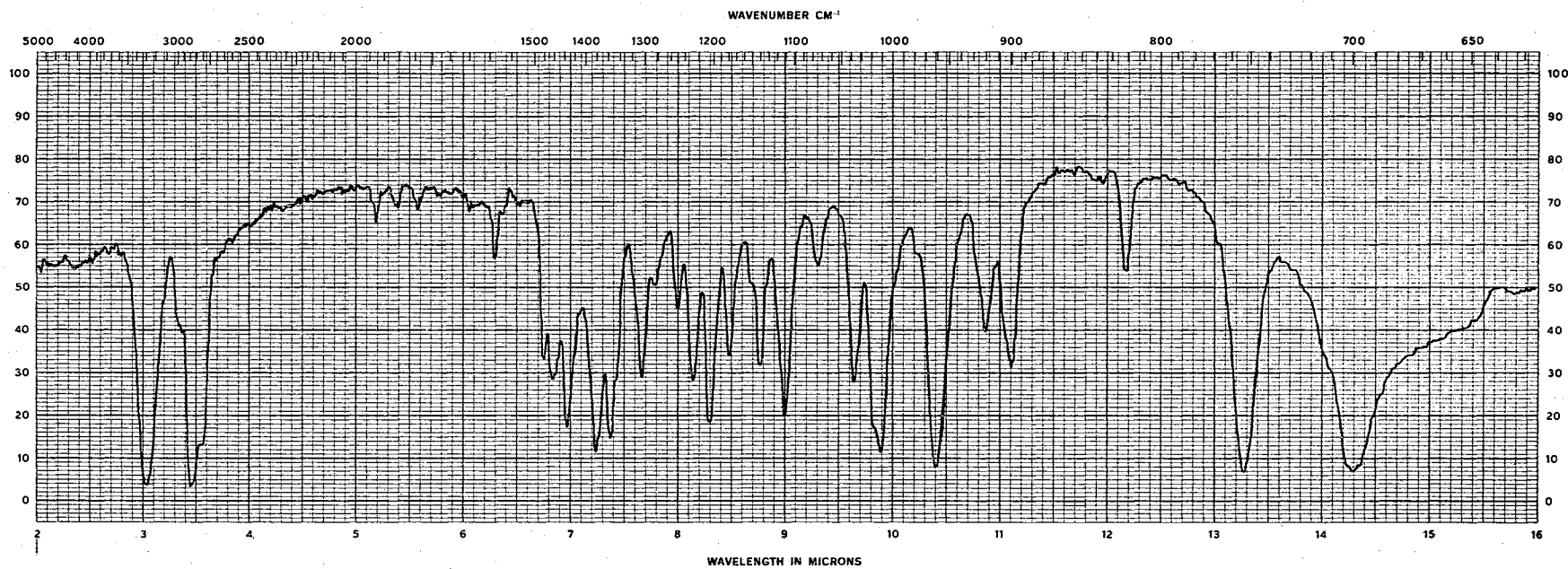
cis-4-tert-Butyl-1-phenylcyclohexyl Chloride (XLI), Nujol Mull on NaCl Plates

Plate IX



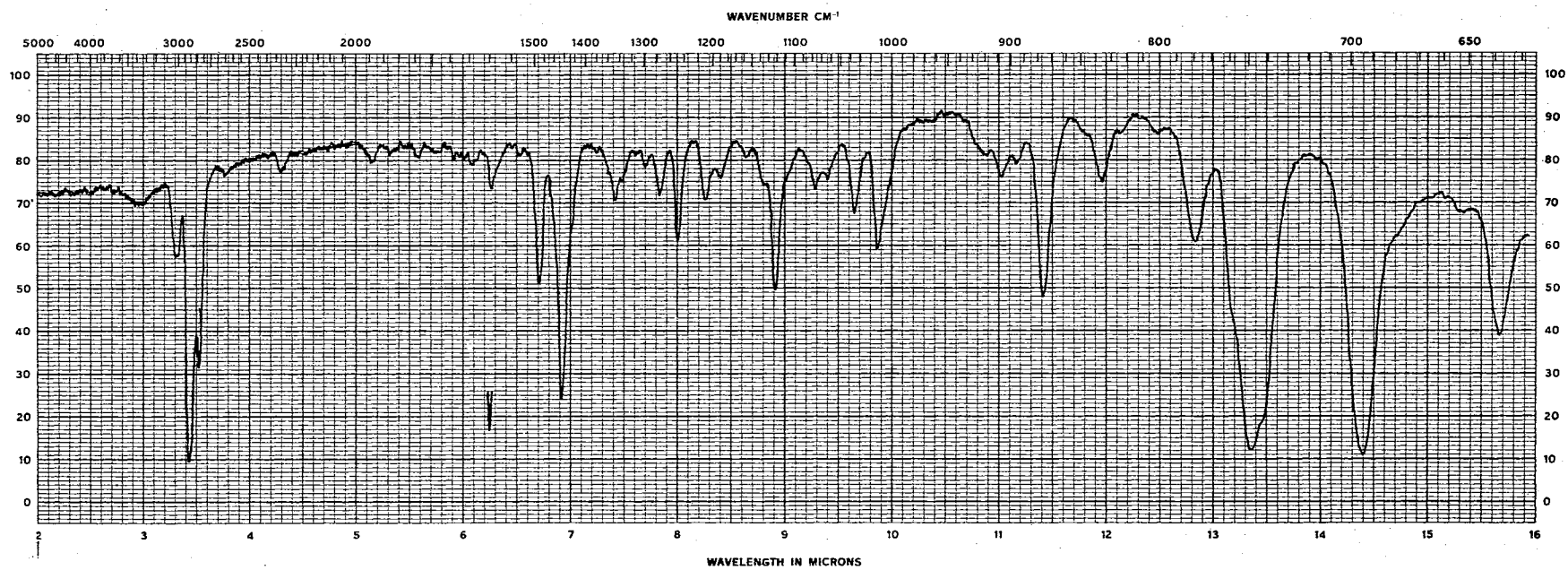
trans-4-tert-Butyl-1-phenylcyclohexyl Chloride (XLII), KBr Pellet

Plate X



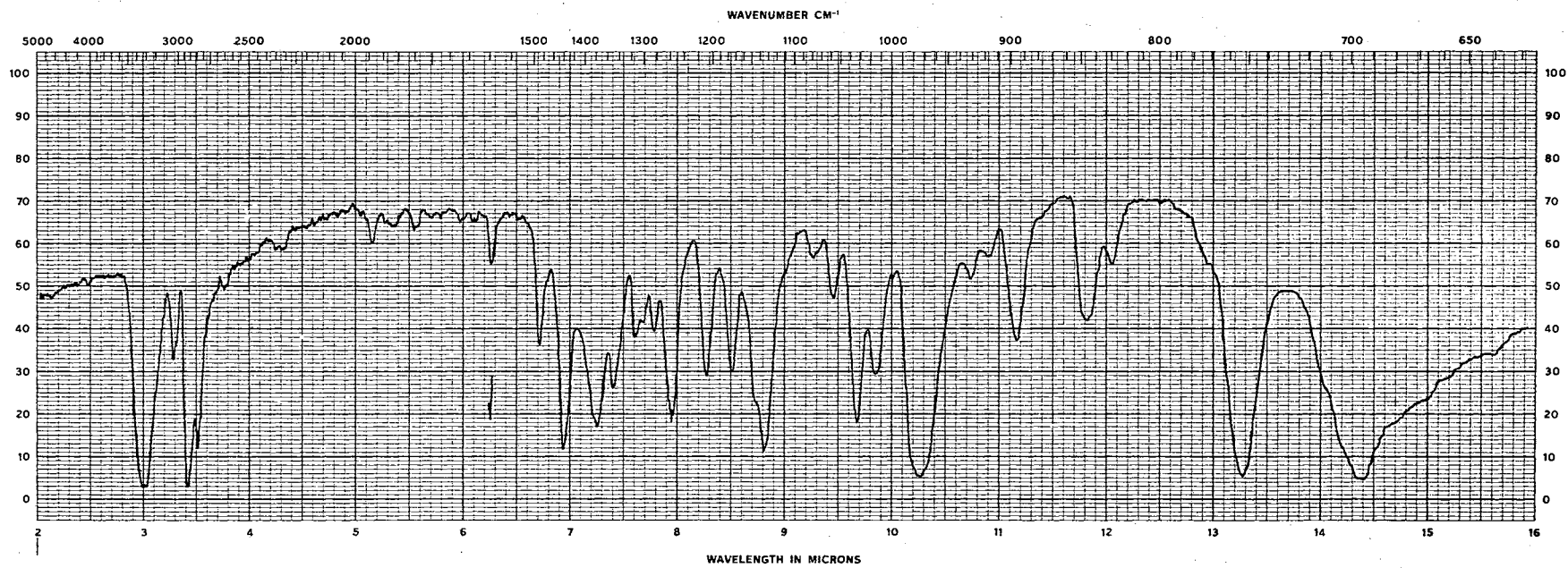
trans-4-tert-Butyl-1-phenylcyclohexanol (XLIV), KBr Pellet

Plate XI



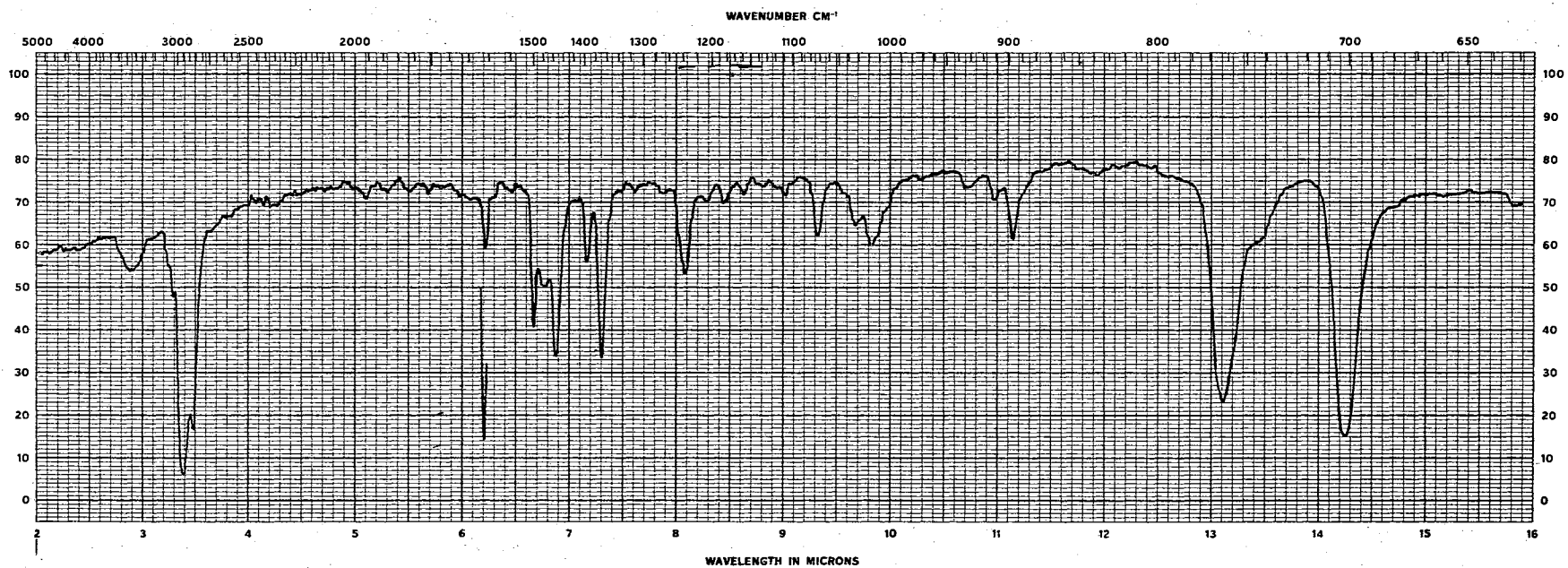
1-Chloro-1-phenylcyclohexane (XLV), Film on NaCl Plates

Plate XII



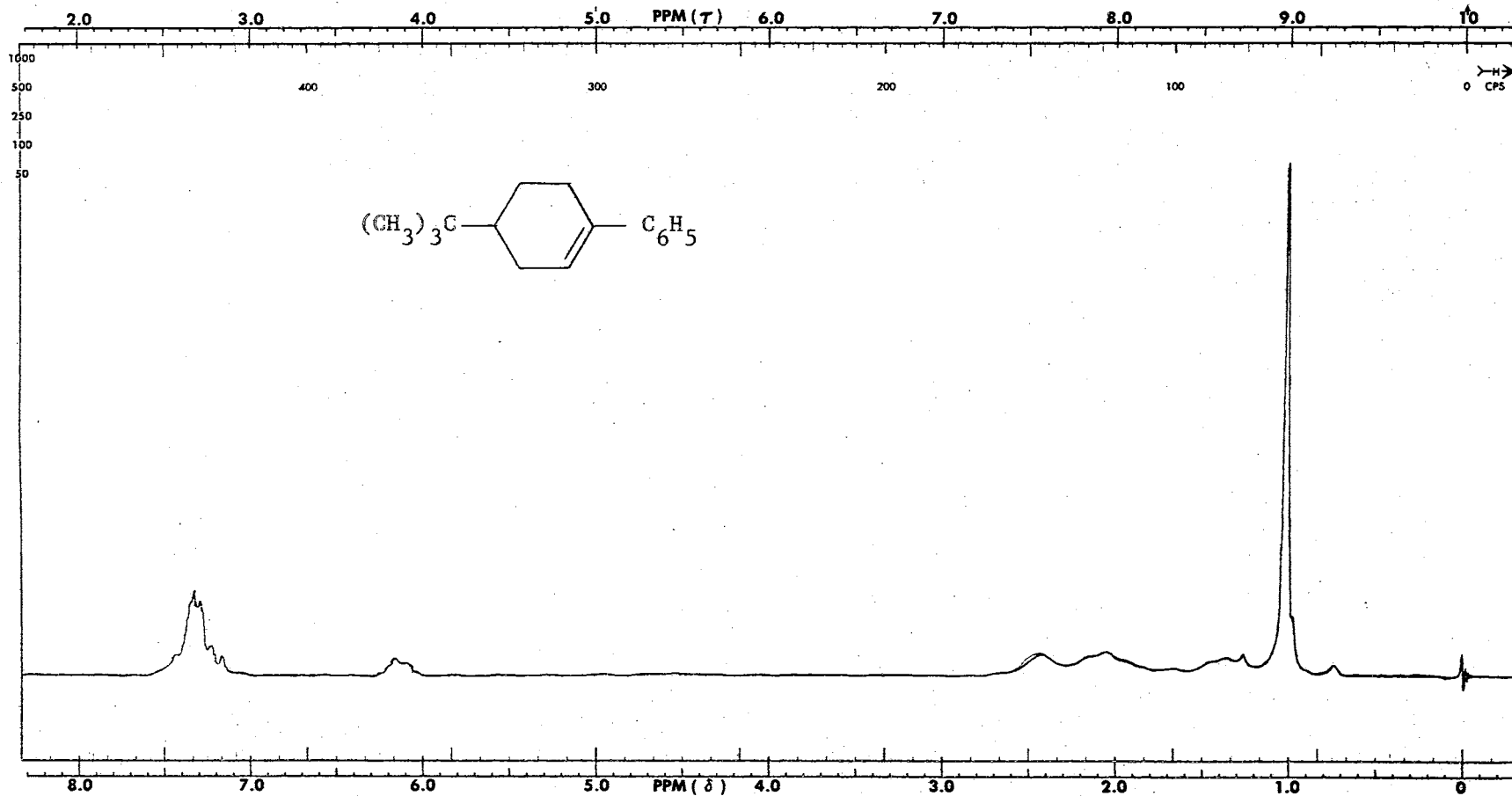
1-Phenylcyclohexanol (LIX), KBr Pellet

Plate XIII



trans-4-tert-Butyl-1-phenylcyclohexane (LXXXI), KBr Pellet

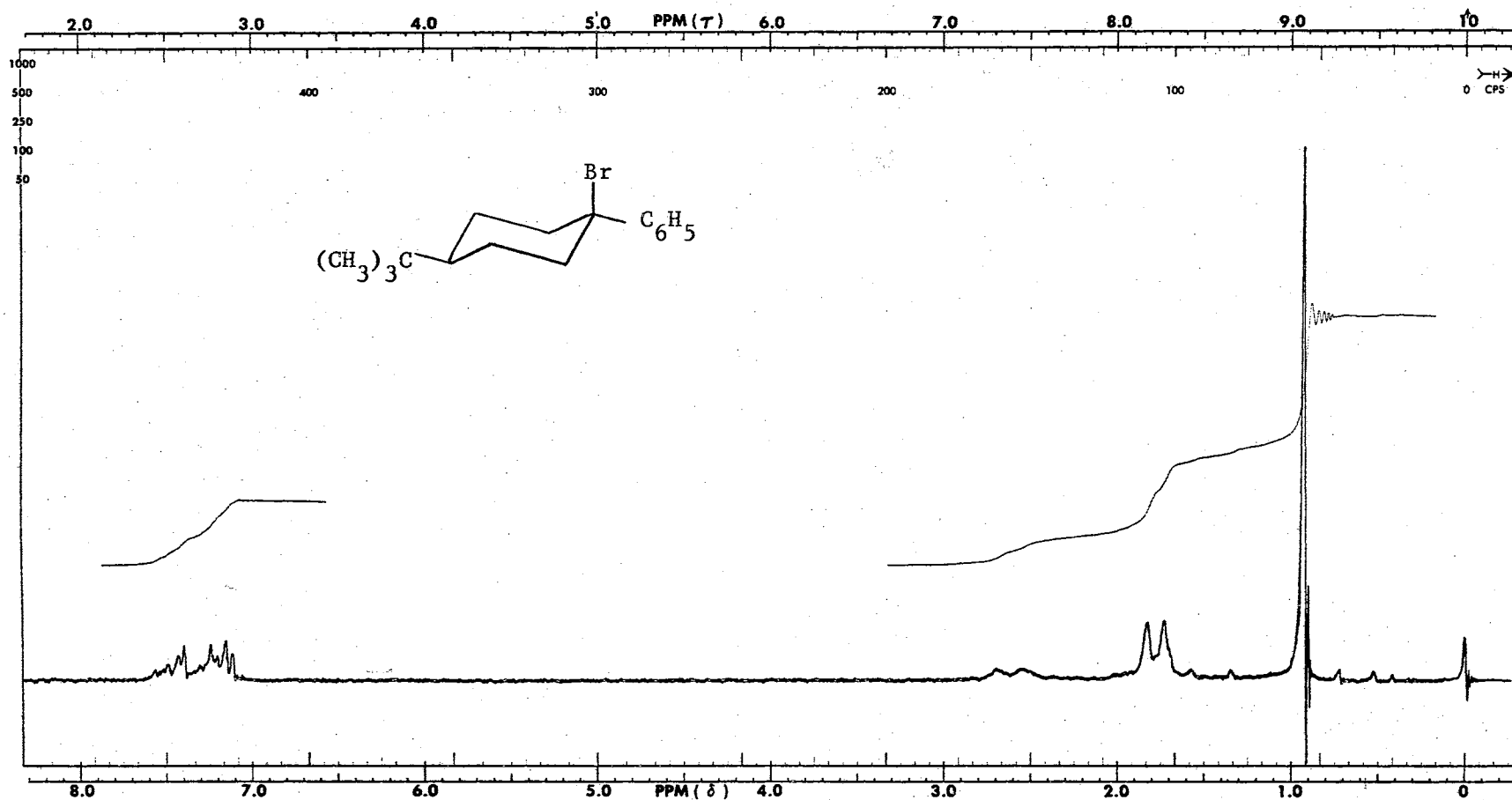
Plate XIV



4-tert-Butyl-1-phenylcyclohexene (XXXVIII)

Solvent.CCl ₄	R.F.	0.05 mg	S.W.	500 cps	S.A.	1.0
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

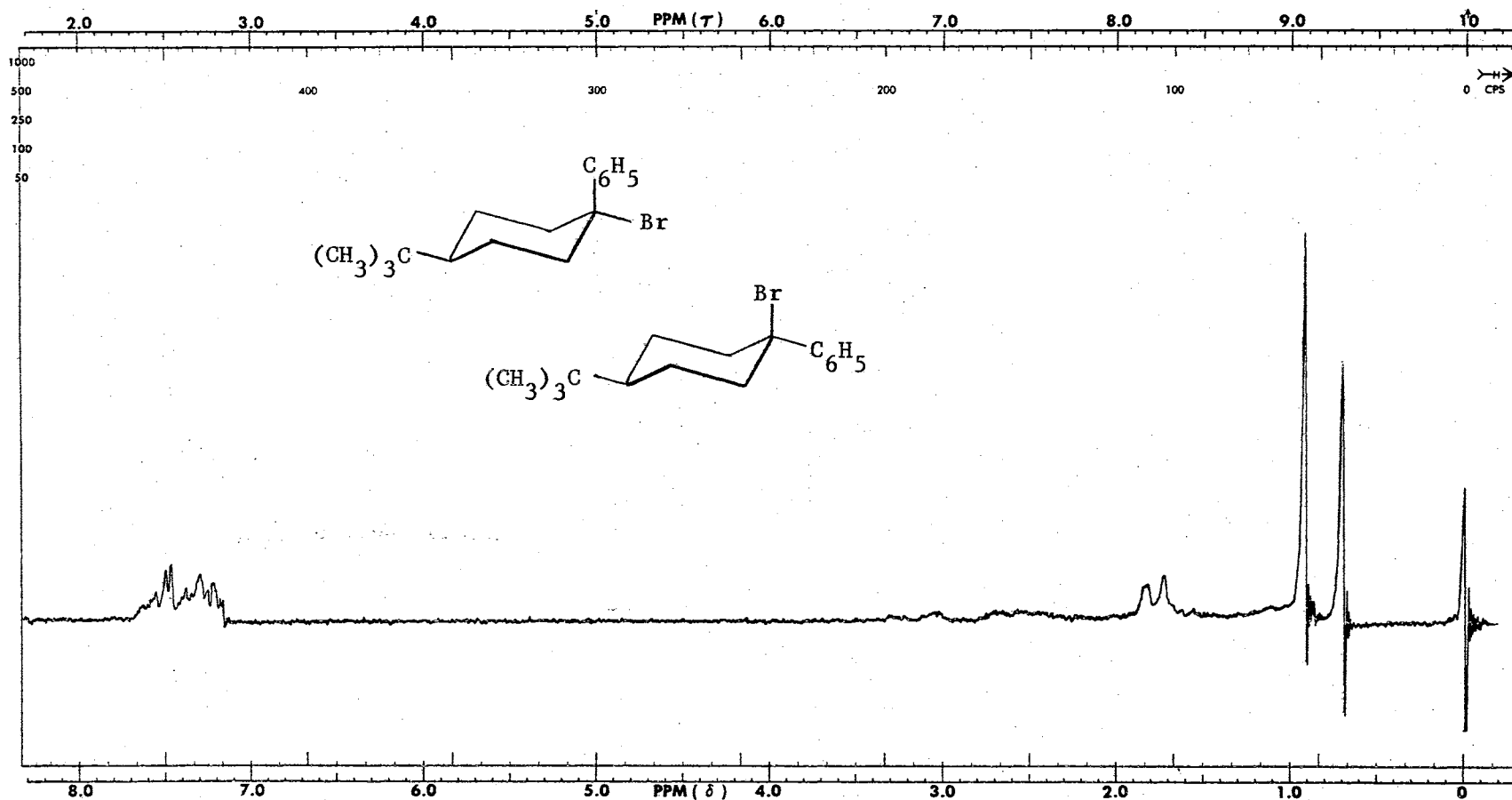
Plate XV



trans-4-tert-Butyl-1-phenylcyclohexyl Bromide (XL)

Solvent	CCl_4	R.F.	0.05 mG	S.W.	500 cps	S.A.	2.5
F.B.	4.0 cps	S.T.	250 sec	S.O.	22 cps	I.A.	80

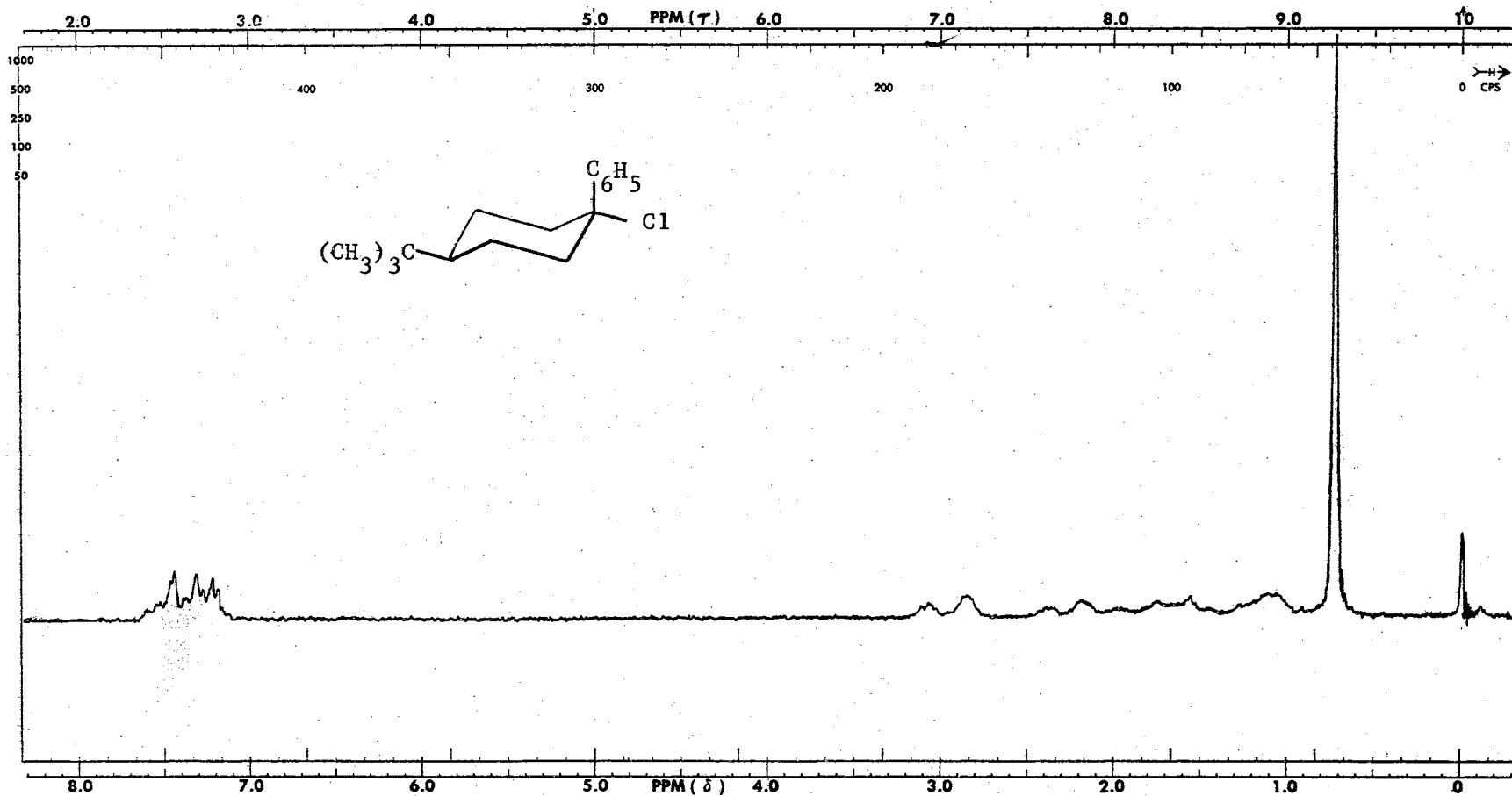
Plate XVI



cis- and trans-4-tert-Butyl-1-phenylcyclohexyl Bromides: (XXXIX and XL)

Solvent	CCl ₄	R.F.	0.015 mG	S.W.	500 cps	S.A.	1.2
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

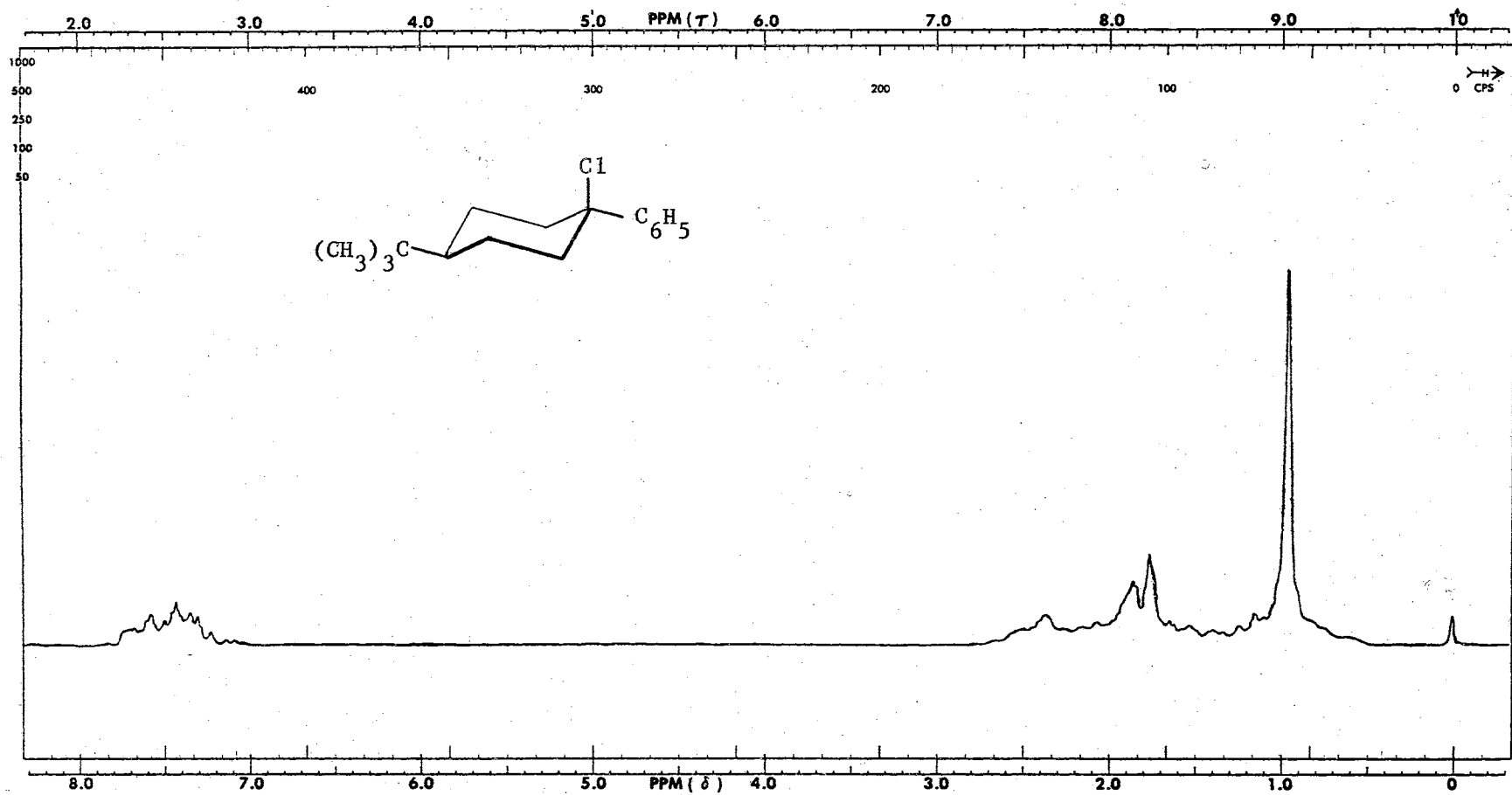
Plate XVII



cis-4-*tert*-Butyl-1-phenylcyclohexyl Chloride (XLI)

Solvent	CCl_4	R.F.	0.025 mg	S.W.	500 cps	S.A.	1.6
F.B.	4.0 cps	S.T.	250 sec	S.O.	36 cps	I.A.	off

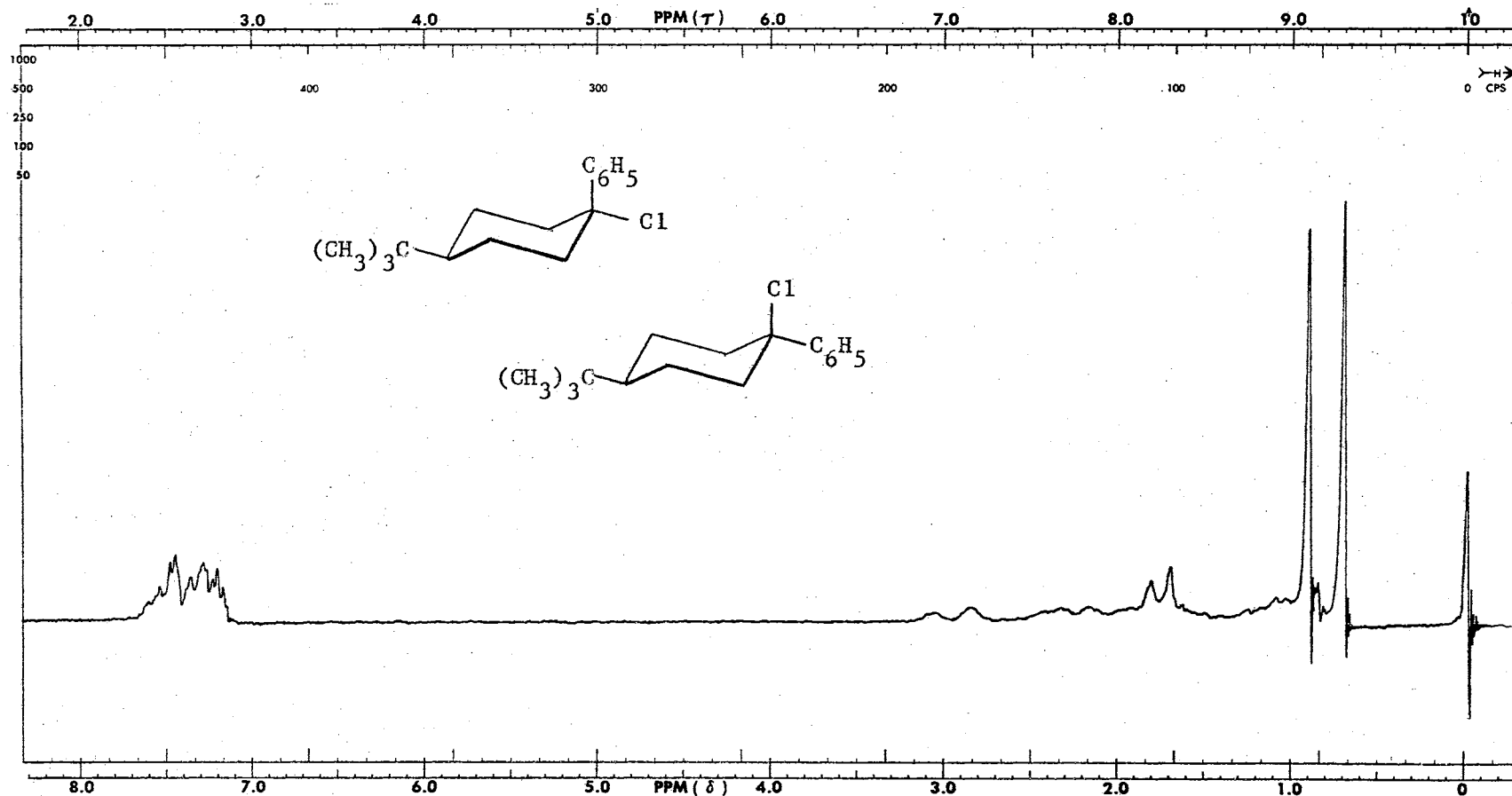
Plate XVIII



trans-4-tert-Butyl-1-phenylcyclohexyl Chloride (XLII)

Solvent	CCl_4	R.F.	0.025 mg	S.W.	500 cps	S.A.	4.0
F.B.	2.0 cps	S.T.	250 cps	S.O.	20 cps	I.A.	off

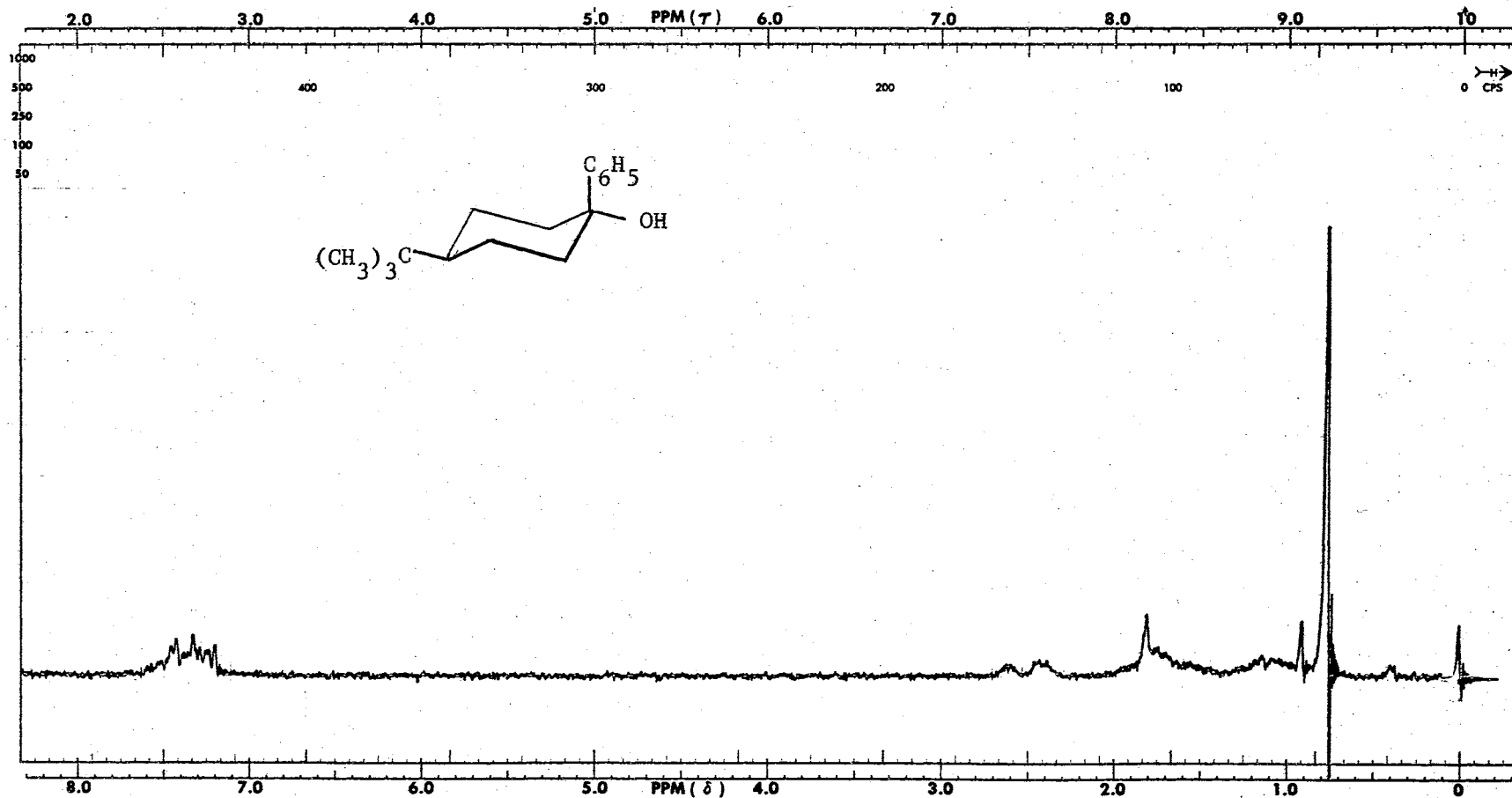
Plate XIX



cis- and trans-4-tert-Butyl-1-phenylcyclohexyl Chlorides (XLI and XLII)

Solvent	CCl ₄	R.F.	0.04 mg	S.W.	500 cps	S.A.	1.6
F.B.	2.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

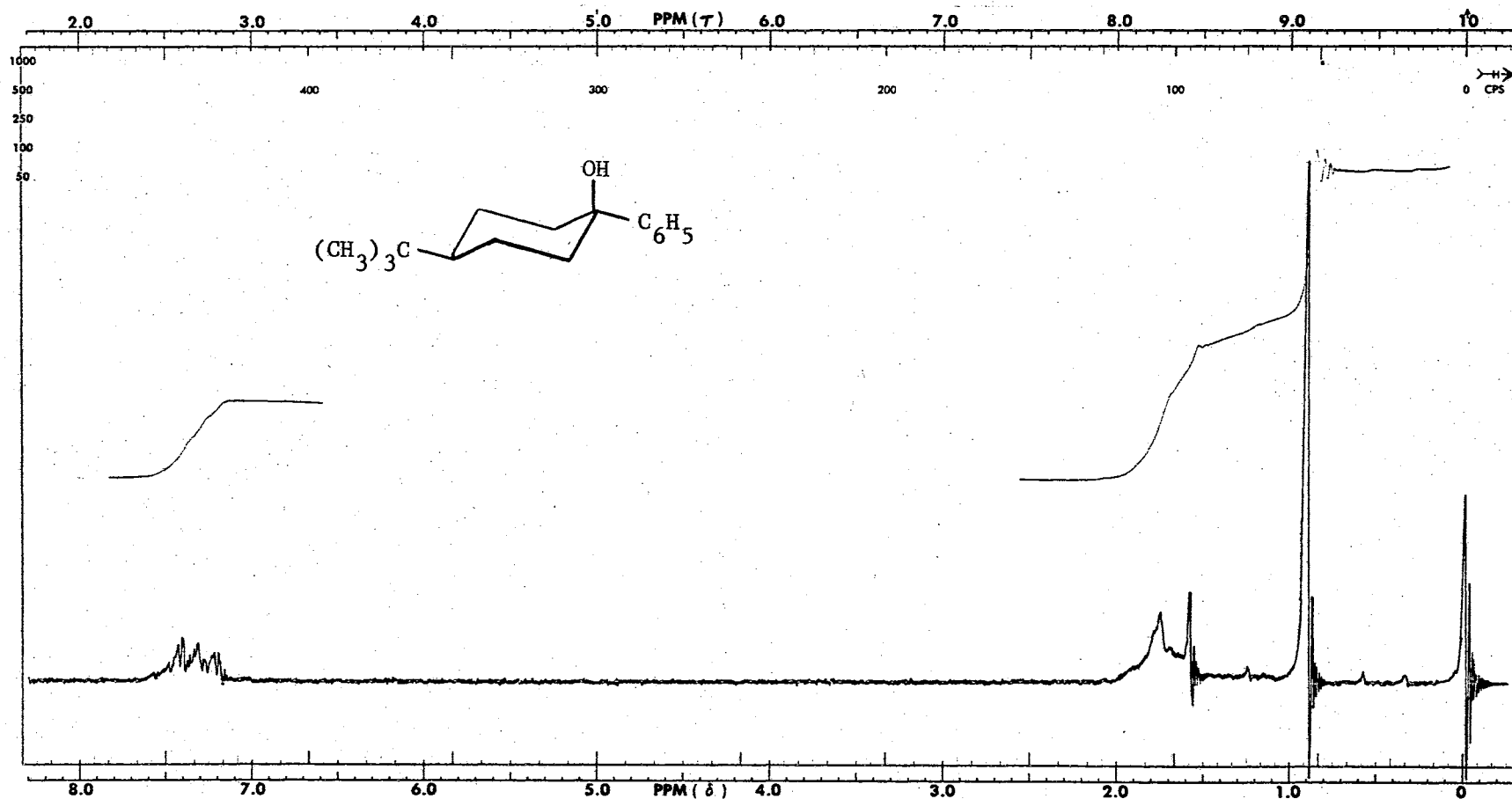
Plate XX



cis-4-*tert*-Butyl-1-phenylcyclohexanol (XLIII)

Solvent	CDCl ₃	R.F.	0.05 mg	S.W.	500 cps	S.A.	16
F.B.	2.0 cps	S.T.	250 sec	S.O.	10 cps	I.A.	off

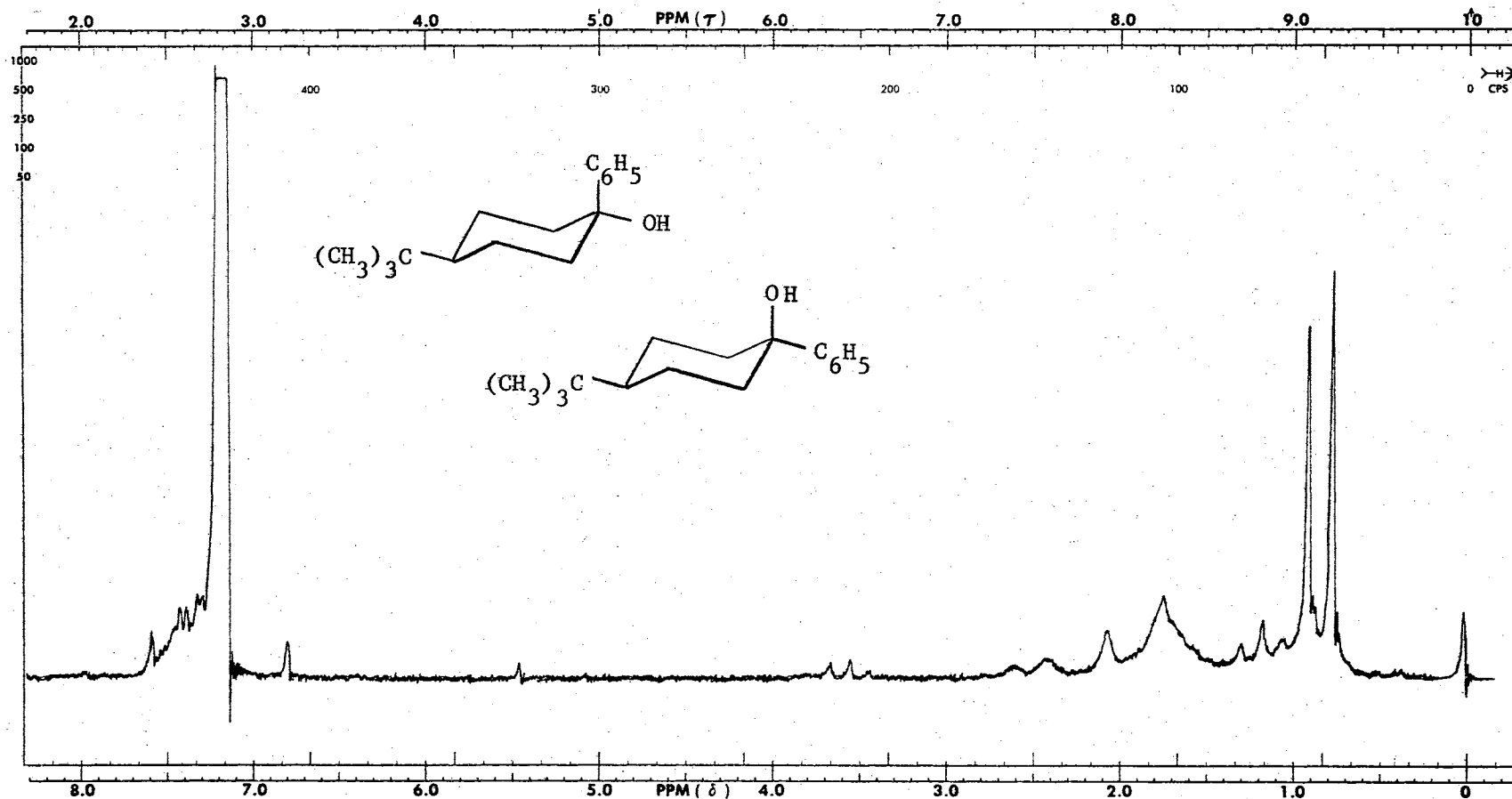
Plate XXI



trans-4-*tert*-Butyl-1-phenylcyclohexanol (XLIV)

Solvent	CDCl ₃	R.F.	0.05 mG	S.W.	500 cps	S.A.	3.2
F.B.	4.0 cps	S.T.	250 sec	S.O.	36 cps	I.A.	80

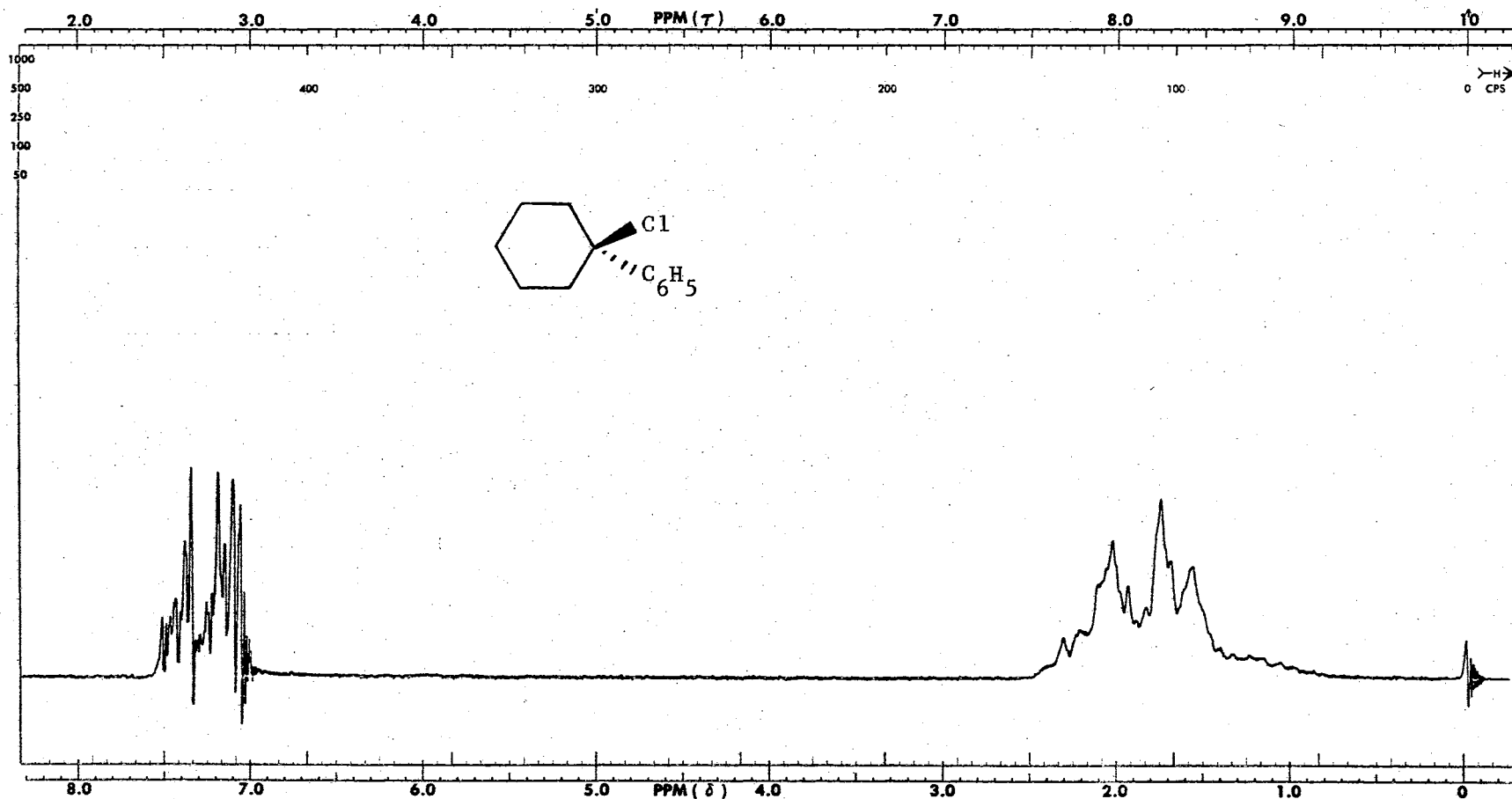
Plate XXII



cis- and trans-4-tert-Butyl-1-phenylcyclohexanols: (XLIII and XLIV)

Solvent	CHCl ₃	R.F.	0.05 mG	S.W.	500 cps	S.A.	4.0
F.B.	4.0 cps	S.T.	250 sec	S.O.	4 cps	I.A.	off

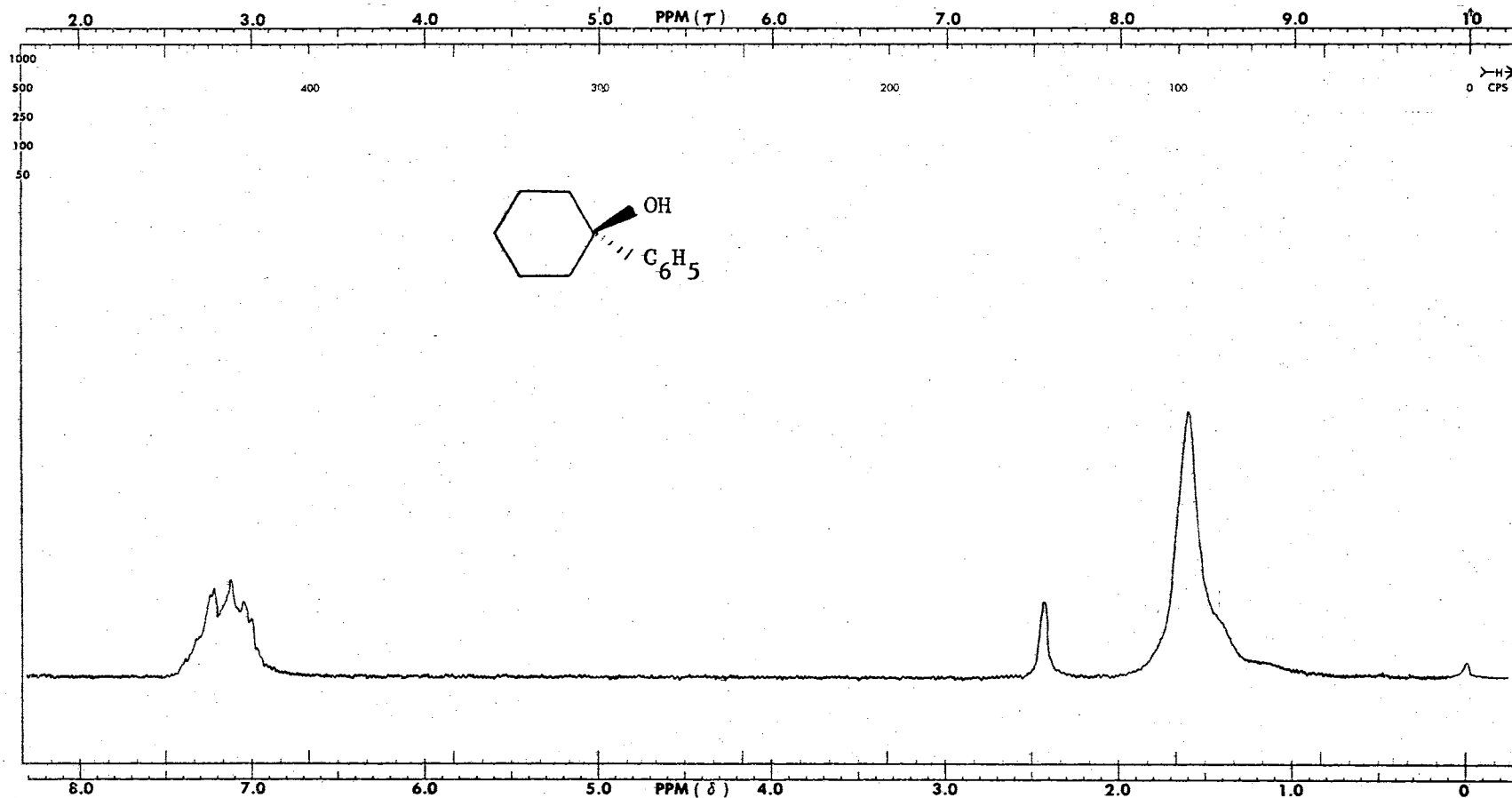
Plate XXIII



1-Chloro-1-phenylcyclohexane (XLV)

Solvent	CCl ₄	R.F.	0.05 mg	S.W.	500 cps	S.A.	2.5
F.B.	4.0 cps	S.T.	250 sec	S.O.	6 cps	I.A.	off

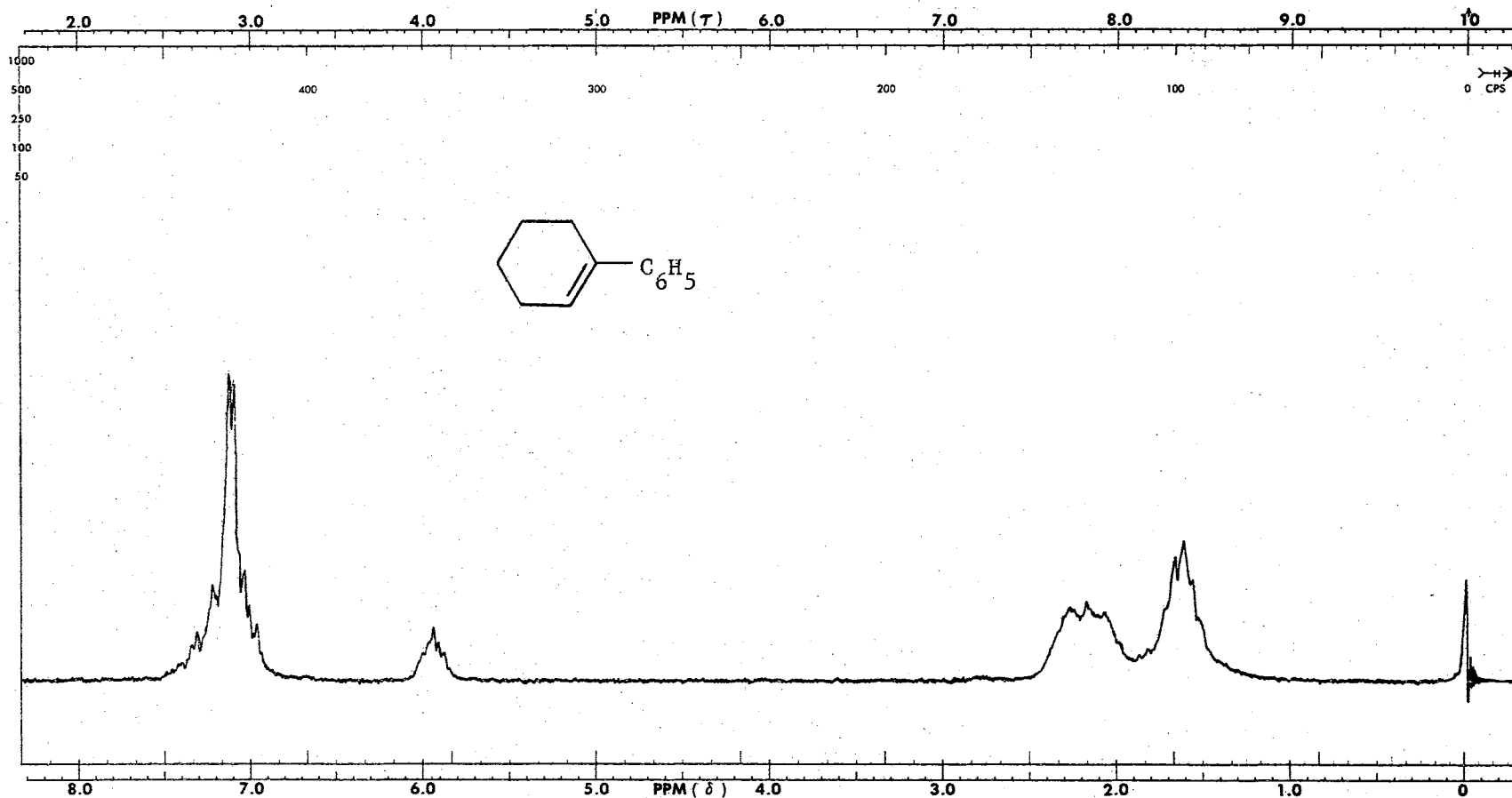
Plate XXIV



1-Phenylcyclohexanol (LIX)

Solvent	CCl ₄	R.F.	0.05 mg	S.W.	500 cps	S.A.	3.2
F.B.	2.0 cps	S.T.	250 sec	S.O.	29 cps	I.A.	off

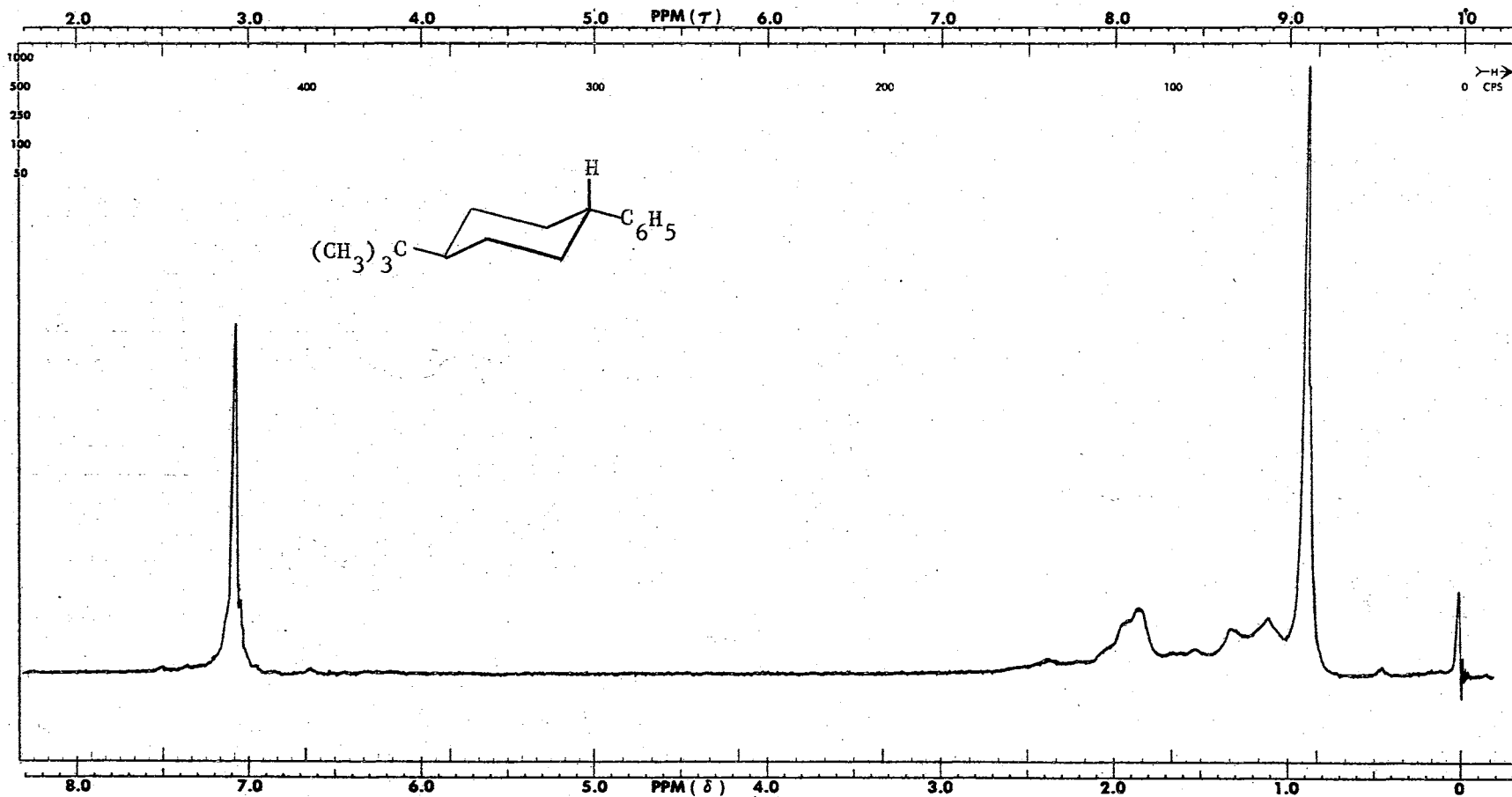
Plate XXV



1-Phenylcyclohexene (LX)

Solvent	CCl_4	R.F.	0.05 mg	S.W.	500 cps	S.A.	3.2
F.B.	2.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

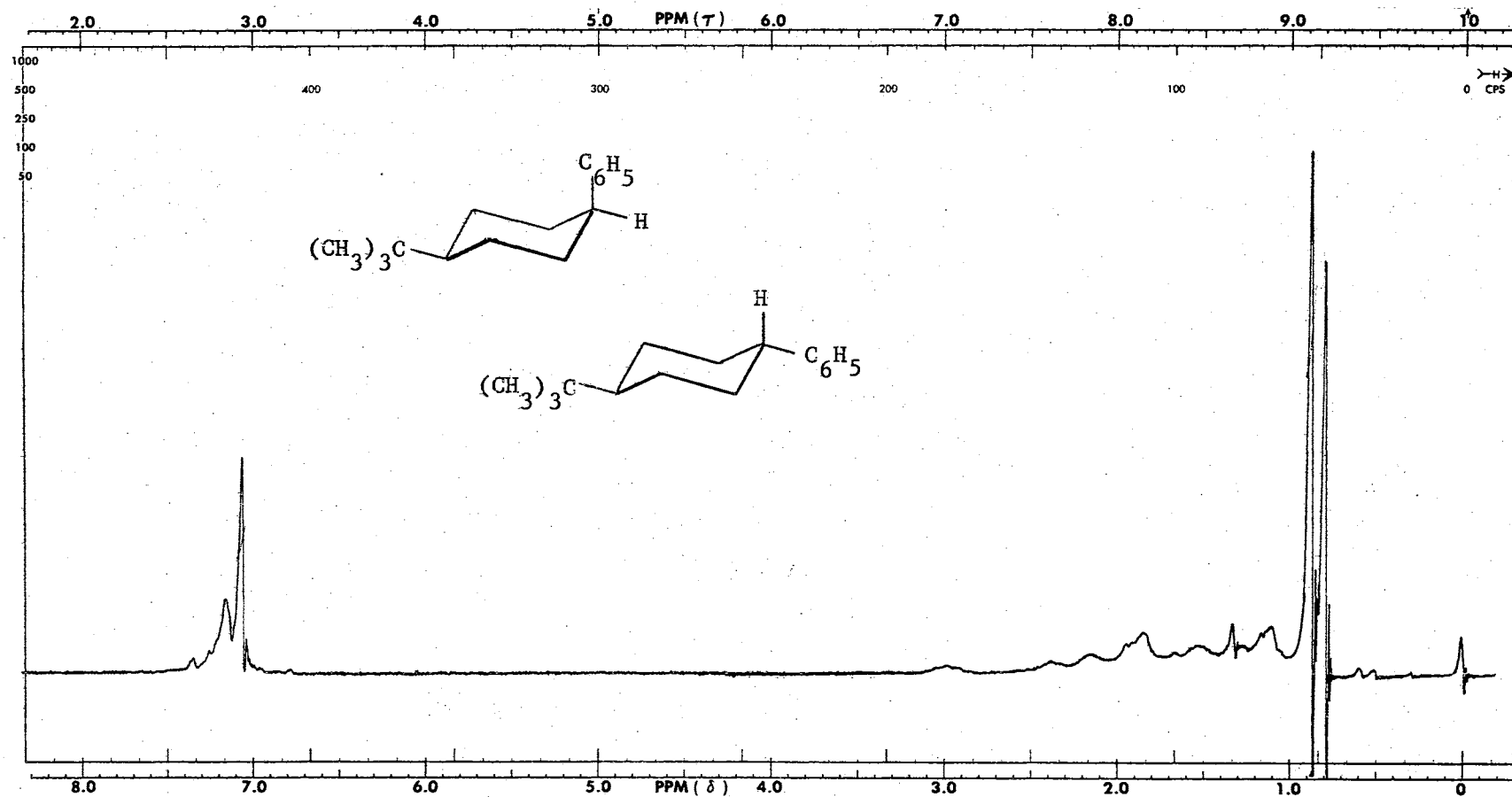
Plate XXVI



trans-4-tert-Butyl-1-phenylcyclohexane (LXXXI)

Solvent	CCl ₄	R.F.	0.05 mG	S.W.	500 cps	S.A.	2.0
F.B.	4.0 cps	S.T.	250 sec	S.O.	30 cps	I.A.	off

Plate XXVII



cis- and trans-4-tert-Butyl-1-phenylcyclohexanes (LXXX and LXXXI)

Solvent	CCl ₄	R.F.	0.05 mg	S.W.	500 cps	S.A.	1.6
F.B.	4.0 cps	S.T.	250 sec	S.O.	5 cps	I.A.	off

BIBLIOGRAPHY

1. Anet, F. A. L., *Can. J. Chem.*, 39, 789 (1961).
2. Barton, D. H. R., *Experientia*, Suppl. II, 121 (1955).
3. Barton, D. H. R., Campos-Neves, A. da S., and Cookson, R. C., *J. Chem. Soc.*, 3500 (1956).
4. Barton, D. H. R., Page, J. E., and Shoppee, C. W., *J. Chem. Soc.*, 331 (1956).
5. Berlin, A. J., and Jensen, F. R., *Chem. Ind. (London)*, 998 (1960).
6. Brown, H. C., *Science*, 103, 385 (1946).
7. Cole, A. R. H., Jones, R. N., and Dobriner, K., *J. Am. Chem. Soc.*, 74, 5571 (1952).
8. Curtin, D. Y., and Kellom, D. B., *J. Am. Chem. Soc.*, 75, 6011 (1953).
9. Dewar, M. J. S., and Fahey, R. C., *J. Am. Chem. Soc.*, 84, 2012 (1962).
10. Dewar, M. J. S., and Fahey, R. C., *J. Am. Chem. Soc.*, 85, 2245 (1963).
11. Dewar, M. J. S., and Fahey, R. C., *J. Am. Chem. Soc.*, 85, 2248 (1963).
12. Dewar, M. J. S., and Fahey, R. C., *J. Am. Chem. Soc.*, 85, 3645 (1963).
13. Eliel, E. L., Allinger, N. L., Angyal, S. J., and Morrison, G. A., "Conformational Analysis," J. Wiley and Sons, New York, N. Y., 1965.
14. Eucken, A., and Hellwege, K. H., Ed., "Landolt-Bornstein Atomic and Molecular Physical Properties," Vol. 1, Pt. 2, Springer, Berlin, 1951.
15. Garbisch, E. W., Jr., *J. Org. Chem.*, 26, 4165 (1961).
16. Garbisch, E. W., Jr., and Patterson, D. B., *J. Am. Chem. Soc.*, 85, 3228 (1963).

17. Gerrard, W., J. Chem. Soc., 741 (1946).
18. Gould, E. S., "Inorganic Reactions and Structure," Holt, Rinehart, and Winston, New York, N. Y., 1955.
19. Hammond, G. S., and Collins, C. H., J. Am. Chem. Soc., 82, 4323 (1960).
20. Hammond, G. S., and Nevitt, T. D., J. Am. Chem. Soc., 76, 4121 (1954).
21. Holder, C. H., and Mass, O., Can. J. Research, 16B, 453 (1938).
22. Hueckel, W., and Heyder, K., Ber., 96, 220 (1963).
23. Huitric, A. C., Stavropoulos, W. S., and Nist, B. J., J. Org. Chem., 28, 1539 (1963).
24. Karabatsos, G. J., Sonnichsen, G. C., Hsi, N., and Fenoglio, D. J., J. Am. Chem. Soc., 89, 5067 (1967).
25. Kharasch, M. S. Kleiger, S. C., and Mayo, F. R., J. Org. Chem., 4, 428 (1939).
26. Kojima, K., and Sakashita, K., Bull. Chem. Soc. Japan, 31, 796 (1958); Chem. Abstr., 53, 14689 (1959).
27. Kwart, H., and Nyce, J. L., J. Am. Chem. Soc., 86, 2601 (1964).
28. Lebas, J. M., J. Chim. Phys., 59, 1072 (1962).
29. Levenne, P. A., and Rothen, A., J. Biol. Chem., 127, 237 (1939).
30. Mare, P. B. D., de la, and Bolton, R., "Electrophilic Additions to Unsaturated Systems," Elsevier, Amsterdam, 1966.
31. Mayo, F. R., and Katz, J. J., J. Am. Chem. Soc., 69, 1339 (1947).
32. Nevitt, T. D., and Hammond, G. S., J. Am. Chem. Soc., 76, 4124 (1954).
33. Radio, P. D., and Skell, P. S., J. Org. Chem., 31, 753 (1966).
34. Richards, T. W., and Hall, N. F., J. Am. Chem. Soc., 39, 531 (1917).
35. Robinson, D. L., and Theobald, D. W., Quart. Reviews, 21, 314 (1967).
36. Sheppard, N., J. Chem. Phys., 17, 79 (1949).
37. Smirnov-Zamkov, J. V., and Piskovitina, G. A., Ukr. Khim. Zh., 28, 531 (1962); Chem. Abstr., 58, 2335 (1963).

38. Vaughan, W. R., Craven, R. L., Little, R. Q., Jr., and Schoentaler, A. C., *J. Am. Chem. Soc.*, 77, 1594 (1955).
39. Walling, C., Kharasch, M. S., and Mayo, F. R., *J. Am. Chem. Soc.*, 61, 2693 (1939).
40. Wechter, W. J., Slomp, G., MacKellar, F. A., Wiechert, R., and Kerb, U., *Tetrahedron*, 21, 1625 (1965).
41. Wellman, K. M., and Bordwell, F. G., *Tetrahedron Letters*, 1703 (1963).
42. Winstein, S., and Holness, N. J., *J. Am. Chem. Soc.*, 77, 5562 (1955).

VITA

3

Don Eldon Gibbs

Candidate for the Degree of

Doctor of Philosophy

Thesis: I. PHOTOLYSIS AND PYROLYSIS OF SILVER BENZOATE IN CYCLOHEXENE
II. STEREOCHEMISTRY OF THE ADDITION OF HYDROGEN BROMIDE AND
HYDROGEN CHLORIDE TO 4-TERT-BUTYL-1-PHENYLCYCLOHEXENE

Major Field: Chemistry

Biographical:

Personal Data: The author was born in Frederick, Oklahoma, on February 7, 1943, the son of Odus and Altus Gibbs. On August 15, 1964, he was married to Linda Lee Carothers; a daughter, Lara Michelle, was born February 29, 1968.

Education: The author was graduated from Weaver High School, Frederick, Oklahoma, in 1960. He received the Bachelor of Science degree from Oklahoma State University, Stillwater, Oklahoma, in 1964. In May, 1969, he completed the requirements for the Doctor of Philosophy degree.

Professional Experience: The author served as a graduate teaching assistant from January, 1967 to May, 1968. He held a National Defense Education Act Fellowship from September, 1964, to May, 1967.

Membership in Professional Societies: The author is a member of Phi Lambda Upsilon and the Society of the Sigma Xi.