

CYCLIALKYLATION STUDIES WITH ISOPRENE

By

John Robert Mattox

Bachelor of Science

Ohio State University

Columbus, Ohio

1963

Submitted to the Faculty of the Graduate School of
the Oklahoma State University
in partial fulfillment of the requirements
for the degree of
MASTER OF SCIENCE
May, 1965

SEP 21 1965

OKLAHOMA
STATE UNIVERSITY
LIBRARY

SEP 21 1965

CYCLIALKYLATION STUDIES WITH ISOPRENE

Thesis Approved:

E. J. Eismann

Thesis Adviser

K. D. Berlin

J. H. Boyce

Dean of the Graduate School

587613

SEP 21 1965

ACKNOWLEDGMENT

The author wishes to thank E. J. Eisenbraun for his enthusiasm and capable assistance. The author is grateful for the facilities put at his disposal by Bill Hamilton of the Continental Oil Company, Ponca City, Oklahoma. The author also wishes to thank A. B. Carel, P. W. Flanagan, and M. Hamming for their assistance in structural determinations.

Appreciation is also extended to the American Petroleum Institute for financial aid in the form of a research assistantship.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION.	1
II. HISTORICAL.	2
III. RESULTS AND DISCUSSIONS	8
General.	8
Experimental Conditions.	14
Structural Assignments from Spectral Data.	17
Mechanistic Discussion	23
IV. EXPERIMENTAL.	31
1,1-Dimethylindan Using Sulfuric Acid.	31
1,1,-Dimethylindan Using Polyphosphoric Acid	33
1,1,4-and 1,1,6-Trimethylindan	33
1,1,4,7-Tetramethylindan	34
1,1,4,6-Tetramethylindan	37
Cyclialkylation of 1,1,4,6-Tetramethylindan.	39
1,1,4,5-; 1,1,5,6-; and 1,1,6,7-Tetramethylindan	39
Cyclialkylation of Ethylbenzene, Isopropylbenzene, and t-Butylbenzene	42
Cyclialkylation of Tetralin.	44
1,1,4,6,7-Pentamethylindan	44
Alkylation of Mesitylene Using Methane Sulfonic Acid	45
Cyclization of the Olefin Product From Mesitylene	46
Aluminum Chloride Rearrangement.	48
Methylation of 1,1,4,7-Tetramethylindan.	48
Cyclialkylation of Durene.	49
Cyclialkylation of 1,2,3,4-Tetramethylbenzene.	50
BIBLIOGRAPHY.	63

LIST OF TABLES

Table	Page
I. Yields of Monoalkylbenzenes Cyclialkylated With Isoprene	7
II. NMR Spectra of Methylindans	19
III. Infrared Absorption Maxima in the 11 - 14 μ Range.	21
IV. Mass Spectra Data of Methylindans	22
V. Product Distribution of Benzene Cyclialkylated With Iso- prene	32
VI. Product Distribution of Toluene Cyclialkylated With Iso- prene	34
VII. Product Distribution of <i>p</i> -Xylene Cyclialkylated With Iso- prene	35
VIII. Experimental Conditions for the Cyclization of 2-Methyl- 4-(2,4,6-trimethylphenyl)-2-butene.	47
VIIIa. Yields from the Cyclization of 2-Methyl-4-(2,4,6-trimethyl- phenyl)-2-butene.	47

LIST OF FIGURES

Figure	Page
1. Flow Sheet for Cyclialkylations Giving Di-, Tri-, and Tetraalkylindans.	9
2. Flow Sheet for Cyclialkylations Giving Penta- and Hexa- alkylindans	10

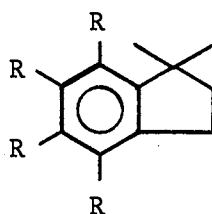
LIST OF PLATES

Plate	Page
1. Cyclialkylation Apparatus	51
2. 5 ml. Samples of GLC Separated Indan Isomers A, XIX; B, XX and C, XXI	52
3. N.M.R. Spectrum of XVI	53
4. N.M.R. Spectrum of XXV	54
5. N.M.R. Spectrum of XIX	55
6. N.M.R. Spectrum of XX.	56
7. N.M.R. Spectrum of XXI	57
8. N.M.R. Spectrum of XI.	58
9. N.M.R. Spectrum of XXVIII From Pseudocumene.	59
10. N.M.R. Spectrum of XXVIII From Mesitylene.	60
11. N.M.R. Spectrum of XXIX	61
12. N.M.R. Spectrum of XXVI.	62

CHAPTER I

INTRODUCTION

The cyclialkylation reaction of benzene or other aromatic homologs with isoprene in sulfuric acid affords a convenient one-step synthesis of some indans of the type



where R = H or alkyl

Because of the recent discovery (1963) of this reaction for the preparation of 1,1-dimethylindans, the description of these indans in the literature is sketchy and experimental conditions are sometimes incomplete. This study was undertaken to elucidate these reactions and to provide physical and spectral data for many of these indans. Several new polymethylindans were synthesized, some having been isolated from isomeric mixtures by preparative scale gas-liquid chromatography (G.L.C.).

The reaction of isoprene with an aromatic molecule lacking two adjacent hydrogen atoms on the ring (e.g., mesitylene) was investigated. Some attempts to further methylate these polymethylindans under Friedel-Crafts conditions were made.

This cyclialkylation reaction also provided a convenient method for the syntheses of hydrocarbons on a large scale (up to 40 moles) for the American Petroleum Institute's Standard Samples Program.

CHAPTER II

HISTORICAL

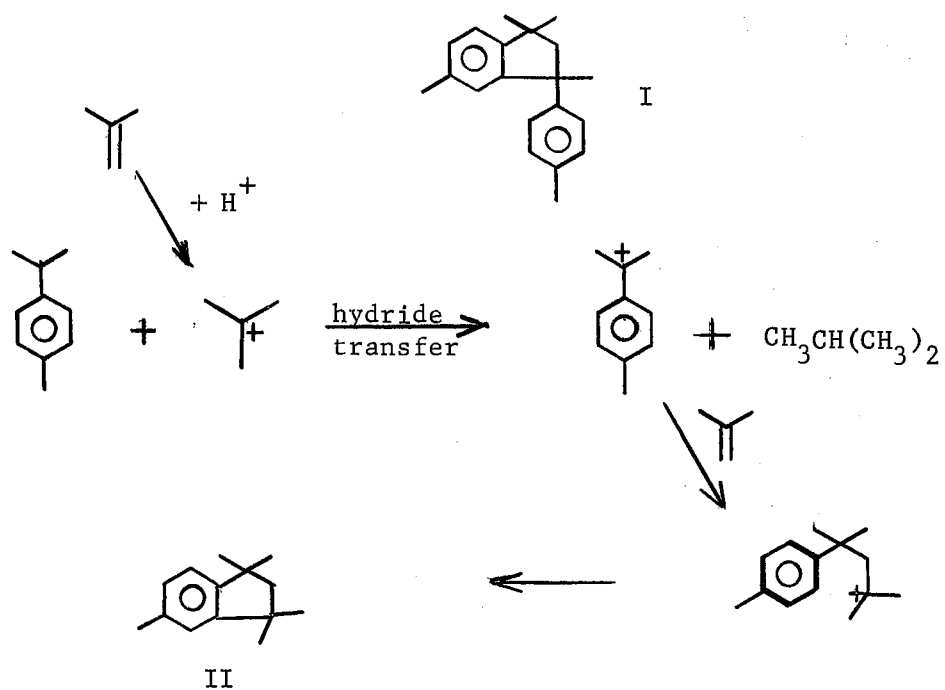
1,1-Dimethylindans have been prepared by a number of multi-step synthetic routes. Bogert and Davidson (1) first prepared 1,1-dimethylindan in 1934 by cyclization of 2-methyl-4-phenyl-2-butanol in the presence of sulfuric acid. This hydrocarbon was also synthesized by Baddeley and Williamson (2) who fused β -benzoyl- α,α -dimethylpropionic acid to give in 60% yield 3,3-dimethyl-1-indanone. This was reduced to 1,1-dimethylindan by a Clemmensen reduction. In 1948 Colonge and Rochas (3) prepared 1,1,4,7-tetramethylindan by cyclodehydration of 4-(2,5-dimethylphenyl)-2-methyl-2-butanol using sulfuric acid at 10⁰C. Catalytic dehydrogenation of 2,2,6-trimethyl-9-methylenebicyclo[3.3.1]non-6-ene is reported to have given 1,1,5-trimethylindan (4). 1,1-Dimethyl-6-isopropyl- and 1,1-dimethyl-6-t-butyl-indans were prepared by malonic ester synthesis using 4-isopropylbenzyl or 4-t-butylbenzyl chloride followed by methylation with methylmagnesium bromide. The resulting tertiary alcohol was cyclodehydrated to give the respectively substituted indan hydrocarbons (5).

The one-step cyclialkylation method for the preparation of 1,1-dimethylindans using isoprene was discovered in 1951 by Schmerling of Universal Oil Products (6). In this reaction hydrindacenes (e.g., 1,1,5,5-tetramethylhydrindacene) are synthesized by the reaction of aromatic hydrocarbons (e.g., benzene) with isoprene or other similar alkylating agents using sulfuric acid as a catalyst. Some 1,1-dimethylindan (one

mole isoprene added to one mole benzene) was obtained as a by-product. However, the disubstituted product (2 moles isoprene added to one mole benzene) is predominant in the case of benzene. The yield of the hydrindacene product can be increased with respect to the indan (monosubstituted) product in the case of other aromatic compounds, such as the xylenes, by controlling the reaction conditions.

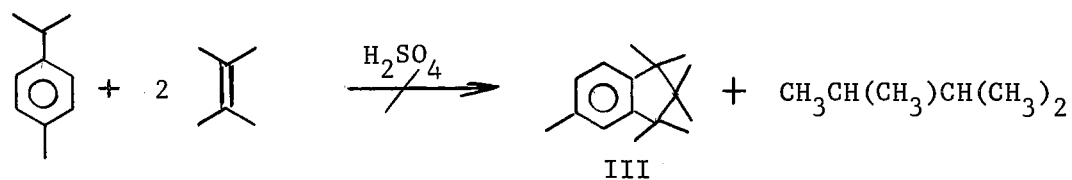
In 1932 Barbier synthesized the musk Moskene by condensing isobutylene with p-cymene under Friedel-Crafts conditions (96% sulfuric acid) and subsequently dinitrating this adduct. He assumed the hydrocarbon adduct to be 1-t-butyl-2-methyl-5-isopropylbenzene. In 1955, while preparing this musk Carpenter (7) noted that the distillation fore-runs contained copious amounts of isobutane. Also further nitration of Moskene under drastic conditions gave no change, whereas, if the Barbier structure were correct, the isopropyl group should have been readily replaced by a nitro group. Carpenter noted that in 1948 Ipatieff, Pines, and Olberg (8) had reported the formation of 1,3,3,6-tetramethyl-1-p-tolylindan (I) in a similar reaction, due to a hydride ion transfer from the isopropyl group to the protonated isobutylene and subsequent condensation with another p-cymylcarbonium ion which had deprotonated to give an alkene.

If an excess (theoretical 1 mole isobutylene per mole p-cymene) of isobutylene is used, the isobutylene itself can condense with p-cymylcarbonium ion resulting from a hydride ion transfer giving 1,1,3,3,5-pentamethylindan (II). This apparently was the case in the alkylation reaction in the synthesis of Moskene. Thus, Carpenter postulated the formation of II, the dinitration product being Moskene. Here two moles of isobutylene per mole of p-cymene are theoretically necessary.

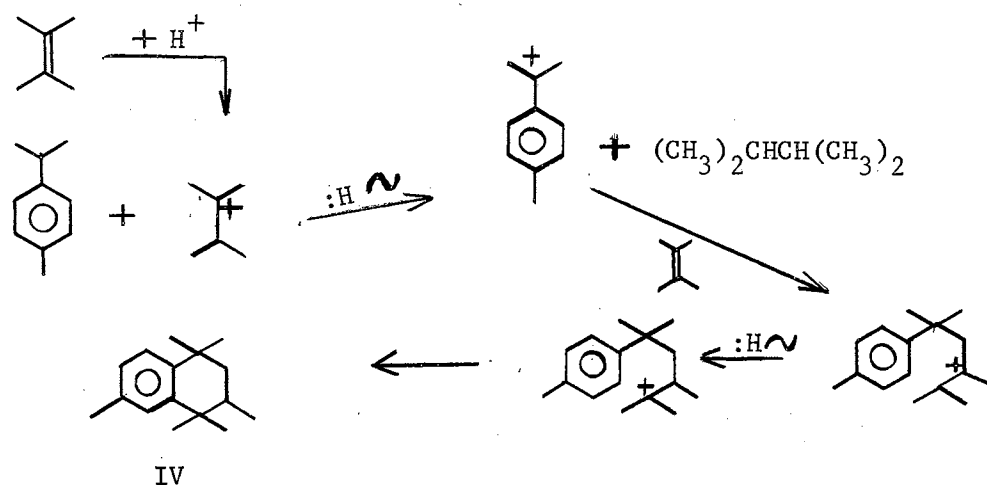


Schlatter (9,10) made similar observations about the same time.

A series of papers have been published on this hydride shift of p-cymene and subsequent cyclization to give indans (11,12,13). Carpenter (7) also reported the formation of 1,1,2,2,3,3,5-heptamethylindan (III) by an analogous reaction using p-cymene and 2,3-dimethyl-2-butene.



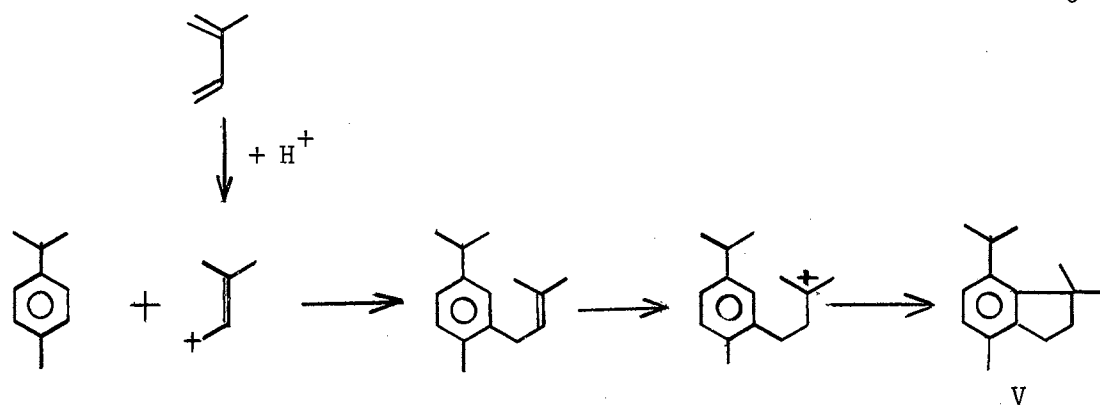
In 1962, Wood (14) showed that the product from the condensation of p-cymene and 2,3-dimethyl-2-butene was not III, but that a second hydride shift had taken place and the tetralin IV was formed.



Structure IV was substantiated by N.M.R. studies.

Wood proposed using a diene as the alkylating agent, incorporating both functions of the double bond into a single molecule, the first double bond into a single molecule, the first double bond to accept the hydride ion from the *p*-cymene and the second to be attacked by the *p*-cymyl cation, with subsequent cyclization. Thus, only one mole of diene per mole of aromatic hydrocarbon would be theoretically needed and the mole of saturated hydrocarbon would not be formed, as is the case when a mono-olefin is used.

When *p*-cymene was allowed to react with 2,3-dimethyl-1,3-butadiene in a 96% sulfuric acid medium and the hydrocarbon product isolated, this hydrocarbon was found to be an indan with the isopropyl group intact on the aromatic ring. The protonated isoprene attacked the ring as in Schmerling's cyclialkylation reaction, in preference to abstracting a hydride ion from the isopropyl group. Isoprene was also found to react with *p*-cymene giving rise to 1,1,4-trimethyl-7-isopropylindan (V). The following mechanism was proposed by Wood.



m-Cymene also gave an indan when treated under cyclialkylation conditions with isoprene. This appeared to be largely a single isomer, 1,1,4,-4,-trimethyl-6-isopropylindan. The reaction was reported to proceed well in the case of mono-, di-, and trialkylbenzenes.

Givaudan Corporation was issued a patent based upon Wood's work pertaining to the cyclialkylation of monoalkylbenzenes with isoprene, giving 1,1-dimethyl-6(and-4-)-alkylindans and with 2,3-dimethyl-1,3-butadiene giving 1,1,2-trimethyl-6(and-4-)-alkylindans (15).

Wood showed that the more bulky R(R = alkyl group of a monoalkylbenzene) gave a higher yield of an isomerically purer product. The suitable temperature for the reaction depended upon the concentration of the acid used: the more concentrated the acid, the lower the temperature required. The effect on the products of the variation in R was the same in both the dimethylbutadiene and isoprene cases.

TABLE I

Alkyl Substituent in 6-position	% Yield 1,1-Dimethyl-6-alkylindan (from isoprene)	% Yield 1,1,2-Trimethyl- 6-alkylindan (from 2,3-dimethyl- 1,3-butadiene)
Methyl	42.2 (80% pure)	22.1
Ethyl	43.6 (90% pure)	23.0
Isopropyl	53.0 (95% pure)	36.0
<u>t</u> -Butyl	57.7 (95% pure)	43.3
Sec-Butyl	32.1	
<u>t</u> -Amyl	35.3 (93% pure)	

(Purities of the desired isomer were determined by gas-liquid chromatography).

1,1-Dimethylindan has been prepared from cymene and ethylene in an autoclave using potassium as a catalyst (16). A hydride shift was postulated to have taken place. Forty-nine per cent of the product was the indan, while 51% t-amylbenzene was formed. By using a mixture of potassium hydride and butyllithium, 62% 1,1-dimethylindan and 38% t-amylbenzene were formed (17). These two previously mentioned methods give a higher yield of 1,1-dimethylindan than the cyclialkylation of benzene with isoprene. Benzene is anomalous among the aromatic compounds giving mostly a hydrindacene on cyclialkylation.

CHAPTER III

RESULTS AND DISCUSSIONS

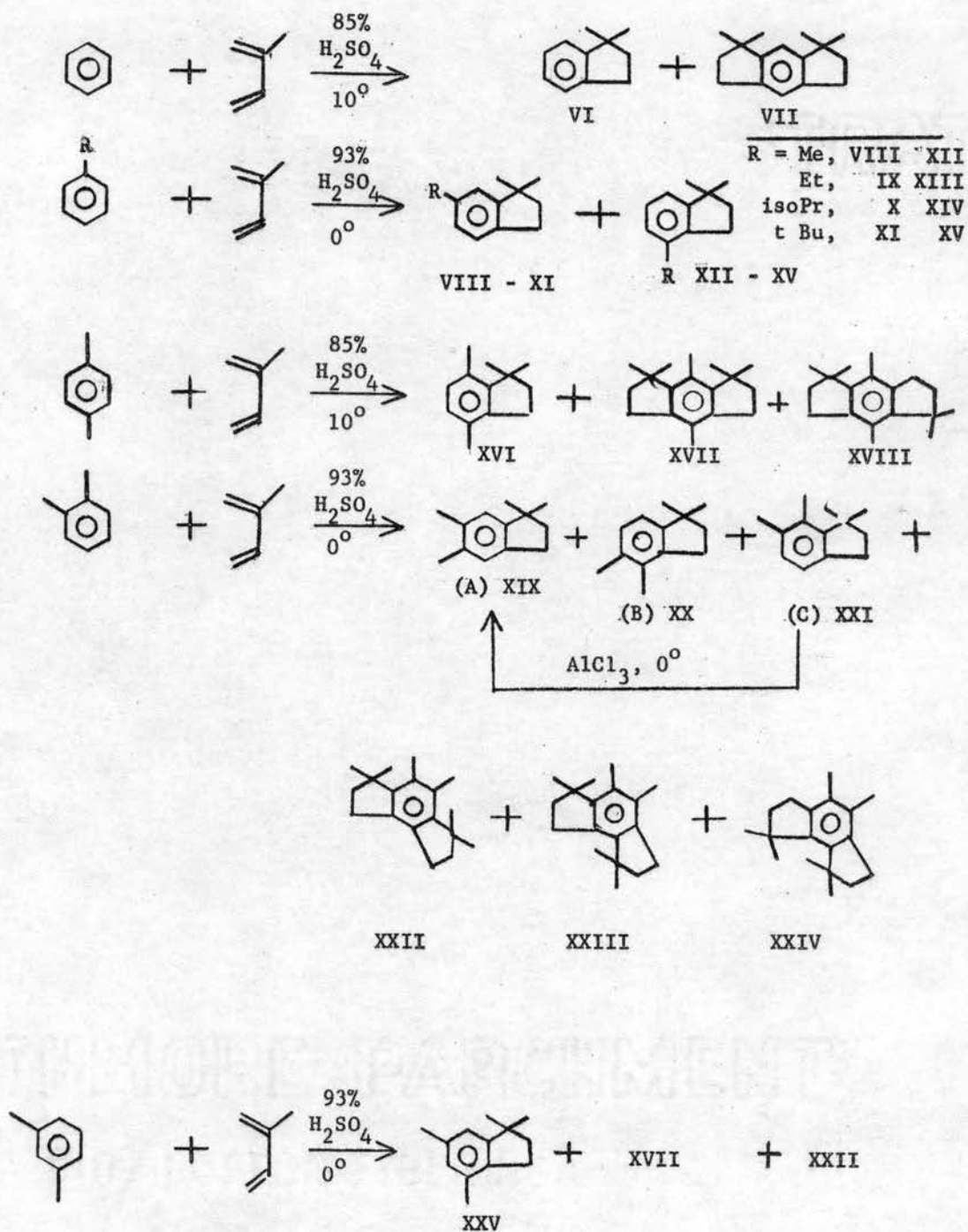
General

Benzene was cyclialkylated with isoprene using a sulfuric acid catalyst to give 1,1,-dimethylindan (VI) in 24% yield and the hydrindacene product (VII) in 28% yield. However, a polyphosphoric acid catalyst gave a mixture of eleven products, some of which were alkenes.

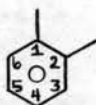
Toluene was cyclialkylated with isoprene using sulfuric acid to give in 58% yield an isomeric mixture of the trimethylindans VIII and XII. The products VIII and XII result from attack at the para and ortho positions of the toluene ring and were found in the ratio of 60:40 respectively. These isomers were separated on G.L.C. Ethylbenzene gave products IX and XIII in the ratio of 70:30 whereas isopropylbenzene gave indans X and XIV in the ratio of 80:20. t-Butylbenzene was cyclialkylated in 68% yield giving XI and XV of which 98% was XI. These data clearly demonstrate that an expected steric effect controls the orientation of the entering alkyenyl group. About 8% yield of p-di-t-butylbenzene formed by transalkylation was isolated from a 15 mole reaction using 89% sulfuric acid.

The xylenes were cyclialkylated with isoprene. p-Xylene reacted to give a single indan (XVI) in 59% yield and an isomeric mixture of hexamethylhydrindacenes (XVII and XVIII) in 14% yield. Equal amounts of XVII and XVIII were formed. o-Xylene gave three monosubstituted

FIGURE 1



(indan) products and three disubstituted (hydrindacene) products upon cyclialkylation. Indan XX resulted from attack at the 3-position of o-xylene while XIX and XXI resulted from attack on the 4-position and cyclization on the 5-position or 3-position of the o-xylene nucleus respectively.

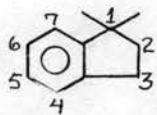


The ratio of initial attack on the 4-position to attack on the 3-position was 89:11. The intermediate resulting from attack at the 4-position was found to cyclize at position 5 and position 3 in the ratio of 56:33. The hydrindacene isomers (XXII, XXIII, and XXIV), formed in the cyclialkylation of o-xylene, were analyzed on G.L.C. The separation of indans XIX, XX, and XXI was shown to be unfeasible by distillation but was accomplished by preparative scale gas chromatography.

When the purified indans XIX, XX and XXI were separately treated with aluminum chloride in nitroethane solvent and stirred for 30 minutes at 0°, neither XIX nor XX was affected but XXI quantitatively rearranged to XIX. The indans XVI and XXV showed no change when subjected to these rearrangement conditions, but XI was shown to give four compounds when treated in the same manner. The t-butyl group from XI was probably involved in a transalkylation reaction in the presence of aluminum chloride to account for the multiplicity of products.

m-Xylene gave a single indan (XXV) in 68% yield. A crystalline hydrocarbon of higher boiling point was found in the reaction mixture. This hydrocarbon was a mixture of two hydrindacene isomers formed from the attack of a second isoprene molecule on either the 5- or 7-position of

the indan (XXV) and the subsequent ring closure involving a methyl shift.



The 1,2-methyl migration leads to a hydrindacene (XVII) derived from *p*-xylene and a hydrindacene (XXII) with the same structure as one of the disubstituted ortho products. Separation of these isomers was not achieved but the components were readily identified by retention times of prepared mixtures of the hydrindacene products on G.L.C. The methyl shift is thought to be intramolecular since no products were found which would result from the loss of a methyl group on the ring. 1,1,4,6-Tetramethylindan (XXV) was shown to be an intermediate in the formation of the hydrindacene products (XVII and XXII) for cyclialkylation of XXV with isoprene under the same conditions gave an identical crystalline product.

Pseudocumene was cyclialkylated to give in 70% yield a crystalline product (XXVIII) which is a single isomer.

Although initial attack of isoprene was postulated by Wood (14) to involve a primary carbonium ion and that the resulting olefin subsequently cyclized, the proposed olefin intermediate was never isolated in the preceding reactions. The existence of the olefin in the presence of sulfuric acid is evidently very brief. Mesitylene was alkenylated with isoprene in sulfuric acid in the hope of isolating an olefin. Two adjacent hydrogen atoms are not available on the mesitylene ring to permit a cyclialkylation reaction. Reactions were carried out using 93%, 85%, and 75% sulfuric acid and only two products (XXVI and XXVII) were found. These were isolated in 4.8% yield and were separated on a preparative gas chromatography. The ratio of XXVI to XXVII was 9:1. Isoprene was condensed

with mesitylene using methane sulfonic acid as a catalyst. This milder, nonsulfonating catalyst provided a higher yield (39%) of the isomeric mixture of XXVI and XXVII which was of approximately the same composition as the alkenylation product with 75% sulfuric acid. A 9% impurity of pseudocumene in the mesitylene starting material afforded some cyclic product upon alkenylation with methane sulfonic acid. Analytical G.L.C. showed the cyclic product due to the pseudocumene impurity was absent when pure (99.8%) mesitylene was used.

The mixture of these olefins from the alkenylation with methane sulfonic acid was cyclized with sulfuric acid of varying concentration. The strengths of the acid used were 85%, 93%, and 96% sulfuric acid. The extent of cyclization was determined by N.M.R. spectroscopy and was shown to be 57%, 78% and 100% respectively when the reaction was stirred for 60 minutes at ambient temperature. The products from the cyclization with 86% sulfuric acid are two pentamethylindans (XXVIII and XXIX). These indans are formed in the ratio of 9:17 respectively in 97% overall yield. These cyclizations were carried out using a 10% solution of olefin in cyclohexane. Because of the high yield of pentamethylindan isomers and the failure to observe any trimethylindans or tetramethylindans, both products were thought to have arisen from an intramolecular methyl migration. This is to be expected in the dilute solution of 10% olefin in cyclohexane which was used. The indan XXVIII would arise from a 1,2-methyl shift and structure XXIX would be the result of a 1,4-intramolecular migration. The methyl shift observed in the disubstitution of m-xylene also appears to be intramolecular, although no inert solvent was used in that case. Presumably the excess m-xylene serves as the inert diluent.

Several cyclizations of the olefin mixture from mesitylene (XXVI and XXVII) were carried out with 96% sulfuric acid (Table VIII) by varying the amount of acid used and the concentration of the olefin in cyclohexane. It was noted (Table VIIIa) that the most dilute solution in Flask 1 gave the highest yield of indan (0.9 g. indan per gram olefin). The poorest yield was found when using an increased amount of sulfuric acid in flask 4. There 0.38 g. of indan per gram of olefin were obtained.

Tetralin was cyclialkylated with isoprene to give a mixture of three indan isomers. The indan product from *p*-xylene (XVI) was methylated in an attempt to isolate 1,1,4,5,6,7-hexamethylindan. A reaction was carried out with methyl chloride at -5° to 0° under a slight pressure. A similar methylation was performed with XXVIII at 65° . Both reactions failed to proceed. Methyl iodide was used in a further attempt to methylate XVI with aluminum chloride at 43° . Two products were isolated by G.L.C. from a complex mixture. These were in the molecular weight range of penta-methylindans. A higher boiling crystalline material was isolated and shown to be hexamethylbenzene rather than the desired hexamethylindan. Apparently isoprene is eliminated and complete methylation of the benzene nucleus takes place.

Durene was treated with methane sulfonic acid and isoprene and the product was distilled to give XXXI in 26% yield. This olefin was cyclized with 96% sulfuric acid to give about 25% cyclization to 1,1,4,5,6,7,-hexamethylindan (XXXII). 1,2,3,4-Tetramethylbenzene was cyclialkylated with isoprene and 85% sulfuric acid to give the hexamethylindan XXXII and the intermediate olefin XXXIII.

Experimental Conditions

In addition to the formation of an indan when an aromatic hydrocarbon is cyclialkylated with isoprene in sulfuric acid, the following competing reactions take place; (a) addition of two moles of isoprene to form hydrindacenes, (b) sulfonation of the aromatic ring, and (c) polymerization of isoprene. Reaction conditions were chosen to minimize the three competing reactions and maximize the yield of indan hydrocarbon. The presence of polymerized isoprene and sulfonated products also created problems in the isolation of the indan product because of the formation of fairly stable emulsions.

Preliminary experiments with equimolar quantities of isoprene and an aromatic hydrocarbon indicated that a large excess of the aromatic hydrocarbon was necessary to limit the addition to one mole of isoprene per mole of aromatic hydrocarbon. The yield of indan was increased from less than 10% to over 50% by increasing the aromatic hydrocarbon to isoprene molar ratio to about 5:1. Using this 5:1 molar ratio the optimum conditions were found when equimolar quantities of the aromatic compound and isoprene were mixed. This mixture is added to a mixture of sulfuric acid and the remaining arene contained in the reaction flask.

Studies were made to determine the optimum temperature for the cyclialkylation reaction for a given concentration of sulfuric acid and a given hydrocarbon, a certain desirable temperature range is dictated by the competing reactions of sulfonation and polymerization. Both the sulfonation and cyclialkylation reactions are temperature dependent although the change in rate is greater for sulfonation than that of cyclialkylation. This is demonstrated by occurrence of excessive sulfonation when the optimum temperature is exceeded. When the temperature is lowered considerably, the polymerization of isoprene becomes predominant,

for this reaction is highly independent of temperature change while the cyclialkylation reaction has been considerably slowed down. The ratio of hydrindacene formation to indan formation does not appear to be temperature dependent. It was found that generally for 96% sulfuric acid a temperature under -15° was necessary, 93%, -10° to $+5^{\circ}$; 85%, $+10$ to $+25^{\circ}$; 75%, 30° to 45° . The two concentrations of sulfuric acid convenient to work with were 93% and 85%. The low temperature required with 96% acid limited its use. The 85% sulfuric acid gave slightly lower yields than 93% acid but its use was necessary for compounds which melted above 0° (e.g. *p*-xylene). With 75% sulfuric acid the yield of indan fell off considerably and with 50% sulfuric acid no reaction occurred.

The variation of the addition time would affect several factors which determine the yield of the reaction. In general with *p*-xylene (see Table VII) which was chosen as a typical aromatic hydrocarbon, the yields of the indan product were less when a longer addition time was used. This is probably due for the most part to the sulfonation of the indan. While the overall yield of the cyclialkylated product (both indan and hydrindacenes) was found to vary inversely with the addition time, it was noted that the per cent of disubstituted (hydrindacene) product increased with the longer addition time. Thus slower addition probably gives greater selectivity of attack, preferentially on the more substituted ring (alkyl indans vs. alkylbenzenes).

It was noted that the yield of hydrindacene product is greater than indan product in the case of benzene whereas alkyl benzenes give a larger indan yield under similar conditions. This is probably because the difference in reactivity toward further substitution of benzene and 1,1,-dimethylindan is greater than the difference in reactivity of a given alkyl benzene

and its indan derivative.

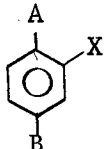
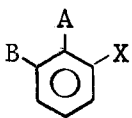
Structural Assignments from Spectral Data

After determining the purity of the isomer under consideration by G.L.C., the structure determination by spectral means was quite definitive with the exceptions of XXVIII and XXX. Mass spectral data was used to determine molecular weight as well as determining impurities of different molecular weight. Fragmentation patterns showed little difference for the various indan isomers. N.M.R. spectra provided the bulk of the information for structural assignments. I.R. spectra were used in determining the alkyl substitution on the benzene ring. All of the indans showed characteristic infrared absorbance maxima at 7.62μ . A doublet in the 7.25 to 7.40μ range is characteristic for symmetrical methyl group bend. This was found due to (a) the gem-dimethyl group in the indans (b) the terminal methyl group in the olefin XXVI and (c) the t-butyl group on the ring of XI. The C-H out-of-plane bending is shown in Table III.

The N.M.R. spectra of all the methylindans were quite similar in appearance. The gem-dimethyl group was at highest field. With the exception of XXX, a signal at $1.17 \text{ ppm}(\delta)$ was observed for the gem-dimethyl when a hydrogen atom was in the 7-position of the indan. The chemical shift was observed to move down field to around 1.32 ppm when a methyl group was present in the 7-position. This information was used to distinguish XIX and XX from XXI (Table II). Compound XIX was distinguished from XX by I.R. spectra which showed C-H out of plane bending (Table III).

The triplet due to the carbon 2 protons ($J = 0.24 \text{ ppm}$) and the triplet of the benzylic protons ($J = 0.25 \text{ ppm}$) have chemical shifts that each seem to fall into two groups but no correlation could be drawn with the assigned

structure. The assignment of ring methyl proton in this case was made as follows: A and B of XXV were assigned from analogous shifts in VIII and XII. The chemical shifts of the ring methyls of the following compounds were recently published (18).

Downfield Shift of A(ppm) ¹ With Respect to B	
	0.10
	0.12
	A, B = -CH ₃ X = -C(CH ₃) ₂ COOH

The assignment of XXV and XVI were made from this analogy. The assignment of XX is made from the analogy with 1,2,3-trimethylbenzene in which the 1- and 3-methyl groups at 2.20 ppm are down field from the 2-methyl at 2.10 ppm.² 1,2,3,4-Tetramethylbenzene has the 2- and 3-methyl groups at 2.16 ppm and the 1- and 4-methyl groups at 2.23 ppm. The assignments of chemical shifts to the ring methyls in the pentasubstituted indans are in doubt. Further N.M.R. work will be done in this area.

The olefins XXVI, XXVII, and XXXI were characterized by their N.M.R. spectra. The spectrum of structure XXVI shows a signal at 6.67 ppm which indicates two hydrogen atoms of a tetrasubstituted benzene with the hydrogens in equivalent environments. The vinylic proton signal centered at 5.00 ppm ($J = 0.18$ ppm) shows a single proton. The methylene doublet at 3.19 ppm is coupled to the vinyl proton ($J = 0.06$ ppm). The aromatic

¹Calculated from published values given in c.p.s.

²A.P.I. Spectrum

TABLE II
NMR SPECTRA PPM(δ)

Compound	VIII	XII	XXV	XVI	XXI	XIX	XX
Structure							
gem-Dimethyl Protons	1.17	1.17	1.17	1.31	1.34	1.17	1.17
Carbon 2 Protons (triplet)	1.83	1.83	1.79	1.86	1.86	1.77	1.79
Ring Methyl Protons	A 2.25	2.15	2.23	2.31	2.22	2.09	2.12
A, B = Methyl	B		2.11	2.16	2.19		2.03
Ring Benzylic Protons (triplet)	2.73	2.75	2.67	2.71	2.74	2.73	2.72
Aromatic Protons	6.96	6.94	6.71 6.76	6.69	6.77	6.86	6.82 6.87

TABLE II (Continued)

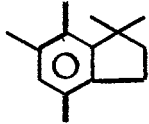
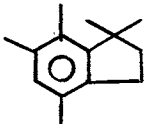
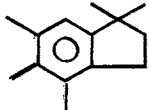
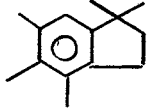
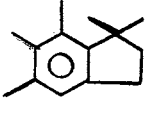
Compound	XXVIII (from pseudocumene)	XXVIII (from mesitylene)	XXIX (from mesitylene)	XXIX (from XVI)	XXX (from XVI)
Structure					
<u>gem</u> -Dimethyl Protons	1.33	1.31	1.19	1.19	1.24
Carbon-2 Protons (triplet)	1.85	1.84	1.84	1.81	1.77
Ring Methyl Protons	A 2.18	2.17	2.22	2.16	1.99
A, B, C = Me	B 2.17	2.15	2.13	2.03	2.26
	C 2.12	2.11	2.09	1.96	2.07
Ring Benzilic Protons (triplet)	2.64	2.65	2.75	2.72	2.67
Aromatic Protons	6.64	6.64	6.63	6.78	6.63

TABLE III
 INFRARED ABSORPTION MAXIMA IN THE 11-14 μ RANGE









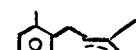



Compound	Structure	Measured Absorbance Maxima (μ)
VIII		12.33, 11.36
XII		13.07, 14.00
XI		12.18, 11.30
XVI		12.45
XIX		11.51
XX		12.32
XXI		12.42
XXV		11.76
XXVI and XXVII		11.80
XXVIII		11.60
XXIX		11.53
XXX		11.59

TABLE IV
 MASS SPECTRA DATA

Compound	Intense Molecular Ion at m/e	Impurity and Volume Per Cent Detected
1,1-Dimethylindan (VI)	146	$\left\{ \begin{array}{l} \text{C}_{12}\text{H}_{16} \text{ 0.3\%} \\ \text{C}_{11}\text{H}_{12} \text{ 0.3\%} \end{array} \right.$
1,1,4-Trimethylindan (XII)	160	$\text{C}_{13}\text{H}_{18} \text{ 0.3\%}$
1,1,6-Trimethylindan (VIII)	160	None detected
1,1,4,5-Tetramethylindan (XX)	174	$\text{C}_{14}\text{H}_{20} \text{ 0.5\%}$
1,1,5,6-Tetramethylindan (XIX)	174	None detected
1,1,6,7-Tetramethylindan (XXI)	174	None detected
1,1,4,7-Tetramethylindan (XVI)	174	None detected
1,1,4,6-Tetramethylindan (XXV)	174	None detected
1,1,4,6,7-Pentamethylindan (XXVIII)	188	None detected

methyl group appears at 2.18 ppm. This signal is equivalent to 9 protons. Six allylic methyl protons are at 1.68 ppm. The spectrum of structure XXXI is essentially the same except four aromatic methyl protons appear at 2.12 ppm and four methyl protons are shifted up field to 2.08 ppm probably due to steric interactions with the alkenyl side chain. The aromatic proton signal is at 6.72 ppm. Structure XXVII shows two aromatic protons at 6.74 ppm. Two vinylic protons are situated at 4.75 ppm. The signal at 2.28 ppm is for 9 aromatic methyl protons. The three allylic protons are found at 1.79 ppm. Two benzylic protons are located at 2.60 ppm.

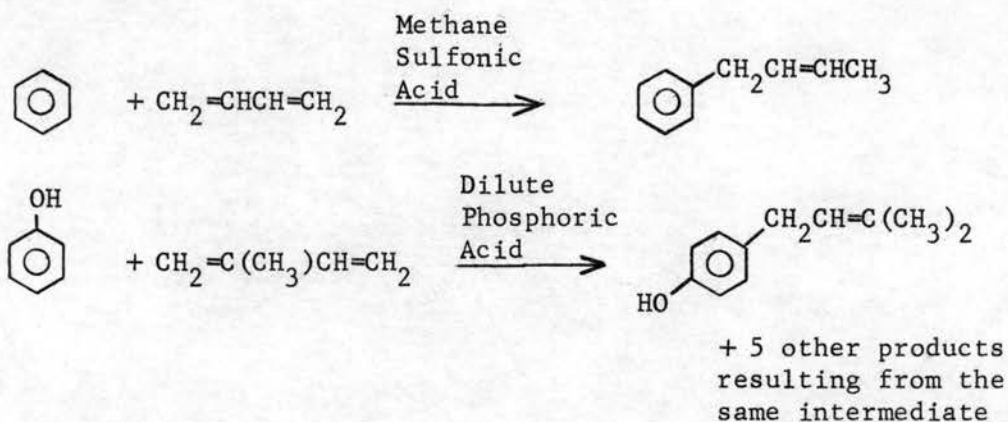
The N.M.R. spectrum of the product from the cyclization of XXXI shows that the cyclization proceeds partially to the hexamethylindan (XXXII). By integration of the 6 allylic methyl protons centered at 1.79 ppm (minus the two allylic protons of the indan at 1.85 ppm) and comparing them with the integration of the gem-dimethyl group of the cyclized indan (at 1.32 ppm), the percentage of cyclization was determined to be 28%.

The product from the cyclialkylation of 1,2,3,4-tetramethylbenzene was shown to be a mixture of the olefin XXXIII and the hexamethylindan XXXII. The percentage of cyclization was determined as before and found to be 33%.

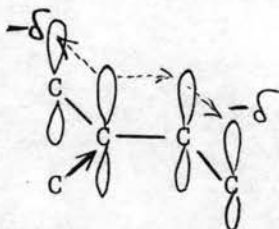
Mechanistic Discussion

The cyclialkylation reaction with isoprene in sulfuric acid appears to involve two steps: first, on attack of some equivalent of a primary carbonium ion and, secondly, reprotonation and cyclization of the resulting tertiary carbonium ion. The attack of a conjugated diolefin, such as isoprene, on an aromatic system under Friedel-Crafts conditions

to give an olefinic product with a secondary benzylic carbon is well known (19,20,21).

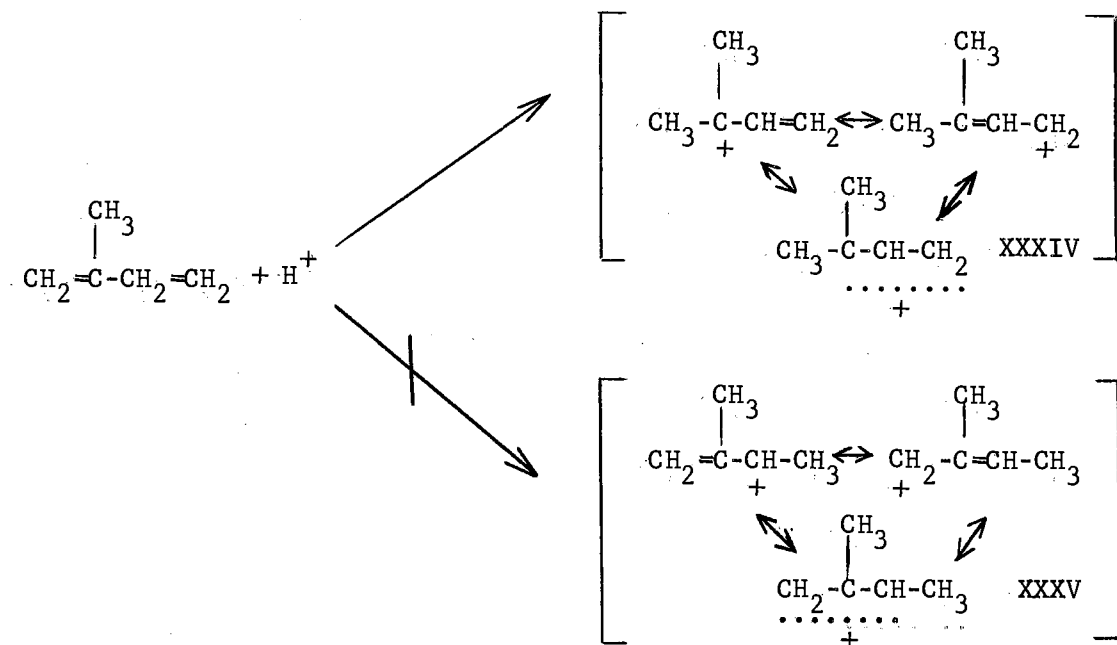


Considering the initial attack, the protonation of isoprene is thought to take place on the 1-carbon. Certainly the electron density of the π -cloud is greatest in the proximity of the 1- and 4-carbons due to the inductive effect of the methyl group and the delocalization by the conjugated π electrons. The ground state is probably the lower energy transoid form.



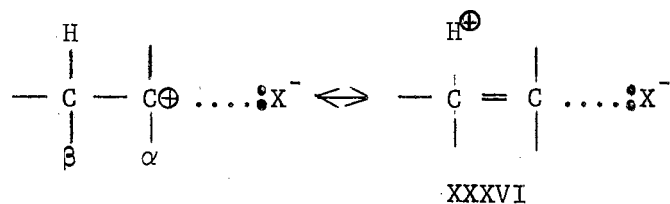
The resonance hybrid forms XXXIV and XXXV would result from protonation of the 1- and 4-carbons respectively.

In no case has a product been identified which could have been derived from the resonance hybrid (resonance forms XXXV) (22). A similar effect has been demonstrated in the hydrohalogenation of isoprene with hydrogen chloride and hydrogen bromide. In both cases, the products are postulated to result from an initial protonation of the 1-carbon giving the resonance hybrid XXIV. The product from the hydrochlorination is the result of 1,2 addition giving 3-chloro-3-methyl-1-butene. Hydrobromination gave 1-bromo-3-methyl-2-butene as a result of a 1,4 addition



(23). Thus it seems the inductive effect of the 2-methyl group increases the electron density at the adjacent 1-position much more than the 4-position, even though the system is conjugated. Koncos and Friedman (24) stated that the main products of alkenylation have been shown in almost all cases to result from the 1,4 addition of the aromatic to the diene.

It seems clear that the resonance hybrid (resonance forms XXXIV) is the attacking specie. The protonated isoprene contains two centers of partial positive charge on carbons 2 and 4. Since a resonance hybrid is of lower energy than any of its canonical forms and the π -electron cloud is quite fluid, the partial positive charges on carbons 2 and 4 must not necessarily be of equal energy. At first thought, since a primary carbonium ion is a much higher energy specie than a tertiary carbonium ion, it would seem that the great majority of the positive charge would be located on the 2-carbon. The stability of tertiary carbonium ion compared to a primary carbonium is due to stabilization resulting from hyperconjugation involving structures such as XXXVI.



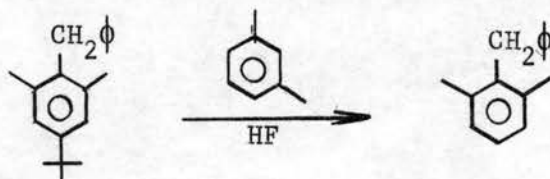
This effect would be expected to be more important if three alkyl groups are on the α carbon (i.e., it is tertiary) than if only one alkyl group is present (i.e., a primary α carbon) (25).

Although the exact electronic nature of the attacking species is unknown, it has been demonstrated from kinetic studies that a π -complex results from protonation of double bonds and it is reasonable that such a complex may be formed from isoprene when treated with acid. Consequently, this is in closer agreement with the known fact that primary carbonium ions are virtually unknown as discrete and free species. Therefore, in the π -complex distribution of charge over several atoms via the allylic double bond seems reasonable.

In a discussion of the alkenylation of phenols with dienes, Bader (26) suggests that the products of the alkenylation by XXXIV are derived from the resonance hybrid of the carbonium ion which "spatially most accessible" (i.e., presumably not the tertiary carbonium ion). If steric factors, which tend to minimize the role of the tertiary carbonium ion, tend to come into play, they certainly would not account for the complete absence of all tertiary alkylate (27,28,29).

An alternative explanation for the products which were found is that attack of the aromatic ring by the 2- and 4-carbons of the resonance hybrid (resonance forms XXXIV) both take place. Since they should not

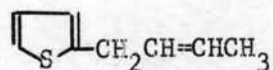
be of equal energy, the rate of attack should be determined by the energy requirement of the respective transition states. Thus it is likely that the reaction involving tertiary attack is reversible and the only product isolated is the result of the thermodynamically more stable (and irreversible) primary alkenylate. Schlatter was able to remove a t-butyl group from a ring merely by stirring the substituted arene with an excess of the original arene in the presence of hydrogen fluoride at 0° (10,30).



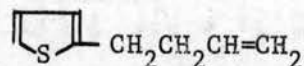
We observed the formation of p-di-t-butylbenzene during the cyclialkylation of t-butylbenzene and cite this as evidence of the transalkylation of the t-butyl group under sulfuric acid cyclialkylation conditions.

When mesitylene was alkenylated with isoprene (described in this paper) and the olefin isolated, it was found to be a mixture of the internal olefin XXVI and the terminal olefin XXVII. If both were a result of the alkenylation, this would necessitate the postulation of a different mechanism. It was shown that when isomer XXVI was shaken with 75% sulfuric acid, it partially isomerized to XXVII in the same proportion as that of the alkenylation product, thus it seems likely that the product of the alkenylation is XXVI which subsequently isomerizes to the observed isomer ratio XXVI and XXVII which are in thermodynamic equilibrium. Since a terminal olefin is generally considered less stable than an internal olefin and XXVII has not been previously observed as a product of alkenylations with isoprene, it is thought that the methyl groups in the 2- and 6-positions of the ring influence the stability of XXVI.

One other case of the formation of a terminal olefin XXXVIII was reported along with XXXVII in the alkenylation of thiophene with butadiene (31). Bader (32) later discounted the structure assignment of XXXVIII by the I.R. band at 970 cm^{-1} and suggested that XXXVIII might be the cis isomer of XXXVII.

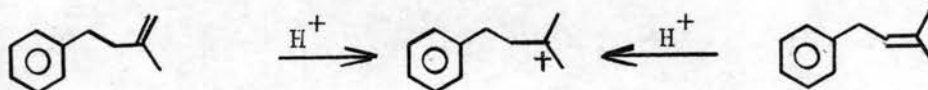


XXXVII



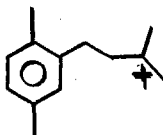
XXXVIII

The second step in the cyclialkylation reaction involves ring closure. Whether an internal olefin such as XXVI which is postulated to be the intermediate or a terminal olefin as XXVII is present, the protonated forms should be identical and the tertiary carbonium ion attacks the ring to



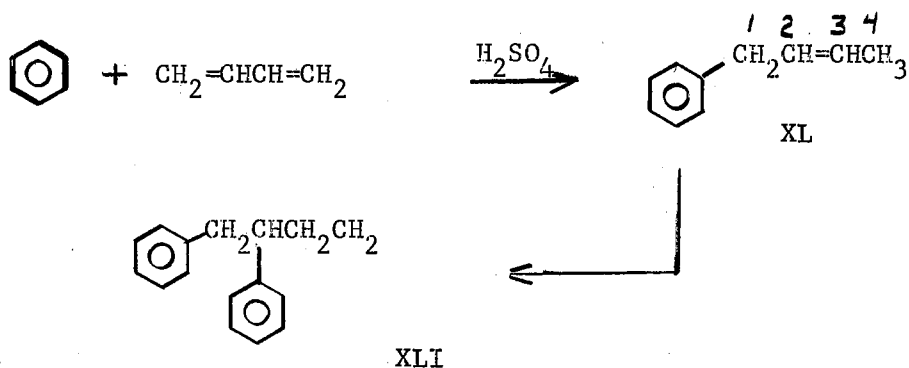
form the indan.

It has been shown that in alkylation of olefins in sulfuric acid the products due to tertiary alkylation predominate (33,34). It is noted that the tertiary carbonium ion will close intramolecularly rather than alkylate another aromatic molecule in a case where methyl group is located on the ring adjacent to the point of attack. It has been shown that t-butylation ortho to a methyl group as in p-xylene (35) or pseudocumene (36) proceeds with difficulty. However, the proposed carbonium ion intermediate (XXXIX in the case of p-xylene) is likewise hindered from alkylating another aromatic molecule (e.g., p-xylene). The frequency of impact on the ortho carbon is many times greater than on a carbon atom



XXXIX

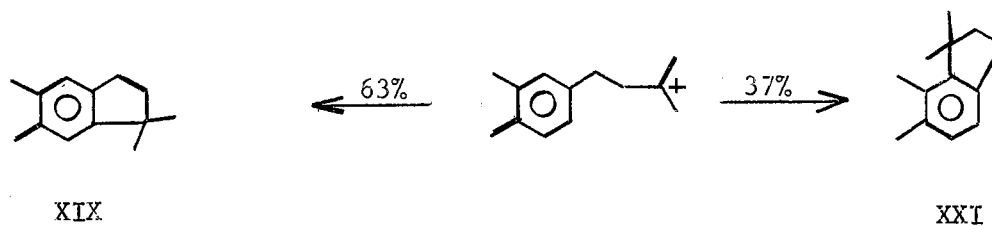
available for substitution of another *p*-xylene molecule. The path of approach of the "whiplashing tail" to its π -cloud would probably be more sterically favored as opposed to the randomness of an intermolecular collision. 2-3-Dimethyl-1,3-butadiene shows the same tendency as isoprene for cyclialkylation (14) but 1-phenyl-2-butene, the primary reaction product of benzene and 1,3-butadiene, is known to alkylate another arene by attack of the secondary carbonium ion of the carbon beta to the ring (37).



In this case the protonation takes place on the 3-carbon of XL since the driving force for the formation of a tertiary carbonium ion as in isoprene in sulfuric acid is absent. With the positive charge residing on the 2-carbon, cyclization is unfavored and alkylation of another arene molecule occurs instead.

The quantitative isomerization of XXI to XIX in aluminum chloride indicates a more bulky complex than that with sulfuric acid. The percentage of alkene which alkylated the position ortho to the methyl group (37%) indicates the effective steric requirement of the attacking tertiary

carbonium ion in this case is minimal.



In the cyclialkylation of 1,2,3,4-tetramethylbenzene, some of the intermediate olefin was observed in the N.M.R. spectrum. This is the only instance wherein the intermediate olefin was detected. Usually those arenes containing two adjacent ring hydrogens readily cyclize to indans. The failure to cyclize is probably due to the increased energy requirements for the cyclization because of steric crowding around the ring.

CHAPTER IV

EXPERIMENTAL

The following reactions were carried out (unless otherwise noted) in a three-necked flask of appropriate size, fitted with a thermometer, stirring assembly, and an addition funnel. Phillips pure grade isoprene was used. All reactants were analyzed using gas-liquid chromatography (GLC) and any appreciable impurities were noted. The cyclohexane used in some of the latter experiments was shaken overnight with 96% sulfuric acid, washed with water and dried over activated silica gel. The resulting liquid was deemed alkene-free by bromine test. Temperatures are given in degrees centigrade.

1,1-Dimethylindan Using Sulfuric Acid

A 1 liter flask was placed in a water bath and 50 ml. of 85% sulfuric acid and 234 g. of benzene were placed in the flask. A mixture of 68.1 g. (1.0 mole) of isoprene and 117 g. of benzene was added to the acid-benzene mixture. Three reactions were carried out varying the addition time and temperature.

TABLE V

Benzene Run No.	Addition Time	°C	Gram Crude Product	Residue	% Yield Monosubstituted Product	% Yield Disubstituted Products
1	2.25 hrs.	15 to 20	60	10	13.8	18.7
2	2.0 hrs.	35 to 40	45	21	10.4	14.0
3	15 min.	15 to 20	96	8	24.4	28.2

In each case the reaction mixture was stirred 15 minutes after the addition was completed. The sulfuric acid layer was drained from the separatory funnel and 25 ml. of water was added to hydrolyze the remaining red-brown complex. The separatory funnel contents were neutralized with aqueous sodium carbonate and the hydrocarbon layer washed with water.

This yellow organic layer was separated, dried over magnesium sulfate, filtered, and the benzene removed on a rotary evaporator. The crude product referred to in the above table consisted of 1,1,-dimethylindan (monosubstituted product) and an isomeric mixture of tetramethylhydrindacenes (disubstituted products). The percentages were determined by G.L.C. analysis (8 ft. x $\frac{1}{4}$ in., 25% LAC-446 at 175°) using a thermal conductivity detector. The crude products (201 g.) were combined and distilled through a 2 ft. column packed with metal helices to give 15.5 g. of 1,1-dimethylindan (b.p. 73°/3mm). A G.L.C. analysis (150 ft., ECNSS-S capillary column at 150°) showed an impurity of about 4%. A 1 ml. sample was prepared by preparative scale gas chromatography on a 3/8 in. x 10 ft. column of 20% XE 60 at 200°. This sample was shown by G.L.C. (150 ft. ECNSS-S capillary column at 100°) to be over 99% pure. The 1,1,-dimethylindan gave a positive bromine test for unsaturation before the G.L.C.

purification. The purified product was saturated to bromine in carbon tetrachloride.

1,1-Dimethylindan Using Polyphosphoric Acid (P.P.A.)

The apparatus was set up as before and 68 g. of P.P.A. and 234 g. of benzene were introduced into the flask. One mole (68.1 g.) isoprene and 117 g. of benzene were mixed and added over a period of 2 hours with an additional 15 minute stirring time. The temperature was maintained at 40-45°. The hydrocarbon layer was decanted from the viscous P.P.A. and washed with aqueous sodium carbonate and with water. After drying over magnesium sulfate and filtering, the unreacted benzene was removed on a rotary evaporator, giving 54 g. of crude product. This was shown by G.L.C. analysis (8 ft. x ¼ in., 20% LAC-446 at 158°) to be a mixture of at least eleven major components. This product had an unusually sweet smell unlike that of the sulfuric acid catalyzed products, and was shown to be unsaturated to bromine. A small portion (3 g.) was placed in a flask and 1 ml. of 85% sulfuric acid was added while stirring with a magnetic stirring bar at ambient temperature. A brown tar formed immediately. The supernatant liquid was decanted, washed with aqueous sodium carbonate and dried over magnesium sulfate. A G.L.C. analysis (8 ft. x ¼ in., 20% LAC-446 at 158°) showed at least three of the peaks diminished in size.

1,1,4-and 1,1,6-Trimethylindan

The 500 ml. flask was fitted with an ice-salt bath and 75 g. of sulfuric acid and 163 g. of toluene were poured in and allowed to cool to -10°. A mixture of 29 g. (0.43 mole) of isoprene and 50 g. of toluene

was added dropwise. Two runs were made varying the addition time.

TABLE VI

Toluene Run No.	Addition Time	°C	Gram Crude Product	Gram Residue	% Yield Monosubstituted Isomers	% Yield Disubstituted Isomers
1	1 hr.	-10 to 0	35	22	39.5	8.8
2	3 hr.	-10 to -3	60	18	58.0	11.5

In both reactions the acid layer was separated from the organic portion and the latter washed with aqueous sodium carbonate, washed with water, dried over magnesium sulfate, and filtered. The unreacted toluene was distilled at atmospheric pressure giving 191 g. and 172 g. recovered toluene for runs #1 and #2 respectively. The products were shown by G.L.C. analysis (4 ft. x $\frac{1}{2}$ in., 20% SE 30 at 150°) to be identical mixtures of two sets of doublet peaks. The product from run #2 (58 g.) was distilled to give a series of lower boiling fractions (b.p. 65°-70°/1mm.) and a higher boiling fraction (120°/1mm.). Analysis by G.L.C. (8 ft. x $\frac{1}{2}$ in., 20% XE 60 at 200°) showed the lower boiling fractions to be the first doublet peak and the higher boiling fraction, the doublet with the longer retention time. The two compounds of the first fractions (1,1,4- and 1,1,6-trimethylindans) were separated preparatively by G.L.C. (10 ft. x $\frac{3}{8}$ in., 20% XE 60 at 200°). About 1 ml. of each isomer was collected. Analytical G.L.C. (150 ft., ECNSS-S capillary column at 100°) indicated each isomer to be over 99% pure.

1,1,4,7-Tetramethylindan

Into a 1 liter flask was placed 300 g. of *p*-xylene and sulfuric acid

of the amount and strength indicated in the table below. These reactants were cooled to -10° and a mixture of 68.1 g. of isoprene (1.0 mole) and 150 g. of *p*-xylene was added. The rate of addition and strength of the acid were varied as indicated below. Five reactions were carried out.

TABLE VII

<i>p</i> -Xylene Run No.	<u>Mole Acid</u> Mole Isoprene	Ml. Acid	% Strength Acid	$^{\circ}\text{C}$	Addition Time	Gram Recovered <i>p</i> -Xylene
1	0.27	50	85	10 to 20	2.25 hr.	380.5
2	0.27	50	85	15 to 20	1 hr.	312
3	0.27	50	85	15 to 20	15 min.	284
4	0.27	57	75	30 to 40	15 min.	408
5	0.27	85	50	30 to 40	15 min.	432

Gram Crude Product	Gram Residue	% Yield Monosubstituted Product	% Yield Disubstituted Product
70	7	23.7	11.9
74	8	27.6	10.7
136	14	58.7	14.0
29	18	10.9	4.2
0	0	0.0	0.0

The reaction mixtures were worked up by draining the acid layer from a separatory funnel and adding 10 ml. of water to hydrolyze the remaining complex. This product was then washed with aqueous sodium carbonate, saturated aqueous sodium chloride, and dried by shaking with activated silica gel and passing through a basic alumina column. *p*-Xylene was

stripped on a rotary evaporator. The product was quickly distilled from the remaining residue under vacuum and the percentages of mono- and disubstituted products were determined by G.L.C. analysis (10 ft. x $\frac{1}{4}$ in., 20% XE 60 at 180^o) using a thermal conductivity detector.

Three large scale runs were made with *p*-xylene to obtain 4 liters of 1,1,4,7-tetramethylindan for purification by the American Petroleum Institute Project 58B for use as API Standard Samples. The apparatus was set up as in Plate 1. A 22 liter three-necked flask was used. A mixture of 4.5 liters of *p*-xylene and 700 ml. of 85% sulfuric acid was cooled to 10^o in the flask. To this mixture 1.5 liters of isoprene (15.1 moles) and 2.0 liters of *p*-xylene were added. The reaction mixture in each case

Run No.	°C	Addition Time
1	15 to 25	1.5 hr.
2	15 to 20	2.25 hr.
3	14 to 23	2.5 hr.

was allowed to stir for 15 minutes after the addition was completed.

In each case the mixture was poured into a 22 liter separatory funnel and allowed to settle. The lower (sulfuric acid) layer was drained and discarded. About 100 g. anhydrous sodium carbonate was then added to the organic layer. This addition caused some effervescing and the solid sodium carbonate settled to the bottom along with most of the polymerized isoprene present. The relatively clear liquid was then passed through a basic alumina column, using about ten pounds pressure of nitrogen to facilitate the flow. The products from the three reactions were distilled separately and the fractions rich in 1,1,4,7-tetramethylindan were combined

for a final distillation (b.p. $98^{\circ}/10\text{mm}$) giving 3584 g. (45.5% of the hydrocarbon. The purity was determined by G.L.C. analysis (150 ft., ECNSS-S capillary column at 102°) to be greater than 99%. A shipment of 3400 g. of the indan was made to Project 58B. A 3 ml. sample was purified by preparative scale gas chromatography (10 ft. x $3/8$ in., 20% XE 60 at 200°) and was shown by analytical G.L.C. (150 ft. capillary ECNSS-S at 100°) to be greater than 99.8% pure. The residues of the three distillations were quickly distilled under vacuum to give 2250 g. (19.5%) of the disubstituted isomer mixture. This was recrystallized three times from ethanol-benzene to give a product having a m.p. $80.3 - 113.0^{\circ}$.

1,1,4,6-Tetramethylindan

Sixty-nine grams (38 ml.) of sulfuric acid (93%) and 164 g. of m-xylene were placed in a 1 liter flask. The contents of the flask were cooled to -10° and to this 29 g. of isoprene (0.43 moles) and 50 g. of m-xylene were added over the period of 2.5 hours. The temperature varied from -5° to 0° . Stirring was continued for 30 minutes with the temperature below 0° . The acid layer was drained off the bottom and the product was washed with water, aqueous sodium carbonate and saturated sodium chloride. This organic layer was dried over magnesium sulfate and filtered. Recovery of 133 g. of m-xylene was made by distillation at atmospheric pressure. Distillation at reduced pressure ($88^{\circ}/6\text{mm.}$) gave 51 g. (68%) of 1,1,4,6-tetramethylindan. A crystalline material was distilled from the residue to give 6 g. of white crystals with 4 g. of tar remaining in the flask. The crystals were purified by successive recrystallizations from ethanol-benzene and isopropyl alcohol-benzene and were found to melt at $136.7^{\circ} - 137.6^{\circ}$.

Three large scale reactions were carried out with m-xylene. The apparatus was set up as in Plate 1 using a 22 liter flask. Four and one-half liters of m-xylene and 912 ml. of 93% sulfuric acid were placed in the flask and stirred until the temperature of the flask and contents reached -10° . A mixture of 1392 ml. m-xylene and 1.0 liter (10.2 moles) of isoprene was added over a period of 4 hours, keeping the temperature below 5° . The reaction mixture was allowed to stir an additional 15 minutes with the temperature below 0° . The acid layer was drained from a separatory funnel and 1 liter of water was added to hydrolyze the remaining organic portion. Run #1 was neutralized with 5% sodium hydroxide (aq.); Run #2 with aqueous sodium carbonate; and Run #3 by adding solid sodium carbonate to the remaining organic layer after draining the water layer. In the first two cases a very stable emulsion formed. Removal of the product by steam distillation was attempted, but the low steam volatility of the indan made this course impractical. In the first two runs, the product was recovered by ether extraction, drying over magnesium sulfate and filtering, and stripping the ether from the product. The third method (anhydrous sodium carbonate) neutralized the solution without emulsion formation and cleared the solution of most of the polymer present. The resulting liquid was then passed through a basic alumina column. The three products were distilled separately. m-Xylene was distilled at atmospheric pressure and the 1,1,4,6-tetramethylindan was distilled at reduced pressure. The appropriate fractions from the three runs were combined for a final distillation giving 3675 g. (70.2% overall) of 1,1,4,6-tetramethylindan (b.p. $85^{\circ}/4.7\text{mm.}$). Analytical G.L.C. (150 ft. ECNSS-S capillary column at 125°) showed the purity exceeded 99%. Of this material 3247 g. were shipped to project 58B. Three milliliters of

1,1,4,6-tetramethylindan were purified by preparative gas-liquid chromatography (10 ft. x 3/8 in., 20% XE 60 at 200°) and G.L.C. analysis showed this material to be over 99.8% pure.

Cyclialkylation of 1,1,4,6-Tetramethylindan

Twenty grams of 1,1,4,6-tetramethylindan along with 10 ml. of 93% sulfuric acid were placed in a 250 ml. flask set up as before. A mixture of 20 g. of isoprene (0.29 mole) and 20 g. of the indan were added over a period of 45 minutes, keeping the temperature between 0° and 25°. The mixture was stirred an additional 15 minutes and was hydrolyzed with 25 ml. water after separating and discarding the bottom (acid) layer. The organic portion was then washed with aqueous sodium carbonate and with water. This material was dried over magnesium sulfate and filtered. The crude material was quickly distilled giving: (1) 19 g. recovered indan which turned dark upon standing, (2) 7.5 g. of the hydrindacene product which was recrystallized to give 6 g. of a material of melting point 136.2 - 138.5°, and (3) 14 g. of residue.

1,1,4,5-; 1,1,5,6-; and 1,1,6,7-Tetramethylindan

A 500 ml. flask was set up as usual and 69 g. (38 ml.) of 93% sulfuric acid and 164 g. of o-xylene were placed in the flask and cooled below 0°. A mixture of 29 g. of isoprene (0.43 mole) and 50 g. of o-xylene was added dropwise over a period of two hours with the temperature reaching a maximum of 2°. A stirring time of 15 minutes was used after the completion of the addition of the isoprene and o-xylene mixture. The acid layer was drained from the upper organic portion in a separatory funnel and the remaining product was washed until neutral with aqueous sodium carbonate

and dried over magnesium sulfate. After filtration, the o-xylene was distilled at atmospheric pressure giving 152 g. of recovered o-xylene and a reduced pressure distillation of the resulting product gave 38 g. (51%) of the monosubstituted isomeric indan mixture (b.p. 65^o/0.5mm) and 7 g. (7%) of the disubstituted isomeric mixture (b.p. 140^o/0.6mm).

A large run was made in order to have enough material to separate the three monosubstituted isomers. The apparatus was set up as in Plate 1. To the 22 liter flask was added 4.5 liters of o-xylene and 700 ml. of 85% sulfuric acid. The contents of the flask were cooled to 10^o and a mixture of 1008 ml. isoprene (10.2 moles) and 1392 ml. o-xylene was added over a period of two hours. The temperature was held between 15^o and 20^o during the addition. An additional 15 minute stirring period was used. The product was poured into a 12 liter separatory funnel and the bottom (acid) layer drained. One liter of water was added to hydrolyze the complex and after separating this from the organic layer about 100 g. of anhydrous sodium carbonate was added and the mixture was shaken. The product was dried by shaking with silica gel and was passed through a basic alumina column. Distillation at atmospheric pressure gave 2763 g. of recovered o-xylene. Distillation at reduced pressure gave 717 g. (41.2%) of monosubstituted isomeric mixture (b.p. 92-94^o/5mm) and 158 g. of residue. When this residue was distilled under reduced pressure, 152 g. (6.3%) of a viscous disubstituted product was obtained. Analytical G.L.C. (10 ft. x 1/4 in., 20% LAC-886 at 185^o) showed the monosubstituted (indan) product to be a set of three peaks A, B, and C with composition 56%, 11% and 33% respectively.

This isomeric mixture of the cyclialkylation product of o-xylene was

distilled through a 4 ft. x 1 in. Podbielniak column packed with 29/17 in. helipack packing material. At a reflux ratio of 60:1, the column had an efficiency rating of 80 theoretical plates. A charge of 400 g. of the indan mixture was distilled continuously at 20mm. taking 5% cuts.¹ A total of seventeen fractions were taken. Analytical G.L.C. (10 ft. x $\frac{1}{2}$ in., 20% LAC-886 at 150°) showed the fraction most pure in component A to be 95% A, the fraction most pure in B, 37% B, and the fraction most pure in component C was 90% C.

The isomers were separated preparatively on G.L.C. (16 ft. x 4 in., 20% Apiezon L at 200°). For the separation of components A and C, 10 ml. injections of the charge stock were made collecting to the top of the first peak (A) and from the top of the last (C) peak. The material collected from a single pass was analyzed on a 10 ft. x $\frac{1}{2}$ in., 20% LAC-886 column at 150° (see Plate 2). The purities of fractions A and C were found to be 99.9% and 99.8% respectively. The material from the above distillation richer than 25% in peak B (cuts 9-12) were injected as four 10 ml. injections and the B component collected. This material was reinjected and collected to give 2 ml. of isomer B. (About 5 ml. each of isomers A and C were collected.) A 10 ft. x $\frac{1}{2}$ in., 20% LAC-886 column at 150° showed a 5% impurity, with a longer retention time than any of the isomers, remained in component B. This collected material was passed through a 16 ft. x 4 in., 20% Carbowax 20M preparative column at 200° and 1 ml. of the B isomer isolated. Analytical G.L.C. showed this compound to be over 99.5% pure (see Plate 2).

¹This distillation was performed under the direction of A. B. Carel in the distillation laboratories of Continental Oil Co., Ponca City, Okla.

Anal. Calcd. for $C_{13}H_{18}$: C, 89.59%; H, 10.41%. Found for Component A: C, 89.57%; H, 10.42%. Component B: C, 89.80%; H, 10.31%. Component C: C, 89.83%; H, 10.30%.

Cyclialkylation of Ethylbenzene, Isopropylbenzene, and t-Butylbenzene

The reaction vessel in the following series of experiments was a flat-bottomed glass tube with a 24/40 standard taper joint at the upper end and two side arms below this opening. One of these side arms was fitted with a dropping funnel. The tube had a capacity of about 100 ml. (24mm. x 192mm.). A magnetic bar was used to stir the reaction mixtures.

In each case 4 ml. of 93% sulfuric acid was placed in the reaction tube along with 16 g. of the alkylbenzene. The vessel and contents were cooled to -10° and a mixture of 2.9 g. of isoprene and 5 g. of alkylbenzene was added with stirring over a period of 20 minutes. The temperature of the reaction vessel was kept below 5° . An additional stirring time of 5 minutes was used. The acid layer was drained from a separatory funnel and the product was washed with aqueous sodium hydroxide and water. The retained organic layer was then dried over magnesium sulfate and filtered. Analytical G.L.C. (4 ft. x $\frac{1}{2}$ in., 20% SE 30 at 150°) showed the products to be isomeric mixtures of the 6-alkyl- and 4-alkyl-1,1-dimethylindans, the former being the major component.

A reaction was carried out to isolate 6-t-butyl-1,1-dimethylindan. A 500 ml. flask was set up as usual. Into the flask were placed 82 g. of t-butylbenzene and 16 ml. of 93% sulfuric acid. The flask and contents were cooled below 0° . A mixture of 26 g. of t-butylbenzene and 15 g. of isoprene (0.22 mole) was added to the flask in 1.5 hours. An

additional 15 minutes stirring time was allowed. The bottom acid layer was drained using a separatory funnel and 50 ml. water was added to hydrolyze the organic complex. The crude reaction mixture was washed with aqueous sodium carbonate, dried over silica gel, and passed through a basic alumina column. This mixture was distilled to give 62 g. of recovered t-butylbenzene and 30 g. (68%) of the indan isomers.

Two large scale reactions were carried out to prepare a hydrocarbon for the Standard Samples program. The apparatus was set up as in Plate 1. In each of these reactions, 5.0 liters of t-butylbenzene and 1 liter of 89% sulfuric acid were added to the 22 liter flask. The flask contents were cooled to 10° and a mixture of 2 liters of t-butylbenzene and 1.5 liters (15.5 moles) of isoprene was added over a period of 3.5 hours in the first reaction and 3 hours in the second. The temperature was kept below 20° in both cases. The work-up procedure was identical for both reactions, draining the acid layer from a 12 liter separatory funnel, hydrolyzing the remaining organic complex with 1 liter of water, then adding anhydrous sodium carbonate. Silica gel was added to dry the crude mixture which was then passed through a basic alumina column. The two reaction products were distilled separately. Run #1 gave 3741 g. of recovered t-butylbenzene and Run #2, 3654 g. The fractions from Runs 1 and 2 in the boiling point range 112°/13mm. to 120°/11mm. (4875 g.) were combined and distilled twice to give 3815 g. (60.3%) of the 6-t-butyl-1,1-dimethylindan (B) (b.p. 87°/2mm.) and 183 g. (3.0%) of a crystalline product (A). The latter product was recrystallized from benzene-ethanol to give 1,4-di-t-butylbenzene melting at 77.6° - 78.6°.

Anal. Calcd. for C₁₅H₂₂: C, 89.04%; H, 10.96%. Found for Component A: C, 89.02%; H, 10.88%. Component B: C, 88.90%; H, 11.03%.

Cyclialkylation of Tetralin

A 1 liter three-necked flask was set up as usual and 38 ml. of 93% sulfuric acid and 234 g. of tetralin were added. When the contents of the flask were cooled to -10° , 66 g. of tetralin was added along with 29 g. of isoprene (0.43 mole) over the period of 3.5 hours. The contents were stirred for an additional 15 minutes with the temperature held below 0° . The acid layer was drained from a separatory funnel and the remaining organic layer was washed with 5% aqueous sodium hydroxide and with water. Ether and a small amount of ammonium hydroxide were added to break the emulsion which had formed. The solution was washed with saturated sodium chloride, dried over magnesium sulfate, and filtered. Distillation gave 126 g. of recovered tetralin, 47 g. (57.4%) of an isomeric mixture of cyclialkylated product and 28 g. of residue. Analytical G.L.C. (10 ft. x $\frac{1}{4}$ in., 25% XE 60 at 200°) showed the product to consist of three components.

1,1,4,6,7-Pentamethylindan

The apparatus was set up as in Plate 1. Into the 22 liter flask were placed 5.1 liters of pseudocumene and 700 ml. of 93% sulfuric acid. The flask and contents were cooled to 0° and a mixture of 1008 ml. of isoprene (10.2 moles) and 1.6 liters of pseudocumene was added over the period of two hours. The reaction mixture was stirred an additional 15 minutes. During the course of addition, the temperature varied from -5° to $+2^{\circ}$. After pouring the crude product into a 12 liter separatory funnel, the acid layer was drained and 500 ml. of water was added to hydrolyze the remaining organic layer. The mixture was neutralized with aqueous sodium

carbonate, dried over magnesium sulfate and filtered. Distillation gave 4030 g. recovered pseudocumene and 1342 g. (70.0%) of the colorless crystalline indan melting at 73.9° - 75.4° . The residue weighed 186 g. The crude indan was recrystallized from ethanol-benzene, Skelly solvent B, and again from ethanol-benzene. The melting range of the purified indan was 75.7° - 76.0° and this product was shown by G.L.C. analysis (10 ft. x $\frac{1}{4}$ in., 20% LAC-886 at 180°) to be one component.

Alkylation of Mesitylene Using Methane Sulfonic Acid (M.S.A.)

A three-necked 2 liter flask was set up as usual and 380 g. of mesitylene and 10 g. of M.S.A. were added. To this mixture 100 g. of mesitylene and 95.2 g. of isoprene (1.4 moles) were added over a period of 2.5 hours maintaining the temperature of the reaction between 20° and 25° . This mixture was stirred for 30 minutes after the addition, neutralized with dilute ammonium hydroxide, and washed with water. Fifty ml. of ether was added to break up the emulsion which had formed. After drying over magnesium sulfate and filtering, the ether was removed on a rotary evaporator and the product was steam distilled to remove the unreacted mesitylene. A fast vacuum distillation of the nonvolatile material from the steam distillation was performed. The residue from this distillation was 118 g. The volatile material from both distillations was dried over magnesium sulfate, filtered, and distilled through a 2 ft. packed column to give 347 g. of recovered mesitylene and 93.5 g. (31.9%) of olefin product. The residue weighed 8 g. Analytical G.L.C. (460 ft., 6-ring polymeta-phenyl ether capillary column at 160°) indicated the product was a mixture of two components. These components were separated preparatively

on G.L.C. (16 ft. x 4 in., 30% carbowax 20M at 210°).

Cyclization of the Olefin Product From Mesitylene

Four 50 ml. Erlenmeyer flasks were set up with magnetic stirring bars. The fourth flask was fitted with a drying tube. In each flask was placed 10 ml. of cyclohexane and 1 ml. of the isomeric mixture of 2-methyl-4-(2,4,6-trimethylphenyl)-2-butene and the corresponding 1-butene. The following were also added:

<u>Flask</u>	<u>Catalyst</u>	<u>Quantity</u>
1	96% sulfuric acid	1 ml.
2	93% sulfuric acid	1 ml.
3	85% sulfuric acid	1 ml.
4	aluminum chloride	0.1 g.

These reaction mixtures were stirred for one hour at ambient temperature and 1 ml. of water was added to stop the reaction. The organic layer of each flask was washed with dilute ammonium hydroxide and analyzed by G.L.C. with a 460 ft., 6-ring polymetaphenyl ether capillary column at 160°.

Four additional reactions were carried out using 96% sulfuric acid as a catalyst. The 50 ml. Erlenmeyer flasks were set up as in the previous experiment and in each case a 10 minute stirring period was allowed.

TABLE VIII

Flask	ml. Cyclohexane	Gram Mesitylene Olefin	ml. 96% Sulfuric Acid	°C
1	8	2	1	30
2	5	5	1	30
3	2	8	1	20
4	5	5	5	20

These reactions were worked up as described in the previous experiment.

The products were distilled from the higher boiling residue under vacuum.

TABLE VIIIa

Flask	Wt. Indan (g.)	Wt. Residue (g.)
1	1.8	0.1
2	4.3	0.5
3	4.7	2.8
4	1.9	1.7

A larger reaction was carried out in a 500 ml. round-bottomed flask equipped with a magnetic stirring bar and containing 15 g. of the olefin mixture from mesitylene along with 150 ml. of cyclohexane and 5 ml. of 96% sulfuric acid. This mixture was stirred 15 minutes at ambient temperature. Fifty ml. of water was added to hydrolyze the product which was then washed with aqueous sodium hydroxide. This organic layer was dried with magnesium sulfate and filtered. The cyclohexane was removed on a rotary evaporator and 14.6 g. (97%) of the product was obtained. Analytical

G.L.C. (8 ft. x $\frac{1}{4}$ in., 20% Carbowax 20M at 210^o) showed this product to be a mixture of two components. These were separated on a 16 ft. x 4 in., 20% Carbowax 20M preparative G.L.C. column at 210^o.

Aluminum Chloride Rearrangement

Into each of six 50 ml. round-bottomed flasks fitted with a drying tube and stirring bar, was placed 5 ml. of nitroethane and 1.3 g. of anhydrous aluminum chloride. The suspension was stirred and the individual flasks were cooled by an ice bath at 0^o. One-half gram of the following compounds were added: (1) 1,1,4,5-tetramethylindan (XX) (2) 1,1,5,6-tetramethylindan (XIX) (3) 1,1,6,7-tetramethylindan (XXI) (4) 1,1,4,7-tetramethylindan (XVI) (5) 1,1,4,6-tetramethylindan (XXV) and (6) 1,1,-dimethyl-6-t-butylindan (XI) (with 2% 1,1-dimethyl-4-t-butylindan impurity). These mixtures were stirred at ice temperature for 30 minutes and then allowed to come to ambient temperature. Ten ml. of water was added to each flask to hydrolyze the complex. These products were worked up by washing with ammonium hydroxide and then water, drying over magnesium sulfate, and filtering. Analytical G.L.C. was performed on a 10 ft. x $\frac{1}{4}$ in., 20% LAC-886 column at 160^o. The only changes noted were XXI isomerizing quantitatively to XIX and some trans-t-butylation of XI to a complex mixture of 4 products.

Methylation of 1,1,4,7-Tetramethylindan

A 1 liter three-necked flask was fitted with a stirring assembly, dropping funnel, and a reflux condenser with a drying tube attached. The flask was flushed with nitrogen and 41 g. 1,1,4,7-tetramethylindan (0.24 mole) was added to the flask along with 66 g. of aluminum chloride.

Stirring was commenced and 199 g. of methyl iodide was added over a period of one hour. The temperature reached 43° during the addition. This reaction mixture was stirred for 2 hours at 60° and 150 ml. of water was added to hydrolyze the complex. Distillation gave 26 g. of recovered 1,1,4,7-tetramethylindan and 9 g. (20%) of a material with a boiling range $60^{\circ} - 65^{\circ}/0.5$ mm., consisting principally of two pentamethylindan isomers. These isomers were separated on preparative G.L.C. (16 ft. x 4 in., 20% Carbowax 20M at 210°) to give two fractions, each greater than 90% pure. The N.M.R. spectra indicated these products were 1,1,4,5,6- and 1,1,5,6,7-pentamethylindan.

Cyclialkylation of Durene

Durene (100 g., 0.75 mole) was placed in a 1 liter flask along with 150 ml. of cyclohexane and 10 g. of M.S.A. To this mixture a solution of 95.2 g. of isoprene (1.4 moles) in 100 ml. of cyclohexane was added with stirring over a period of 20 minutes. The reaction became quite vigorous and the temperature rose to 60° . This mixture was cooled before adding 50 ml. of water to hydrolyze the complex. Aqueous sodium carbonate was used to neutralize the reaction mixture. After drying over magnesium sulfate and filtering, the mixture was distilled to give 74.3 g. (26%) of the durene-isoprene product. Recrystallization from ethanol yielded a single isomer. Twenty grams of the above olefin was dissolved in 200 ml. of cyclohexane and 5 ml. of 96% sulfuric acid was added. This mixture was stirred for 30 minutes and the sulfuric acid layer was drained. After washing with water and aqueous sodium carbonate, the reaction product was dried over magnesium sulfate and filtered. The

cyclohexane was removed on a rotary evaporator to give 16 g. of material. Analytical G.L.C. (10 ft. x $\frac{1}{4}$ in., 20% SE 30 at 196^o) showed this to be a mixture of two components, one of which was the olefinic starting material. The other component was the cyclized hexamethylindan.

Cyclialkylation of 1,2,3,4-Tetramethylbenzene

The reaction vessel was set up as in the monoalkylbenzene experiments. Into the reaction tube was placed 4 g. of 1,2,3,4-tetramethylbenzene along with 4 drops of 85% sulfuric acid. A solution of 3 g. of isoprene in 5 ml. of cyclohexane was added over a period of 15 minutes keeping the temperature between 10^o and 15^o. Water was added to hydrolyze the complex and the mixture was neutralized with aqueous sodium carbonate. This product was then dried over magnesium sulfate and filtered. Analysis by G.L.C. was done on a 10 ft. x $\frac{1}{4}$ in., 20% SE 30 column at 196^o and the mixture was shown to contain a number of components. Distillation gave a mixture of two components in the boiling range of hexamethyl indans as determined by retention time on the SE 30 G.L.C. column. The N.M.R. spectra showed the mixture comprised XXXII and XXXIII.

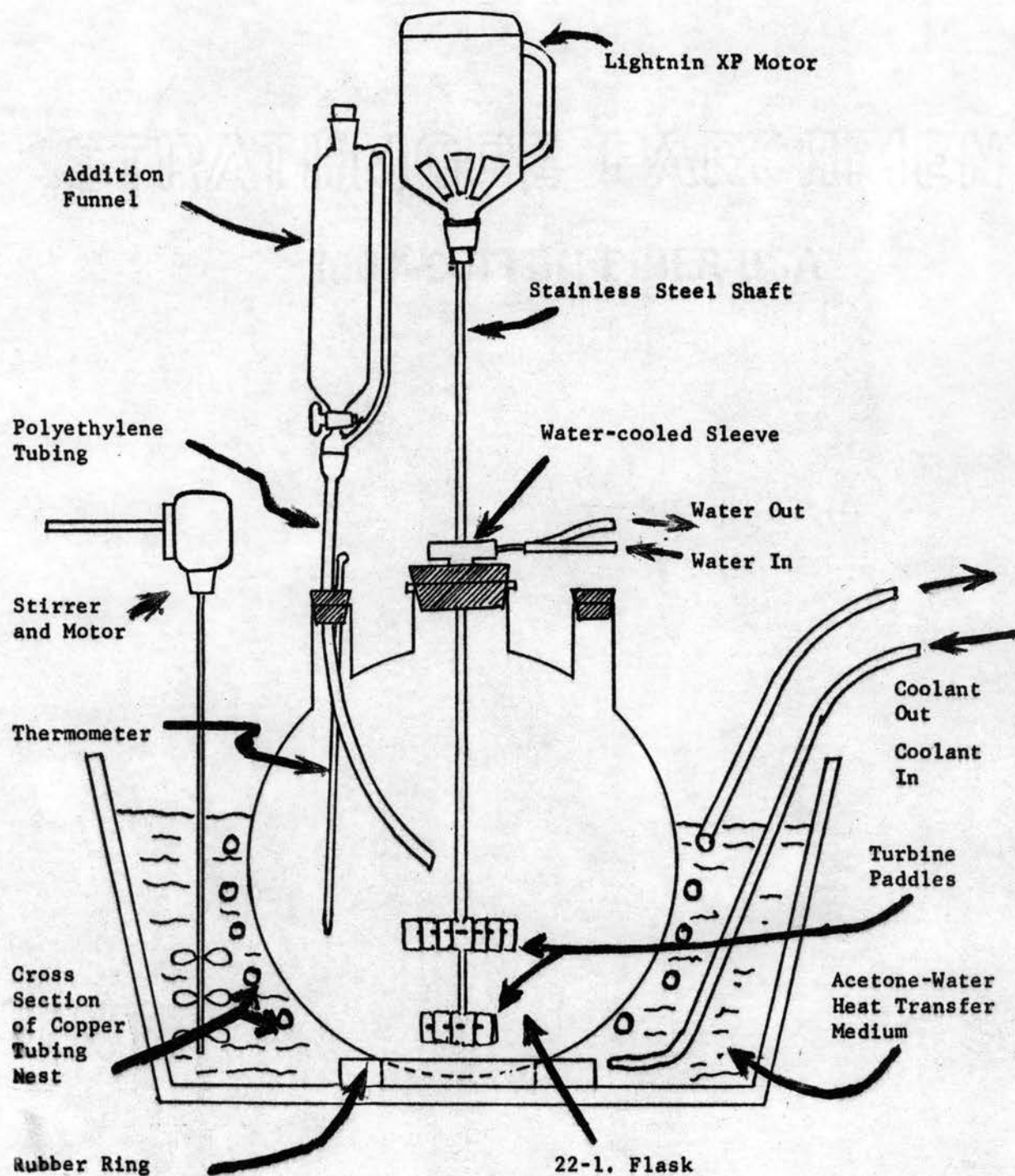


Plate 1 CYCLIALKYLATION APPARATUS

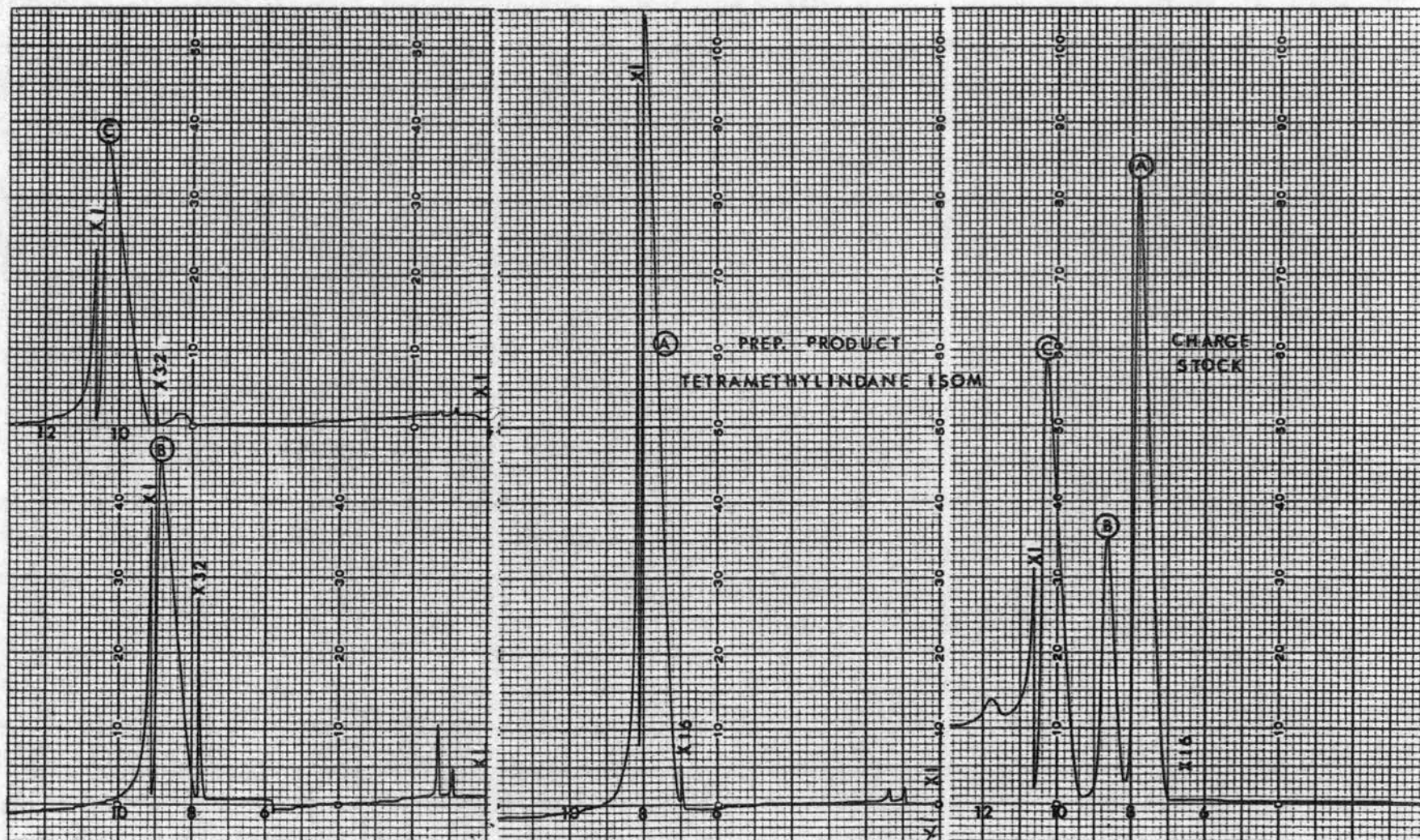


Plate 2 5 ml. Samples of GLC Separated Indan Isomers A, XIX; B, XX and C, XXI

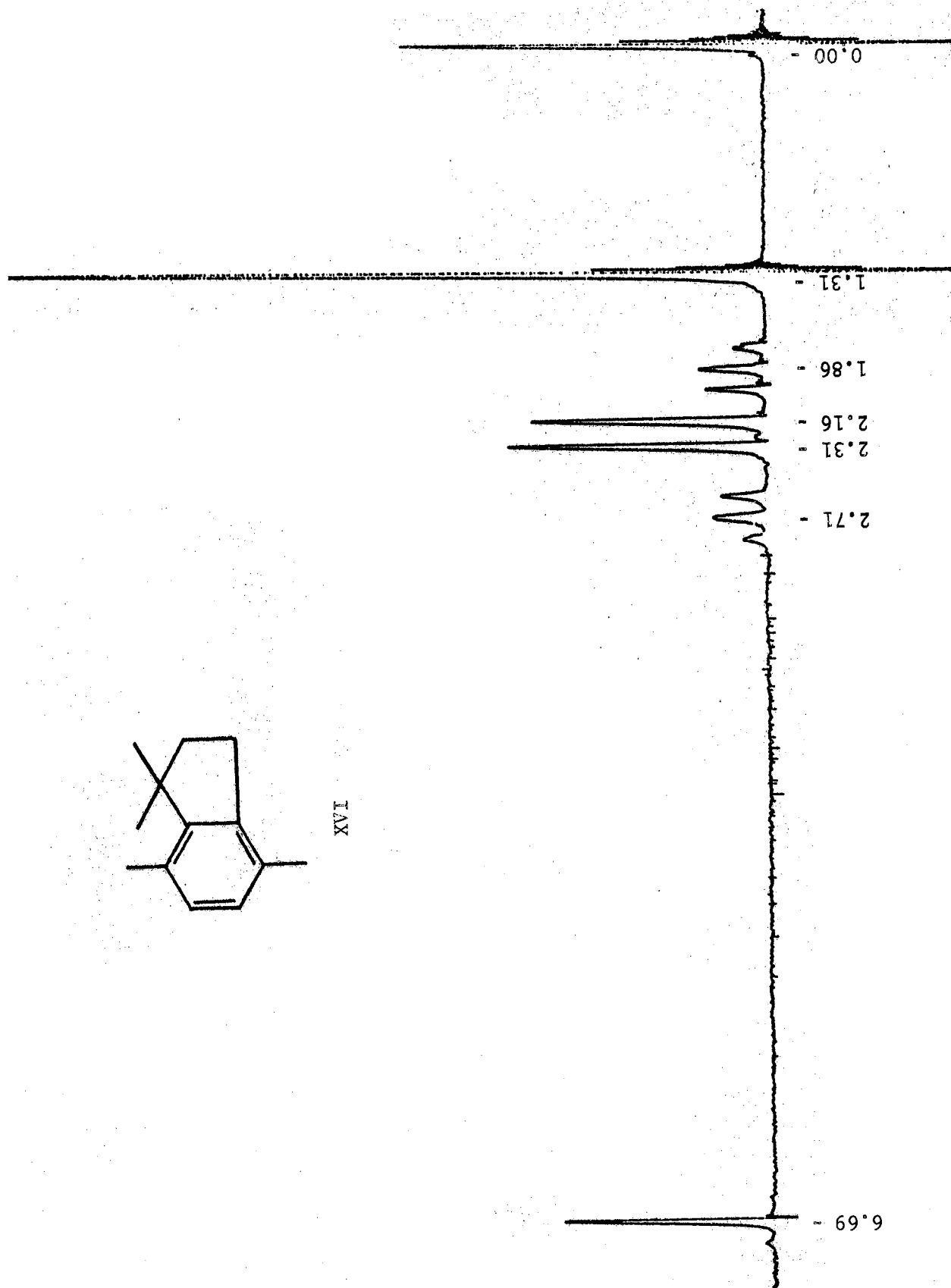


Plate 3 N.M.R. Spectrum of XVI PPM(δ)

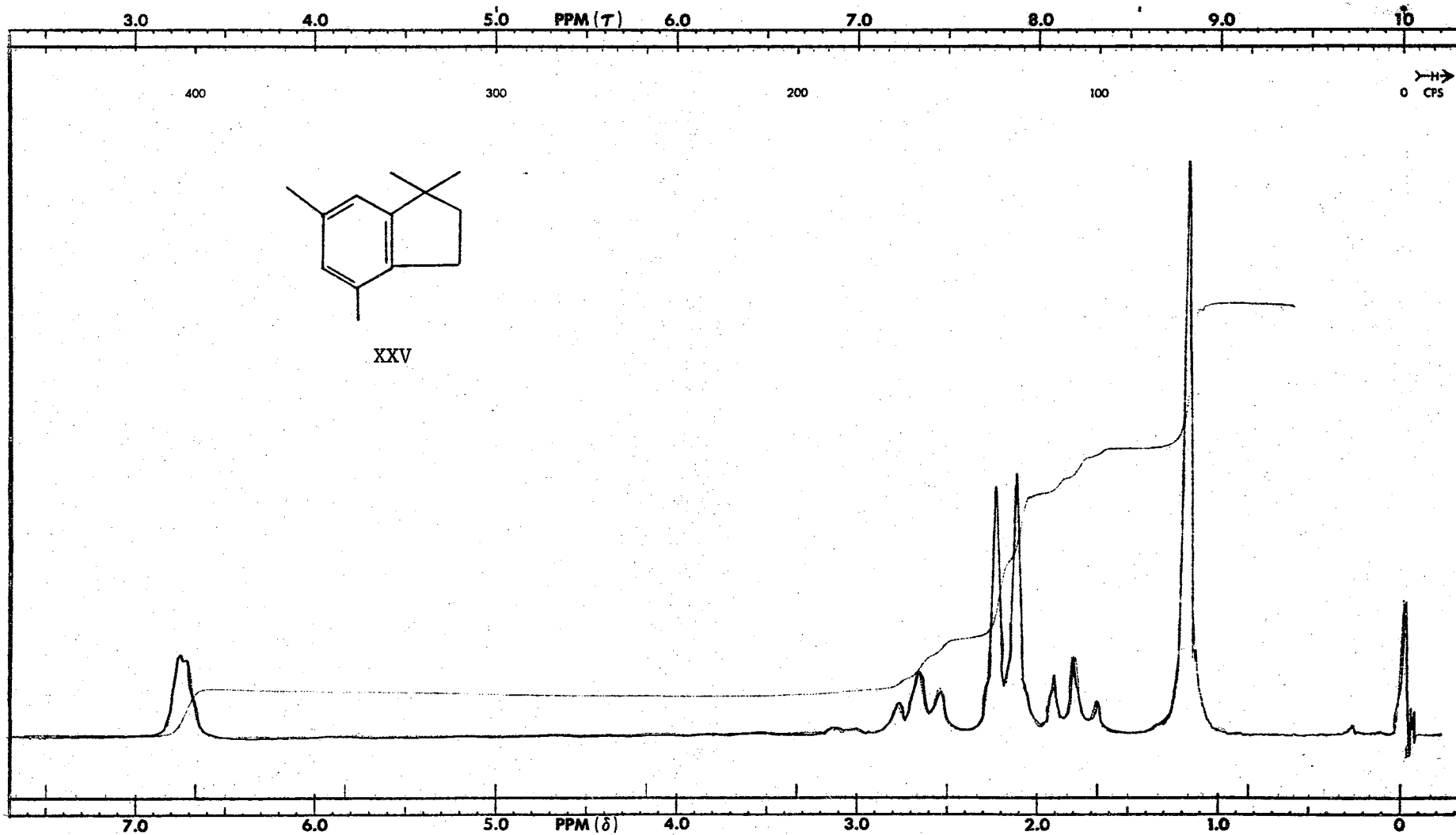


Plate 4 N.M.R. Spectrum of XXV

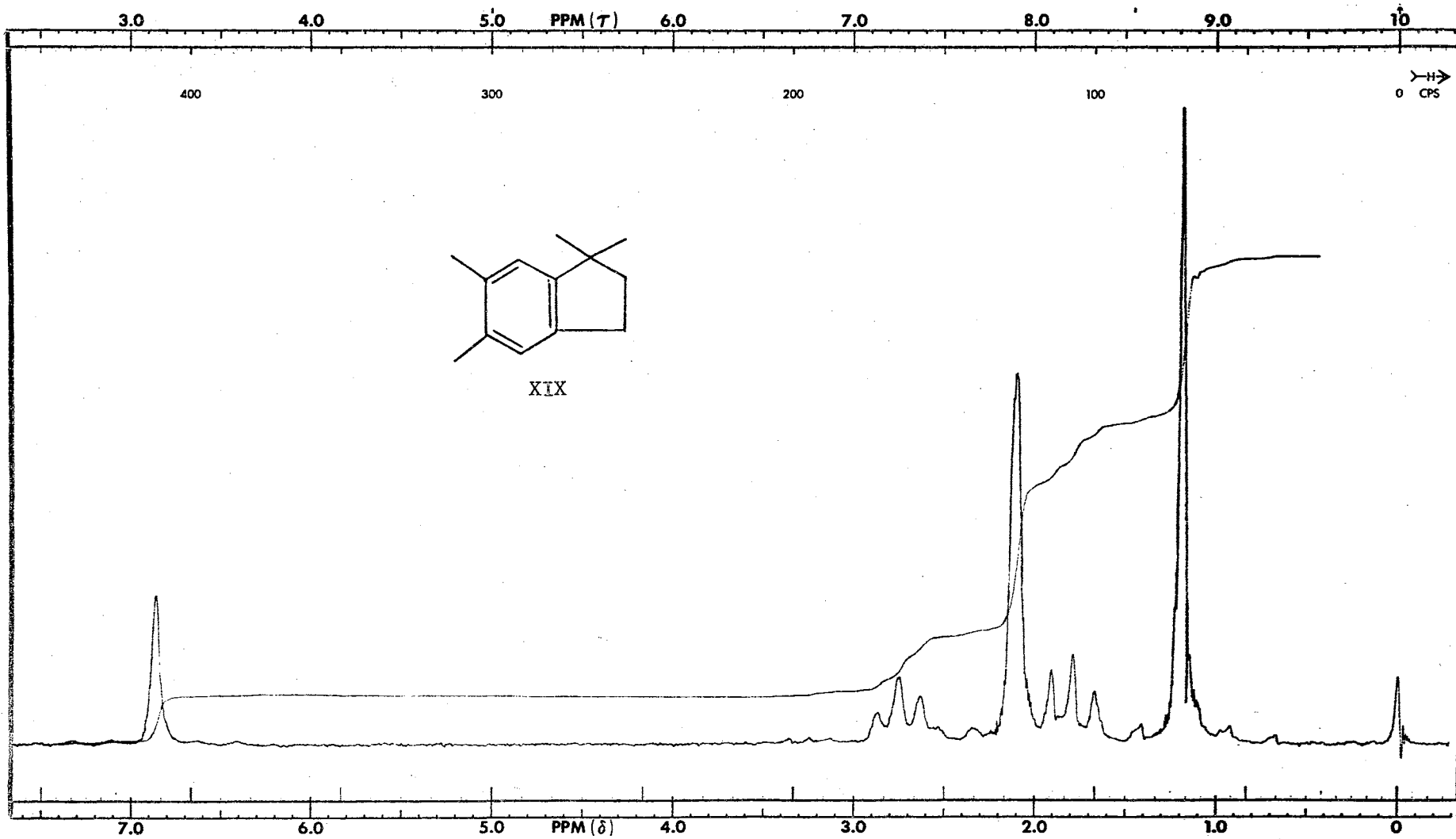


Plate 5 N.M.R. Spectrum of XIX

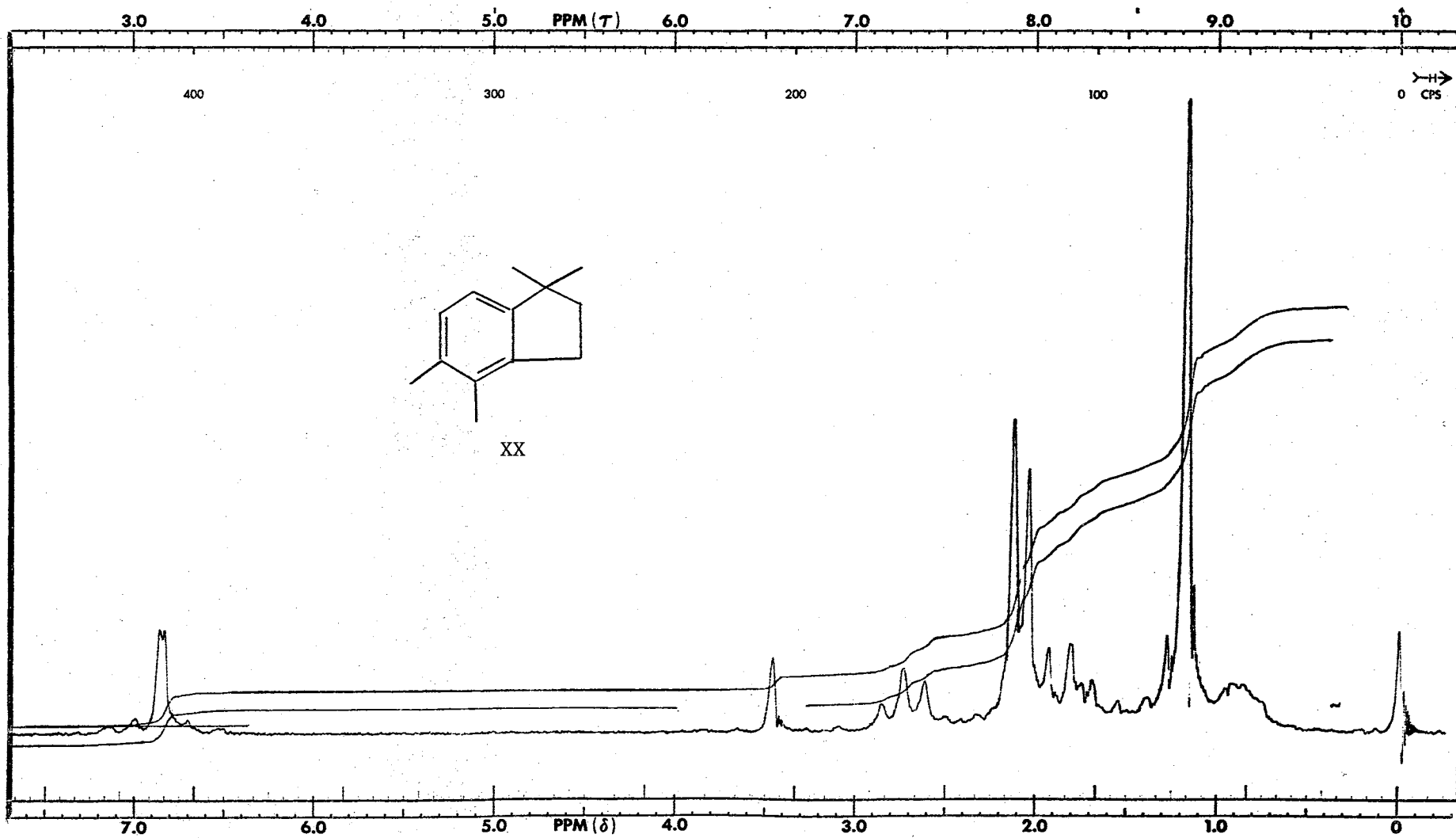
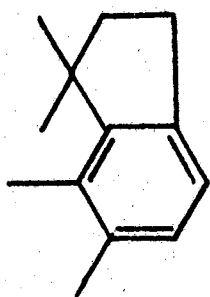


Plate 6 N.M.R. Spectrum of XX



XXI

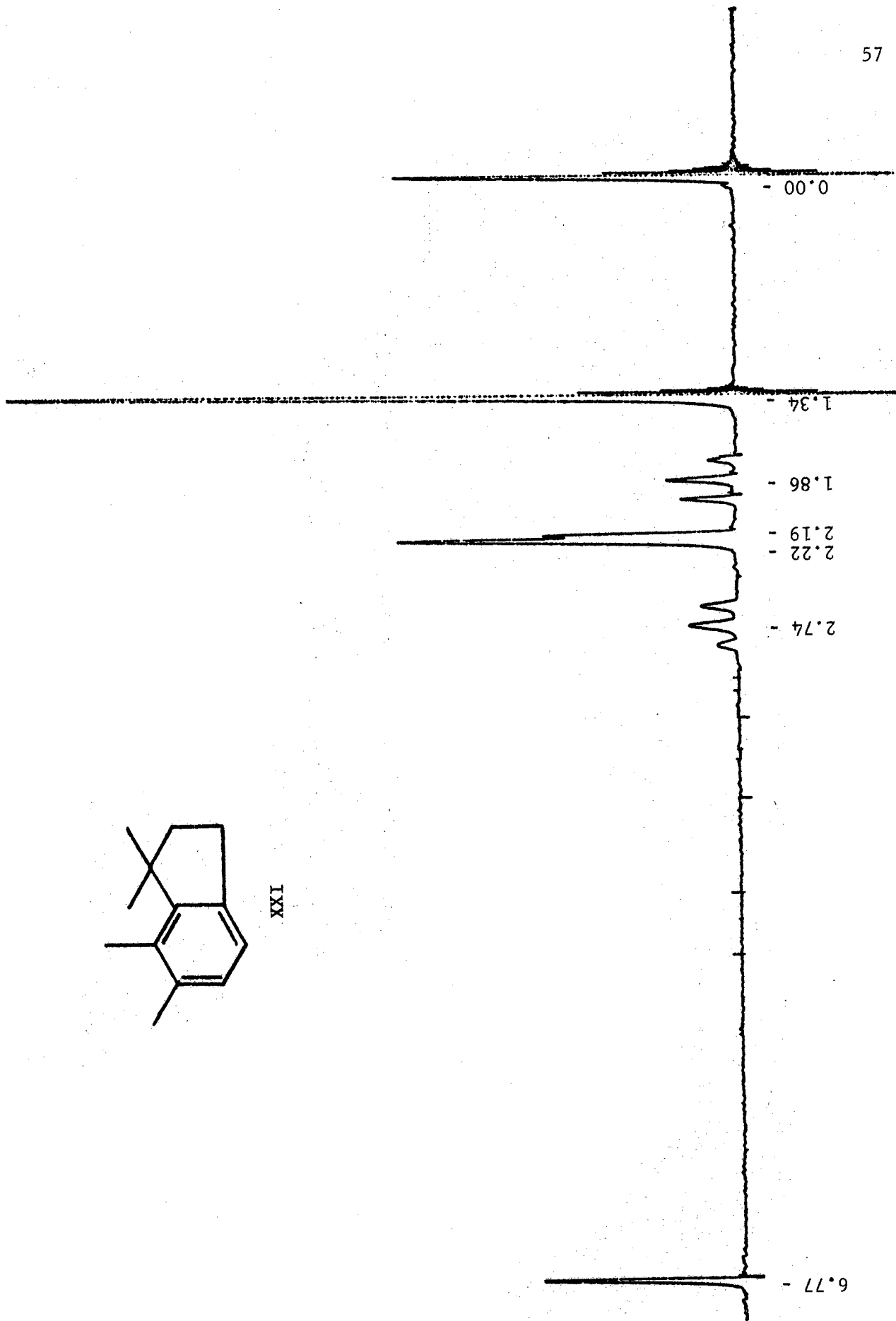


Plate 7 N.M.R. Spectrum of XXI PPM(δ)

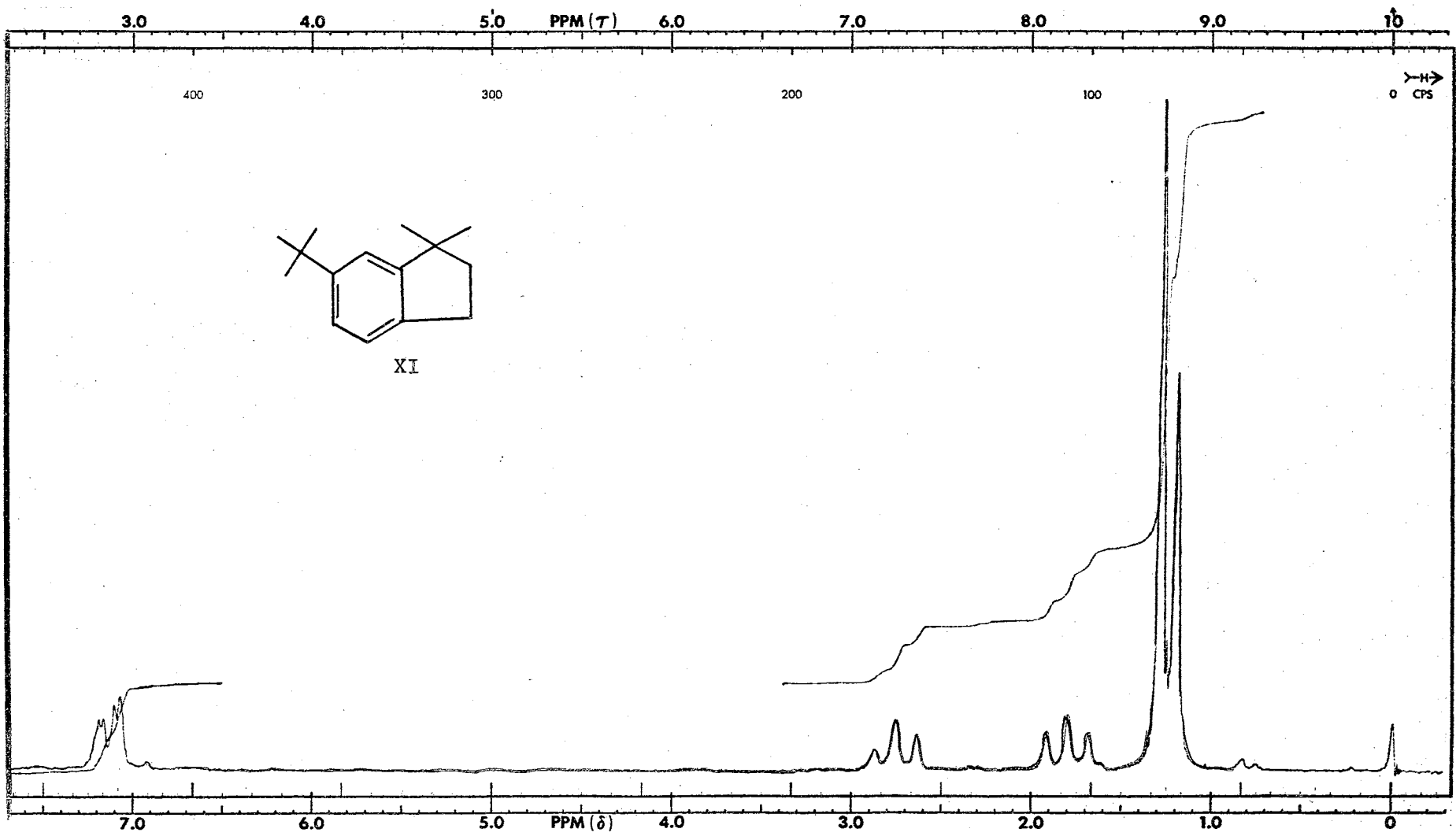
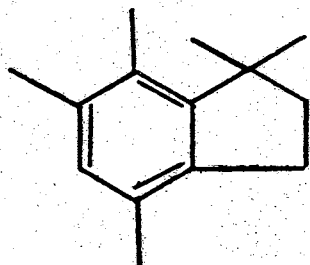


Plate 8 N.M.R. Spectrum of XI



XXVIII

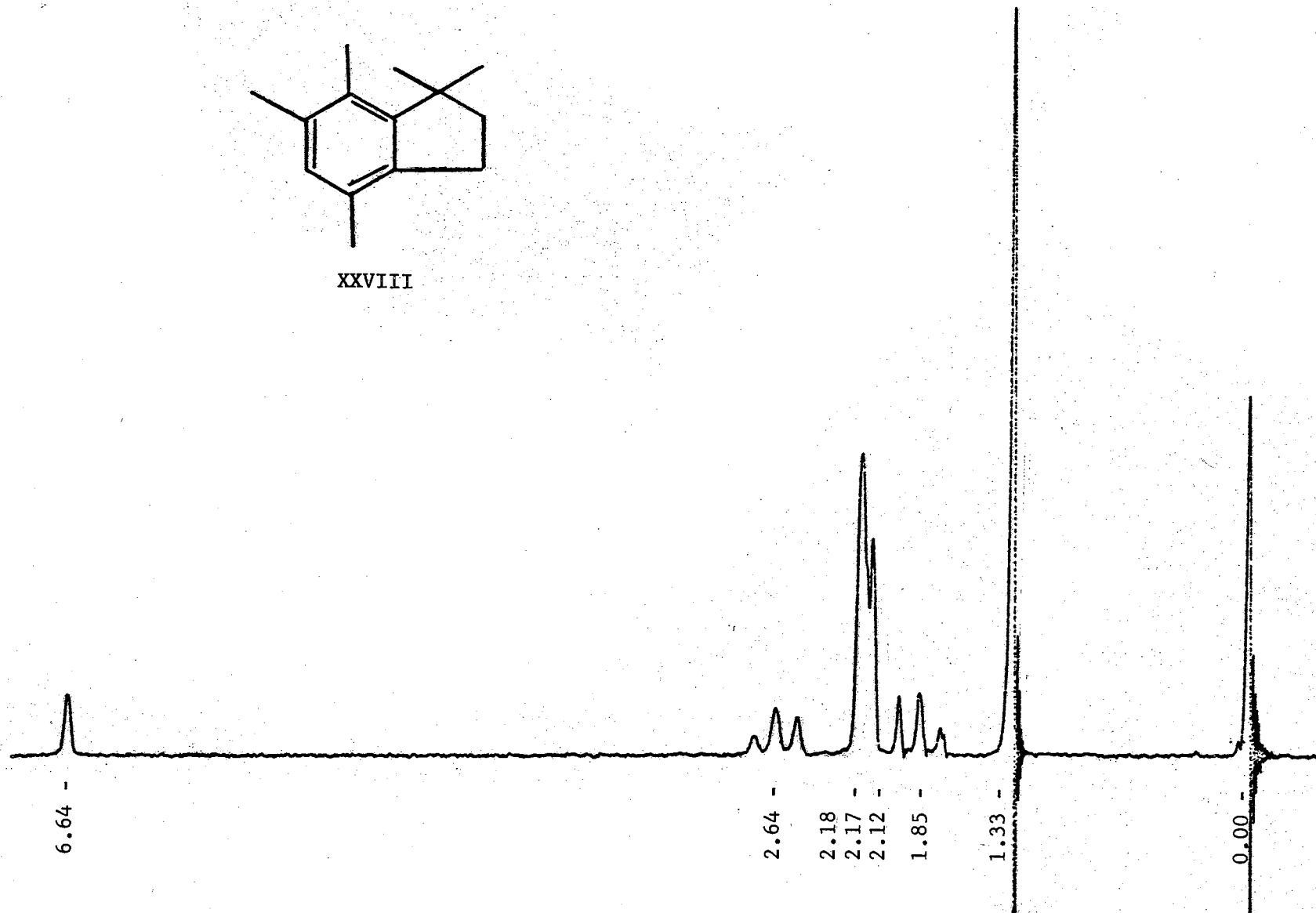
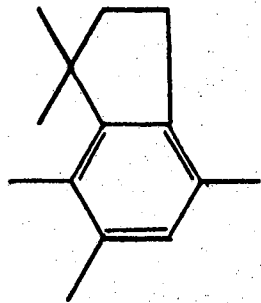
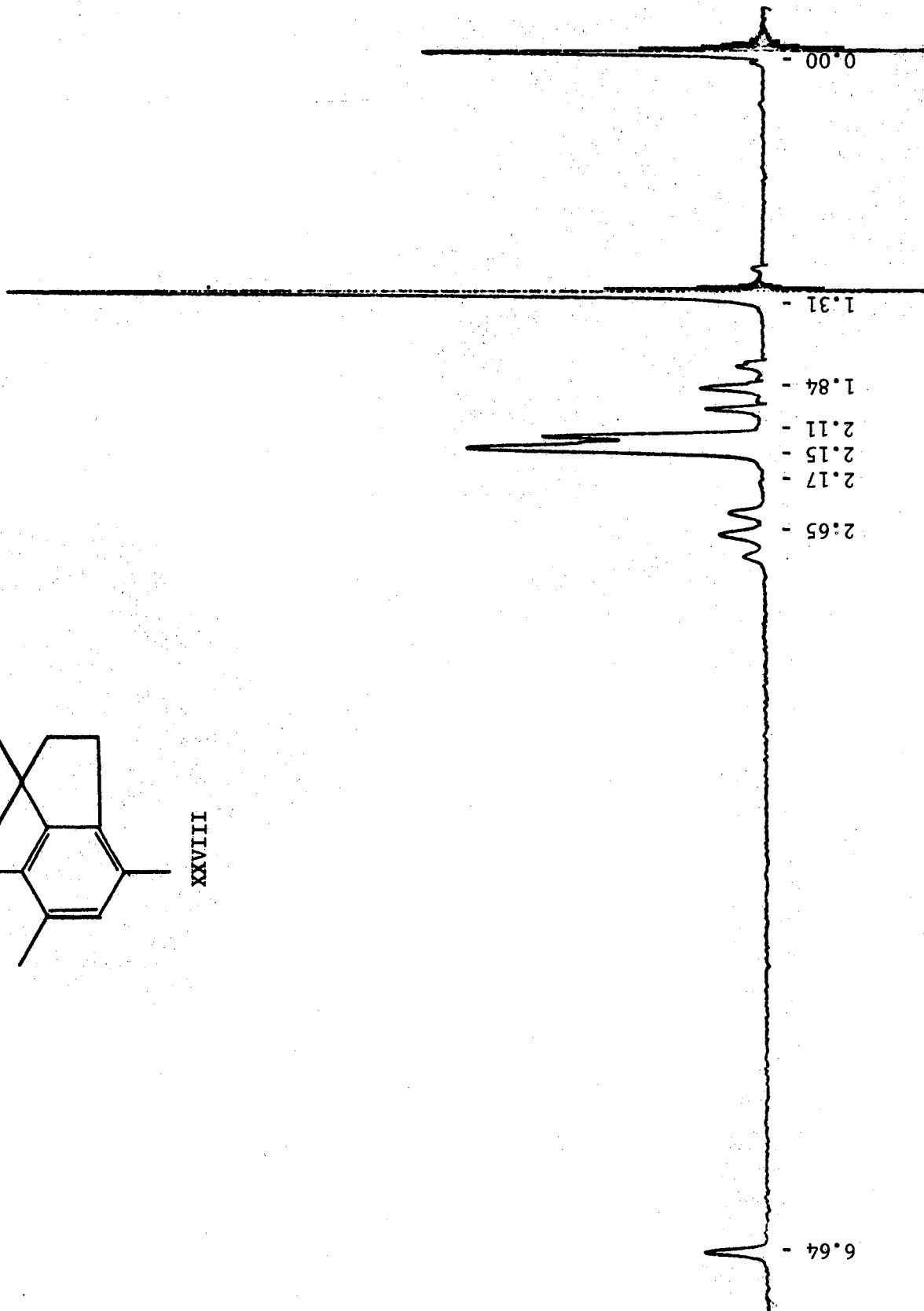


Plate 9 N.M.R. Spectrum of XXVIII From Pseudocumene PPM(δ)



XXVIII

Plate 10 N.M.R. Spectrum of XXVIII From Mesitylene PPM(δ)

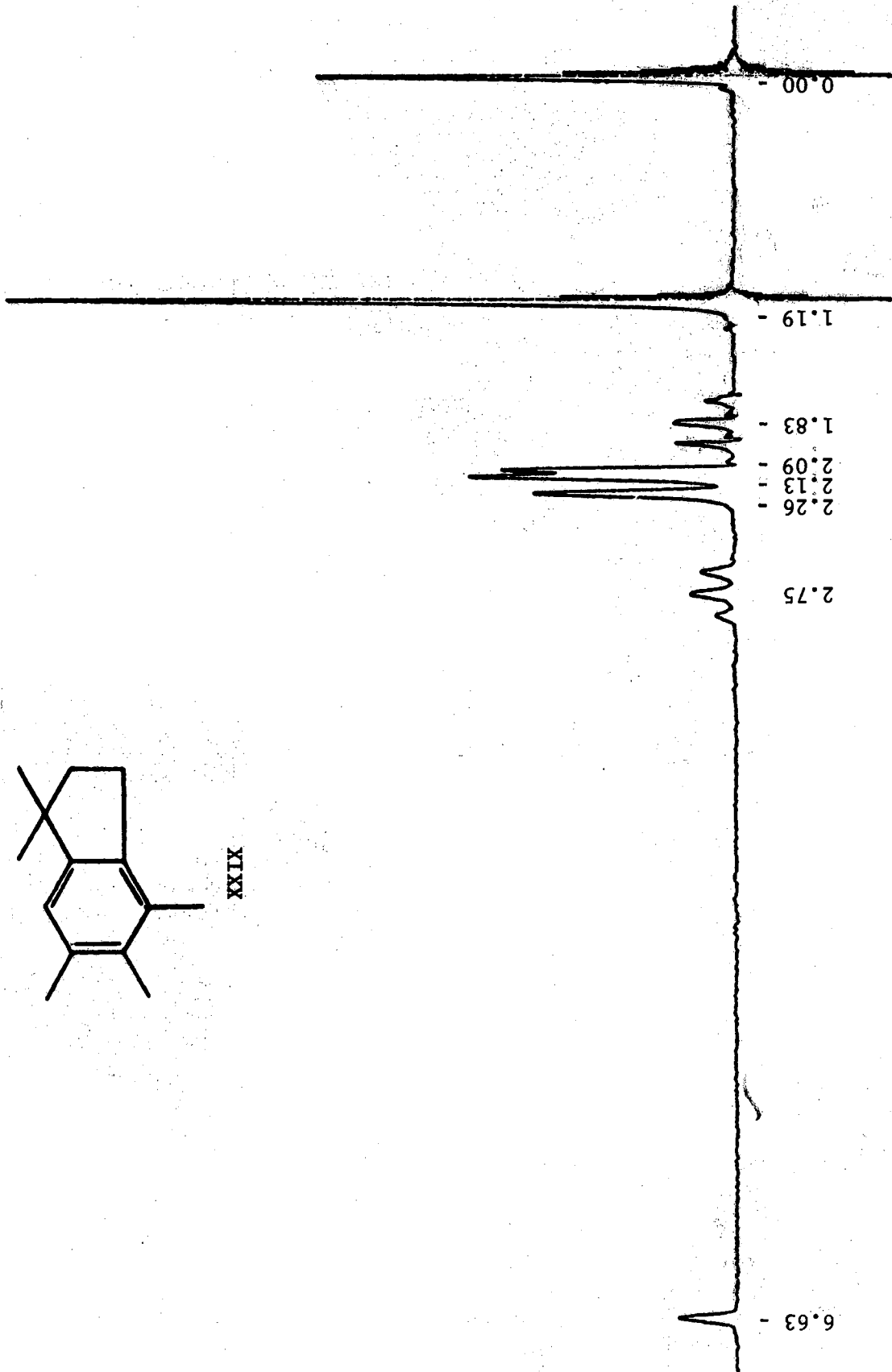


Plate 11 N.M.R. Spectrum of XXIX PPM(6)

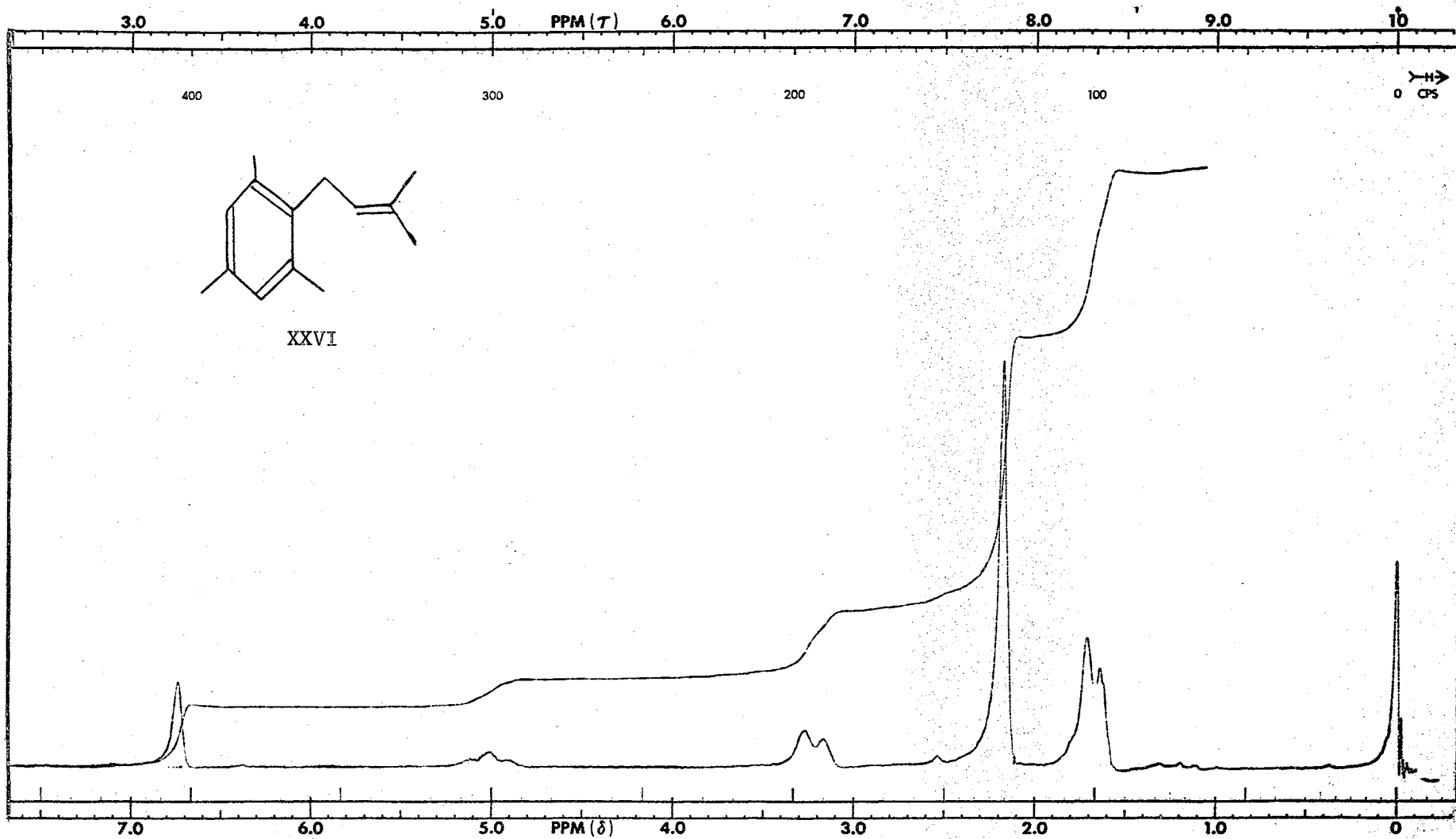


Plate 12 N.M.R. Spectrum of XXVI

BIBLIOGRAPHY

1. M. T. Bogert and D. Davidson, *J. Am. Chem. Soc.*, 56, 185 (1934).
2. G. Baddeley and R. Williamson, *J. Chem. Soc.*, 4647-53 (1956).
3. J. Colonge and P. Rochas, *Bull. Soc. Chim., France*, 822 (1948).
4. G. Buchi, K. Biemann, B. Vittimberga, and M. Stoll, *J. Am. Chem. Soc.*, 78, 2622 (1956).
5. M. Beets, H. Vanessen, and W. Meerburg, *Rec. Trav. Chim.*, 77, 857 (1958).
6. Universal Oil Products Co., L. Schmerling, U.S. Pat. 2,848,512.
7. M. S. Carpenter, *Proc. Sci. Sect., Toilet Goods Assoc.*, 23, 1 (1955).
8. V. N. Ipatieff, H. Pines, and R. C. Olberg, *J. Am. Chem. Soc.*, 70, 2123 (1948).
9. M. J. Schlatter, *Symposium on Petrochemicals in The Postwar Years*, Am. Chem. Soc. (Chicago), 79 (1953).
10. M. J. Schlatter, *Symposium on Chemicals from Petroleum, Division of Petroleum Chemistry*, Am. Chem. Soc., (Dallas), 17 (1956).
11. S. H. Weber, D. B. Spoelstra, and E. H. Polak, *Rec. Trav. Chem.*, 74, 1179 (1955).
12. S. H. Weber, J. Stofberg, D. B. Spoelstra, and R. J. C. Kleinpool, *ibid.*, 75, 1433 (1956).
13. S. H. Weber, R. J. C. Kleinpool, and D. B. Spoelstra, *ibid.*, 76, 196 (1957).
14. T. F. Wood and J. Angiolini, *Tetrahedron Letters*, 1, 1 (1963).
15. The Givaudan Corp., T. F. Wood, U.S. Pat. 3,078,319.
16. L. Schaap and H. Pines, *J. Am. Chem. Soc.*, 79, 4767 (1957).
17. G. G. Eberhardt, *J. Org. Chem.*, 29, 643 (1964).
18. J. L. Adelfang, *ibid.*, 29, 2756 (1964).

19. W. Proell, *J. Org. Chem.*, 16, 178 (1951); U.S. Pat. 2,565,077 (Aug. 14, 1951).
20. K. E. Moeller, *Brennstoff - Chem.*, 42, 361 (1961).
21. A. R. Bader, *J. Am. Chem. Soc.*, 79, 6164 (1957).
22. R. Koncos and B. S. Friedman, *Friedel-Crafts and Related Reactions*, Ed. Olah, Vol. II, Part 1, p. 297, John Wiley, New York (1964).
23. *Ibid.*, 290.
24. E. S. Gould, *Mechanism and Structure in Organic Chemistry*, p. 532, Holt, Rinehart, and Winston (Revised, 1962).
25. *Ibid.*, p. 262.
26. A. R. Bader and W. C. Bean, *J. Am. Chem. Soc.*, 80, 3073 (1958).
27. S. Natelson, *Ibid.*, 56, 1584 (1934).
28. Ya. M. Paushkin, A. V. Topchiev, and M. V. Kurashev, *Kokl. Akad. Navk S.S.S.R.*, 130, 1033 (1960).
29. M. A. Dalin, R. E. Spivak, and E. F. Burmistrov, *Azerb. Khim. Zh.*, No. 6, 21 (1960).
30. M. J. Schlatter, *J. Am. Chem. Soc.*, 76, 4952 (1954).
31. H. Pines, B. Kvetinskas, J. A. Vesely, and E. Bacłowski, *Ibid.*, 73, 5173 (1951).
32. A. R. Bader, *Ibid.*, 79, 6164 (1957).
33. N. C. Deno, H. E. Berlkheimer, W. L. Evans and H. J. Peterson, *Ibid.*, 81, 2344 (1959).
34. N. C. Deno, H. J. Peterson, and G. S. Sainey, *Chem. Rev.*, 60, 7 (1960).
35. B. S. Friedman, F. L. Morritz, C. J. Morrissey, and R. Koncos, *J. Am. Chem. Soc.*, 80, 5867 (1958).
36. H. Hart and F. A. Cassis, *Ibid.*, 73, 3179 (1951).
37. V. N. Ipatieff, H. Pines, and R. E. Schaad, *Ibid.*, 67, 1060 (1945).

VITA

John Robert Mattox

Candidate for the Degree of

Master of Science

Thesis: CYCLIALKYLATION STUDIES WITH ISOPRENE

Major Field: Chemistry

Biographical:

Personal Data: The author was born in Columbus, Ohio, on August 31, 1940, the son of Robert W. and Elsie Mattox.

Education: The author attended North High School in Columbus, Ohio, and received a Bachelor of Science Degree from the Ohio State University in March, 1963.

Professional Experience: The author was employed on a part-time basis by the American Petroleum Institute project 58A then at Ohio State University from June, 1959 to March 1962. From June 1962 to March 1963 the author was employed by Professor M. S. Newman of Ohio State University.