THE HEXAMETHYLHYDRINDACENES DERIVED

FROM ISOPRENE AND THE XYLENES

By

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Bachelor of Science

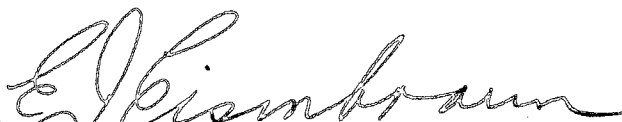South Dakota State University

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# INTRODUCTION

The cyclialkylation reaction of an aromatic hydrocarbon having unoccupied vicinal positions with a conjugated diene in the presence of a protonic acid is well documented. However, in most of these cases, the aromatic hydrocarbon was selected to insure formation of a single hydrindacene.

Alkyl-substituted hydrindacenes have been studied extensively, not only as they are novel hydrocarbons but also because they have been used as intermediates for the preparation of oxidation inhibitors, detergents, perfumes, and pharmaceutical products.

This study was undertaken to investigate the cyclialkylation reaction of the xylenes and isoprene using sulfuric acid as a catalyst and to determine if a cyclialkylation reaction would be a feasible means of preparing hydrindacenes for the American Petroleum Standard Samples Program. In every case, isomeric mixtures of hexamethylhydrindacenes were formed and highly efficient distillation was ineffective in separating the individual components. Recrystallization and preparative gas chromatography were valuable tools for separating some of the individual isomers. Liquid-solid column chromatography provided a means of separating the ketone derivatives of these hydrindacenes.

Cyclialkylation reactions are believed to proceed through attack of an allyl carbonium ion on an aromatic ring. This study has established that the initial attack is from C-4 of isoprene since a

noncyclic intermediate from the reaction of mesitylene and isoprene has been isolated and subsequently cyclized to two pentamethylindans.

Spectral data, chemical reaction studies, and elemental analyses were used to establish the structure of individual hydrindacenes and indans.

# CHAPTER I

# HISTORICAL

The term cyclialkylation was first used by Bruson and Kroeger[1] to describe condensation reactions of aromatic compounds with difunctional molecules such as diols, dichlorides, and diolefins. Reactions of these compounds with aromatic systems proceed at each end of the difunctional chain to attach a new ring to the aromatic nucleus as shown in Fig. 1.

The course of the reaction probably involves alkylation of the aromatic compound to produce an aryl-substituted intermediate. This intermediate can then undergo an intramolecular alkylation and aromatization to form the new ring. Bruson and Kroeger also introduced the use of 1,4-glycols and 1,5-diolefins in addition to 1,4-dihalides as cyclialkylating reagents in these Friedel-Craft reactions.
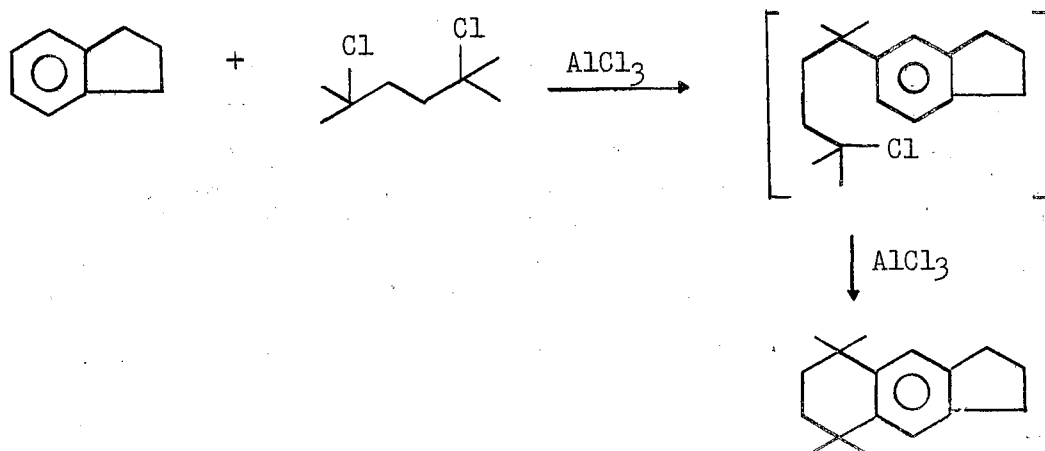
Figure 1. Cyclialkylation of Indan

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A convenient one-step cyclialkylation reaction used to synthe-
size hydrindacenes was reported by Schmerling[2] in 1958. In this case,
isoprene served as the cyclialkylating reagent which resulted in
1,1,5,5-tetramethyl-s-hydrindacene (1) from benzene.



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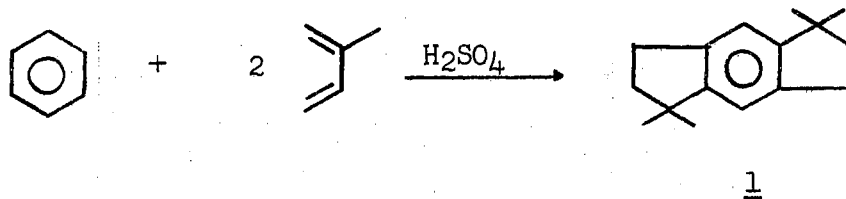
The hydrindacene 1 was accompanied by a lower yield of 1,1-
dimethylindan  and it was also reported that 1 can be converted to
4-hydroxy-1,1,5,5-s-tetramethylhydrindacene and 4,8-dihydroxy-1,1,5,5-
s-tetramethylhydrindacene.  Both hydroxy compounds show marked activity
as oxidation inhibitors.  Schmerling's patent[2] claims all cyclialkyla-
tion reactions of aromatic hydrocarbons containing at least two pairs
of unoccupied vicinal positions separated by at least one carbon atom
(e.g., benzene, toluene, p-xylene, etc.) with conjugated dienes in
which at least one of the doubly bonded carbon atoms is a tertiary
carbon atom (e.g., isoprene, 2,3-diethyl-1,3-butadiene, 2-ethyl-1,3-
pentadiene, etc.).  Examples of catalysts described in this patent are
concentrated sulfuric acid, hydrogen fluoride, and phosphoric acid.

A unique cyclialkylation reaction of p-disubstituted alkyl-
benzenes in which both alkyl groups contain a reactive α-tertiary
hydrogen atom was described by Schlatter.[3]  With these compounds, a
"double cyclialkylation" accounted for the formation of symmetrical
hydrindacenes.  The following mechanism was proposed.[3]
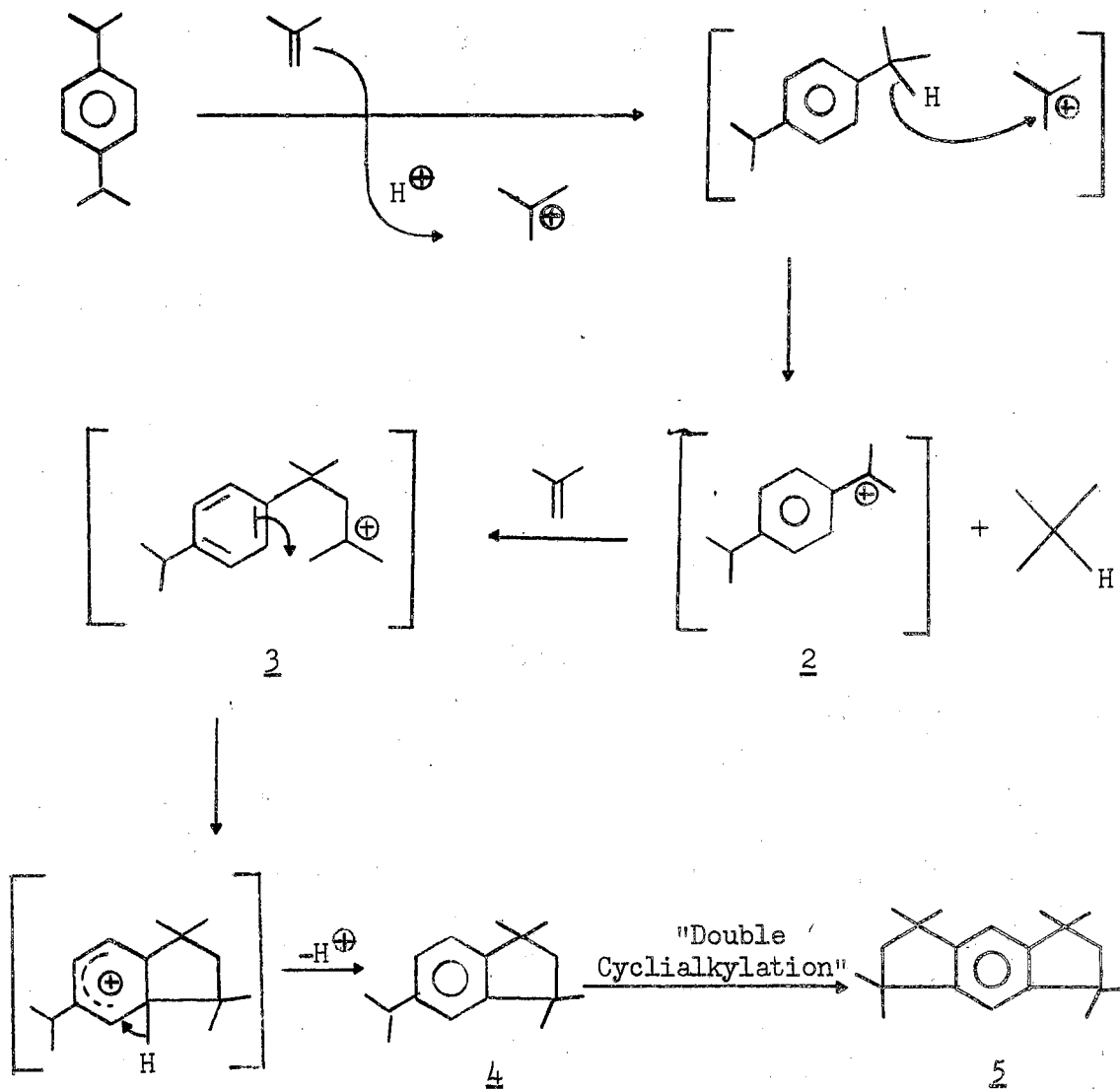
The concept of hydride transfer was first postulated in 1948 by Ipatieff, Pines, and Olberg.[4]

The overall mechanism involves a hydride ion transfer from the isopropyl side-chain of p-diisopropylbenzene to protonated isobutylene and an attack by isobutylene on the carbonium ion 2 to produce carbonium ion 3. The latter subsequently undergoes ring closure and aromatization to yield 5-isopropyl-1,1,3,3-tetramethylindan (4). A second or "double cyclialkylation" gives 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene (5).

Barclay and co-workers[5] reported that the reaction between 1,3,5-triisopropylbenzene and various olefins (e.g., isobutylene, 2-methyl-2-butene, or 2,4,4-trimethyl-1-pentene) in the presence of aluminum chloride and an alkyl halide gave polyalkylhydrindacenes. The reaction of isopropyl chloride and 1,3,5-tri-t-butylbenzene produced 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene (5). These authors postulated replacement of t-butyl groups by isopropyl groups followed by cyclialkylation as previously described for p-diisopropylbenzene.

Table I shows examples of hydrindacenes synthesized in cyclialkylation reactions. The formation of the first four compounds have been rationalized by employing the hydride-ion-transfer mechanism previously described. The last two examples do not involve a hydride-transfer mechanism and their mode of formation will be described in Chapter II.

Methods other than one-step cyclialkylation reactions have been used to prepare hydrindacenes. Theimer and Blumenthal[6] reported the addition of 2-methyl-2-propenylmagnesium chloride to $\alpha,\alpha'$-dichloro-m-xylene and the cyclization of the adduct 6 with 88% sulfuric acid to a mixture of the tetramethylhydrindacenes 7 and 8. Acetylation of 7 with acetyl chloride and aluminum chloride produced 4-acetyl-1,1,6,6-tetramethyl-as-hydrindacene, which has been used as a perfume.
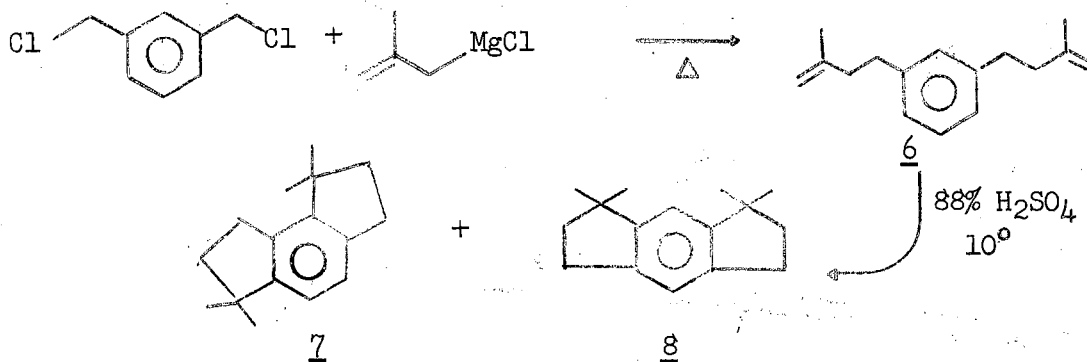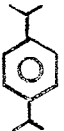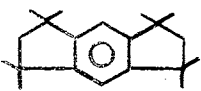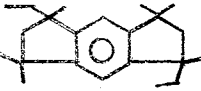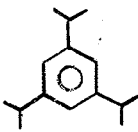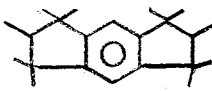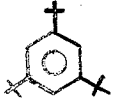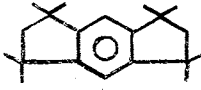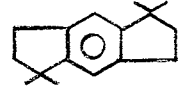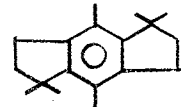
# TABLE I

## CYCLIALKYLATION OF ALKYLBENZENES TO POLYALKYLHYDRINDACENES

| Polyalkylbenzene | Cyclialkylating Reagent | Catalyst | Polyalkylhydrindacene | Reference |
|---|---|---|---|---|
|  | Isobutylene | HF |  | 3 |
|  | Isobutylene | HF |  | 3 |
|  | 2,methyl-2-butene | $AlCl_3$ |  | 5 |
|  | Isopropyl chloride | $AlCl_3$ |  | 5 |
|  | Isoprene | $H_2SO_4$ |  | 2 |
|  | Isoprene | $H_2SO_4$ |  | 2 |

Muller[7] synthesized as-hydrindacene (9) by passing 1,5,9-cyclo-
dodecatriene vapors at 450° over a catalyst consisting of chromium
(III) oxide and potassium oxide on an alumina support.



$$\xrightarrow[\text{450°, 100 min.}]{\text{Cr}_2\text{O}_3,\ \text{K}_2\text{O}}$$
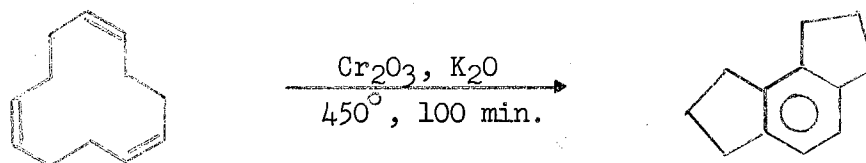
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Bushick[8] reported the formation of 9 by treating indan with boron
trifluoride-hydrogen fluoride catalyst. The reaction mixture also con-
tained a small amount of 1-(2-indanyl)-3-phenylpropane. The authors
did not advance a mechanism for the formation of either of these
compounds.

Labunskii and Tsukervanik[9] also prepared 5 in 18% yield by cycli-
alkylating benzene with 2,4-dimethyl-2,4-pentanediol in the presence
of aluminum chloride. A 53% yield of 1,1,3,3-tetramethylindan was
also produced.

A multistep synthesis of alkyl-substituted hydrindacenes has been
developed by Fleischer.[10] Toluene with diethylmalonyl chloride and
aluminum chloride gave 2,2-diethyl-5-methylindan-1,3-dione (10). A
Clemmensen reduction of 10 gave 2,2-diethyl-5-methylindan (11).

Reaction of 11 with another mole of diethylmalonyl chloride pro-
duced 2,2,7,7-tetraethyl-4-methyl-as-hydrindacene-1,3-dione (12) which
was reduced by the Clemmensen method to 2,2,7,7-tetraethyl-4-methyl-
as-hydrindacene (13).
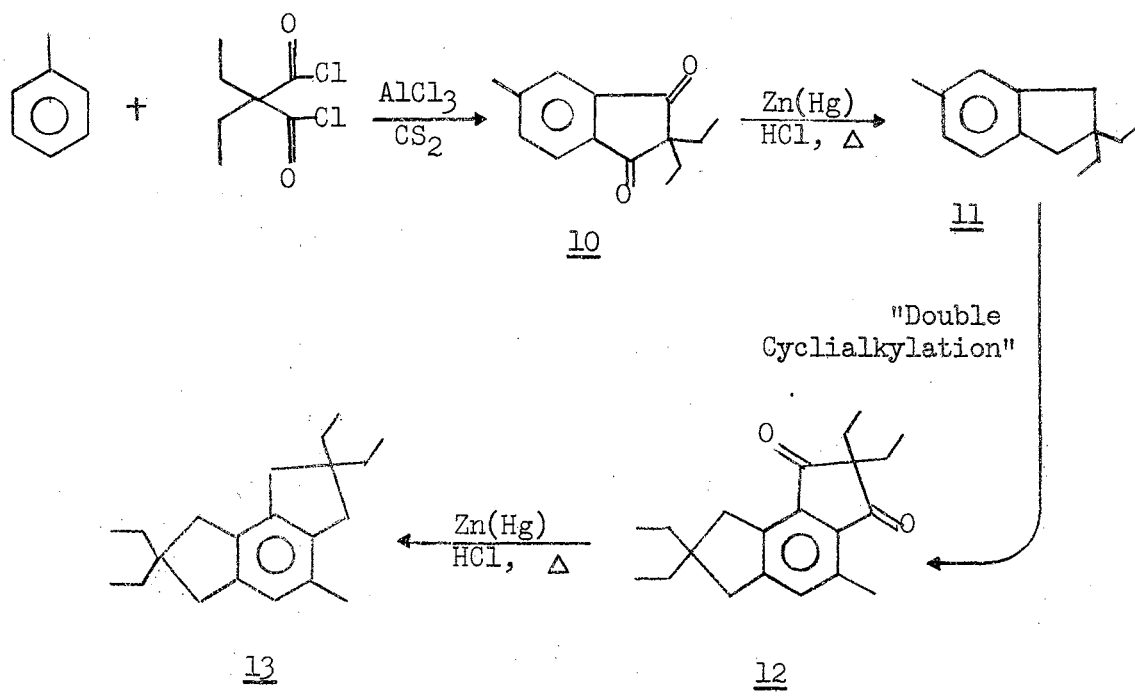
Benzene was cyclialkylated in the above manner and an isomeric mixture of 2,2,7,7-tetraethyl-as-hydrindacene and 2,2,6,6-tetramethyl-s-hydrindacene was obtained.

There are numerous references in the literature describing the formation of alkyl-substituted hydrindacenes.[11-15] However, since the majority of these are U. S. patents, a detailed description of the reagents and conditions is lacking.

CHAPTER II

RESULTS AND DISCUSSIONS

Isoprene and benzenoid hydrocarbons having unoccupied vicinal positions combine, in the presence of sulfuric acid, in a 1:1 ratio to yield indans. These indans may react with a second mole of isoprene to form hydrindacenes.

The cyclialkylation reaction with isoprene, a xylene, and sulfuric acid appears to involve several steps: first, attack of the aromatic hydrocarbon by a carbonium ion; second, loss of a proton from the aromatic hydrocarbon and reprotonation; and finally, cyclization of the resulting tertiary carbonium ion. The sequence is shown for p-xylene in Fig. 2.

If the sequence is repeated with the indan, the formation of the hydrindacene can be rationalized in the same manner.

At present, the exact nature of the attacking species is unknown, but it seems clear that resonance-stabilized hybrid 14, owing to its partial tertiary carbonium ion character, would be preferred over 13. It is known from kinetic studies that a π-complex results from protonation of double bonds and it is reasonable that such a complex results when isoprene is treated with sulfuric acid. A π-complex distribution of positive charge over several atoms via the allylic double bond seems reasonable.

Various side reactions compete with hydrindacene formation during cyclialkylation of xylenes with isoprene in the presence of sulfuric
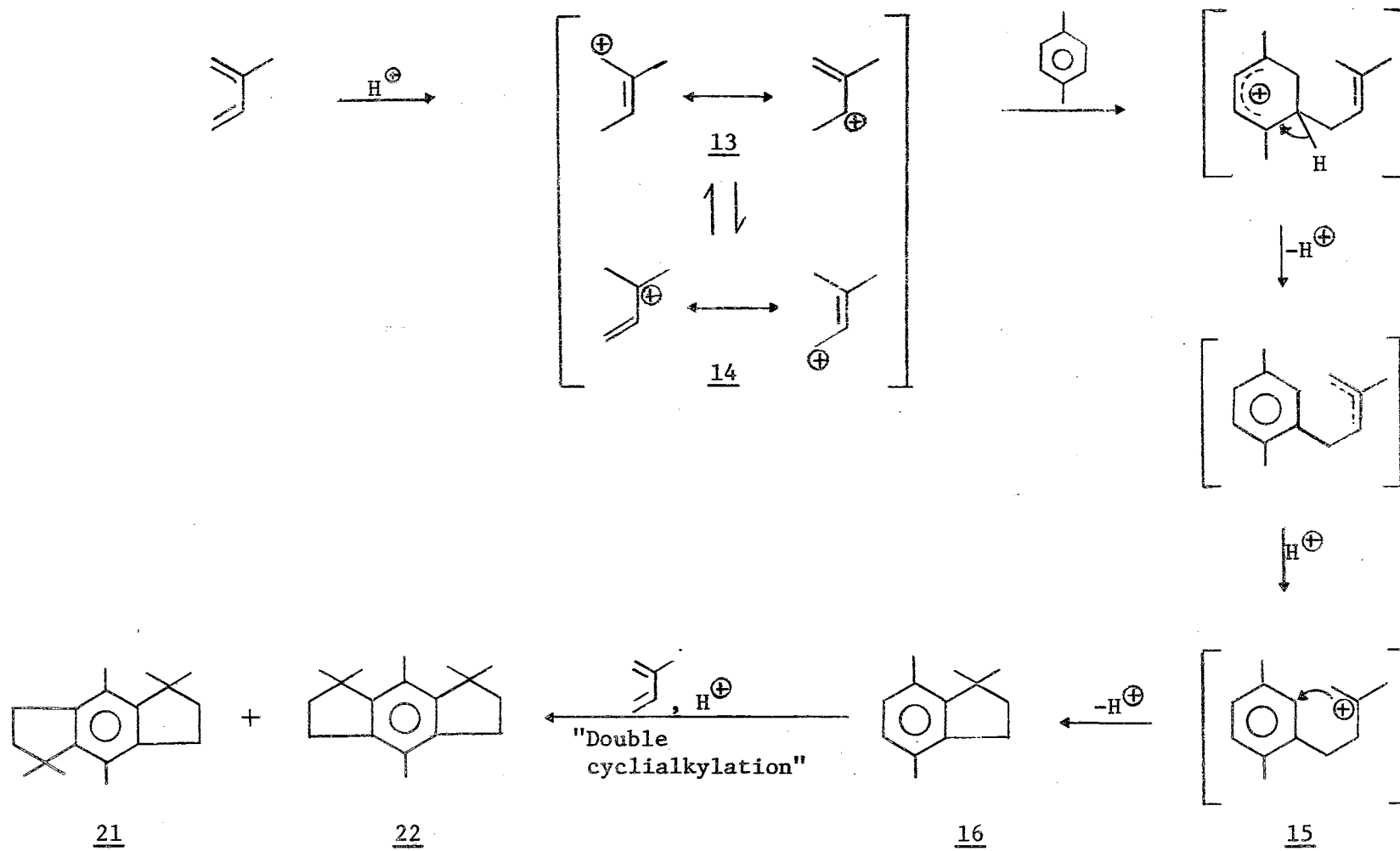
Figure 2. Cyclialkylation of p-Xylene

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acid: monoalkylation to form indans and polyalkylation to form higher alkylation derivatives, sulfonation of the aromatic ring, and polymerization of isoprene and intermediate olefins. Surface-active sulfonation products probably account for the formation of soap-like emulsions which interfered with the isolation and purification of the cyclialkylation products. The use of solid sodium carbonate in work-up minimized the formation of these emulsions. The yield of hydrindacene products can be increased with slower addition of isoprene. However, with slow addition, sulfonation becomes a more serious side reaction.

The optimum reaction temperature for cyclialkylation of p-xylene with isoprene was determined for several concentrations of sulfuric acid: 96%, below $-15^{\circ}$; 93%, $-10^{\circ}$ to $5^{\circ}$; 85%, $10^{\circ}$ to $25^{\circ}$; and 75%, $30^{\circ}$ to $40^{\circ}$. The 93% concentration of sulfuric acid was convenient and gave best yields for those hydrocarbons which were liquid at $-10^{\circ}$. The 85% concentration gave low yields of cyclialkylation products and 50% sulfuric acid caused no cyclialkylation.[16] It is well known that olefins and aromatic hydrocarbons, under the influence of sulfuric acid, yield products which vary considerably with the concentration of the acid.[17] These principles may be used to explain the formation of cyclialkylation products. At relatively low concentrations of sulfuric acid (50-70%), isoprene is converted primarily to the alkyl sulfonate. In approximately 75-80% sulfuric acid, the principal reaction is probably polymerization of isoprene, accompanied by ester formation. At concentrations of sulfuric acid greater than 80%, the cyclialkylation reaction increases. These results can be explained as follows: the carbonium ion formed will react with the nucleophilic species which is the most active and present in the greatest concentration. In aqueous

acid (less than 70%), the predominant nucleophilic species is water.

In 70% sulfuric acid, the hydrogen sulfate anion concentration predominates as the most active nucleophile. As the acid concentration is increased to 80% or more, there is a decrease of olefin concentration as more isoprene is converted to the resonance hybrid 14. Then the rate of isoprene polymerization and ester formation decreases and cyclialkylation becomes the dominant reaction.

Fig. 3 shows the cyclialkylation products obtained from the xylenes, isoprene, and sulfuric acid. The indans (16-20) were isolated and characterized previously in this Laboratory.[16]

The proposed tertiary carbonium ion intermediate 15, in the case of p-xylene, should present steric requirements similar to a t-butyl cation and thus is somewhat hindered toward attack of another molecule of p-xylene in an intermolecular alkylation. The frequency of collision of the charged center of 15 with the ortho carbon is evidently many times greater than with a carbon atom available for substitution in another p-xylene molecule. Intramolecular ring closure to give the hydrindacene then becomes the driving force for completion of the reaction. However, in the case of m-xylene, one intermolecular alkylation product, 30, was isolated by preparative gas chromatography. This case is significant because it is the only intermolecular alkylation observed in cyclialkylation reactions involving the xylenes. This new compound has been tentatively identified through nmr and mass spectroscopy as 2-methyl-2-(2,4-dimethylphenyl)-4-(2,6-dimethylphenyl)butane (30).

The formation of 30 may be explained by considering the possible points of attack for the resonance-stabilized hybrid 14 at the various positions on the m-xylene skeleton. If attack by the carbonium ion 14
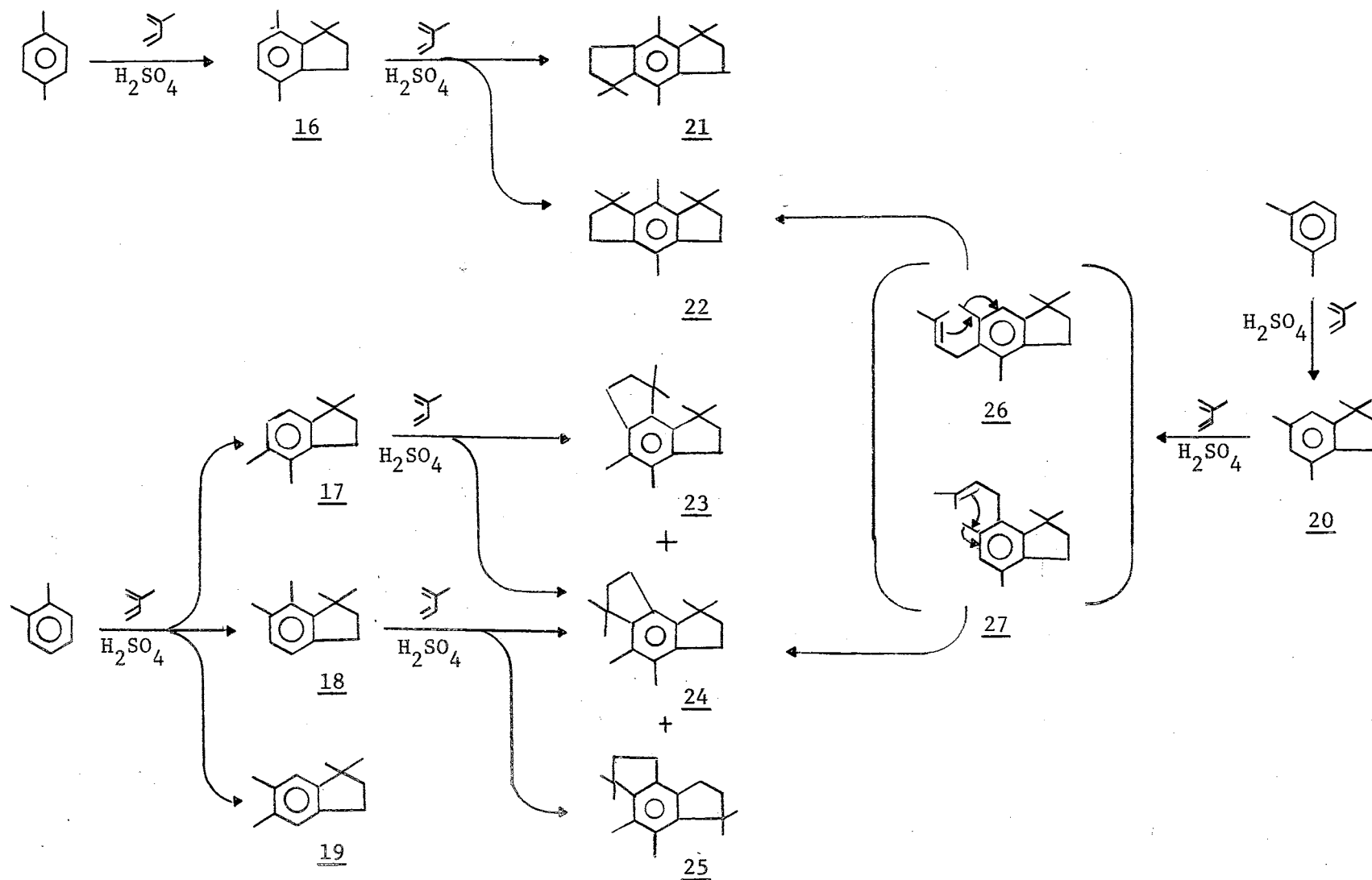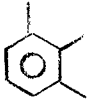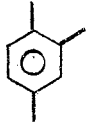
Figure 3. Cyclialkylation Products from the Xylenes

takes place at C-4, the previously observed indan 20 results. If attack takes place at C-5, 1,1,5,7-tetramethylindan should result. Since this isomer has not been observed, and the equally unstable isomer 18 has been isolated, we conclude that attack is selective at an ortho or para position which leaves position 2 for consideration. Attack at this position provides the carbonium ion 29 which cannot cyclize without causing methyl group migration or elimination. Since the indan 16 has not been observed as a product from m-xylene, nor have we observed trimethylindans, we may further conclude that these processes are not significant. Instead, it is suggested that the intermediate 29 gains sufficient stability and is sufficiently reactive to attack another molecule of m-xylene.

It is also suggested that attack by 29 occurs at C-4 of m-xylene in order to explain the quartet appearing at $\delta = 6.78$, 6.85, 7.09 and 7.23 in the nmr spectrum of 30. This quartet may be attributed to the two adjacent aromatic protons flanked by p-alkyl groups. Additional evidence for the correctness of structure of 30 may be found in the infrared spectrum which shows absorptions at 6.7, 6.8, 9.1, 11.45, 12.3, and 13.1 μ. These bands appear to be a composite of the necessary absorption bands for a mixture of 1,2,3-trialkyl- and 1,2,4-trialkylbenzenes. The elements of this mixture appear in the structure 30. Comparison of the infrared spectrum of 30 with the spectra of 1,2,3-trimethyl- and 1,2,4-trimethylbenzene was made and striking similarities were observed. These data are compiled in Table II. Despite many references[18-20] which point out that the steric requirement of a tertiary carbonium ion is sufficiently large to prevent alkylation ortho to a methyl group, it has been our experience with sulfuric

acid alkylations that alkylation equivalent to t-butylation proceed
readily in some cases. Therefore, structure 30 seems reasonable.

TABLE II

COMPARISON OF THE INFRARED SPECTRUM[a] OF 30 WITH MODEL HYDROCARBONS

| 30 | 6.7 | 6.8 | 9.1 | 11.45 | 12.3 | 13.1 |
|---|---|---|---|---|---|---|
| (structure) | | 6.8 | 9.1 | | | 13.1 |
| (structure) | 6.7 | 6.9 | | 11.45 | 12.4 | |

[a]Measured absorbance maxima (μ)

We realize that the mesitylene–isoprene adducts 34a and 34b
readily cyclize to indans with intramolecular methyl group migration.
However, the presence of a third nuclear methyl group in 34a and 34b
which is absent in 29 may be the deciding factor.
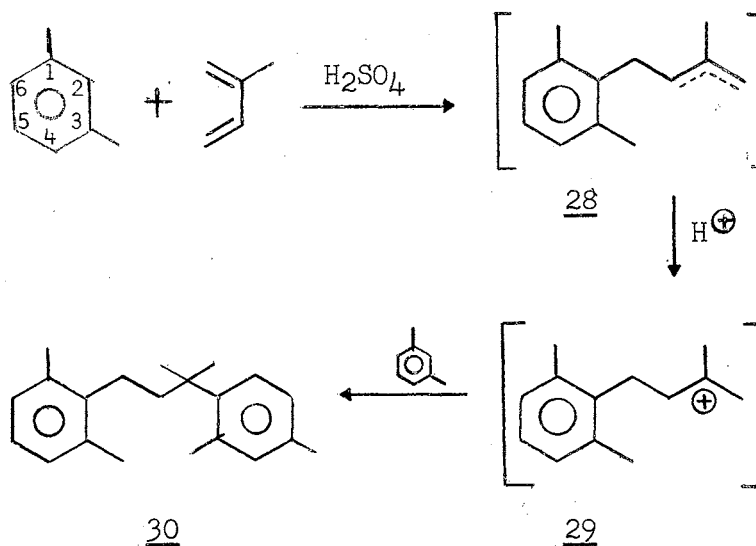
p-Xylene was converted to a mixture of the hexamethylhydrindacenes 21 and 22 in 14% yield in the cyclialkylation reaction with isoprene in the presence of 85% sulfuric acid.[16] Capillary gas chromagraphy studies indicate two minor components and one major component in the ratio 1:4:72 (Plate 1). The retention time of the smallest peak matched that of one of the isomers, 24, from m-xylene, in Table III. The other components of the chromatogram are 22 and 21 in order of elution, with 21 being the major component. Presumably 24 resulted from the presence of m-xylene impurity and not an o-xylene impurity, since 23 and 25 were absent. Isolation of compound 21 was achieved by oxidizing a mixture of 21 and 22 with chromium trioxide in glacial acetic acid to yield, as one of the products, a red, ether-insoluble compound identified as 3,3,4,7,7,8-hexamethyl-s-hydrindacene-1,5-dione (31). The mass spectrum of this diketone showed a parent ion at m/e 270. The infrared spectrum showed strong carbonyl absorption at 5.99 μ. These data and information from the nuclear magnetic resonance spectrum (Plate 4) were used to assign structure 31 to the oxidation product. The Wolff-Kishner reduction of 31 provided a crystalline
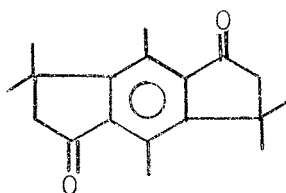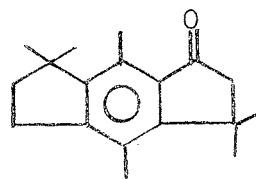
31                          32

compound, mp 97-98°, in 83% yield. The infrared and mass spectra and the nuclear magnetic resonance data are consistent with 1,1,4,5,5,8-hexamethyl-s-hydrindacene (21).

A monoketone, identified as 3,3,4,7,7,8-hexamethyl-s-hydrindacene-
1-one (32) was isolated from a sample of the oxidation products from the
mixed p-xylene-derived hydrindacenes by eluting the mixture of ketones
through a column packed with neutral alumina. The fraction eluted with
petroleum ether was shown by thin-layer chromatography to contain a
single ketone. The mass and nuclear magnetic resonance spectra were
consistent with structure 32.

m-Xylene combined with isoprene and sulfuric acid to give a 10%
yield of two hexamethylhydrindacenes.[16] Capillary gas chromatography
indicated the presence of two major components with retention times
corresponding to the first two components eluted from the mixture ob-
tained from p-xylene (Plate 2). The two components were in a ratio of
1:1.7 with the smaller of the two corresponding to 22 of the p-xylene
derivatives and the major component corresponding to 24 of the o-xylene-
derived hydrindacenes. Since 1,1,4,6-tetramethylindan (20) from m-
xylene lacks the requisite vicinal positions for ring closure during
second-stage cyclialkylation, it is believed that methyl group migration
takes place as indicated in the conversion of 20 via 26 to 22 and via
27 to 24, in Fig. 3. That 20 is a precursor to 22 and 24 was estab-
lished by treating 20 with additional isoprene in the presence of sul-
furic acid to give a mixture of 22 and 24. This was established by com-
parison studies using capillary gas chromatography.[16]

o-Xylene was cyclialkylated with isoprene in the presence of 97%
sulfuric acid to yield an isomeric mixture of the hexamethylhydrinda-
cenes 23, 24, and 25 in 6% yield, as shown in Fig. 3. These hydrin-
dacenes presented formidable separation problems and highly efficient
distillation was unsuccessful in separating these compounds. Analysis

of the higher-boiling residue, after distillation of the reaction mix-
ture, on a 150-ft x .01-in. capillary column lined with DC-550 silicone
oil showed four components present; two major components and two minor
components (Plate 3). These components were eluted at 12.5, 17.1, 18.8
and 22.8 min in the ratio of 1:36:42:20, respectively. The elution
time for the second component matches that of 24 of the m-xylene-
derived hydrindacenes, indicating additionally that the rearrangement
of 27 → 24 had taken place.

By the reaction sequence indicated in Fig. 3, there should
exist only three major components in the o-xylene-derived isomers. It
then was necessary to determine which of the four components was extran-
eous and not a hexamethylhydrindacene. This was shown to be the peak
appearing at 12.5 min on the chromatogram by collecting a sample and
obtaining its nmr spectrum which indicates that approximately 50% of
4-isopentyl-1,1,5,6-tetramethylindan is present. The mass spectrum of
this sample gave an m/e 244 which clearly eliminates a hexamethyl-
hydrindacene structure. Two of the remaining three peaks (17.1 and
22.8 min) were shown to be due to the hexamethylhydrindacenes 24 and
23. The remaining peak appearing at 18.8 min is assumed to be due to
25.

The hydrindacene 23 corresponding to peak 4, having a retention
time of 22.8 min as shown on Plate 3, was isolated by preparative gas
chromatography. The mass spectrum showed a parent ion at m/e 242 and
the nuclear magnetic resonance spectrum is that expected for 1,1,4,5,8,8-
hexamethyl-as-hydrindacene, structure 23. The hydrindacene 24 was dif-
ficult to purify and corresponding peaks 2 and 3 respectively (Plate 3)
could not be separated from 25 in the same manner. However, when a

mixture of 23 and 24 was passed through a column containing silica gel

impregnated with picric acid, compound 24 crystallized in block-like

crystals after the solvent was allowed to evaporate. Again, mass

spectroscopic and nuclear magnetic resonance spectra confirmed structure

24.

Evidence that compound 19 is not a precursor to any of the hydrin-

dacenes was established by treating 19 with additional isoprene in the

presence of 97%, 93% and 70% sulfuric acid. Analysis of each reaction

mixture by capillary gas chromatography showed no hydrindacene product.

Because 19 lacks the required unoccupied vicinal positions necessary

for a second cyclialkylation reaction, reformation of the tertiary car-

bonium ion, 33, would be a necessary step. Since an equilibrium situ-

ation is probably operative and because considerable 19 was recovered,

the equilibrium would lie far in the direction of structure 19. Addi-

tionally, when 18 was treated with aluminum chloride, a high yield



| 19 | | 33 |
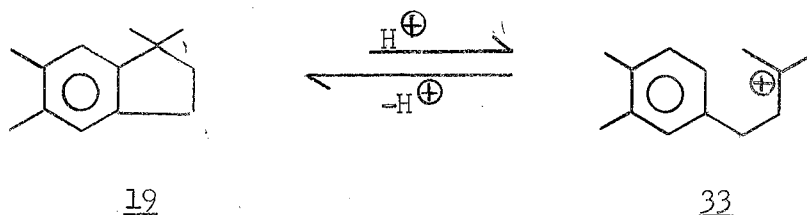
rearrangement to 19 was observed which suggests that structure 19

represents a very stable indan.[21]

Attempts to isolate an olefin or identify an olefin intermediate

resulting from the direct condensation of isoprene and the xylenes were

not successful. The acidic conditions necessary to cause alkylation

are sufficiently vigorous to cause immediate cyclialkylation to the

indan and hydrindacene. However, when mesitylene was condensed with

isoprene in the presence of methanesulfonic acid, a 35% yield of the

olefins 34a and 34b in the ratio of 15:1 resulted. This mixture of

olefins was cyclized to a mixture of the pentamethylindans 35 and 36

in the ratio 1:2 in high yield by contact with 96% sulfuric acid at 0°

for one hour.[21] Since the cyclization reaction afforded pentamethyl-

indans in high yield and formation of tri- or tetramethylindans was not

observed, a 1,2-methyl shift as observed in the formation 22 and 24

from m-xylene is plausible in forming 35 from 34a and 34b. However, a

Jacobsen-like shift of methyl groups would be required to explain the

formation of 36.[22]
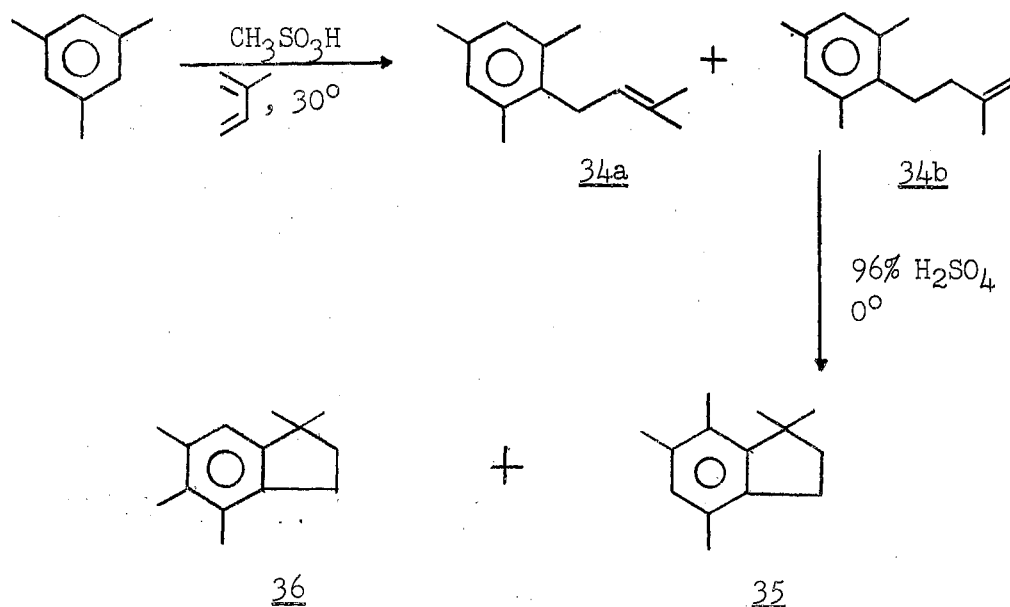


The retention times of the hexamethylhydrindacenes derived from

isoprene and the xylenes are shown in Table III.

TABLE III

CAPILLARY GLC ANALYSIS OF THE HEXAMETHYLHYDRINDACENES

| Compound and Source | Relative Percentage | Retention Time (min) |
|---|---|---|
| p-Xylene | | |
| 24 | 1.2 | 17.1 |
| 22 | 5.2 | 17.8 |
| 21 | 93.6 | 18.4 |
| m-Xylene | | |
| 24 | 63.0 | 17.1 |
| 22 | 37.0 | 17.8 |
| o-Xylene | | |
| 4-Isopentyl-1,1,5,6-<br>tetramethylindan | 1.1 | 12.5 |
| 24 | 36.4 | 17.1 |
| 25 | 42.0 | 18.8 |
| 23 | 20.5 | 22.8 |

Column:  150 ft x 0.01 in. DC-550 silicone oil

Column temperature:  160° isothermal

Flow rate:  3 cc/min of helium

Block temperature:  250°

Detector temperature:  165°

Sample size:  0.1 - 0.2 µl; split with #2 splitter

# CHAPTER III

## EXPERIMENTAL

Melting points were taken in capillary melting-point tubes using a Thomas-Hoover apparatus and are uncorrected. The centigrade scale was used for all temperature measurements. NMR spectra were obtained with a Varian HR-60 spectrometer, using tetramethyl silane (TMS) as an internal standard ($\delta = 0$). Mass spectra were obtained with a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer. Gas chromatography analyses were obtained with an F & M Model 700, an Aerograph Autoprep Model A-700, or an Instruments, Inc. valved gas chromatograph. The chromatographs were equipped with thermal conductivity detectors except the valved gas chromatograph which was fitted with a flame ionization detector. Helium was used as the carrier gas. Infrared spectra were obtained with a Beckman IR-5A spectrometer as films on sodium chloride cells or as potassium bromide pellets.

The cyclohexane used in the reactions was stirred for 24 hours with 97% sulfuric acid, washed with water, dried over activated silica gel and distilled. Phillips pure grade isoprene was used in all cyclialkylation reactions.

For capillary gas chromatography, a 150-ft x 0.01-in. stainless steel column lined with Dow Corning 550 silicon oil was used. For preparative gas chromatography, a 12-ft x 3/8-in. column packed with Chromosorb P coated with 20% SE-30 (60-80 mesh) was used.

1,1,5,6-Tetramethylindan (19) was purified by preparative gas chroma-tography using 20% Carbowax on Chromosorb W in 4" O.D. columns through the courtesy of R. E. Laramy, Continental Oil Company.

Samples of the cyclialkylation products from m- and p-xylene were furnished by J. R. Mattox.

The numbering system of the hexamethylhydrindacenes was obtained from The Ring Index.[23]

## Cyclialkylation of o-Xylene

Sulfuric acid (120 g, 97%) and 3605 g (34 moles) of o-xylene were added to a 12-l. three-necked flask fitted with an addition funnel, high-speed mechanical stirrer, and thermocouple. To the stirred solution was added dropwise 1496 g (22 moles) of isoprene and 735 g (6.94 moles) of o-xylene while keeping the reaction mixture between 0 - 10° at all times. The addition time was 90 minutes. A 12-l. separatory funnel was used to drain the acid layer from the upper organic layer. The organic layer was poured over solid sodium carbon-ate, filtered, and dried (MgSO$_4$). After filtering again, the organic layer was steam distilled, giving 3100 g of recovered o-xylene. The nonvolatiles from the steam distillation were distilled at reduced pressure, giving 250 g of the monosubstituted indan product (bp 61-65°/ 0.2 mm) and 450 g of disubstituted hydrindacene product (140-155°/0.2 mm) plus a large amount of pot residue. Analysis of the higher boiling fraction by capillary gas chromatography showed four peaks to be pres-ent. Three peaks were shown by mixed injections to be compounds 24, 25, and 23 respectively, in order of elution. The remaining peak has been tentatively identified as 4-isopentyl-1,1,5,6-tetramethyl-indan as previously mentioned.

Preparation of 3,3,4,7,7,8-Hexamethyl-s-hydrindacene-1,5-dione (31)

A 61.5 g (0.25 moles) sample of the mixed hydrindacene isomers from p-xylene in 150 ml of glacial acetic acid and 100 ml of methylene chloride were added to a 2-l. three-necked flask, equipped with a high-speed mechanical stirrer, addition funnel and thermometer. To the stirred solution, a mixture of 150 g (1.5 moles) of chromium tri-oxide in 100 ml of distilled water and 500 ml of glacial acetic acid was added over a period of one hour, keeping the temperature between $15^\circ$ and $25^\circ$. The reaction mixture was stirred for 36 hours at room temperature and then poured over 500 g of ice, neutralized with a saturated solution of sodium bicarbonate and extracted with ether. The ether extract was washed with water, dried over anhydrous sodium sulfate, and filtered. After standing overnight at room temperature, a red, insoluble solid deposited from the ether solution. The solid was filtered, recrystallized from chloroform-petroleum ether, and sub-limed at $260^\circ/0.3$ mm, giving 4.0 g of red-colored crystals, mp $204-206^\circ$. The mass spectrum for 31 showed a parent ion at m/e 270 and the nuc-lear magnetic resonance spectrum showed absorption at $\delta = 1.54$ (12H, gem-dimethyl protons, singlet); 2.64 (4H, C-2 and C-6 protons, singlet); and 2.76 (6H, aromatic ring methyl protons, singlet) (Plate 4).

Wolff-Kishner Reduction of 31 to 1,1,4,5,5,8-Hexamethyl-s-hydrinda-cene (21)

To a 200-ml three-necked flask equipped with a mechanical stirrer, thermometer, and splash head, 60 ml (0.64 moles) of diethylene glycol and 1.2 g (0.005 moles) of 31 were added. After warming the stirred slurry to $40^\circ$, 2.24 g (0.4 moles) of potassium hydroxide and 4 ml (0.125 moles) of hydrazine were added. The green solution was heated

at 190° for 11 hours and an additional 4 ml of hydrazine were added.

Heating at 190° for six more hours produced white crystals in the

splash head which were washed into a beaker with anhydrous ether. The

white crystals were sublimed twice at 220°/0.3 mm giving 1.0 g (83%)

of crystals, mp 97-98°. The mass spectrum showed a parent ion at

m/e 242, and the nuclear magnetic resonance spectrum (Plate 5) indi-

cated absorption at $\delta$ = 1.3 (12H, gem-dimethyl protons, singlet);

1.85 (4H, C-2 and C-6 protons, triplet); 2.18 (6H, aromatic ring

methyl protons, singlet); and 2.70 (4H, C-3 and C-7 protons, triplet).

Isolation of 3,3,4,7,7,8-Hexamethyl-s-hydrindacene-1-one (32)

One gram of the crude product from the oxidation of the mixed

p-xylene-derived hydrindacenes was dissolved in a minimum amount of

benzene and eluted through a 2-ft x 1-in. column packed with 30 g of

neutral alumina. The eluent (1.4 l.) was gradually changed from

petroleum ether to benzene. The eluate was collected in 100-ml frac-

tions. These fractions were concentrated in a vacuum evaporator and

then tested on a thin-layer plate coated with an 0.30-mm thickness of

silica gel (Silica Gel PF$_{254 + 366}$, Brinkmann Instruments, Inc.).

Fractions 2 and 3 were shown by thin-layer chromatography to be com-

posed of one ketone while the remaining fractions contained three com-

pounds. Fractions 2 and 3 were combined and sublimed at 230°/0.3 mm

giving 0.4 g of white crystals, mp 129-130°. The mass spectrum

showed a parent ion at 256 and the nuclear magnetic resonance spectrum

(Plate 6) gave absorption at $\delta$ = 1.37 (6H, C-7 gem-dimethyl protons, sing-

let); 1.48 (6H, C-3 gem-dimethyl protons, singlet); 1.93 (2H, C-6 pro-

tons, triplet); 2.33 (3H, C-4, one methyl group, singlet); 2.55 (2H, C-2

protons, singlet); 2.66 (3H, C-8, one methyl group, singlet); 2.80 (2H,

C-5 protons, triplet).

## Isolation of 1,1,4,4,7,8-Hexamethyl-as-hydrindacene (24)

A 1-g sample of a mixture of the hydrindacenes 23 and 24 was dis-
solved in a minimum amount of petroleum ether and eluted through a
2-ft x 1-in. column packed with 50 g of silica gel impregnated with
0.25 g of picric acid. The eluent used was n-hexane and 50-ml frac-
tions were collected. Capillary gas chromatography showed than no
separation had been achieved. However, after evaporation of the sol-
vent, block-like crystals appeared in the bottom of each flask. These
crystals were collected, recrystallized from 2-propanol and sublimed
at $230^\circ/0.3$ mm, giving 0.4 g of 24 as white crystals, mp 127-129$^\circ$.
Mass spectral analysis showed a parent ion at m/e 242. The nuclear
magnetic resonance spectrum (Plate 7) showed absorption at $\delta = 1.25$
(6H, C-1 gem-dimethyl protons, singlet); 1.32 (6H, C-6 gem-dimethyl
protons, singlet); 1.82 (4H, C-2 and C-7 protons, triplet); 2.08 (3H,
C-4, one methyl group, singlet); 2.20 (3H, C-5, one methyl group, sing-
let); 2.76 (2H, two different benzylic methylene group protons,
staggered triplets).

## Isolation of 1,1,4,5,8,8-Hexamethylhydrindacene (23)

The mixture of the higher boiling components from the o-xylene
cyclialkylation reaction was chromatographed on the Autoprep unit
equipped with a 12-ft x 3/8-in. column packed with 20% SE-30 on Chromo-
sorb P (60-80 mesh). Settings on the chromatograph were as follows:
column, 240$^\circ$; helium flow, 20 cc/min; injector, 290$^\circ$; detector, 320$^\circ$;
collector, 265$^\circ$. A 200-µl injection was made and the analysis showed
three components to be present with retention times of 19 min, 24 min,
and 28 min respectively. The component eluting at 28 min was collected

in a small glass collector tube immersed in a dry ice-acetone bath.
After the first few injections, it was found that the materials formed
aerosols when emerging from the collection port. Hot air from a heat
gun applied directly to the glass collector destroyed the aerosol and
gave more efficient collection. After about 20 of the 200 μl injec-
tions, the collection tube was warmed to room temperature and the solid
material present in the tube was washed into a separate vial with ether.
Analysis of the solid material by capillary gas chromatography indica-
ted only one component to be present. Mass spectral and nmr analysis
indicated the compound to be 23, mp 128-130$^\circ$. The nmr spectrum
(Plate 8) gave signals at $\delta$ = 1.39 (12H, gem-dimethyl protons, sing-
let); 1.80 (4H, C-2 and C-7 protons, triplet); 2.08 (6H, aromatic ring
methyl protons, singlet); and 2.71 (4H, C-3 and C-6 protons, triplet).

Isolation and Tentative Identification of 4-Isopentyl-1,1,5,6-Tetra-
methylindan

The same technique and conditions were used as those employed in
isolating 23 except the peak eluting at 19 min was collected. The
mass spectrum showed a parent ion at m/e 244.

Reaction of 1,1,5,6-Tetramethylindan (19) with Isoprene and Sulfuric
Acid

A 250-ml, two-necked flask was equipped with a mechanical stirrer,
a thermometer, and an addition funnel. To this flask was added 5 g
(0.029 moles) of 1,1,5,6-tetramethylindan (19) and 5 drops of 97%
sulfuric acid. After cooling the stirred solution to 10$^\circ$ by an ice-
water bath, the addition funnel was charged with 3 g (0.044 moles) of
isoprene and 5 ml of cyclohexane. This solution was added dropwise
over 20 minutes while keeping the temperature between 0-10$^\circ$ at all

times. When the addition was complete, the reaction mixture was stirred for 2 hours while warming to room temperature. After the 2-hour period, the dark brown reaction mixture was added to approximately 10 g of solid, anhydrous sodium carbonate and the entire solution was allowed to stand overnight and then filtered through a glass wool plug. The cyclohexane was removed on a rotary evaporator. Analysis of the reaction mixture by capillary gas chromatography indicated a major peak to be present which had a retention time of 12.5 min. Mixed injections with known samples from the o-xylene cyclialkylation reaction mixture confirmed the results given by retention times. The same results were obtained by analysis of the reaction mixtures obtained from the reaction of 19, isoprene, and 93% and 70% sulfuric acid respectively.

## Chromic Acid Oxidation of Hexamethylhydrindacenes from m-Xylene

A 20-g sample of the hexamethylhydrindacenes obtained from m-xylene was oxidized with chromium trioxide in the manner described for the hexamethylhydrindacenes derived from p-xylene. This reaction provided mainly recovered hydrocarbons but also gave orange crystals (4.3 g) which deposited from a concentrated ether solution.

The integral of the nmr spectrum showed the proper ratio of gem-dimethyl protons ($\delta = 1.56$) to all other hydrogens; however, the expected ratio of 4:6:12 for methylene protons, aromatic-methyl protons and gem-dimethyl protons was not observed. Instead the signal due to methylene hydrogens was only 61% of what is expected based on the aromatic methyl proton signal. Therefore, this sample probably represents impure 3,3,4,5,8,8-hexamethylhydrindacene-1,6-dione.

## Isolation of 2-Methyl-2-(2,4-dimethylphenyl)-4-(2,6-dimethylphenyl) butane (30)

The hydrocarbon 30 was isolated by preparative gas chromatography from the mixture of hydrocarbons obtained from the cyclialkylation of m-xylene. The retention time of 30 was 58 min on the 12-ft x 3/8-in. SE-30 column operating at 240°. The structure of 30 was derived from the mass spectrum (m/e 280). The nmr spectrum in $CDCl_3$ gave the expected signals as follows: $\delta$ = 1.47 (6H, gem dimethyl protons); 2.15 and 2.24 (12H, three aromatic methyl groups); 2.50 (3H, aromatic methyl group ortho to the gem-dimethyl group, singlet); 6.78, 6.85, 7.09 and 7.23 (6H, six aromatic protons, AB quartet). The infrared spectrum of 30 showed pertinent absorption at 3.4, 6.7, 6.8, 9.1, 11.45, 12.3 and 13.1 μ. Comparison of these bands with corresponding bands of 1,2,3- and 1,2,4-trimethylbenzene may be found in Table II.

Capillary Gas Chromatogram of the Hexamethyl-
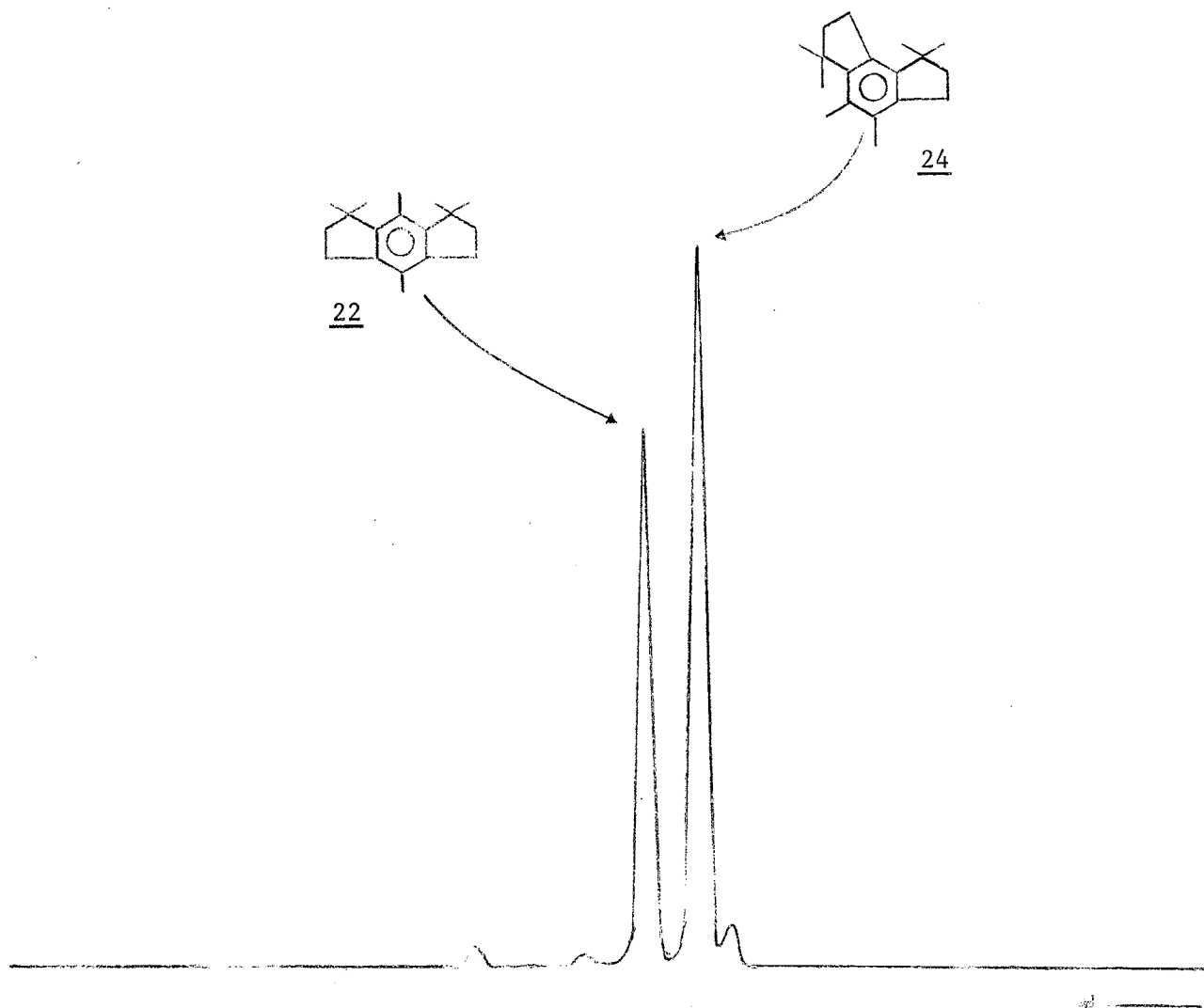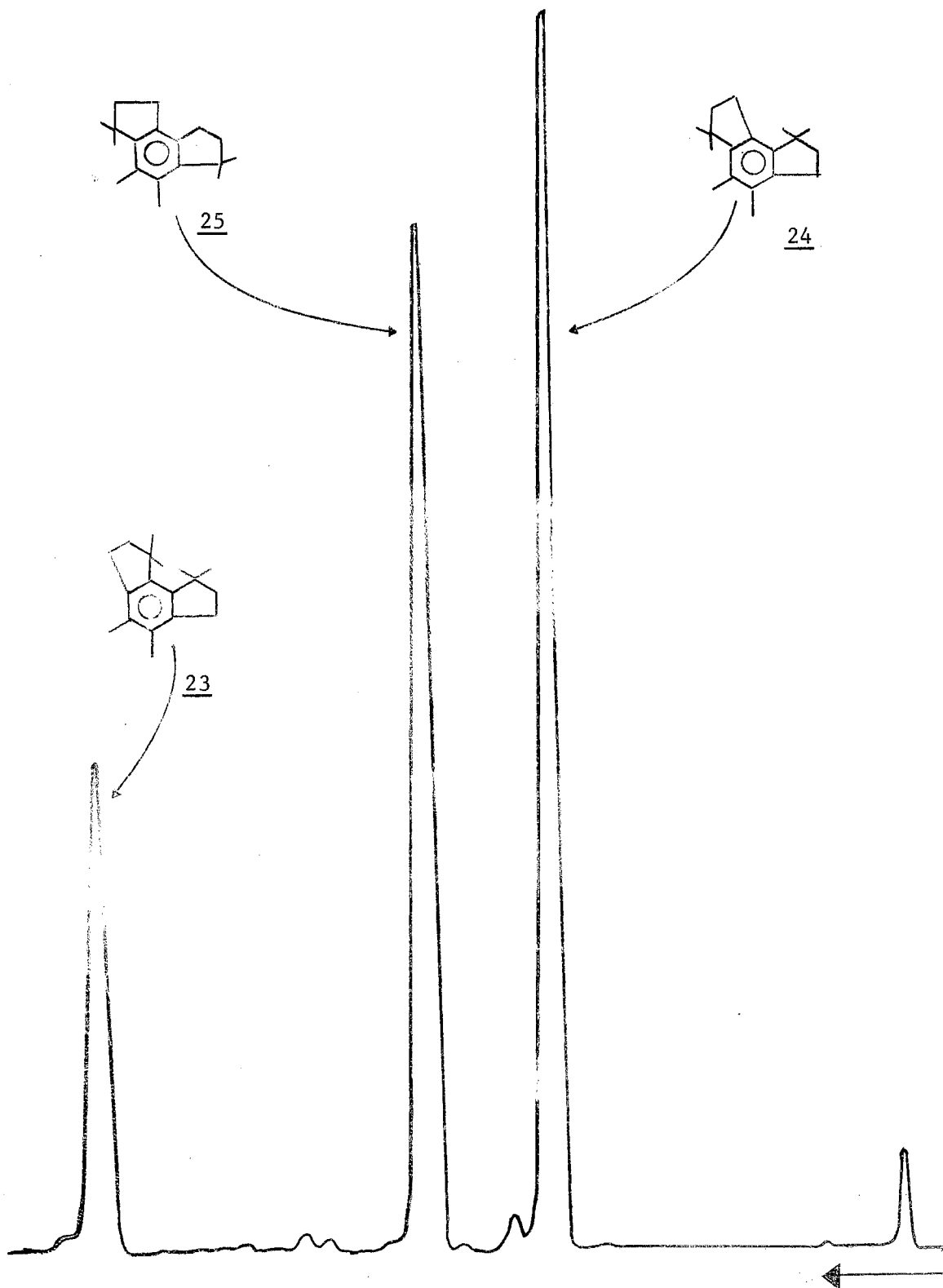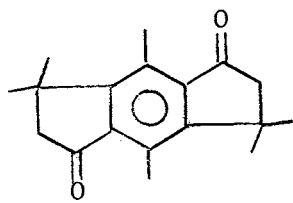hydrindacenes Derived from p-Xylene
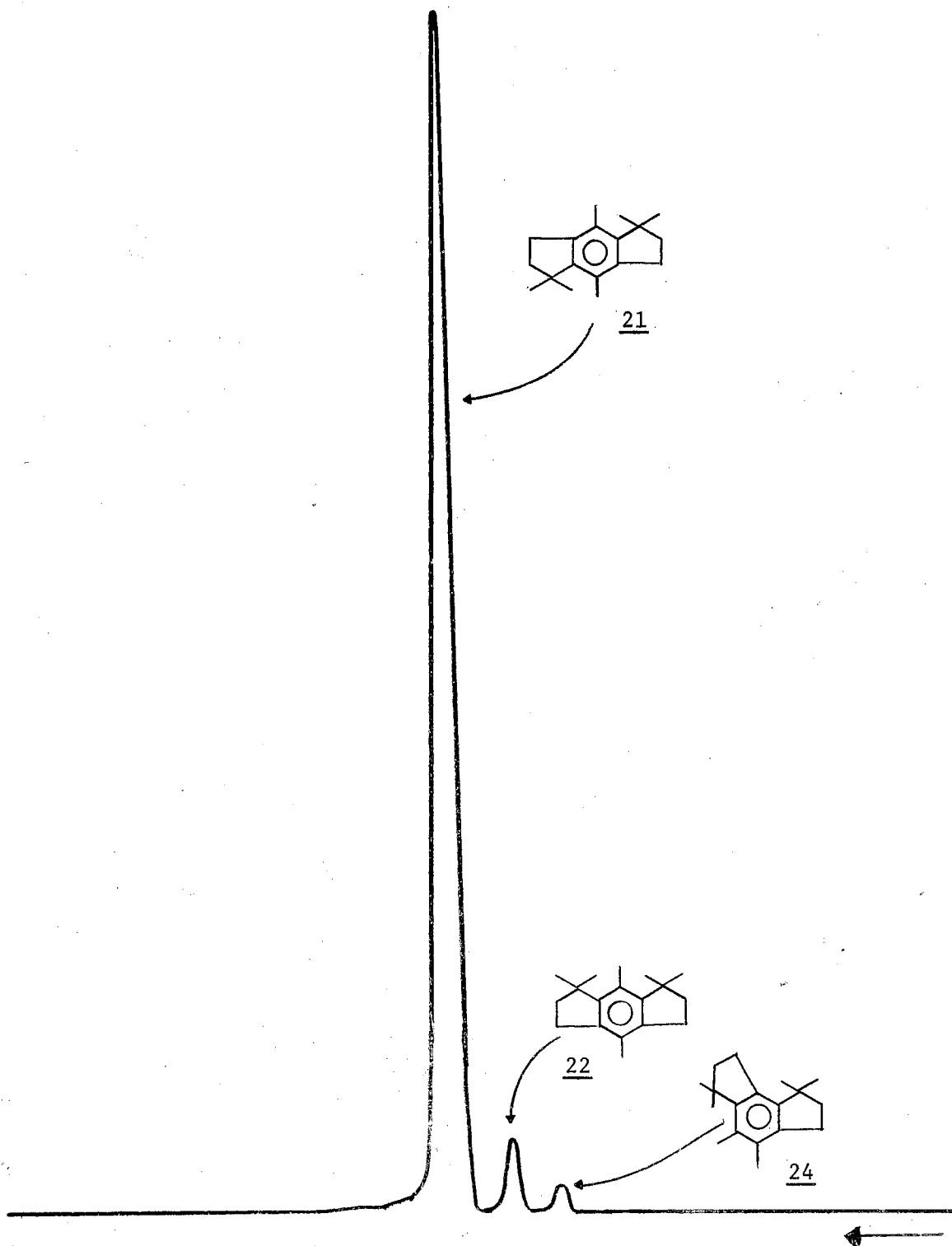


Plate 1

Capillary Gas Chromatogram of the Hexamethyl-
hydrindacenes Derived from m-Xylene



Plate 2

Capillary Gas Chromatogram of the Hexamethyl-
hydrindacenes Derived from o-Xylene



Plate 3

31

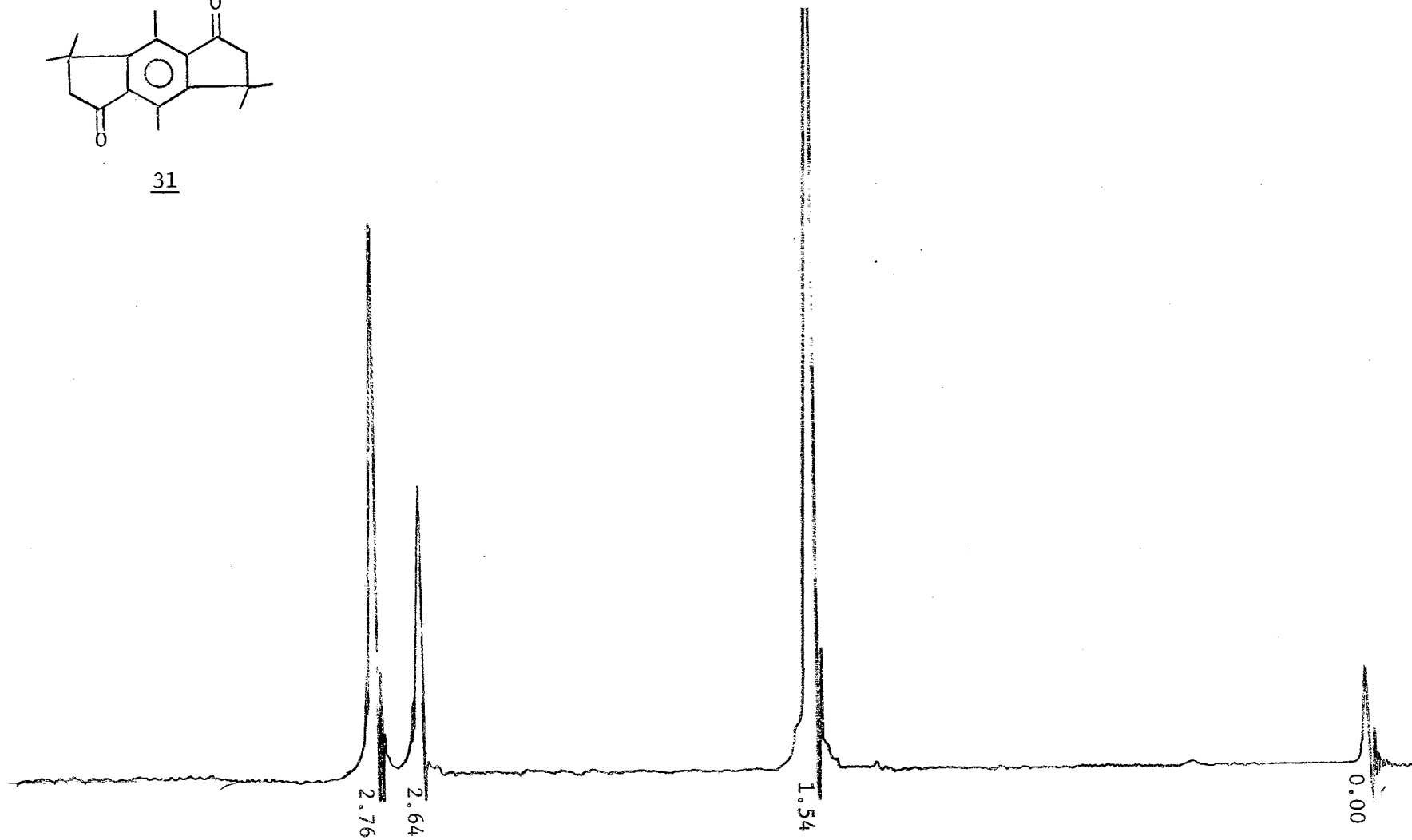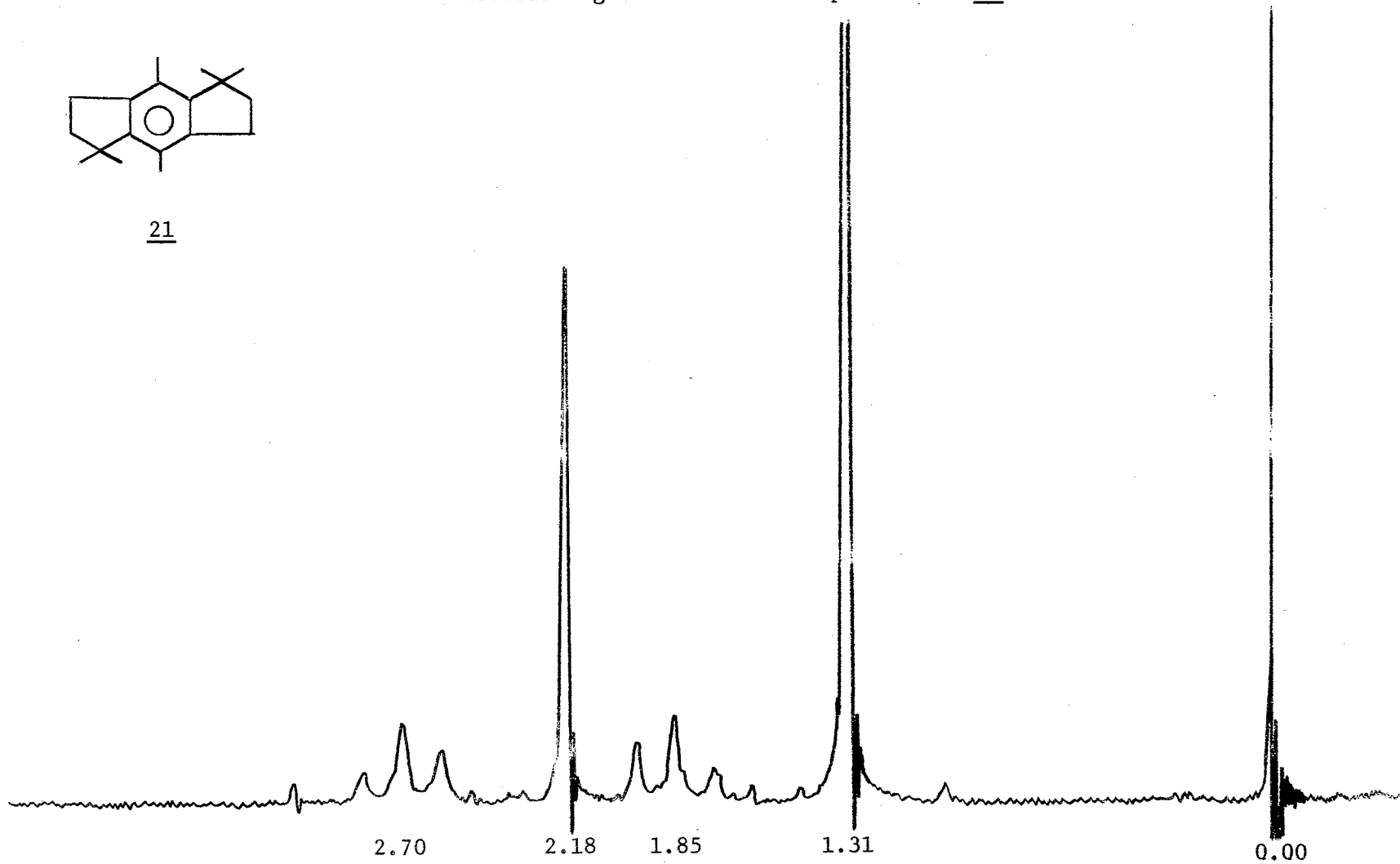2.76   2.64                                        1.54                                      0.00
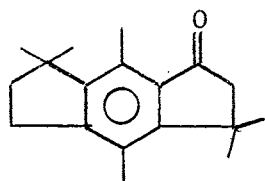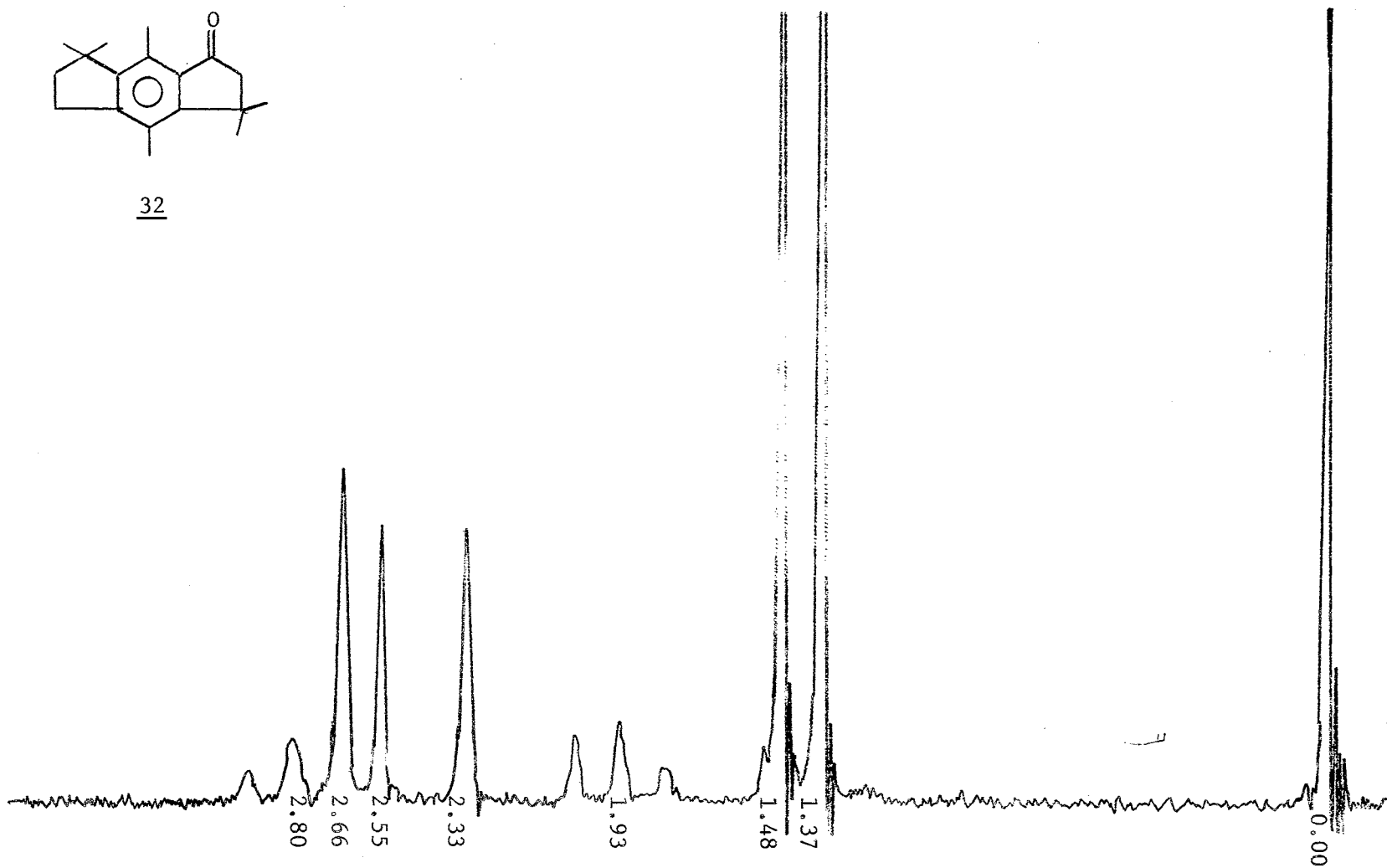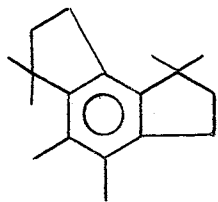
Plate 4

Nuclear Magnetic Resonance Spectrum of 21
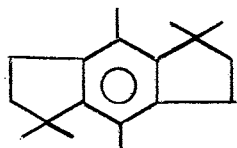
21

2.70    2.18    1.85    1.31    0.00

Plate 5

33

32

2.80  2.66  2.55  2.33  1.93  1.48  1.37  0.00

Plate 6

34

Nuclear Magnetic Resonance Spectrum of 24



24

2.76   2.20   2.08   1.82   1.32   1.25   0.00

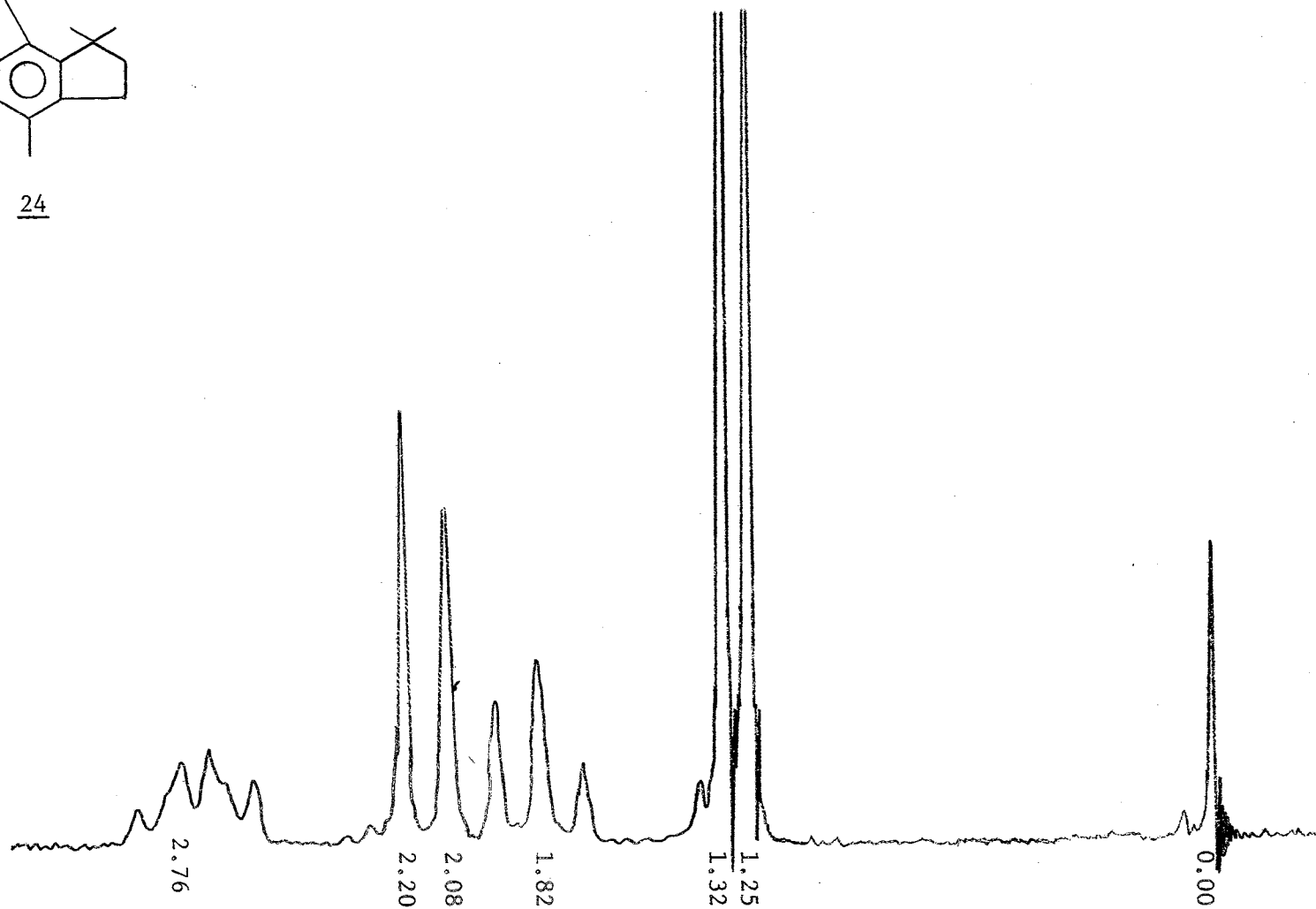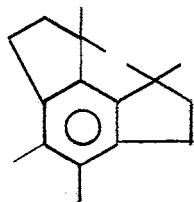Plate 7

Nuclear Magnetic Resonance Spectrum of 23



23

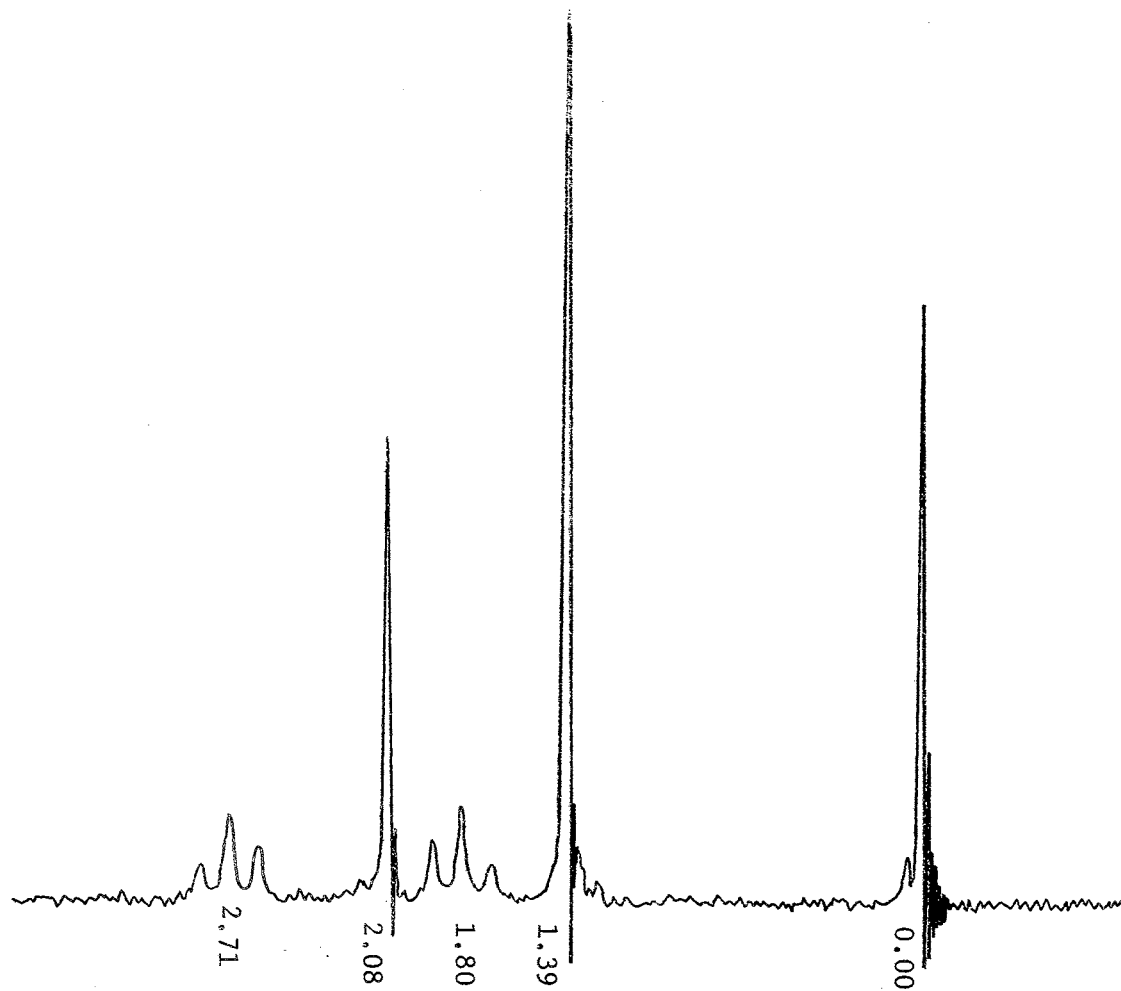Plate 8

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