ACID-CATALYZED REACTIONS OF *ORTHO-*, *META-*,

AND *PARA*-CYMENE WITH ISOBUTYLENE

AND RELATED OLEFINS

By

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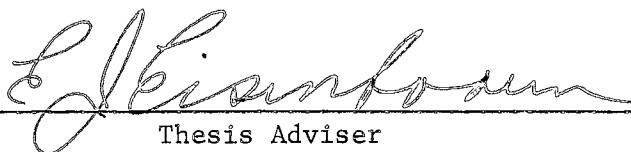Oklahoma State University

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CHAPTER I

HISTORICAL

The term "cyclialkylation" was originated by Bruson and Kroeger[1]
to describe reactions between diols, dienes, and dichlorides or other
difunctional molecules and aromatic compounds. The ends of the difunc-
tional molecule react with the aromatic nucleus to attach a new ring.
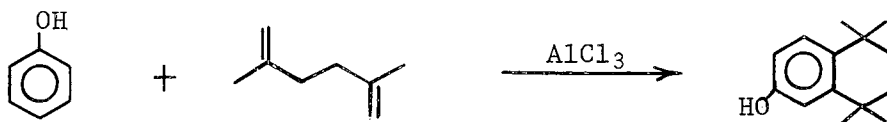
Barclay, in a recent review of the subject, used "cyclialkylation"
in a more general sense "to cover all electrophilic ring closures on to
aromatic systems, including intramolecular ring closures of aryl-sub-
stituted functional compounds as well as ring closures with difunction-
al compounds..."[2]

Cyclialkylation reactions initiated by hydride-ion transfer were
first reported by Ipatieff, Pines and Olberg.[3] It was found that the
reaction of *p*-cymene with 3-methylcyclohexene in the presence of either
sulfuric acid or hydrogen fluoride gave 1,3,3,6-tetramethyl-1-*p*-tolyl-
indan (1). Their mechanism is shown in Fig. 1.

1
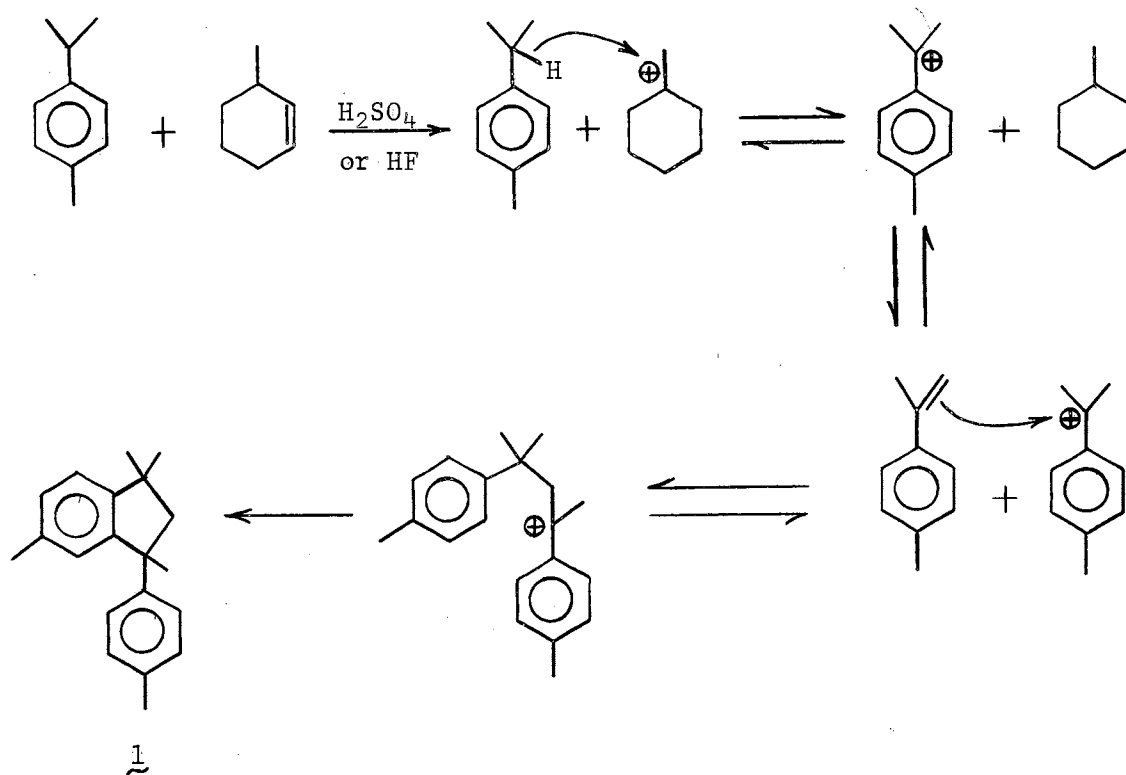
Figure 1. Hydride Transfer Mechanism

The reaction of *m*-cymene with a branched olefin in the presence of sulfuric acid or hydrogen fluoride was reported[4] to have yielded 1,3,3,5-tetramethyl-1-*m*-tolylindan (2). It was later claimed[5] that

2

3
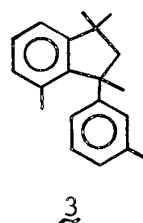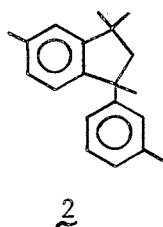
this product was a mixture of $\underset{\sim}{2}$ and 1,3,3,7-tetramethyl-1-*m*-tolylindan (3) in a ratio of about 1:2 with the major product resulting from ring closure ortho to the methyl group. *o*-Cymene when treated with 4-methylcyclohexene in the presence of hydrogen fluoride gave only methylcyclohexyl-*o*-cymene.[4] Thus only the alkylation product was observed, and no products resulting from hydride transfer were reported.

The acid catalyzed reaction between *p*-cymene and isobutylene was found[6] to yield 1,1,3,3,5-pentamethylindan (4) instead of the previously reported 2-*tert*-butyl-*p*-cymene.[7] The hydride transfer mechanism shown in Fig. 1 was used to rationalize the formation of $\underset{\sim}{4}$.

$\underset{\sim}{4}$
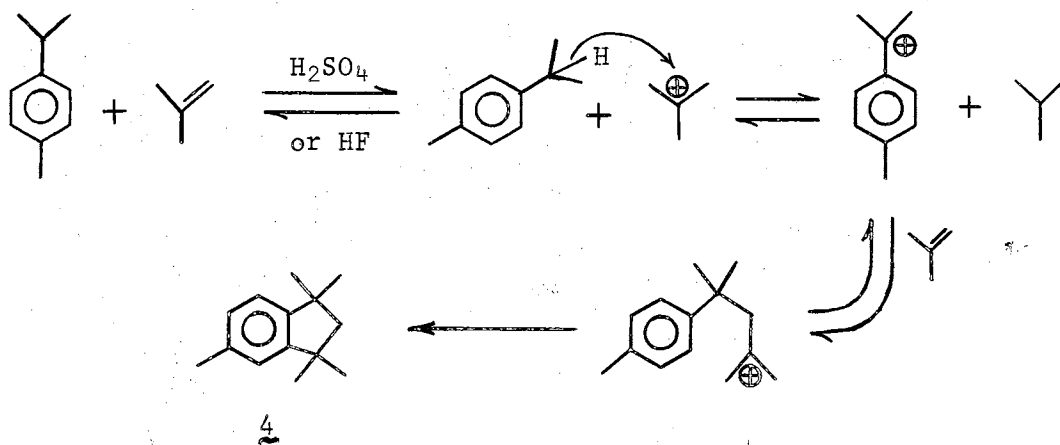
In addition to $\underset{\sim}{4}$, Schlatter also reported a C_{18} hydrocarbon which was thought to result from the reaction between *p*-cymene and isobutylene dimer.[8]

It had long been known that the dinitro derivative of the major product from the p-cymene – isobutylene reaction was useful as an artificial musk in perfumery.[7] The discovery that this product was an indan precipitated an intense effort in this area by the perfume companies. The polyalkylindans and polyalkyltetralins which have been prepared by cyclialkylation have been reviewed by Barclay.[2]

The cyclialkylation reaction was extended to p-disubstituted alkylbenzenes in which both alkyl groups contain a reactive α-tertiary hydrogen.[9] Later work showed that 1,3,5-triisopropylbenzene yielded 1,1,3,3,5,5,7,7-octamethyl-s-hydrindacene (5) and other polyalkylhydrindacenes upon treatment with certain olefins in the presence of aluminum chloride and an alkyl halide.[10]
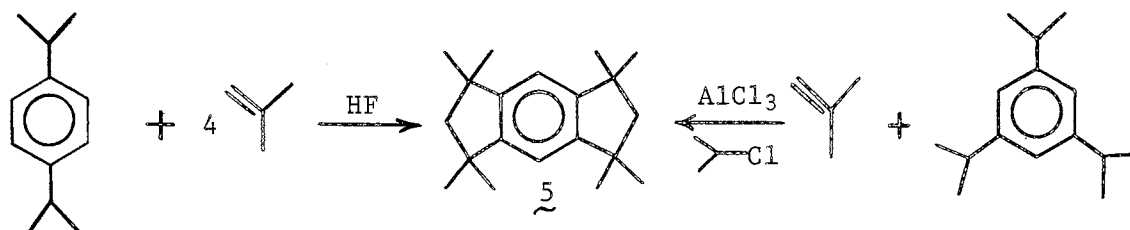
The reaction of benzene with isoprene was found[11] to yield hydrindacene products with lower yields of 1,1-dimethylindan. Other workers[12] applied this cyclialkylation reaction to m- and p-cymene and found 6 and 7. Later work[13,14] has shown that a variety of indans and hydrindacenes are formed in the reaction of isoprene with o-, m-, or p-xylene.

6   7

or

8   9
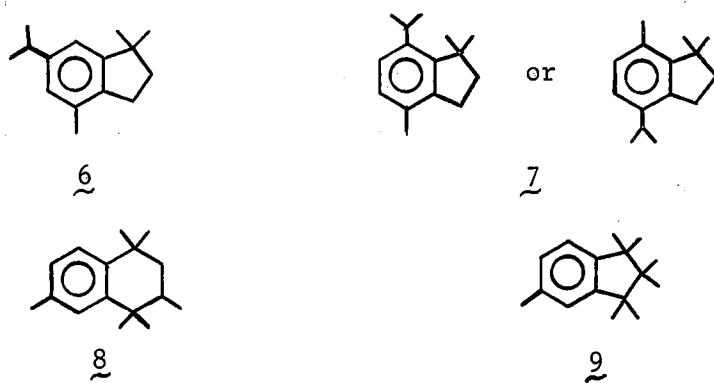
Wood et al. found[15a] that the reaction of 2,3-dimethyl-2-butene with p-cymene gave the tetralin 8 instead of the indan 9 previously reported.[15b] The formation of 8 is shown in Fig. 2. A small amount of 10 which results from ring closure without apparent hydride shift[15a] was also identified.

+   R ⊕   ⟶   +

8 ⟵   ⇌   →   10
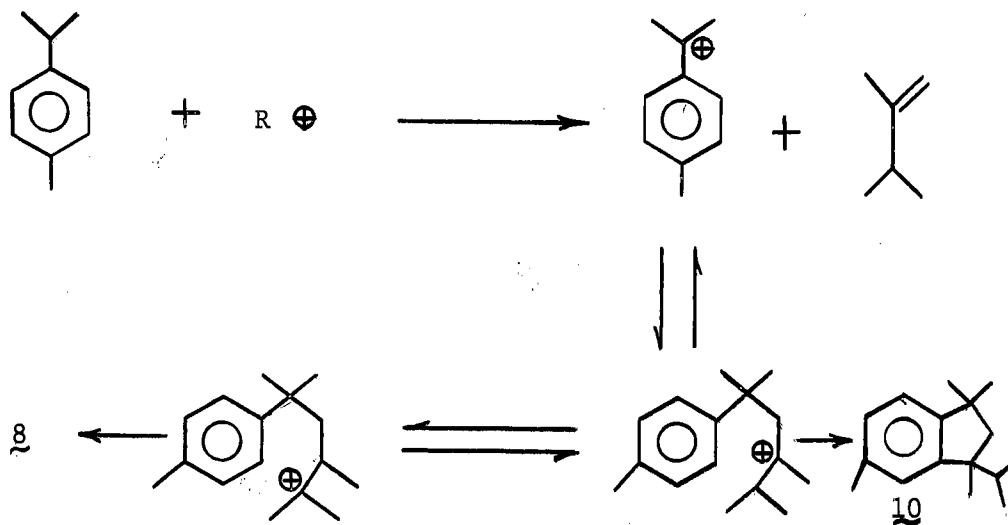
Figure 2. Formation of 1,1,3,4,4,6-Hexamethyltetralin

Roberts and Khalaf[16] found that 3-chloro-5-phenylpentane (11)

gave 98% 1-methyltetralin (12) in the presence of aluminum chloride –

ferric chloride catalyst, whereas ethylindan (13) was not detected.
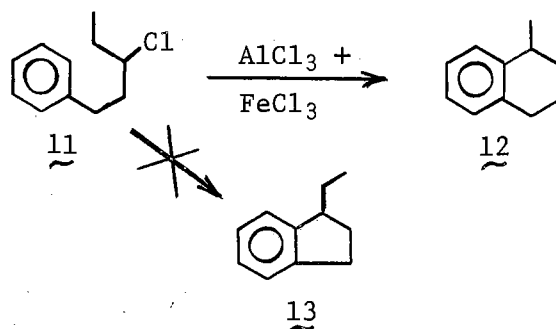
The alkylation of isoparaffins is used in the petroleum industry

to produce gasoline components with exceptionally good anti-knock pro-

perties. Commonly, this alkylation combines isobutane with butenes in

the presence of a strongly acidic catalyst to produce highly branched

octanes.[17] It is commonly accepted that these reactions proceed via

carbonium ions.[18]

The two most important hydride transfer reactions in this type of

alkylation are:
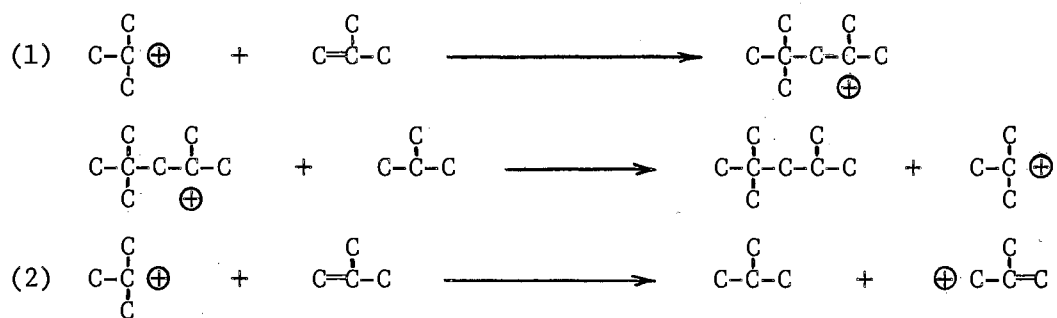
The hydride transfer shown in reaction 1 produces the desired branched octane. Reaction 2, called[19] "conjunct polymerization", is less desirable since the $C_4H_7^\oplus$ allyl cation is soluble in the acid catalyst where it contributes to acid deactivation and a reduced yield.[18]

Only strong acids catalyze either of these hydride transfer reactions and consequently, concentrated sulfuric acid or hydrofluoric acid are used. At present there appears to be no satisfactory explanation for the apparent relationship between acid strength and hydride transfer.

Table I shows the composition of C_8 alkylate from the alkylation of isobutane with isobutylene.[20] It is evident that rearrangements of some sort occur during the reaction.

TABLE I

COMPOSITION OF ALKYLATES BY NAME

2,2,4-Trimethylpentane	49.6	2,3-Dimethylhexane	3.2
2,2,3-Trimethylpentane	3.4	2,4-Dimethylhexane	5.0
2,3,3-Trimethylpentane	19.1	2,5-Dimethylhexane	7.0
2,3,4-Trimethylpentane	12.7	3,4-Dimethylhexane	---
Total	84.8	Total	15.2

Examination of the composition of total alkylates shown in Table

II indicates the complexity of the alkylation reaction.[18]

TABLE II

COMPOSITION OF ALKYLATES BY NUMBER OF CARBON ATOMS

Paraffin Isomers	C_5	C_6	C_7	C_8	C_9
Volume %	8.4	5.9	6.5	73.1	6.1

Thus only about three-fourths of the product is C_8. Schneider and Kennedy[21] postulated that the C_5, C_6, and C_7 hydrocarbons arise from a C_{12} carbonium ion which undergoes β-scission (cracks) to form C_5 and C_7 or two C_6 fragments before hydride transfer. In more recent work, Hofmann and Schriesheim[22] studied the alkylation of isobutane with ^{14}C-labeled butylenes. Their work supported the proposed reaction path involving the C_{12} carbonium ion.

Work utilizing the measurement of rates of tritium exchange between tritiated sulfuric acid and a series of isoparaffins[23] points to rapid rearrangements and exchange during the lifetime of the carbonium ion. It appears that intramolecular methide and hydride shifts are rapid compared to intermolecular hydride transfer. As long as a decrease in chain branching is not involved, isomerization will occur when possible. β-Scission of the carbonium ion also becomes important with C_8

and higher hydrocarbons.

The reactions of the 2,4,4-trimethylpentyl cation in concentrated, tritiated sulfuric acid at room temperature were studied.[23a] It was found that "the primary reactions of the 2,4,4-trimethylpentyl cation include isomerization to other trimethylpentyl cations and β-fission to form C_4 fragments." The dimethylhexanes are not formed primarily by rearrangement but appear to arise from a combination of isobutylene with the methallyl cation and some C_{12} cracking.

$$R \oplus \quad + \quad C\!\!=\!\!\overset{\overset{\textstyle C}{|}}{C}\!\!-\!\!C \quad \longrightarrow \quad RH \quad + \quad C\!\!=\!\!\overset{\overset{\textstyle C}{|}}{C}\!\!-\!\!C \oplus$$

$$C\!\!=\!\!\overset{\overset{\textstyle C}{|}}{C}\!\!-\!\!C \oplus \quad + \quad C\!\!=\!\!\overset{\overset{\textstyle C}{|}}{C}\!\!-\!\!C \quad \longrightarrow \quad C\!\!=\!\!C\!\!-\!\!C\!\!-\!\!\overset{\overset{\textstyle \oplus}{}}{\underset{\underset{\textstyle C}{|}}{C}}\!\!-\!\!C \quad \text{Saturation via hydride transfer}$$
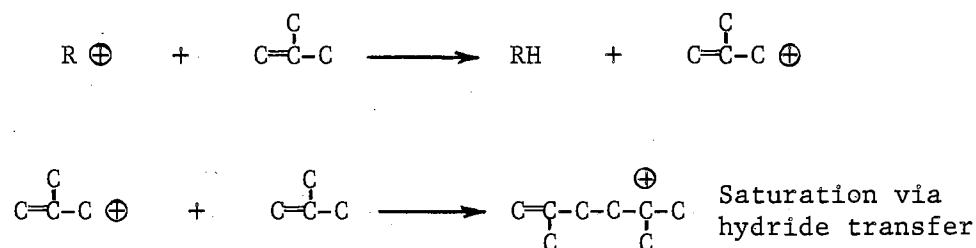
It has been found that "1-Butanol, 2-butanol, *tert*-butyl alcohol, or 2,4,4-trimethylpentenes all produce the same products in 96% sulfuric acid, but at different rates."[24] The products consist of 50% of sulfuric acid-insoluble alkanes and about 50% of sulfuric acid-soluble alkylcyclopentenyl cations as observed by nmr spectroscopy. The alkyl-cyclopentenyl cations formed are mainly in the C_{10} – C_{18} range. This is to be contrasted with the yield of dimers, trimers, etc., of C_4H_8 obtained when 75% sulfuric acid is used.

The effect of acid strength on the products obtained is quite evident in the case of sulfuric acid.[25] Isobutylene when mixed with ben-

zene and 70% sulfuric acid at 6-15° is converted to *tert*-butyl hydrogen

sulfate. In 80% sulfuric acid the principal reaction is polymerization

of isobutylene along with some ester formation. The principal product

in 96% sulfuric acid is *tert*-butylbenzene. For a more involved dis-

cussion of the acids used in Friedel-Crafts reactions, some of the re-

views in this area should be consulted.[26,27]

The predominant olefin products from the acid-catalyzed dimeriza-

tion of isobutylene are the 2,4,4-trimethylpentenes. The mixture of di-

isobutylenes which is formed from the intermediate carbonium ion,

$(CH_3)_3CH_2\overset{\oplus}{C}(CH_3)_2$ (14), consists of 80% 2,4,4-trimethyl-1-pentene (15)

and 20% 2,4,4-trimethyl-2-pentene (16), though 16 is reported[15] to be

thermodynamically more stable.

A simplified olefin reaction scheme is shown in Fig. 3. The re-

action conditions and the acid used determine the path(s) which pre-

dominate. The effect of various concentrations of sulfuric acid on

the products obtained with isobutylene has been previously discussed.

The reaction temperature also has a large effect.[18]

It has been proposed[28] that liquid-phase bimolecular reactions

can account for rearrangements of secondary and tertiary carbonium ions

and thus avoid the hypothetical participation of primary carbonium

ions. It is still necessary however to invoke secondary carbonium

ions in the rationalizations.

As shown in Fig. 3, the formation of 17 can be rationalized by at

least two paths. Both of these require the formation of secondary

carbonium ions from tertiary carbonium ions.

The reaction involving the methide shift in going from 17 to 18 is

evidently rapid compared to the reverse, i.e., from 18 to 17. There
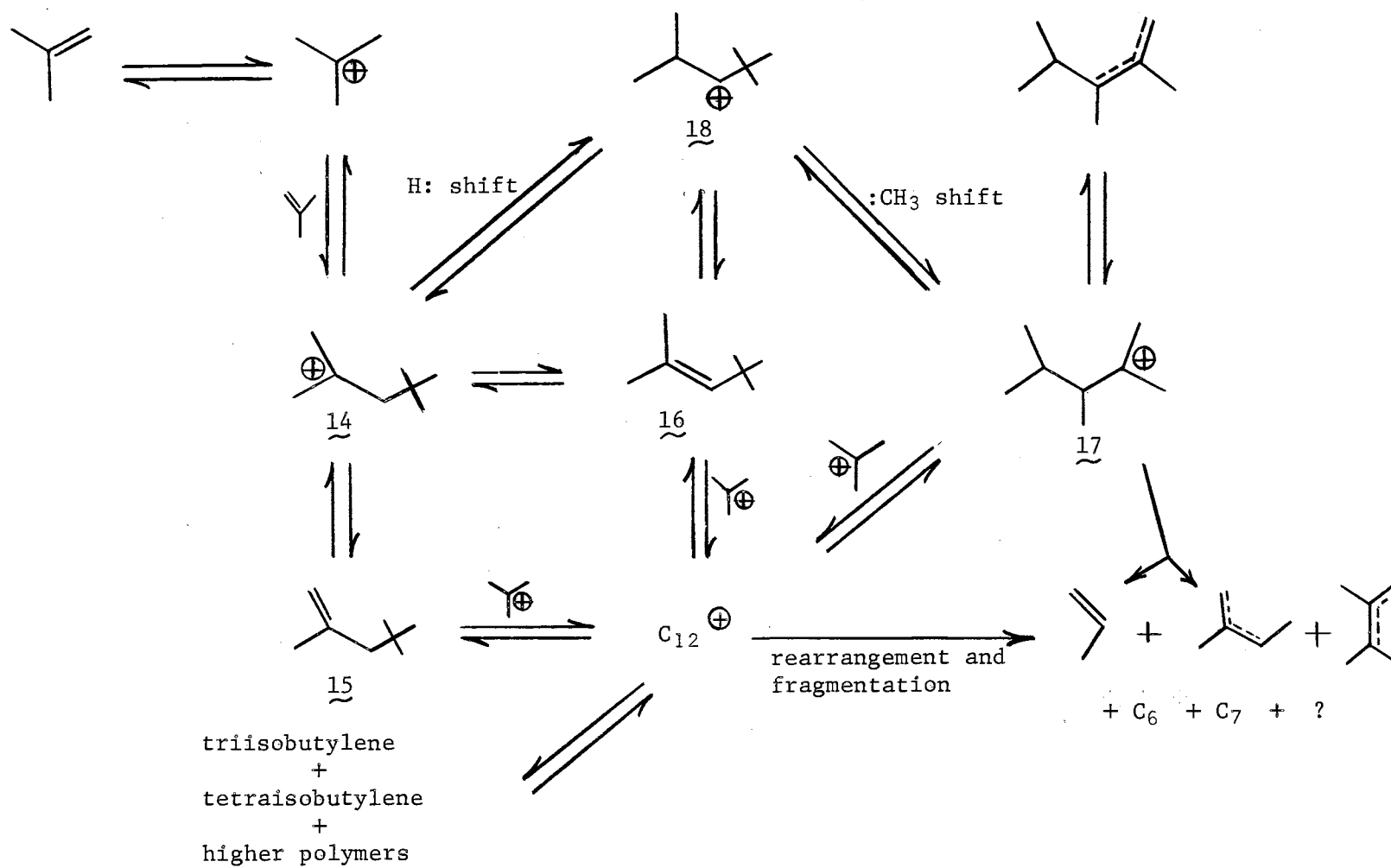
Figure 3. Olefin Reactions

triisobutylene
+
tetraisobutylene
+
higher polymers

are, however, literature discrepancies on the acid-catalyzed equilibra-
tion. It has been reported[29] that the order of velocity of polymeriza-
tion and isomerization is: 2,3,3- > 2,4,4- > 2,3,4-trimethylpentene.
No double bond locations or sulfuric acid concentrations were given in
the abstract. It was also reported that 2,3,4-trimethylpentene is the
chief product of the isomerization of the 2,2,3- and 2,4,4-trimethyl-
pentenes, and that 2,4,4-trimethylpentene is the thermodynamically most
stable isomer.

Recent studies[30] on the reaction of 2,3,4-trimethylpentane in con-
centrated sulfuric acid indicate that once 17 is formed it rearranges
to 14 which undergoes β-scission to form a *tert*-butyl cation and isobu-
tylene. It appears that there is no accurate thermodynamic data for
the acid-catalyzed equilibration of trimethylpentenes.[31]

Table III gives a rough comparison of the heats of formation of
different carbonium ions.[32] These data were obtained by electron im-
pact from gas-phase reactions and do not involve the energy of solva-
tion.

The β-scission of 17 to form 2-methyl-2-butene (19) and the iso-
propyl cation would not be expected to be a major pathway owing to the
higher energy of formation of the isopropyl cation compared to other
secondary carbonium ions and especially tertiary carbonium ions. Due
to the rapidity with which acid-catalyzed hydride and methide shifts
occur in hydrocarbon carbonium ions, it would be expected that β-scis-
sion would occur only when a relatively stable carbonium ion would
result.

TABLE III

HEATS OF FORMATION OF UNSOLVATED CARBONIUM IONS

	H_f(kcal/mole)
$CH_3 \oplus$	262
$CH_3CH_2 \oplus$	224
$CH_3CH_2CH_2 \oplus$	216
$CH_3\overset{\oplus}{C}HCH_3$	190
$CH_3CH_2CH_2\overset{\oplus}{C}H_2$	207
$CH_3CH_2\overset{\oplus}{C}HCH_3$	181
$(CH_3)_3C \oplus$	166

CHAPTER II

RESULTS AND DISCUSSION

p-Cymene. The acid-catalyzed reaction[6] of p-cymene with isobuty-
lene was repeated to prepare 4 for the American Petroleum Institute
standard samples program. A complex array of products shown in Fig. 4
was found when the reaction products were examined by gas liquid phase
chromatography (glpc).

The identification of these components was accomplished by instru-
mental methods utilizing mass, nmr, and ir spectra. Samples for analy-
sis were usually obtained by distilling the reaction mixture to concen-
trate the desired components and then separating the individual hydro-
carbons by preparative glpc.

Some of the reaction products were found to contain thermally un-
stable polymers which interfered with the analyses. This contaminant
could not be entirely removed with preparative glpc, distillation, col-
umn chromatography on silica gel and alumina, or stirring with concen-
trated sulfuric acid.

The major product of the p-cymene - isobutylene reaction was found
to be 4 as previously reported.[8] The formation of this compound by a
hydride-transfer mechanism has been discussed.

The hydrocarbon dimer 1, whose formation is shown in Fig. 1, was
usually found in less than five per cent yield. In addition, a small
amount of 2-*tert*-butyl-p-cymene (20) was identified.

14
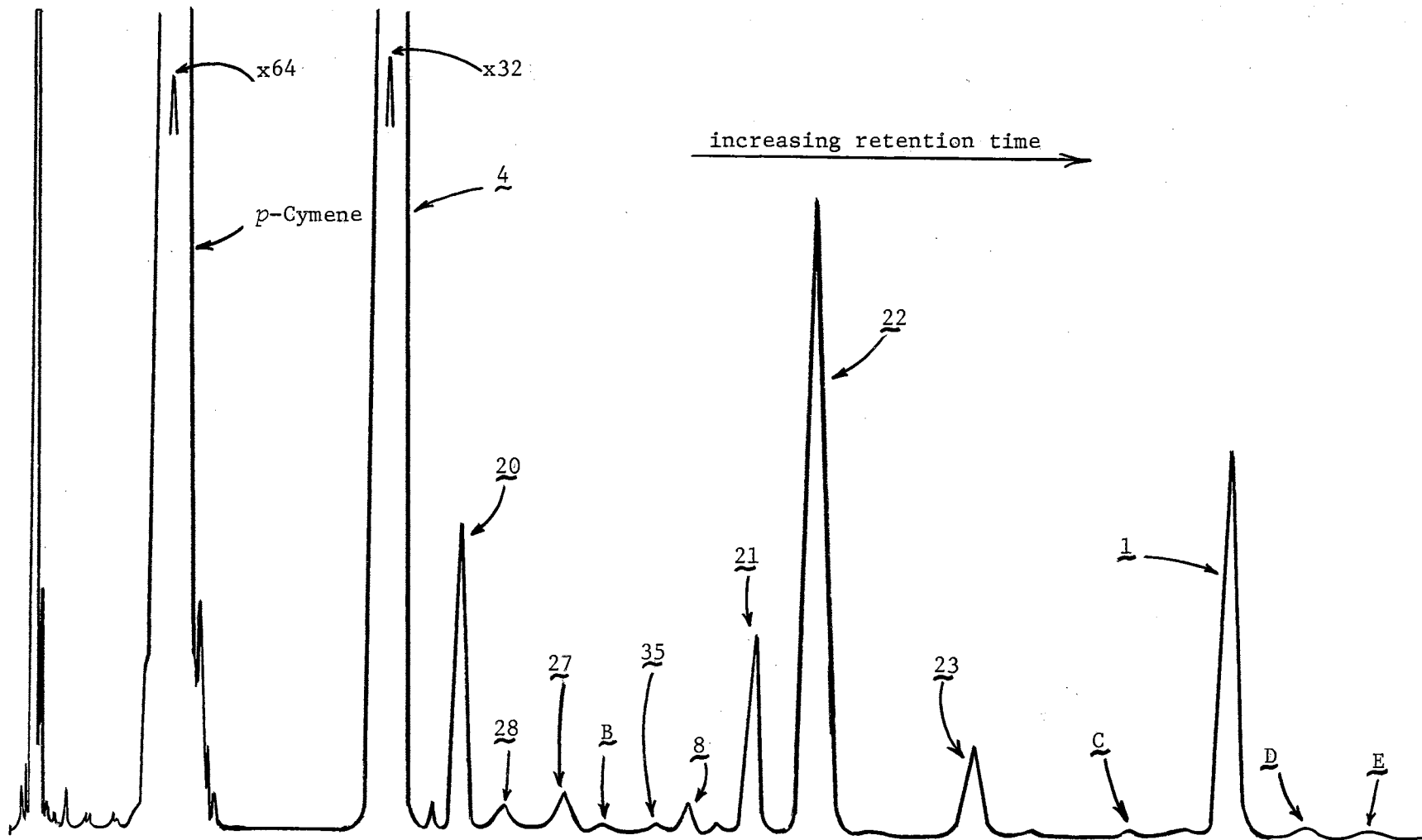
Figure 4. Gas Chromatogram of The *p*-Cymene - Isobutylene Reaction Mixture

The fact that compounds other than 1, 4, and 20 are formed shows that hydride abstraction by the *tert*-butyl cation is slow enough to allow competition through attack of olefin, intramolecular rearrangement, or proton loss. Thus, the formation of the *p*-cymyl cation may be the rate-determining step provided stirring is sufficiently rapid to make any mass-transfer factor negligible.

5-*tert*-Butyl-1,1,3,3,6-pentamethylindan (21) can be formed by the two pathways shown below. It is not clear which predominates or whether both contribute. Each route involves the same reaction steps only in different order, and each requires that *tert*-butylation occur ortho to a methyl group.
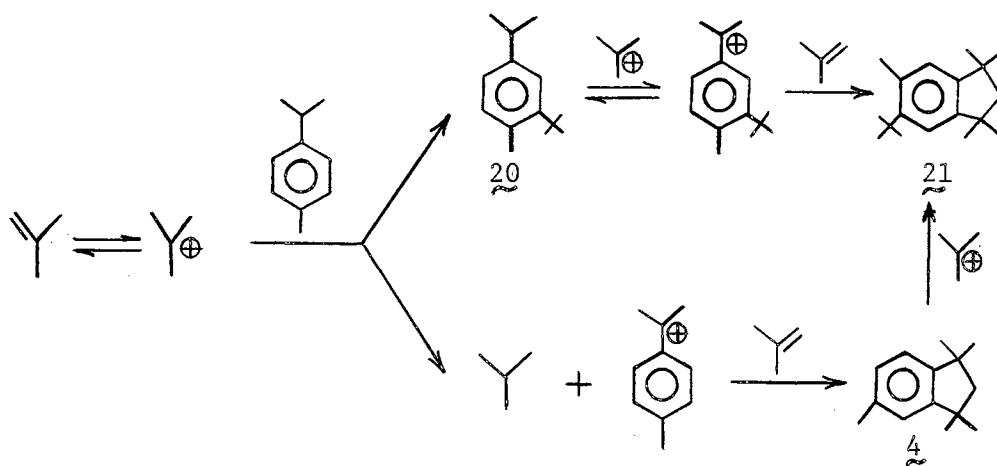
The dealkylation of *tert*-butyl groups from aromatic rings is reported[6] to readily occur when the compound is stirred with sulfuric acid or other strong acids in the presence of toluene or other

acceptors to which the *tert*-butyl group can be transferred.

The products 20 and 21 are not observed in every reaction with isobutylene or diisobutylene and *p*-cymene. They were isolated from a reaction in which there was a large excess of *p*-cymene relative to isobutylene. The transfer agent, in this case probably an olefin, was therefore diluted with *p*-cymene. When the reaction was run with an equal molar ratio of isobutylene to *p*-cymene, only trace amounts, if any, of 20 and 21 were observed.

Two attempts were made to produce 21 by combining 4 with isobutylene. In one case 96% sulfuric acid was used, and in the other Amberlyst-15 was the catalyst. The reaction catalyzed by sulfuric acid at 5° afforded a low yield of 21, while the reaction with Amberlyst-15 at 100° gave only a trace of 21. Evidently dealkylation with loss of *tert*-butyl group occurs rapidly at the higher temperature.

An attempt was made to cyclialkylate 20 by treating it with isobutylene. It was found that 4 formed but 21 did not. A large amount of triisobutylene was produced, and since *p*-cymene has the same glpc retention time as one of these C_{12} compounds, it was not determined whether *p*-cymene was present. However, since 4 was produced, it is apparent that loss of the *tert*-butyl group from 20 had occurred. The reaction of 20 with isobutylene will be discussed in more detail when the reactions of a series of *tert*-butylcymenes with isobutylene are presented.

1,3,3,6-Tetramethyl-1-neopentylindan (22) is formed by reaction of the *p*-cymyl carbonium ion with 15. This indan can be prepared in over 60% yield when diisobutylene is used instead of isobutylene. Isobutylene readily dimerizes and 22 is usually a major product.
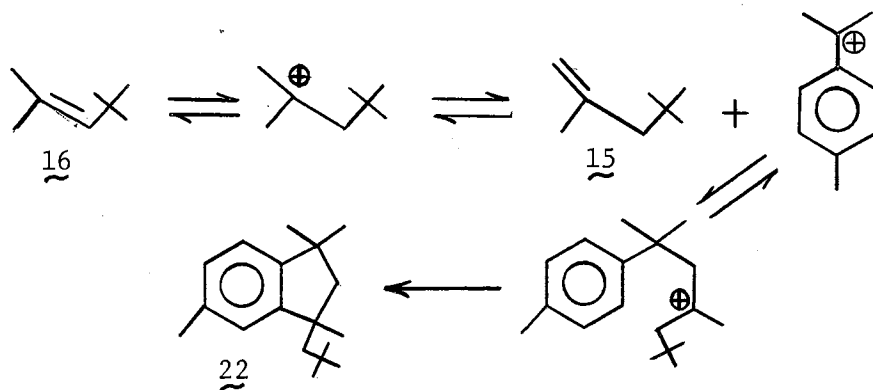
The nmr spectrum of 22 shows an interesting case of two nonequi-
valent methylene groups, each having nonequivalent hydrogens. Each
methylene group appears as an AB quartet with one being centered at
1.65 ppm, and the other centered at 2.03 ppm.
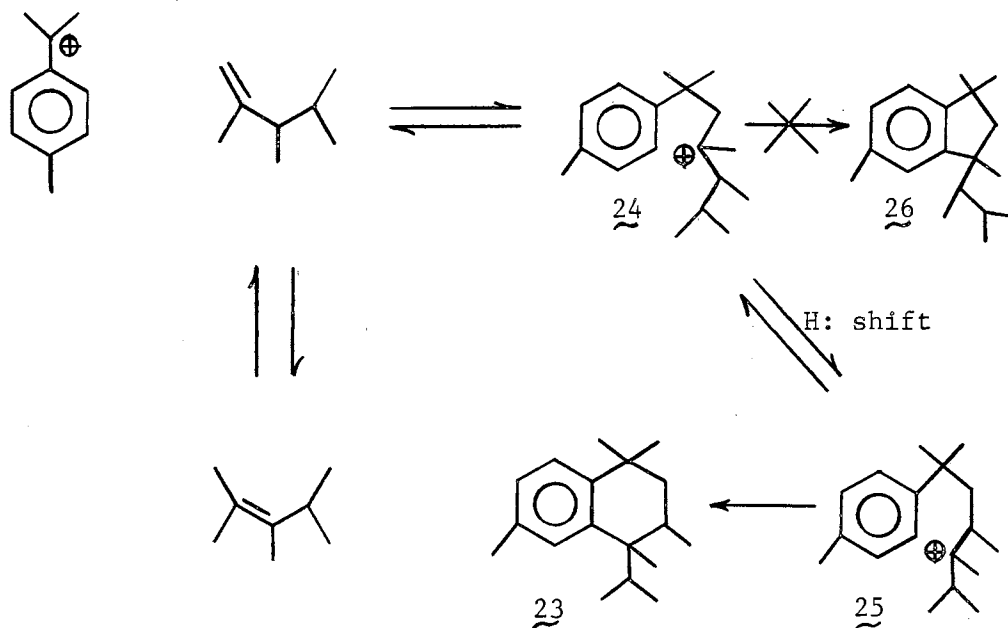
The formation of 23 is analogous to the described formation[15a] of

8. The exo isomer, 2,3,4-trimethyl-1-pentene, though expected to be

thermodynamically less stable than the endo isomer, is present in

greater quantities in acid media, as in the case of 15 in diisobutylene.

In addition, 2,3,4-trimethyl-1-pentene would be expected to react more

rapidly with the p-cymyl cation than 2,3,4-trimethyl-2-pentene does

since there is greater steric hindrance for the latter.

Once the p-cymyl cation has reacted with olefin to form the car-

bonium ion 24, a rapid hydride shift occurs to give 25 which then forms

23. The hydride shift is evidently much faster than the ring closure

since none of the indan 26 has been found in the reaction products.

Alternatively, 26 could be unstable under the reaction conditions.

When 2,3,4-trimethyl-2-pentene was treated with p-cymene in the

presence of sulfuric acid, three principal products were obtained.

These were 4, 22, and the expected 23. The ratios of these and other

reaction products are shown in Table IV.

TABLE IV

RATIOS OF PRODUCTS FROM THE REACTION OF
2,3,4-TRIMETHYL-2-PENTENE AND p-CYMENE[a]

Moles olefin / Moles p-cymene	1	4	22	23	27	28
0.1	1.7	1.0	8.2	14.6	0.5	0.4
0.5	3.5	1.0	6.4	12.5	0.5	0.4
2.0	0.2	1.0	1.3	2.0	0.6	0.5

[a]Ratios are relative glpc peak areas.

The hydrocarbons 27 and 28 are formed[33] from the 2-methylbutenes which result from olefin rearrangements and fragmentation as shown in Fig. 3. The reactions of these C_5 olefins with p-cymene are discussed in more detail later.

19 27 28 29
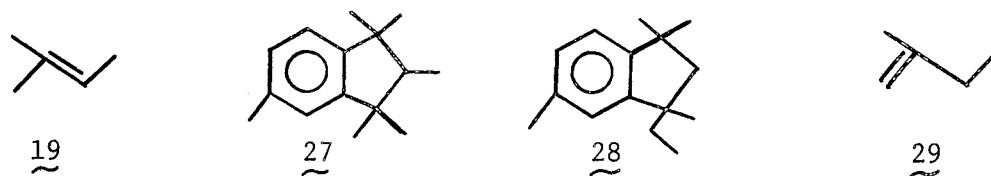
When an excess of p-cymene was used, more of 23 was formed relative to other products, and there was less olefin fragmentation as evidenced by the lower yields of 4, 27, and 28. It is to be expected that the yields of 27 and 28 would decrease as the concentration of p-cymene is increased, since their C_5 olefin presursor is probably formed for the most part from the C_{12} cation as shown in Fig. 3. If the olefin concentration is low, the likelihood of a carbonium ion abstracting a hydride ion from p-cymene or of the p-cymyl cation reacting with the olefin is increased.

The ratio of 22 and 23 in Table IV is not readily explained. At all three concentrations, this ratio is approximately 1:2 and appears to be independent of p-cymene concentration. Additional studies are planned to clarify this point.

The "odd molecular weight" products, i.e., those not formed from

p-cymene and one or more C_4H_8 units, appear to result from rearrangements and cracking which take place at the carbonium ion stage of the reaction shown in Fig. 3. Thus 27 and 28 are formed from 19 and 29 respectively.

The indans 27 and 28 had been previously prepared by chemists in the perfume industry[34] by two methods. The first[34a] was the reaction of p-cymene with *tert*-pentyl alcohol in sulfuric acid, which gave a mixture of 4, 27, and 28 in 12, 41, and 23% yields respectively. The indan 4 evidently results from a series of reactions involving dimerization of the C_5 olefin 19, subsequent rearrangements, and β-scission forming C_4 and C_6 fragments.[35] These olefins can then react with p-cymene or, in the case of the C_6 olefin, undergo further reactions with other olefins in the system.

The second method consisted of reacting a C_5 olefin with α,p-dimethylstyrene.[34b] It was found that a mixture of 27 and 28 in an approximate ratio of 2:1 was obtained regardless of whether 19 or 29 or a mixture of both was used.

In a reexamination of the reaction of p-cymene with 19, we found that the hexamethylindan 27 was indeed the major product, but the pentamethylindan 4 is also formed. In addition, it was found that 28 was formed along with about an equal amount of a $C_{15}H_{22}$ hydrocarbon designated A which is structurally similar. Since 28 and A show intense M-15 (loss of CH_3) and M-29 (loss of C_2H_5) peaks in their mass spectra, both products could be represented by structure 28 or an isomer. The molecular weight 202 indicates that these compounds must result from a C_5 olefin reacting with p-cymene, assuming that there is no loss of isopropyl group from p-cymene under these reaction conditions. Dis-

proportionation of the type that would be required here, i.e., migration of an alkyl group to another ring at a position adjacent to an alkyl group, does not readily occur.[36] Products resulting from this sort of rearrangement are not observed in related reactions.

There are three structures $\underset{\sim}{31}$, $\underset{\sim}{32}$, and $\underset{\sim}{33}$ other than $\underset{\sim}{28}$ which fit the requirements of having ethyl and methyl groups that are easily lost and having the *gem*-dimethyl group characteristic of *p*-cymene.
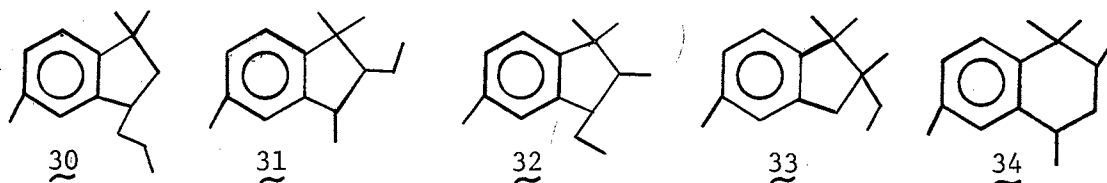
Structures $\underset{\sim}{30}$, $\underset{\sim}{31}$, and $\underset{\sim}{32}$ may be formed by reaction of the *p*-cymyl cation with *n*-pentenes. Their formation would involve a secondary carbonium ion which would then alkylate the aromatic ring. Structure $\underset{\sim}{30}$ should show an intense M-43 peak in the mass spectrum which was not observed. Since the formation of $\underset{\sim}{32}$ is similar to that of $\underset{\sim}{8}$ and $\underset{\sim}{12}$, it would seem likely that a hydride shift would occur to form the pentamethyltetralin $\underset{\sim}{34}$. The latter should not show the intense M-29 (loss of C_2H_5) peak in the mass spectrum.

The formation of $\underset{\sim}{33}$, while not requiring conversion of a methyl butene to an *n*-pentene, does involve the formation of a primary car-

bonium ion in the transition state which would then alkylate the aromatic ring. This process would not be expected to compete with the formation of 28. Thus structure 31 seems most likely, but the structure for this hydrocarbon should still be considered to be unknown.

The molecular weights of several other hydrocarbons which are formed in trace amounts in the sulfuric acid-catalyzed reaction of isobutylene and p-cymene were obtained by mass spectrometric analysis of preparative glpc samples.

A $C_{17}H_{26}$ hydrocarbon (MW 230) was isolated which showed an intense M-57 peak in the mass spectrum. The nmr spectrum of this sample (contaminated by isobutylene polymers) indicates the presence of a sec-butyl group. Structure 35 fits the available data.
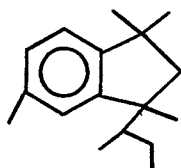
35

A $C_{16}H_{24}$ hydrocarbon (B) (MW 216) which showed an intense M-43 (loss of C_3H_7) peak in the mass spectrum was isolated from the p-cymene -isobutylene reaction mixture. The mass spectrum of hydrocarbon B was compared with the spectrum of a hydrocarbon isolated from the p-cymene - 2,3-dimethyl-1-butene reaction mixture and identified[33] as 10. It was found that the relative intensities of the peaks were in good

agreement except for the M-15 peak. The difference could be explained

by assuming either that there is an impurity of molecular weight 216 in

sample $\underset{\sim}{B}$ or that structure $\underset{\sim}{10}$ represents a closely related isomer of $\underset{\sim}{B}$.

The mass spectrum of sample $\underset{\sim}{C}$ showed it to be a mixture of hydro-

carbons of molecular weights 258 ($C_{19}H_{30}$), 272 ($C_{20}H_{32}$), and 286

($C_{21}H_{34}$).

Two additional samples, $\underset{\sim}{D}$ and $\underset{\sim}{E}$, were found to be hydrocarbons of

molecular weight 300 ($C_{22}H_{36}$). Hydrocarbon $\underset{\sim}{D}$ had intense peaks in its

mass spectrum at M-15 (loss of CH_3) and M-71 (loss of C_5H_{11}) while $\underset{\sim}{E}$

had intense peaks at M-15, M-43 (loss of C_3H_7) and M-99.

When methanesulfonic acid was used as a catalyst, it was found

that in addition to the "odd molecular weight" hydrocarbons discussed

above several other hydrocarbons of this type were formed. One of

these, $\underset{\sim}{F}$, was shown to have structure $\underset{\sim}{8}$ by comparison of ir, nmr, and

mass spectral data.[33] Hydrocarbon $\underset{\sim}{G}$ was also found to have a molecular

weight of 216 but showed intense M-15 (loss of CH_3) and M-29 (loss of

C_2H_5) peaks in the mass spectrum.

A hydrocarbon $\underset{\sim}{H}$, $C_{23}H_{28}$ (MW 304), crystallized out of the product

mixture from the methanesulfonic acid-catalyzed reaction of p-cymene

with isobutylene. The molecular weight indicates that the numbers of

rings plus double bonds equal ten. Therefore if two aromatic rings are

involved, there must be two additional rings or double bonds or one

ring and one double bond. The mass spectrum shows an intense M-15

(loss of CH_3) peak.

The sulfuric acid-catalyzed reaction of 2,3-dimethyl-1-butene

with excess p-cymene was performed to obtain a sample of $\underset{\sim}{8}$ (known sam-

ples of $\underset{\sim}{8}$ and $\underset{\sim}{10}$ were later received from another source[33]). There

were four major products formed, 1, 4, 8, and 10. The formation of 4 requires that the C$_6$ olefin undergo dimerization, rearrangement and fragmentation reactions to form isobutylene.

The products obtained are the same whether isobutylene, diisobutylene, or triisobutylene is combined with *p*-cymene. The olefin used does affect the product yields. The ratios of the products of these olefins are compared in Table V.

When sulfuric acid was used, the best results were obtained when the reaction temperature was kept below 10°. As the reaction temperature was increased, the yield of polyisobutylenes increased until, at 65°, only a few percent of the products resulted from the cyclialkylation reactions, and the major products observed on glpc were tetraisobutylenes.

Within certain limits, the quantity of sulfuric acid used seemed to have little effect on the products formed. When a small quantity of acid was used, more tetraisobutylene and other olefinic polymers resulted. Large amounts of sulfuric acid, e.g., acid to *p*-cymene ratio of 2:1 or greater, resulted in loss of material due to sulfonation and consequent emulsion formation during isolation.

Anhydrous hydrogen fluoride was effective in catalyzing the cyclialkylation reaction. In Run 4, the isobutylene introduced into the reaction did not approach the stoichiometric amount; therefore the 12% yield of 4 formed is not a true indication of this acid's ability to catalyze the reaction.

When diisobutylene was used, the hydrogen fluoride reaction gave much less of the intact cyclialkylation product, 22, than did sulfuric acid. More fragmentation of the diisobutylene occurred when hydrogen

TABLE V

RATIOS OF PRODUCTS FROM ACID-CATALYZED REACTIONS OF p-CYMENE AND OLEFINS

Run	Olefin, Acid, Temp °C		Ratios of Hydrocarbons[a]						
			4[b]	1	35	21	22	23	27
	Isobutylene								
1a	H_2SO_4	5°	41	0.093		0.069	0.15	0.027	
1b	H_2SO_4	5°	42	0.096		0.023	0.094	0.012	
2a	MSA[c]	10°	2				0.32	0.53	
2b	MSA	115°	43	0.022			0.044	0.022	0.026
3a	A-15[d]	25°	1				2.00	0.71	
3b	A-15	85°	15			0.028	0.095	0.030	
3c	A-15	130°	33	0.047			0.057	0.067	
4	HF	5°	12	0.027			0.32	0.033	0.016
	Diisobutylene								
5a	H_2SO_4	5°	9	0.52	0.060		5.04	0.61	0.24
5b	H_2SO_4	5°	7	1.46	0.084		7.53	1.05	0.18
5c	H_2SO_4	5°	7	0.13	0.054		7.40	0.74	0.19
6a	H_2SO_4	25°	8	0.14			2.40	0.41	
6b	H_2SO_4	25°	17	0.43	0.060		2.76	0.53	0.071
6c	H_2SO_4	25°	10	0.42	0.003		2.22	0.50	0.079
7	H_2SO_4	65°	2				1.40	0.47	
8a	MSA	70°	25		0.071	0.054	0.39	0.19	0.12
8b	MSA	70°	27	0.03	0.07		0.31	0.16	0.15

TABLE V (Continued)

Run	Olefin, Acid, Temp °C		4^b	1	35	21	22	23	27
8c	MSA	115°	43	0.086			0.075	0.050	0.047
8d	MSA	140°	35		0.054		0.19		0.12
9	A-15	100°	12	0.11			1.20	0.54	
10a	HF	5°	15	0.037	0.003		2.05	0.18	0.12
10b	HF	5°	23		0.057		1.19	0.16	0.15
11a	AlCl$_3$	5°	trace^e				50		0.036
11b	AlCl$_3$	70°	13				2.7	0.17	
Triisobutylene									
12a	H$_2$SO$_4$	5°	18	0.13	0.075		0.74	0.061	0.105
12b	AlCl$_3$	5°	5	1.06			10.2		0.48

Column header note: Ratios of Hydrocarbons[a]

[a] Product ratios normalized to 4 = 1.00. [b] Values given are percent yields of 4. [c] Methanesulfonic acid. [d] Amberlyst-15. [e] Peak ratios are compared to 22 = 1.00. The value given for 22 is percent yield.

fluoride was used than with sulfuric acid, and an increased concentration of hydrogen fluoride caused formation of larger yields of fragmentation products.

Methanesulfonic acid gave only olefin polymerization at temperatures below 30°. This catalyst at 70° still caused formation of reaction products which were badly contaminated by polymeric material, but it also afforded cyclialkylation products. Under the conditions necessary for the formation of cyclialkylation products, little of indan 22 was formed, i.e., dealkylation of diisobutylene was occurring to a large extent. The yields of 4 increased when the reaction temperature was raised to 115°.

When Amberlyst-15 was the catalyst, it was necessary to use temperatures in excess of 100° to minimize the polyisobutylene formation. Comparison of Run 9 with Run 8a shows that while the yield of 4 is over twice as great in the methanesulfonic acid-catalyzed reaction as when A-15 was used, the ratio of 22 to 4 is several times greater in the A-15 reaction. This shows that even at a higher temperature the A-15 gives more intact cyclialkylation products than the methanesulfonic acid.

Aluminum chloride at 5° gave essentially no products resulting from depolymerization of diisobutylene, i.e., no 4 and a large yield of 22 were obtained. When the reaction temperature was increased, indan 4 was formed, but 22 was still the major product. Though aluminum chloride caused formation of a large amount of 22, when triisobutylene was used no intact cyclialkylation products were observed. Instead, the major product as seen in Run 12b was 22.

m-Cymene. The reaction of *m*-cymene with 4-methylcyclohexene in

the presence of sulfuric acid or hydrogen fluoride gave a 42% yield of 6-(1-methylcyclohexyl)-*m*-cymene.[4] In addition, about 25% of a cyclialkylation product thought to be 1,3,3,5-tetramethyl-1-*m*-tolylindan (2) was isolated. As discussed earlier, other workers reported[5] that a mixture of 2 and 1,3,3,7-tetramethyl-1-*m*-tolylindan (3) was formed in a 1:2 ratio.

The reaction of *m*-cymene with isobutylene using sulfuric acid as the catalyst gave the complex mixture shown in Fig. 5. As in the case of *m*-cymene, preparative gas chromatography was used to obtain samples for analysis with compound identifications being made by instrumental methods using nmr, ir, and mass spectrometry.

Structures of the products which have been identified in the *m*-cymene - isobutylene reaction are shown in Fig. 6.
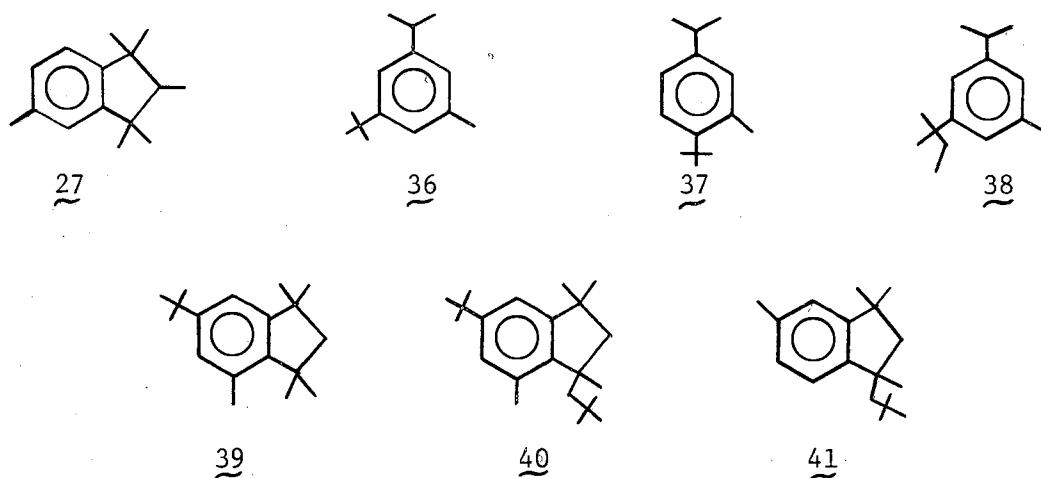
Figure 6. Reaction Products From The
m-Cymene - Isobutylene Reaction
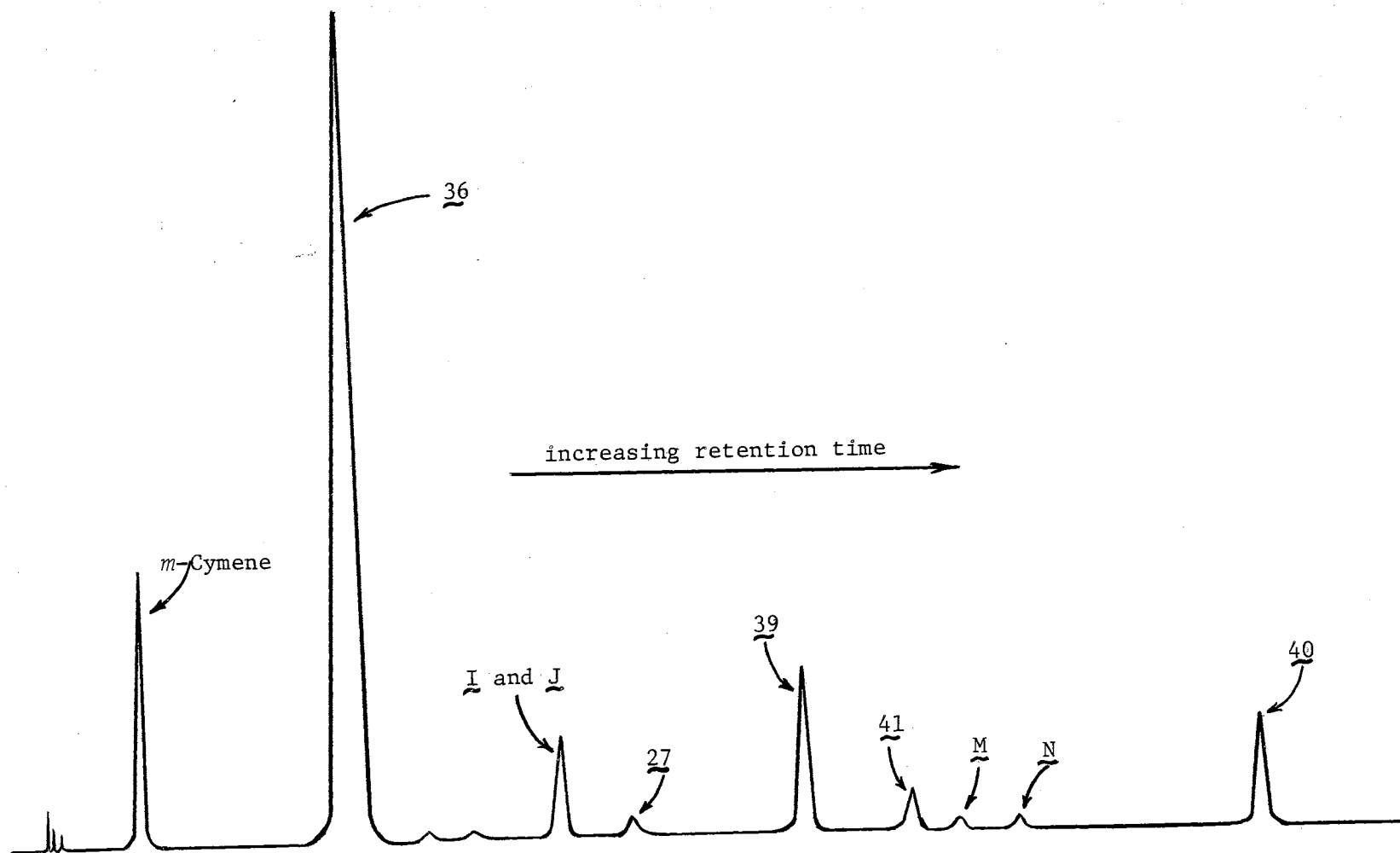
Figure 5. Gas Chromatogram of The *m*-Cymene – Isobutylene Reaction Mixture

The major product shown in Fig. 5, is 5-*tert*-butyl-*m*-cymene (36). This product results from *tert*-butylation of *m*-cymene, and it should be thermodynamically more stable than 2-*tert*-butyl-*m*-cymene (37).

Although 37 has not been definitely identified as a product of the *m*-cymene – isobutylene reaction, the hydrocarbon material corresponding to the peak for I + J in Fig. 5, collected by preparative glpc, was found to be a mixture since the mass spectrum showed molecular ions at m/e = 190 ($C_{14}H_{22}$), hydrocarbon I, and m/e = 204 ($C_{15}H_{24}$), hydrocarbon J, in a ratio of 5:1. The ir spectrum of the mixture showed a 1,2,4-substituted benzene to be present in a greater amount than a 1,3,5-substituted benzene. The glpc peak has the same retention time as that of a sample of 5-*tert*-pentyl-*m*-cymene (38) which was obtained from the *m*-cymene – 2-methyl-2-butene reaction. In addition, the major characteristics in the ir, nmr, and mass spectra of 38 match those of J. Thus the 1,3,5-substituted alkylbenzene, J, is considered to be 38.

The $C_{14}H_{22}$ (MW 190) hydrocarbon, I, is most likely 37. In order for it to be some other alkylbenzene, either migration of an isopropyl or methyl group or transalkylation must occur, and transalkylation has been reported not to occur in similar cases.[37a]

The high ratio of 36:37 of 12:1 from the *m*-cymene – isobutylene reaction is not surprising when their relative stabilities are considered. There should be severe steric hindrance between the adjacent methyl and *tert*-butyl groups of 37 whereas no crowding exists in 36.

A hydrocarbon resulting from alkylation in the 5-position of *m*-cymene is the principal product in the reaction of *m*-cymene with 2-methyl-2-butene. As mentioned earlier, this hydrocarbon has been identified as 38. The polyalkylbenzene which would be formed from alkyla-

tion ortho to the methyl group, i.e., 6-*tert*-pentyl-*m*-cymene (42), has not been found in this reaction mixture. The other products which have been identified will be discussed later.

As seen in Fig. 6, two types of *m*-cymene cyclialkylation products have been found———1,2,4-substituted benzenes, 27 and 41, and 1,2,3,5-substituted benzenes, 39 and 40. The formation of the 1,2,4-substituted benzene products can be rationalized by assuming that a cation, e.g., 43 in Fig. 7, attacks the aromatic ring para to the methyl group. This is also shown in Fig. 8 by the formation of 41.

The formation of the cyclialkylation products which are 1,2,3,5-substituted benzenes can be rationalized by either of two routes. The first path involves initial cyclialkylation to form a mixture of 1,2,4- and 1,2,3-substituted benzenes as shown in the upper path in Fig. 7 to give 4 and 44, and in Fig. 8 by the formation of 41 and 46. This competition in the direction of ring closure has been previously discussed in the formation of 2 and 3. Once the 1,2,3-substituted benzene is formed, it can be alkylated in the 5-position by a *tert*-butyl cation.

The second route is shown as the lower path in Fig. 7 and 8 and involves *tert*-butylation of *m*-cymene in the 5-position to form 36 which then undergoes the cyclialkylation reaction. The steric requirements of the *tert*-butyl group of the cation 45 would favor ring closure ortho to the methyl group.

There are several observations which help to clarify which paths of Fig. 7 and 8 are followed. Cyclialkylation products 39 and 40 were formed when hydrocarbon 36 (as part of a mixture from the isobutylene – *m*-cymene reaction with added *n*-dodecane internal standard) was combined with isobutylene using sulfuric acid as the catalyst.

As can be seen from Table VI, the relative amounts of hydrocarbons 39 and 40 were increased by the reaction. There are two possible explanations. First, 36 may lose the *tert*-butyl group to form *m*-cymene, which then reacts by the upper path of Fig. 7 and 8. This does not seem likely since, as will be discussed in more detail later, neither 4-*tert*-butyl-*o*-cymene nor 5-*tert*-butyl-*o*-cymene loses a *tert*-butyl group under similar reaction conditions. An increase in 41 should also be observed if formation of *m*-cymene were occurring in the reaction.

TABLE VI

REACTION OF 5-*tert*-BUTYL-*m*-CYMENE (36) WITH ISOBUTYLENE

Ratio[b] of compounds in:	Hydrocarbons present						
MC[a]	:dode-:cane :	36 :38+37:	39 :	41 :	M :	40
starting material	0.48 :1.00 :	7.2 :0.52 :	0.48 :trace:	0.0 :0.0			
final reaction	0.00 :1.00 :	1.0 :trace:	1.7 :trace:	1.2 :1.6			

[a] *m*-Cymene. [b] Ratios relative to *n*-dodecane found from glpc peak areas.

The other explanation is that the lower path of Fig. 7 and 8 is being followed, i.e., a hydride ion is abstracted from 36 and a cation formed which can react with olefins present in the system. Once a cation such as 45 is formed, because of the presence of the bulky *tert-*

butyl group, cyclization takes place in favor of 39 or 40. The final
ratio of 1:1 for 39 and 40 in Table VI is in marked contrast to the
ratio 2:1 for these hydrocarbons shown in the isobutylene reaction of
Table VII.

When α,m-dimethylstyrene reacted with diisobutylene in the pre-
sence of sulfuric acid, it was found that hydrocarbon 46 was formed a-
long with 41 in approximately a 1.0:1.5 ratio. This suggests that the
ring closure can occur by attack of a cation such as 45 either ortho or
para to the methyl group as previously reported.[5] The ortho:para pro-
duct ratio for 46 and 41 of 1.0:1.5 found in this reaction provides an
interesting contrast with the 2.0:1.0 (ortho:para) ratio reported for
3 and 2.

A small amount of 40, presumably formed from 46 via the upper
path of Fig. 8, was also formed in the reaction of diisobutylene with
α,m-dimethylstyrene. Thus the diisobutylene depolymerizes to a limited
degree to form isobutylene and *tert*-butyl cations, which then alkylate
46 in the 5-position. There was none of hydrocarbon 4 or 39 observed
in the final reaction mixture; thus isobutylene was not reacting with
the α,m-dimethylstyrene.

Since 46, a 1,2,3-substituted benzene, is formed in the reaction
of diisobutylene with α,m-dimethylstyrene (where a hydride abstraction
is unnecessary), products of this sort would be expected in the cycli-
alkylation reactions of olefins with m-cymene. Evidence for this has
been found only in the reaction of m-cymene with diisobutylene. In
this reaction a hydrocarbon (K) with the same glpc retention time as
46 was observed. The ir spectrum of K compares well with that of 46.
Mass spectral and nmr analyses of K are planned.
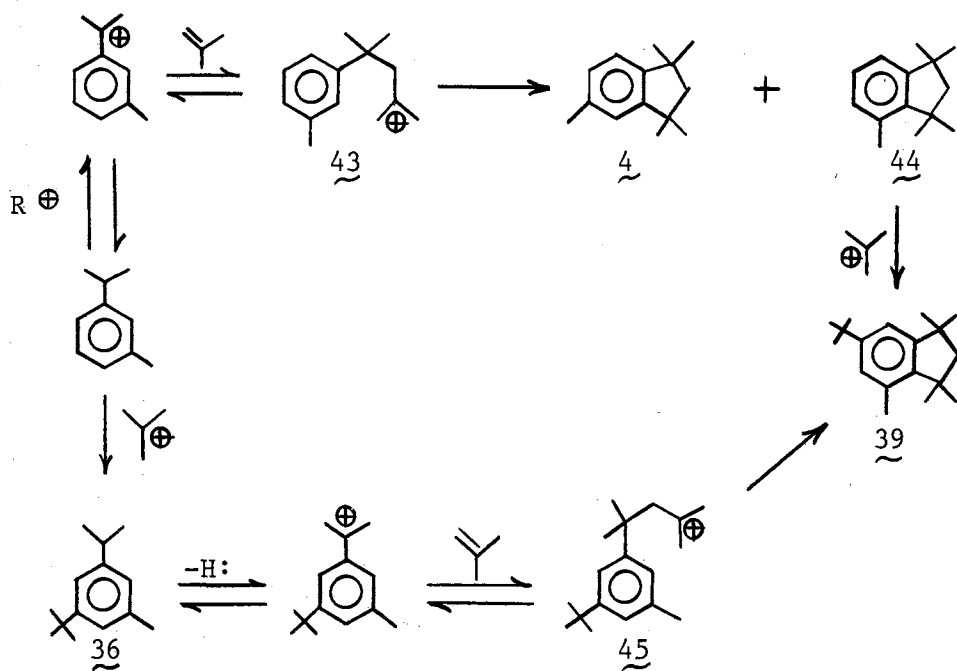
Figure 7.   Formation of 6-*tert*-Butyl-
1,1,3,3,4-pentamethylindan (39)
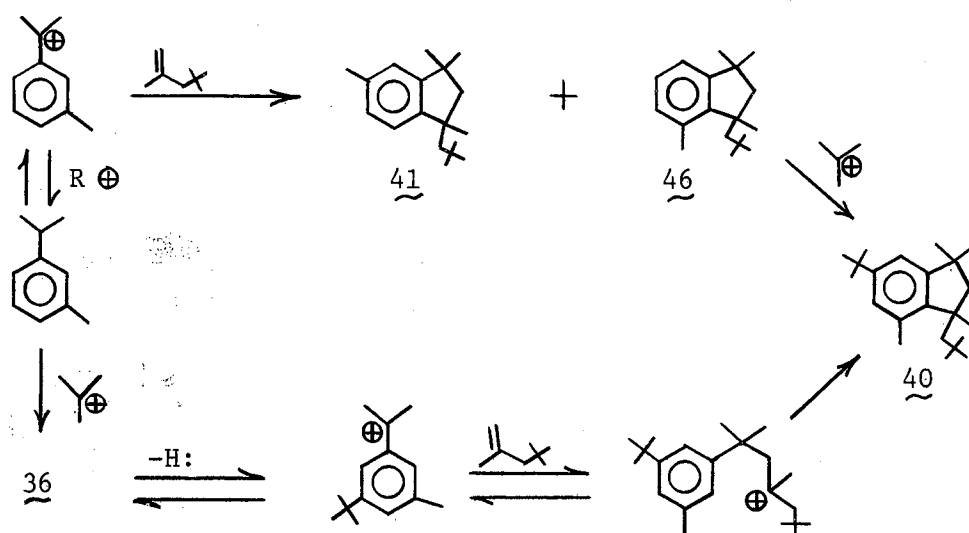
Figure 8.   Formation of 5-*tert*-Butyl-1,3,3,7-tetra-
methyl-1-neopentylindan (40)

Thus, of the three different olefins combined with *m*-cymene as shown in Table VII, only diisobutylene appears to yield a 1,2,3-substituted benzene. Since similar 1,2,3-substituted benzenes would be expected to form in the reaction of *m*-cymene with isobutylene (i.e., 44 in Fig. 7) and 2-methyl-2-butene (i.e., 49 and 50 in Fig. 9), there must be rapid alkylation in the 5-position of these compounds.

TABLE VII

PRODUCT RATIOS FROM REACTIONS OF *m*-CYMENE
WITH DIFFERENT OLEFINS

Olefins	MC[a]	27	36	I,J[b]	39	40	41	M	N
IB[c]	0.76	0.011	1.00	0.091	0.21	0.12	0.072	0.019	0.025
DIB[d]	1.08	0.0	1.00	0.97	0.25	1.14	2.53		0.0
MB[e]	9.94	1.08	1.00	2.25	0.02	0.0	0.019	0.069	0.37

[a]*m*-Cymene. [b]Compounds could not be separated by glpc. [c]Isobutylene. [d]Diisobutylene. [e]2-Methyl-2-butene.

Alkylation of 46 in the 5-position to form 40 must be rapid compared to either alkylation in the 5-position or cyclialkylation reactions of *m*-cymene, since the reactions are run in an excess of *m*-cymene, and there are no glpc peaks which appear and then disappear during the reaction.

Alkylation of toluene with isobutylene has been reported to yield 93% para- and 7% meta-*tert*-butyltoluene.[37b] It should be noted that alkylation of hydrocarbons 44 and 46 in the 5-position involves attack on the aromatic ring para to an alkyl group, whereas meta attack is suf-fered by *m*-cymene.

It appears that in the *m*-cymene – isobutylene reaction the rela-tively rapid formation of 36 is the factor which most influences the reaction path. When diisobutylene is the olefin, cyclialkylation ap-pears to be the predominant initial reaction followed by alkylation in the 5-position of the 1,2,3-substituted benzenes to give 40.

These conclusions are supported by the observation that the 40:41 ratio is 2:1 in the isobutylene – *m*-cymene reaction, but this ratio is 1:2 in the diisobutylene – *m*-cymene reaction. This means that with isobutylene the ring closure is predominately ortho to the methyl group of *m*-cymene. With diisobutylene, however, the major direction of ring closure is para to the methyl group. The 40:41 ratio of 1:2 seen in the diisobutylene reaction is in reasonable agreement with the direc-tion of ring closure observed in the previously mentioned reaction of α,*m*-dimethylstyrene with diisobutylene. Thus the lower paths of Fig. 7 and 8 appear to be the major routes followed when isobutylene is the olefin.

Several hydrocarbons whose structures have not been definitely es-tablished were found in the isobutylene – *m*-cymene reaction mixture. One of these, L, appears to be hydrocarbon 4. It is seen as a shoul-der to the glpc peak assigned to 36 in Fig. 5 in a 1:10 ratio.

The mass spectrum of this mixture of 36 and L shows, in addition to the parent ion m/e 190 resulting from 36, a second parent ion m/e

188 ($C_{14}H_{20}$). The $C_{14}H_{20}$ formula indicates that the rings plus double bonds in the unknown hydrocarbon must equal five, i.e., it may be an indan or a tetralin. Since no hydrocarbons resulting from a butene other than isobutylene were observed in the reaction of p-cymene with isobutylene, it seems likely that L is formed from isobutylene and is therefore an indan.

Hydrocarbon 44 was eliminated as a possibility when the ir spectrum of the mixture (36 and the indan) was compared with that of known compounds. The ir spectrum of the mixture, as seen in Table VIII, shows a strong absorbance at 12.28μ which indicates the presence of 4, a 1,2,4-substituted benzene. The ir spectrum of 1,2,3-substituted benzenes show strong absorbance at 13.09μ whereas the mixture shows no absorbance at this position.

TABLE VIII

COMPARISON OF THE INFRARED SPECTRUM OF AN UNKNOWN MIXTURE WITH SPECTRA OF MODEL HYDROCARBONS[a]

36 + L	11.33 (11.40)[b]			12.28		14.08
4	11.40			12.28		
			12.10	12.60	13.09	14.19
					13.07	14.00

[a]Measured absorbance maxima (μ). [b]Appears as shoulder on 11.33 peak.

Two other hydrocarbons of unknown structure were isolated from the
m-cymene – isobutylene reaction mixture and analyzed by mass spectro-
metry. One of these, hydrocarbon $\underset{\sim}{M}$, $C_{19}H_{30}$ (MW 258), shows an intense
M-29 (loss of C_2H_5) peak in the mass spectrum. The ir spectrum of this
sample indicates it to be a mixture probably consisting of 1,2,3- and
1,2,3,5-substituted benzenes.

The other sample, hydrocarbon $\underset{\sim}{N}$, $C_{19}H_{30}$ (MW 258), shows intense
M-15 and M-29 peaks in the mass spectrum. The ir spectrum of this sam-
ple indicates 1,2,3,5-substitution on a benzene ring. These two hydro-
carbons remain under study.

The products of the m-cymene – 2-methyl-2-butene ($\underset{\sim}{19}$) reaction and
proposed paths of formation are shown in Fig. 9. As previously men-
tioned and shown in Table VII, the major product in this reaction is
$\underset{\sim}{38}$, formed by alkylation of m-cymene in the 5-position with 2-methyl-
2-butene. The hydrocarbon $\underset{\sim}{27}$ is also formed in a ratio $\underset{\sim}{27}:\underset{\sim}{38}$ of 1:2.

Another hydrocarbon $\underset{\sim}{O}$ not listed in Table VII is formed in a ratio
$\underset{\sim}{36}:\underset{\sim}{O}$ of 1.0:0.91. The mass spectrum of $\underset{\sim}{O}$ shows a molecular ion of 272
($C_{20}H_{32}$) with M-15 and M-29 peaks. Two possible structures, $\underset{\sim}{47}$ and $\underset{\sim}{48}$,
are shown in Fig. 9. The ir spectrum of $\underset{\sim}{O}$ indicates that the sample
is probably a mixture, with the major component being a 1,2,3,5-sub-
stituted benzene. Since $\underset{\sim}{27}$ was found and no $\underset{\sim}{28}$ was observed in this
reaction, structure $\underset{\sim}{48}$ is favored.

The two reaction paths shown in Fig. 9 are similar to those dis-
cussed in Fig. 7 and 8. The upper path involves alkylation of m-
cymene in the 5-position followed by the cyclialkylation reaction. In
the lower path, the cyclialkylation reaction occurs initially followed
by alkylation of the 1,2,3-substituted cyclialkylation product in the
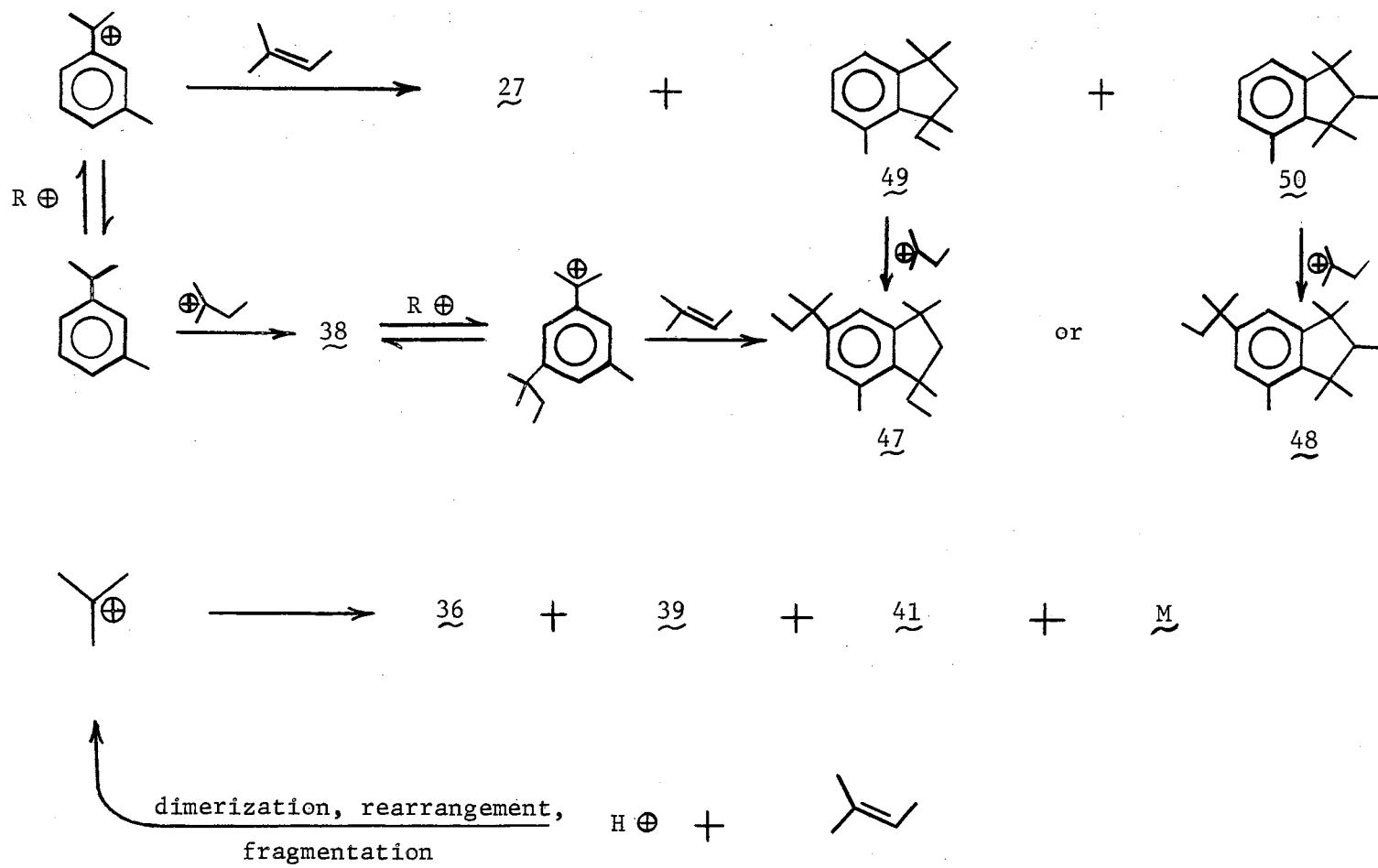
Figure 9. Products From The Reaction of *m*-Cymene and 2-Methyl-2-butene

5-position. No 1,2,3-substituted cyclialkylation products have been identified in this reaction, so there must be rapid alkylation of any 49 or 50 present.

In addition to the products resulting from the C_5 olefin and m-cymene reaction, hydrocarbon 36 was also identified in a ratio 1.0:2.2 (36:38). Thus, the C_5 olefin is evidently dimerizing and then rearranging and fragmenting to form the *tert*-butyl cation (or isobutylene) which then alkylates m-cymene. Peaks with the same glpc retention time as 39, 41, M, and N are also seen. The hydrocarbon 40 was not observed.

The sulfuric acid-catalyzed reactions of a series of *tert*-butyl-cymenes with isobutylene were studied to learn whether cyclialkylation products would form. These hydrocarbons are shown in Fig. 10 along with the expected products from their reaction with isobutylene.
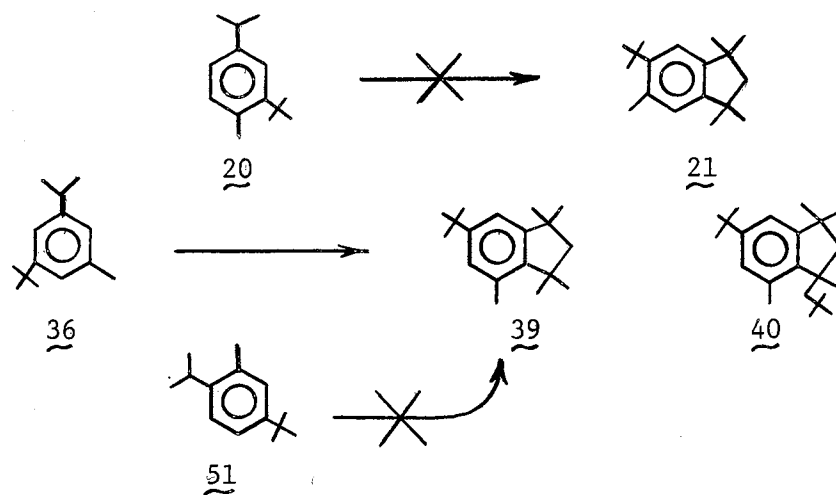
Figure 10. Possible Reaction Products of
tert-Butylcymenes with Isobutylene

The reaction of 36 with isobutylene gave 39 and 40 in a ratio of
1:1 as shown in Table VI. If 36 were dealkylating to *m*-cymene which
could then react, 41 should be formed.

The hydrocarbon 20 with isobutylene appeared to lose the *tert*-
butyl group and form *p*-cymene which then reacted in the usual manner
with isobutylene. Glpc peaks with the same retention time as 4 and
p-cymene were observed to increase as the peak for 20 decreased. A
compound showing a small peak with the same glpc retention time as 21
was found in the final reaction mixture.

5-*tert*-Butyl-*o*-cymene (51) failed to react with isobutylene. An
equal mixture of 51 and 4-*tert*-butyl-*o*-cymene (52) was obtained from
the *o*-cymene – isobutylene reaction. Hydrocarbon 52 would not be ex-
pected to react with isobutylene, but it is somewhat surprising that
51 did not undergo cyclialkylation to form 39. Perhaps the methyl
group which is ortho to the isopropyl group prohibits abstraction of
the tertiary hydride and thus inhibits the cyclialkylation reaction.

o-Cymene. It has been reported[4] that *o*-cymene gave no cyclialky-
lation products when reacted with 4-methylcyclohexene in the presence
of hydrogen fluoride. This was also found to be true in the reaction
with isobutylene.

The gas chromatogram of the *o*-cymene – isobutylene reaction mix-
ture is shown in Fig. 11. The major products were found to be 51 and
52, i.e., *tert*-butylated-*o*-cymene, with essentially equal amounts of
these two hydrocarbons being formed. While the groups attached to the
benzene ring were identified by nmr, ir, and mass spectrometric analy-
ses, positions on the ring could not be definitely assigned.

Mass spectral data were obtained on six other hydrocarbon products
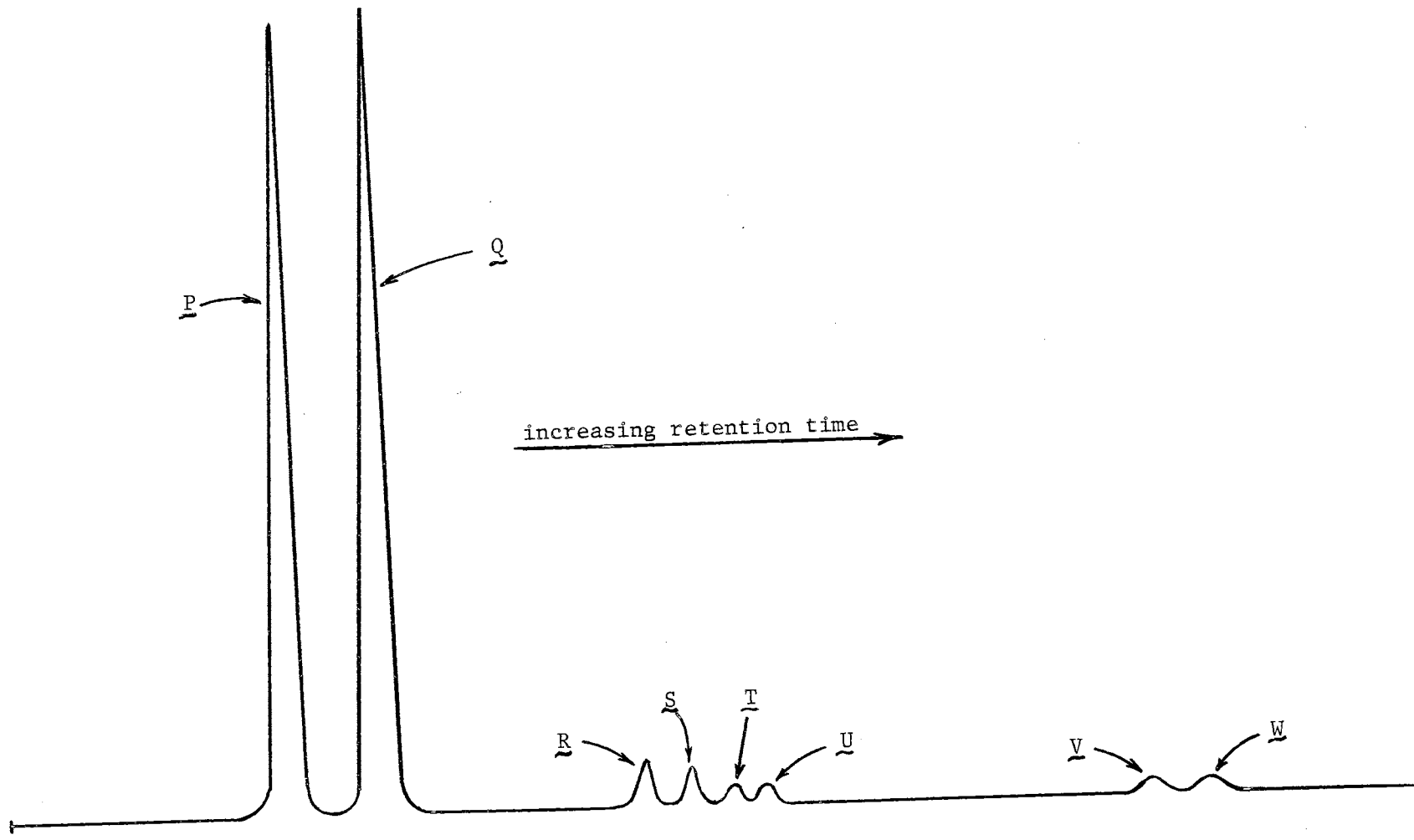
Figure 11. Gas Chromatogram of the *o*-Cymene – Isobutylene Reaction Mixture

(R, S, T, U, V, W) in this reaction, and all of these proved to be al-
kylbenzenes. Cyclialkylation products were not found.

Three of the hydrocarbons, R, S, and T, showed molecular weight
246 ($C_{18}H_{30}$), and all lost a C_5 group during mass fragmentation. These
data fit structures 53, 54, and 55; the hydrocarbons could arise from
alkylation with C_8 olefins.

53   54   55
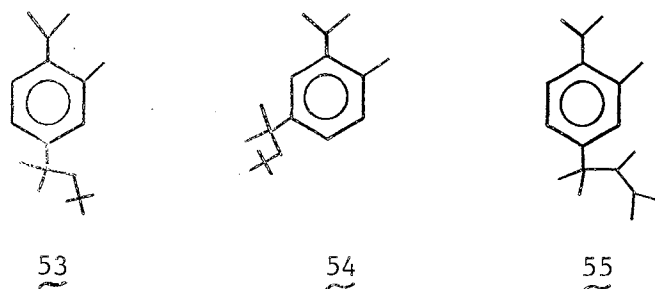
A sample corresponding to peak U in Fig. 11 proved to be a mixture
of phenylalkanes of molecular weight 218 ($C_{16}H_{26}$), 246 ($C_{18}H_{30}$), and
260 ($C_{19}H_{32}$). These could be formed by alkylation of o-cymene with C_6,
C_8, and C_9 olefins respectively.

Mass spectral data indicated molecular weights of 302 ($C_{22}H_{38}$) for
hydrocarbons V and W, and both show loss of a C_{10} group during fragmen-
tation. These could be formed by alkylation of o-cymene with C_{12}
molecules, i.e., triisobutylenes.

Diisobutylene and triisobutylene were also reacted with o-cymene,
and a comparison of the products is shown in Table IX.

TABLE IX

COMPARISON OF REACTION PRODUCTS OF DIFFERENT
OLEFINS AND o-CYMENE

Olefins	Compounds[a]							
	P	Q	R	S	T	U	V	W
IB[b]	1.00	1.01	0.024	0.025	0.004	0.003	0.006	0.007
DIB[c]	1.00	0.98	1.06	1.06	0.43[d]	0.00	0.00	0.00
TIB[e]	1.00	0.94	0.16	0.31[d]	0.23[d]	0.070	0.084	0.078

[a]Compounds correspond to peaks in Fig. 11. [b]Isobutylene. [c]Diiso-
butylene. [d]Value given is the sum of two nonseparable peaks. [e]Triiso-
butylene.

As would be expected, diisobutylene gives a large amount of C_8-
alkylates, especially R and S. It is of interest that while large
amounts of P and Q are formed, indicating dealkylation of diisobutylene,
there is none of the compounds resulting from C_{12} alkylation, i.e.,
V and W.

A gas chromatogram of the o-cymene – triisobutylene reaction mix-
ture is shown in Fig. 12. Comparison of Fig. 11 and Fig. 12 shows that
a more complex array of compounds is obtained with triisobutylene
than with isobutylene. This is also the case for diisobutylene which
shows that the two reactions produce the same compounds as shown by
comparison of glpc retention times. Table X shows the relative amounts
of compounds. These have not been analyzed by mass spectrometry, how-
ever these studies are planned.

TABLE X

RATIOS OF UNKNOWN COMPOUNDS FROM o-CYMENE REACTIONS

Olefin	Compounds[a]			
	P	X	Y	Z
Isobutylene	1.00	trace	trace	trace
Diisobutylene	1.00	0.55	0.57	0.38
Triisobutylene	1.00	0.14	0.14	0.12

[a]Compounds correspond to peaks in Fig. 12.
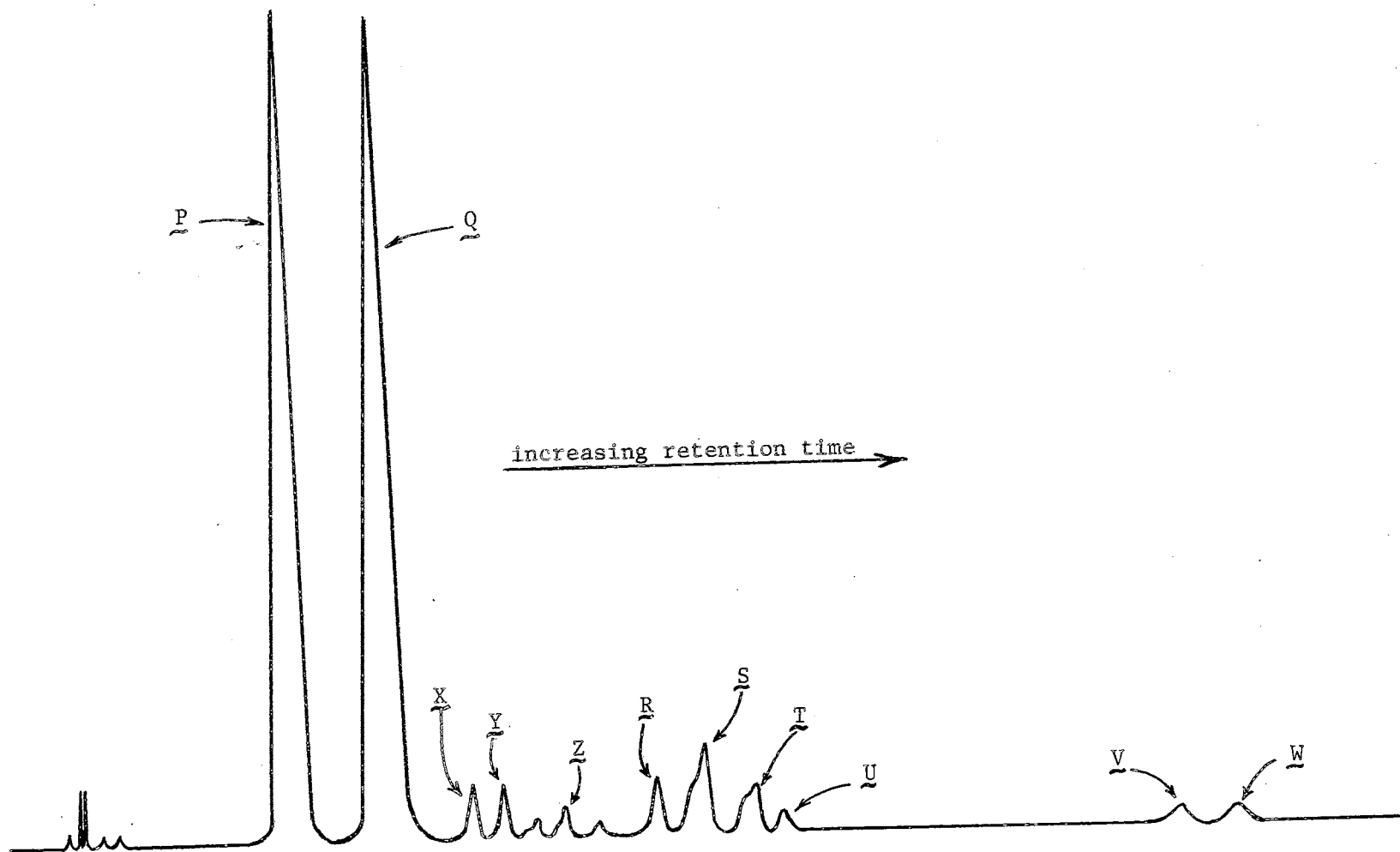
Figure 12. Gas Chromatogram of the *o*-Cymene – Triisobutylene Reaction Mixture

CHAPTER III

EXPERIMENTAL

Mass spectra were obtained with a Consolidated Electrodynamics
Corporation Model 21-110B high resolution mass spectrometer operated
under low-resolution conditions using electron energy of 70 ev. Nuclear
magnetic resonance (nmr) spectra were obtained with a Varian HR-60 and
A-60 sprectrometers. Peak positions are reported in terms of δ = parts
per million (ppm) downfield from internal tetramethylsilane standard
in carbon tetrachloride solvent. Infrared spectra were obtained with
a Beckman IR-5A spectrometer as films on sodium chloride plates unless
otherwise stated. Melting points were taken in capillary melting-point
tubes using a Thomas-Hoover apparatus and are corrected. The centi-
grade scale was used for all temperature measurements.

Qualitative gas chromatographic analyses were obtained with an
F&M Model 5750 gas chromatography apparatus fitted with dual thermal
conductivity and hydrogen flame detectors using helium as a carrier
gas. A 12-ft x 1/8-in. column containing 10% silicone UCW-98 on 80-100
mesh, dimethyldichlorosilane (DMCS) treated, acid-washed Chromosorb W
was used.

Samples for instrumental analyses were obtained by preparative gas
chromatography with an F&M Model 700 gas chromatograph equipped with
dual thermal conductivity detectors. A 13-ft x 1/4-in. column contain-
ing 5% silicone UCW-98 on 80-100 mesh, DMCS-treated, acid-washed Chro-

mosorb G was used with helium as a carrier gas.

Hydrocarbons 4 and 22 were purified by preparative gas chromatography using an F&M Model 776 gas chromatograph fitted with hydrogen flame detectors. An 8-ft x 4-in. column containing Carbowax 20M on 80-100 mesh, acid-washed Gas Pack was used with nitrogen as a carrier gas.

The sulfuric acid used was 97%. The Amberlyst-15 was a gift from the Rohm and Haas Company.

Acid-Catalyzed Reactions of p-Cymene With Isobutylene. Run 1a. Sulfuric acid on large scale at 5°.—In a 5-l. Morton flask equipped with a 0.25 in. (o.d.) stainless steel gas inlet tube, and a thermocouple, were placed 1734 g (12.9 mol) of p-cymene. This was cooled to 0° and 112 g of H_2SO_4 were added. Isobutylene was bubbled into the reaction mixture stirred with a large Vibromixer at a rate which kept the reaction mixture at 10° (the flow was approximately 1250 ml/min). The isobutylene flow was stopped after 6 hr, and the H_2SO_4 layer was separated. The organic layer when poured over solid Na_2CO_3, filtered, washed with saturated Na_2CO_3 soln, and dried ($MgSO_4$) gave 2135 g of reaction products.

Analysis of the reaction mixture by glpc gave the results shown in Table V. Indans 27 and 28 were identified by mass spectral comparisons. The data from mass spectral analyses for B and all other hydrocarbons listed below are given in Table XI.

Hydrocarbons with similar boiling points were concentrated by distillation and separated as previously described by preparative glpc. From one distillation fraction [bp 90-105° (1.9 mm)], six samples were collected by glpc at 120°. Additional data for the hydrocarbons isolated are given below in order of increasing glpc retention times.

4: ir 815 (s) and 878 (m) cm^{-1}; nmr δ 1.24 (s, 12, -CH$_3$ β to aromatic ring), 1.86 (s, 2, -CH$_2$-), 2.27 (s, 3, ArCH$_3$), 6.81-6.87 (m, 3, ArH).

20: ir 812 (s) and 881 (m) cm^{-1}; nmr δ 1.15 and 1.25 (d, 6, -CH(CH$_3$)$_2$), 1.38 (s, 9, -C(CH$_3$)$_3$), 2.43 (s, 3, ArCH$_3$), 2.73 (m, 1, -CH-), 6.80-7.11 (m, 3, ArH).

27: ir identical with 27 identified in Run 13.

35: ir 815 (s) and 878 (m) cm^{-1}; (See Run 8b for additional data).

The data for three other hydrocarbons isolated from another distillation fraction [bp 80-90° (0.5 mm)] are given below in order of increasing glpc retention times.

21: mp 81-82°; ir (CS$_2$ soln) 880 (s, appears as a shoulder on the next peak) and 887 (s) cm^{-1}; nmr δ 1.26 (s, 12, geminate -CH$_3$), 1.40 (s, 9, -C(CH$_3$)$_3$), 1.86 (s, 2, -CH$_2$-), 2.49 (s, 3, ArCH$_3$), 6.70 (s, 1, ArH), and 6.96 (s, 1, ArH).
Anal. Calcd for C$_{18}$H$_{28}$: C, 88.45; H, 11.55. Found: C, 88.57, H, 11.63.

22: ir 815 (s) and 878 (m) cm^{-1}; nmr δ 1.03 (s, 9, -C-(CH$_3$)$_3$), 1.24, 1.28, 1.32 (three s, 3 protons each, -CH$_3$ β to benzene ring), 1.65 (center of AB quartet, 2, -CH$_2$-), 2.03 (center of AB quartet, 2, -CH$_2$-), 2.27 (s, 3, ArCH$_3$), and 6.81-6.87 (m, 3, ArH).

23: bp 87-88° (0.5 mm); ir 758 (w), 816 (s), 887 (m), and 895 (w, appears as a shoulder on the 887 peak) cm^{-1}; nmr δ 0.71, 0.82, 0.91, 1.01 (the four preceding peaks account for 9 protons), 1.44 and 1.54 (account for 2 protons), 2.03 (m, 2 protons), 2.22 (s, 3, ArCH$_3$), 6.73-7.16 (m, 3, ArH).

<u>Anal.</u> Calcd   for $C_{18}H_{28}$: C, 88.45, H, 11.55. Found: C, 88.24; H, 11.56.

Four samples were obtained from the pot residue of the distillation (material boiling above 100° at 0.5 mm).

<u>1</u>: mp 40-41° (lit.[5] 37-38°, 40°); ir agrees with published[3] spectrum: nmr δ 1.03, 1.30, 1.62 (three s, 3 protons each, -C<u>H</u>$_3$ β to the aromatic ring), 2.21 (center of partially hidden AB quartet, 2, -C<u>H</u>$_2$-), 2.21, 2.28 (two s, 3 protons each, ArC<u>H</u>$_3$), and 6.71-7.10 (m, 7, Ar<u>H</u>).

Three other samples, <u>C</u>, <u>D</u>, and <u>E</u>, were analyzed only by mass spectrometric means.

<u>Separation and purification of 1,1,3,3,5-pentamethylindan (4)</u>.—The distillation fraction [bp 40-45° (0.5 mm)] of Run 1a in which <u>4</u> was concentrated was subjected to preparative glpc at 150° using the apparatus previously described. The material collected was distilled and then passed through a column of silica gel and alumina (acidic and basic) to give <u>4</u>, bp 42° (0.5 mm) [lit.[8] 153.6 (100 mm)], in greater than 99 mol % purity.

<u>Anal.</u> Calcd   for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.27, H, 10.56.

<u>Run 1b. Sulfuric acid on small scale at 10°</u>.—A 250-ml, 3-necked Morton flask was equipped with a gas inlet tube, a magnetic bar, a thermometer, and a dry-ice condenser with a $CaCl_2$ drying tube attached. In the flask were placed 33.5 g (0.25 mol) of p-cymene and 19.0 g of H_2SO_4. After cooling the reaction vessel to 5°, isobutylene was bubbled into the stirred reaction mixture for 3 hr at a rate which kept the temp below 10°. The reaction was worked up as in Run 1a to yield

71.4 g of reaction products. The results of gas chromatographic anal-
ysis are shown in Table V.

Run 2a. Methanesulfonic acid at 10°.—A mixture of p-cymene, 67 g
(0.5 mol), and methanesulfonic acid, 6.5 g (0.068 mol), was placed in
a 500-ml, 2-necked flask equipped with a gas inlet tube, a magnetic
bar, and a thermometer. This was cooled to 5°, and isobutylene was
bubbled into the stirred reaction mixture for 9 hr at a rate which kept
the reaction temp below 10°. The mixture was then allowed to stir for
10 hr.

The methanesulfonic acid layer was separated and discarded. The
organic layer was washed with a saturated soln of Na_2CO_3 and dried
($MgSO_4$) giving 145 g of material.

Gas chromatographic analysis showed, in addition to the data in
Table V, that the major products were tetraisobutylenes in a ratio of
1:17 (4:total tetraisobutylenes). Mass spectral analyses verified that
the major products were aliphatic hydrocarbons.

Run 2b. Methanesulfonic acid at 115°.—In addition to the appar-
tus used in Run 2a, a dry-ice condenser – reflux condenser assembly was
fitted to the reaction flask with the reflux condenser being attached
to the flask. A drying tube ($CaCl_2$) was attached to the top of the
dry-ice condenser. p-Cymene, 45 g (0.34 mol), was placed in the reac-
tion vessel and heated to 115°. Methanesulfonic acid, 25 g (0.26 mol),
was added, and isobutylene was bubbled into the stirred reaction mix-
ture for 6.4 hr. The workup procedure of Run 2a was used.

In addition to the hydrocarbons identified through studies shown
in Table V, a compound which does not coincide in retention time with
any analyzed compound was found in a ratio to 4 of 0.07:1.0.

Hydrocarbon H, mp 132.5°, was formed in a ratio of 0.06:1 (H:4).

The following data were obtained for H: ir (CS$_2$ soln) 773 (m), 784

(s), 815 (s), 878 (m), and 883 (m) cm^{-1};   nmr δ 1.31 (s), 1.37 (s),

2.24 (s), 6.48 (s), and 6.92 (d).

Run 3a. Amberlyst-15 (A-15) at 25°.—The same equipment was used

as in Run 2a. In the reaction flask were placed 67 g (0.50 mol) of

p-cymene and 7.0 g A-15. The A-15 had been powdered and heated over-

night at 90°, then heated to 110° at 2 mm for 1 hr. Isobutylene was

bubbled into the stirred reaction mixture for 24 hr at a rate which

kept the reaction temp at 25°. The A-15 was removed by filtration

giving 113 g of reaction products.

In addition to the glpc results given in Table V, it was found

that tetraisobutylene was formed in the ratio of 40:1 (total tetra-

isobutylene:4).

Run 3b. Amberlyst-15 at 85°.—A 300-ml, 3-necked flask was e-

quipped with a gas inlet tube, a magnetic bar, a thermometer, and a re-

flux condenser to which a drying tube (CaCl$_2$) was attached. A mixture

of p-cymene, 33.5 (0.25 mol) and 3.5 g of A-15, treated as in Run 3a,

was added to the reaction vessel and heated to 85°. Isobutylene was

bubbled into the stirred reaction mixture for 48 hr at a rate of about

10 ml per min. About 27 hr after the reaction was begun, 2.0 g more

A-15 was added. The workup was the same as in Run 3a and yielded 97 g

of reaction products.

The gas chromatographic analysis indicated 4, 21, 22, and 23 were

formed in amounts shown in Table V. There was also a large quantity of

tetraisobutylene formed in a ratio of 0.6:1 (total tetraisobutylene:4).

Run 3c. Amberlyst-15 at 130°.—The same apparatus and procedure

described in Run 3b were used in this reaction except that the *p*-cymene, 33.5 g (0.25 mol), was heated to 130° before 3.5 g of A-15 were added. The isobutylene flow was about 9 ml per min and was continued for 39 hr. The reaction was worked up as described in Run 3a to yield 91.4 g of organic material.

Gas chromatographic analysis showed 1, 4, 22, and 23 were formed in the ratios given in Table V.

Run 4. Hydrogen fluoride at 5°.—The equipment, which was all polyethylene, consisted of a 500-ml, wide-mouth bottle fitted with a 3-holed lid in which a sintered gas dispersion tube, a gas exit tube, and a thermocouple were fitted. In the bottle were placed 144 g (1.07 mol) of *p*-cymene, and after cooling to 5°, 28 g (1.4 mol) of anhydrous HF were introduced. Isobutylene was bubbled into the magnetically stirred reaction mixture for 2 hr at a rate which kept the reaction temp below 10°.

The reaction mixture was poured over ice, and a soln of 40% NaOH was added. The organic layer was separated and dried ($CaCl_2$) yielding 165 g of reaction products. The aqueous layer was extracted twice with ether, and after drying ($CaCl_2$), the extract was freed of ether yielding 10 g of organic material.

Gas chromatographic analysis indicated that 1, 4, 22, 23, and 27 were formed in ratios given in Table V.

Acid-Catalyzed Reactions of *p*-Cymene With Diisobutylene. Run 5a. Sulfuric acid to *p*-cymene ratio of 0.25 at 5°.—A 250-ml, 3-necked Morton flask was equipped with thermometer, pressure-equalizing dropping funnel, magnetic bar, and a gas exit tube fitted with a drying tube ($CaCl_2$). *p*-Cymene, 33.5 g (0.25 mol), was added to the flask and

cooled to 5°; then 19 g of H_2SO_4 were added. Diisobutylene, 56 g (0.50 mol), was dripped into the stirred mixture over a 1-hr period, and the stirring was continued for 40 min. The reaction temp was kept below 10° throughout the procedure. The reaction was worked up as in Run 1a to yield 77.6 g of products.

The results of gas chromatographic analysis of the recovered reaction products are given in Table V.

Run 5b. Sulfuric acid to *p*-cymene ratio of 0.78 at 5°.—The same procedure was used as in Run 5a. In the reaction 33.5 g (0.25 mol) of *p*-cymene, 56 g (0.50 mol) of diisobutylene, and 74 g of H_2SO_4 were used.

The acid layer (84 g) was separated, and the organic layer when washed with a 10% NaOH soln formed an emulsion. The emulsion was extracted with ether, and when the ether was evaporated, 56 g of organic material were recovered.

In addition to the results shown in Table V, gas chromatographic analysis of the recovered organic material indicated that 28 was formed in a ratio of 1:10 (28:4).

Run 5c. Large scale with sulfuric acid to *p*-cymene ratio of 0.09 at 5°.—The apparatus of Run 1a with a 2-1. dropping funnel replacing the gas inlet tube and containing 1100 g (8.2 mol) of *p*-cymene cooled to 5° was used. Sulfuric acid, 72 g, was introduced, and 1480 g (13.2 mol) of diisobutylene was added dropwise to the stirred reaction mixture. The temp was kept below 10° throughout the 2.5 hr required to add the olefin and during the additional 3 hr the reaction was stirred. The reaction was worked up as in Run 1a to give 2800 g of reaction products.

The results of gas chromatographic analysis are shown in Table V.

Separation and purification of 1,3,3,5-tetramethyl-1-neopentyl-
indan (22).—A distillation fraction [bp 82-88° (0.5 mm)] from Run 5c
was treated as in the purification of 4 to give 92 g of 22, bp 84-85°
(0.5 mm), in greater than 99 mol % purity.

Anal. Calcd for $C_{14}H_{20}$: C, 88.45; H, 11.55. Found: C, 88.63,
H, 11.39.

Run 6a. Sulfuric acid to *p*-cymene ratio of 0.4 at 30°.—A 200-ml
Morton flask was equipped with a thermometer, a magnetic bar, a pres-
sure-equalizing dropping funnel, and a dry-ice condenser fitted with
a drying tube ($CaCl_2$). A mixture of 33.5 g (0.25 mol) of *p*-cymene
and 5.5 g of H_2SO_4 was placed in the flask, and 56 g (0.50 mol) of di-
isobutylene were added dropwise to the stirred mixture over a 1.5-hr
period. During the olefin addition the reaction temp increased, and a
H_2O bath was used to keep the temp close to 30°. After the diisobuty-
lene was added, the reaction mixture was stirred for 20 min, and then
5.5 g more of H_2SO_4 were added. After stirring for an additional 1.5
hr, the mixture was worked up as in Run 1a to yield 76 g of organic
material.

In addition to the results given in Table V, gas chromatographic
analysis of the reaction mixture also showed tetraisobutylene to be
formed in a ratio of 3:1 (tetraisobutylene:4).

Run 6b. Sulfuric acid to *p*-cymene ratio of 0.8 at 30°.—The same
procedure and quantities of *p*-cymene and diisobutylene were used as in
Run 6a. The 19 g of H_2SO_4 used were added to the *p*-cymene before the
diisobutylene addition was started.

The workup procedure of Run 1a yielded 66 g of reaction products
which, when analyzed by gas chromatography, gave the results shown in

Table V. In addition glpc indicated that tetraisobutylene and H̰ were
formed in a ratio of 100:50:6 (4̰:tetraisobutylene:H̰).

Run 6c. Sulfuric acid to *p*-cymene ratio of 1.6 at 30°.—The same
procedure as in Run 6a was used except that 38 g of H₂SO₄ were added
to the reaction vessel before the diisobutylene was introduced.

The workup of Run 1a yielded 47 g of organic material. Gas chro-
matographic analysis gave the results shown in Table V. In addition,
glpc indicated that tetraisobutylene and H̰ were formed in a ratio of
100:43:12 (4̰:tetraisobutylene:H̰).

Run 7. Sulfuric acid to *p*-cymene ratio of 0.3 at 65°.—To a 1-1.,
3-necked flask equipped with a thermometer, a magnetic bar, a reflux
condenser, and a pressure-equalizing funnel, were added 67 g (0.50 mol)
of *p*-cymene. After heating the reaction flask to 65°, 10 g of H₂SO₄
were introduced, and 112 g (1.0 mol) of diisobutylene were dripped into
the stirred reaction mixture. Addition of the diisobutylene took 1 hr.
The reaction was stirred for 2 hr, and an additional 5.0 g of H₂SO₄
were added. After stirring for another hour, the reaction was worked
up as in Run 1a to yield 158 g of organic material.

Gas chromatographic analysis of this recovered material showed,
in addition to the results in Table V, that tetraisobutylenes were
formed in a ratio of 1:120 (4̰:tetraisobutylenes).

Run 8a. Methanesulfonic acid at 70°.—To a 200-ml, 3-necked Mor-
ton flask equipped with a pressure-equalizing funnel, thermometer, and
reflux condenser with CaCl₂ drying tube attached, *p*-cymene, 33.5 g
(0.25 mol), was added and heated to 70°. The MSA, 19.0 g (0.20 mol),
was introduced, and diisobutylene, 56.0 g (0.50 mol), was dripped into
the reaction mixture which was stirred by a high-speed mechanical

stirrer. The diisobutylene addition took 1.25 hr, and the reaction

mixture was then stirred for 17 hr. The mixture was worked up as in

Run 2a to yield 78 g of organic material.

Analysis by gas chromatography showed, in addition to the results

in Table V, that 28 and B were formed in the ratio of 100:11:2 (4:28:B).

Also, a trace of H was observed.

Run 8b. Methanesulfonic acid at 70°.—The reaction procedures and

apparatus described for Run 8a were used with a dry-ice condenser

and a magnetic bar being substituted for the reflux condenser and me-

chanical stirrer. p-Cymene, 12.5 g (0.093 mol), 20.8 g (0.19 mol) of

diisobutylene, and 10 g (0.10 mol) of MSA were used. The p-cymene and

diisobutylene had been purified by preparative glpc.[38] The addition

of diisobutylene required 25 min, and the reaction mixture was then

stirred for 24 hr at 70°. The mixture was worked up as in Run 2a to

yield 30 g of reaction products.

In addition to the information in Table V, gas chromatographic

analysis of the reaction mixture indicated that F, 28, and B were pre-

sent in ratios to 4 of 100:64:11.3 (4:F:28:B). The samples with the

same glpc retention times as 4 and 27 gave ir, nmr, and mass spectra

which were the same as those from samples identified elsewhere. Hy-

drocarbon F gave ir, nmr, and mass spectra which were essentially

identical to those of 8. The samples collected from this reaction were

contaminated by polymeric material which interfered with the instrumen-

tal analysis, particularly the nmr determination. The mass spectral

data from F and G are given in Table XI. The data obtained which have

not been reported elsewhere are given below.

28: ir 815 (s) and 878 (m) cm^{-1}.

$\underset{\sim}{G}$: ir 815 (s) and 878 (m) cm^{-1}.

$\underset{\sim}{35}$: ir 814 (s) and 878 (m) cm^{-1}; nmr δ 0.75-1.25 (m), 1.30 (s,

9, -C$\underline{H}_3$ β to benzene ring), 1.34-2.25 (m), 2.29 (s, 3, ArC$\underline{H}_3$),

6.75-6.95 (m, 3, Ar$\underline{H}$) [integration values were given only

when the contaminants did not interfere].

Run 8c. Methanesulfonic acid at 115°.—The apparatus of Run 8a

was used with a magnetic stirrer being substituted for the mechanical

stirrer. The reaction was carried out as in Run 8a with 44.7 g (0.33

mol) of p-cymene, 75.0 g (0.67 mol) of diisobutylene, and 25.0 g (0.26

mol) of MSA being used. The diisobutylene addition took 4 hr. The

reaction mixture was stirred for an additional 15 hr and then was

worked up as in Run 2a to give 69.0 g of reaction products.

Gas chromatographic analysis showed very little low molecular

weight material (below C$_{12}$) to be present. In addition to the results

shown in Table V, it appeared that $\underset{\sim}{28}$ and $\underset{\sim}{H}$ were also formed in a ratio

of 100:5:5 ($\underset{\sim}{4}$:$\underset{\sim}{28}$:$\underset{\sim}{H}$).

Run 8d. Methanesulfonic acid at 140°.—The same reagents, quan-

tities of reagents, and procedure was used as in Run 8a except the

reaction temp was 140°. A magnetic stirrer was used in place of the

mechanical stirrer, and a dry-ice condenser was attached to the top of

the reflux condenser. The diisobutylene addition took 2 hr, and the

reaction mixture was stirred for 1.5 hr to yield 56 g of reaction pro-

ducts when worked up as in Run 2a.

The results of gas chromatographic analysis are shown in Table V.

Glpc also indicated that $\underset{\sim}{28}$ was formed in a ratio of 100:11 ($\underset{\sim}{4}$:$\underset{\sim}{28}$).

Run 9. Amberlyst-15 at 100°.—A 500-ml, 3-necked flask was

equipped with a pressure-equalizing dropping funnel, a thermometer, and

a reflux condenser to which a drying tube ($CaCl_2$) was attached. *p*-Cymene, 38.4 g (0.29 mol), was placed in the flask and heated to 100°, and then the first quantity of A-15, 39 g, treated as described in Run 3a, was introduced. Diisobutylene, 98.3 g (0.88 mol), was added dropwise in two aliquots of 63.3 g and 34.0 g while the reaction mixture was stirred with a Vibromixer. About 1 hr was required for the addition of the first quantity of diisobutylene. The reaction was then stirred for 3 hr, and the second aliquot of diisobutylene was added over a 30-min period. Three 10-g portions of A-15 were added after 9, 12, and 20 hr.

After a total reaction time of 22.5 hr, the A-15 was removed by filtration and 79 g of reaction products isolated. The filtered A-15 was washed with H_2O three times, and the washings were extracted with ether. The ether extract was dried ($CaCl_2$), and concentrated yielding 16.0 g of organic material.

Analysis by gas chromatography showed, in addition to the results of Table V, that tetraisobutylene was formed in a ratio of 10:7 (4:tetraisobutylene).

Run 10a. Hydrogen fluoride to *p*-cymene ratio of 4.—The apparatus of Run 4 was used with a polyethylene dropping funnel replacing the gas dispersion tube. *p*-Cymene, 33.0 g (0.25 mol), was placed in the reaction vessel, cooled to 5°, and then 20 g (1.0 mol) of anhydrous HF were cautiously added. Diisobutylene, 61.0 g (0.54 mol), was added dropwise to the stirred reaction mixture over a 1-hr period. The stirring was continued for 30 min while the reaction temp was maintained at 5°. The reaction was worked up as described in Run 4 yielding a total of 76.4 g of reaction products.

The results of gas chromatographic analysis of the reaction products are shown in Table V.

Run 10b. Hydrogen fluoride to p-cymene ratio of 10.—The same apparatus and procedure was used as in Run 10a. The same quantities of p-cymene and diisobutylene were also used, but the amount of HF was increased to 50 g (2.5 mol). The workup described in Run 4 gave 72 g of reaction products.

Gas chromatographic analysis gave the results shown in Table V and also indicated that 28 was formed in a ratio of 100:8 (4:28).

Run 11a. Aluminum chloride at 5°.—To a 1-l., 3-necked Morton flask equipped with a pressure-equalizing dropping funnel, a thermometer, and a magnetic bar, were added 33.5 g (0.25 mol) of p-cymene. The AlCl$_3$, 16.0 g (0.12 mol), was placed in a 100-ml Erlenmeyer flask which was then attached to the reaction vessel by means of Gooch tube. After cooling the reaction vessel to 5°, about one-fourth of the AlCl$_3$ was introduced into the stirred p-cymene, and the diisobutylene, 56.0 g (0.50 mol) was added dropwise over a 45-min period. The rest of the AlCl$_3$ was added in increments throughout the diisobutylene addition. The reaction mixture was stirred for 2 hr while the temp was kept below 10°.

The reaction mixture was quenched by pouring over ice and washing with H$_2$O. The organic layer was separated and dried (CaCl$_2$) to give 75 g of reaction products.

The results of gas chromatographic analysis are shown in Table V.

Run 11b. Aluminum chloride at 70°.—The same quantities of reagents were used as in Run 11a. A 250-ml, 3-necked Morton flask was equipped as described in Run 8a. The p-cymene was placed in the re-

action vessel and heated to 50°. About one-half of the $AlCl_3$ was added,
with the rest being introduced in increments as the diisobutylene was
added. The olefin was added dropwise while the reaction was stirred
with a high-speed mechanical stirrer. The reaction temp increased
from 50° to 70° as soon as the olefin addition was begun and remained
close to 70° throughout the reaction. When the olefin addition was
complete, the reaction mixture was stirred for 1.5 hr and quenched by
pouring over ice. After sitting for several hr, the reaction product –
H_2O mixture was filtered to remove a film which formed between the or-
ganic and aqueous layers. The organic layer was separated and dried
($CaCl_2$) to give 74 g of organic products. Ether extraction of the
aqueous layer did not yield additional organic material.

The mixture of reaction products was analyzed by glpc giving, in
addition to the results in Table V, a ratio of 21:100 (H:4).

Acid-Catalyzed Reactions of *p*-Cymene with Triisobutylene. Run 12a.
Sulfuric Acid.—*p*-Cymene, 27 g (0.20 mol), was placed in the apparatus
described in Run 5a and cooled to 5°. Sulfuric acid, 5.0 g, was added
and triisobutylene, 23.6 g (0.14 mol), was introduced dropwise to the
stirred reaction mixture over a 40-min period. The stirring was con-
tinued for 1.5 hr while the temp was kept below 8°. At this time,
5.0 g more H_2SO_4 were added, and the reaction mixture was stirred for
30 min.

The acid layer was separated, and the organic layer was washed
with a 30% NaOH soln and then dried ($CaCl_2$) to yield 36 g of reaction
products.

Gas chromatographic analysis of the reaction products gave the
results shown in Table V with 28 also indicated in a ratio of 100:5

(4:28).

Run 12b. Aluminum Chloride.—A 250-ml, 3-necked Morton flask was

equipped as described in Run 11a. The procedure of Run 11a was used

to combine 27.0 g (0.20 mol) of p-cymene, 30.0 g (0.18 mol) of triiso-

butylene, and 9.0 g (0.067 mol) of $AlCl_3$. The triisobutylene addition

took 30 min, and then the reaction mixture was stirred for 2 hr with

the temp kept below 5°.

The mixture was worked up as described in Run 11a to yield 45 g

of organic material. The gas chromatographic analysis of this reaction

mixture gave the results shown in Table V. A compound which has a glpc

retention time between those of 23 and 1 was also formed in a ratio of

100:127 (4:unknown compound). It has not been studied further.

Sulfuric Acid-Catalyzed Reaction of p-Cymene With 2-Methyl-2-

butene[39] (19). Run 13.—The same apparatus and reaction procedure des-

cribed in Run 6a were used except that the H_2SO_4, 10g, was introduced

in one addition when the p-cymene, 67.0 g (0.50 mol), had been cooled

to 5°. The 2-methyl-2-butene, 14.0 g (0.20 mol), addition took 20 min.

The reaction mixture was then stirred for 1 hr and worked up as in

Run 1a to yield 72 g of reaction products.

Gas chromatographic analysis showed the following compounds to be

present in order of increasing glpc retention times in the ratio of

10:21:46:3 (4:28:27:1). The structure of 4 was verified by ir and nmr

comparisons. The mass spectrum of a hydrocarbon, A, showed it to be

closely related to 28. The mass spectral data for A, 27, and 28 are

given in Table XI. Additional data not listed elsewhere are given

below for 27 and 28.

27: ir 815 (s) and 879 (m) cm^{-1}; nmr δ 0.91 (This is half of a

doublet from $-CH-CH_3$ and corresponds to 1.5 protons. The

other half is hidden by the 1.04 peak.), 1.04 (s, 7.5, gemi-

nate dimethyl protons, hides half of the previously listed

doublet), 1.26 (s, 6, geminate dimethyl protons), 1.75 (q, 1,

$-C\underline{H}-$), 2.30 (s, 3, ArC$\underline{H}_3$), 6.83-6.89 (m, 3, Ar$\underline{H}$).

28: nmr δ 0.80 (t), 1.02 (s), 1.22 (s), 1.25 (s), 1.58 (m), 1.81

(m), 2.29 (s, 3, ArC$\underline{H}_3$), 6.74-6.86 (m, 3, Ar$\underline{H}$).

Sulfuric Acid-Catalyzed Reaction of p-Cymene With 2,3,4-Trimethyl-

2-pentene.[39] Run 14a. Olefin to acid ratio of 0.10.——In a 250-ml,

3-necked Morton flask equipped with a pressure-equalizing dropping

funnel and a thermometer was placed p-cymene, 134.0 g (1.00 mol).

This was cooled to 5°, and 2.5 g of sulfuric acid was added. 2,3,4-Tri-

methyl-2-pentene, 11.2 g (0.10 mol), was added dropwise to the mixture

which was stirred with a high-speed mechanical stirrer and maintained

at 7°. The addition took about 30 min, and the stirring was continued

for 15 min. The sulfuric acid layer was separated, and the organic

layer washed with saturated Na_2CO_3 soln. The results of gas chromato-

graphic analysis of the organic layer are shown in Table IV.

Run 14b. Olefin to acid ratio of 0.50.——The equipment and proce-

dure were the same as described in Run 14a except a magnetic bar was

used for stirring. There were 67 g (0.50 mol) of p-cymene, 28 g (0.25

mol) 2,3,4-trimethyl-2-pentene, and 10 g of H_2SO_4 used. The olefin

addition was made over a 1.3-hr period while the reaction mixture was

stirred, and the temp maintained at 5°. The reaction mixture was

worked up as in Run 14a and 86.7 g of organic material recovered. The

results of analysis by gas chromatography are shown in Table IV.

Hydrocarbons 4, 22, 23, 27, and 28 were identified as being pre-

sent by comparison of ir and mass spectra with previously identified
samples. The nmr spectra of 22 and 23 from this reaction were found to
be identical with those of samples of these indans.

Run 14c. Olefin to acid ratio of 2.05.—The equipment, procedure,
and conditions were the same as used in Run 14b. The reagents used
were p-cymene, 9.0 g (0.062 mol), 2,3,4-trimethyl-2-pentene, 14.3 g
(0.128 mol), and H_2SO_4, 2.5 g. The olefin addition took 45 min, and
the reaction mixture was then stirred for 1 hr. The results of gas
chromatographic analysis of the final reaction mixture are shown in
Table IV. Hydrocarbons 22 and 23 were identified by nmr and mass spec-
tral comparisons whereas 4 and 27 were identified by mass spectral com-
parisons only.

Run 15. Reaction of p-cymene with 2,3-dimethyl-1-butene.[39]—The
same apparatus, procedure and conditions were used as in Run 14b; p-
cymene, 50.0 g (0.38 mol), 10.0 g (0.12 mol) of 2,3-dimethyl-1-butene
and 7.0 g of H_2SO_4 were used. The olefin was added over a 1-hr period,
and the mixture was stirred for 1 hr. The acid layer was separated,
and the organic layer was washed with a 10% NaOH soln to yield 56.1
g of reaction products.

Gas chromatographic analysis indicated several products. The hy-
drocarbons formed, given in order of increasing glpc retention times,
and the relative amounts of each were respectively 1.00:0.16:0.29:0.72:
5.56:1.90 (4:28:27:B:8:1). Additional data were obtained on three of
these hydrocarbons.

4: ir and mass spectral data were identical with those of a pre-
    viously identified sample of 4.

B: ir spectrum was identical with that of a known[33] sample of

10, and the mass spectrum also was in agreement with this structure.

8: ir, nmr,[15a] and mass spectra all agree with those of the known[33] compound, mp 64-66° [lit.[15] mp 66-67.5°]. The mass spectral data from 8 is given in Table XI.

Sulfuric Acid-Catalyzed Reactions of *m*-Cymene With Three Olefins.

Run 16a. Isobutylene.—To the apparatus described in Run 3b, assembled without the reflux condenser, were added 67.0 g (0.50 mol) of *m*-cymene. After cooling the reaction vessel and contents to 5°, 6.5 g of H_2SO_4 were introduced, and isobutylene was bubbled into the stirred reaction mixture for 4 hr while the reaction temp was kept below 10°. The acid layer was separated, and the organic layer was washed with a saturated Na_2CO_3 soln and dried ($MgSO_4$).

The ratios of products formed in the reaction were obtained by gas chromatographic analysis and are shown in Table VII. The mass spectral data for all hydrocarbons listed below are given in Table XI unless otherwise stated. Additional data presented below were obtained for these hydrocarbons.

27: This was identified by ir and mass spectral comparisons. See Run 13 for these data.

36 and L: ir 711 (s), 815 (w), 857 (s), and 882 (w) cm^{-1}; nmr δ 1.17 (3 H, one-half of doublet from -CH(C$\underline{H}_3$)$_2$), 1.28 (s, 12, -C-(CH$_3$)$_3$ also covers the other half of isopropyl doublet), 2.29 (s, 3, ArC$\underline{H}_3$), 2.81 (m, 1, Ar$\underline{H}$), 6.72 (s, 1, Ar$\underline{H}$), and 6.88 (s, 2, Ar$\underline{H}$).

I and J: ir 712 (m), 823 (s), 857 (m), and 880 (m) cm^{-1}; nmr δ 1.14 (s), 1.25 (m), 2.37 (s), 2.28 (two s, ArCH$_3$ in a 1:2

ratio), and 6.70-7.20 (m, Ar$\underline{H}$).

3̰9̰: ir 655 (m), 770 (m), and 872 (s) cm^{-1}; nmr δ 1.26 (s, 6, un-
hindered geminate dimethyl group), 1.28 (s, 9, -C-(C$\underline{H}_3$)$_3$),
1.37 (s, 6, hindered geminate dimethyl group), 1.86 (s, 2,
-C$\underline{H}_2$-), 2.34 (s, 3, ArC$\underline{H}_3$), and 6.82 (s, 2, Ar$\underline{H}$).

4̰0̰: ir 653 (m), 774 (w), and 870 (s) cm^{-1}; nmr δ 1.03 (s, 9,
-C-(C$\underline{H}_3$)$_3$), 1.24 (s, 3, a geminate methyl group), 1.28 (s,
12, ArC(C$\underline{H}_3$) and a geminate methyl group), 1.46 (s, 3, methyl
group geminate to the neopentyl group), 1.50-2.50 (m, 4, two
nonequivalent CH$_2$ appearing as two overlapping AB quartets),
2.37 (s, 3, ArC$\underline{H}_3$), and 6.75-6.90 (m, 2, Ar$\underline{H}$).

4̰1̰: ir 815 (s) and 878 (m) cm^{-1}; nmr δ (This sample was contam-
inated with polymeric material; thus the integration values
are not included). 1.00 (s, C-(C$\underline{H}_3$)$_3$), 1.25 and 1.28 (two
s, the latter being stronger and having a shoulder), 2.37-
2.33 (m, two overlapping AB q from two nonequivalent CH$_2$
groups), 2.28 (s, ArC$\underline{H}_3$) and 6.75-6.88 (m, Ar$\underline{H}$).

M̰: ir 655 (w), 765 (s), 790 (m), 815 (w), and 870 (s) cm^{-1}.

N̰: ir 653 (m), 769 (m), and 870 (s) cm^{-1}.

Run 16b. Diisobutylene.—In a 200-ml, 3-necked Morton flask e-
quipped with a pressure-equalizing dropping funnel, a magnetic bar,
and a thermometer, were placed 10.1 g (0.074 mol) of m-cymene. This
was cooled to 5°, and 2.0 g of H$_2$SO$_4$ were added. Diisobutylene, 25.0
g (0.22 mol), was introduced dropwise over a 1.3-hr period to the stir-
red reaction mixture which was kept below 8°. The mixture was stirred
for 1 hr, and the acid layer was then separated. The organic layer
upon washing with saturated Na$_2$CO$_3$ soln and drying (CaCl$_2$) yielded

30.6 g of material. The aqueous layer was extracted with ether and this extract afforded 1.6 g of concentrated product.

The results of the gas chromatographic analysis are shown in Table VII. The hydrocarbon with the same glpc retention time as 41 was collected by preparative glpc and was found to have nmr and ir spectra identical with those of 41 obtained from the m-cymene – isobutylene reaction. The hydrocarbon K having the same retention time as M gave the following data: ir 728 (w), 762 (s), and 788 (s) cm^{-1}. This spectrum is very similar to that of 46.

Run 16c. 2-Methyl-2-butene.[39]—The equipment and procedure used were the same as those used for Run 16b except a dry-ice condenser was included. The temperature was held at 10° throughout the reaction, and the olefin addition took 1 hr. The reaction was then stirred for an additional 45 min. The yield of organic material was 38.4 g.

The results of gas chromatographic analysis are shown in Table VII. Hydrocarbons 27 and 36 were identified by nmr, ir, and mass spectral comparisons. The mass spectra of 38 and O are in Table XI. Additional data are shown below.

38: ir 711 (s) and 858 (s) cm^{-1}; nmr δ (No integration values

are given since the sample was contaminated with polymeric

material). 1.17, 1.23, 1.27 (-C-CH$_3$), 1.40-1.80 (m, -CH$_2$-),

2.38 (s, ArCH$_3$), 2.45-2.90 (m, Ar-C-H), 6.70-6.89 (m, ArH).

O: ir 658 (m), 722 (w), 790 (m), 815 (s), and 869 (s) cm^{-1}.

Sulfuric Acid-Catalyzed Reactions of o-Cymene With Three Olefins.

Run 17a. Isobutylene.—The same apparatus and procedure were used for this reaction and workup as in Run 16a. There were 67.0 g (0.50 mol) o-cymene and 6.5 g H$_2$SO$_4$ used. The isobutylene was bubbled into the

reaction mixture for 6 hr while the temp was maintained below 10°.

The reaction products weighed 65 g. The gas chromatogram of the final

reaction mixture is shown in Fig. 11, and a comparison of these data is

shown in Table IX. The results of mass spectral analyses of the prin-

cipal products are shown in Table XI. Additional data were obtained

for the two major products:

P: ir 645 (w), 733 (m), 816 (s), 862 (w), and 888 (m) cm^{-1}; nmr

δ 1.16 (3, half of doublet resulting from the isopropyl me-

thyls, -CH-(C$\underline{H}_3$)$_2$, the other half is covered by the next peak

mentioned), 1.29 (s, 12, C(C$\underline{H}_3$)$_3$ and three of -CH(C$\underline{H}_3$)$_2$),

2.25 (s, 3, ArC$\underline{H}_3$), 3.08 (m, 1, ArC-$\underline{H}$), 6.94 (m, 2, Ar$\underline{H}$), 7.14

(m, 1, Ar$\underline{H}$).

Q: ir 825 (s) and 881 (m) cm^{-1}; nmr δ 1.14 (3, half of the doub-

let from -CH(C$\underline{H}_3$)$_2$), 1.27 (s, 12, C(C$\underline{H}_3$)$_3$ and three protons

from CH(C$\underline{H}_3$)$_2$), 2.29 (s, 3, ArC$\underline{H}_3$), 3.07 (m, 1, ArC-$\underline{H}$),

7.03 (m, 3, Ar$\underline{H}$).

Run 17b. Diisobutylene.—o-Cymene, 20.1 g (0.15 mol), 33.6 g

(0.30 mol) of diisobutylene, and 6 g of H$_2$SO$_4$ were used. The equipment

and reaction procedure was the same as used in the m-cymene – diisobu-

tylene reaction, except the H$_2$SO$_4$ was added in increments during the

diisobutylene addition. The temp was maintained at 5° during the 35

min of diisobutylene addition and for the extra 1.5 hr of stirring.

The acid layer did not separate when the stirring was stopped, so the

reaction mixture was shaken with 30% NaOH and the resulting emulsion

extracted with ether and dried (CaCl$_2$). There were 44.4 g of organic

material recovered upon ether removal.

Results of analysis by glpc are shown in Table IX and Table X.

Run 17c. Triisobutylene.—The same apparatus was used as in the m-cymene – diisobutylene reaction along with 20.1 g (0.15 mol) of o-cymene, 26.3 g (0.16 mol) of triisobutylene, and 6.0 g of H_2SO_4. About half of the o-cymene was placed in the reaction vessel and cooled to 5°, with the other half being mixed with the olefin. Sulfuric acid (2.5 g) was added to the reaction vessel, and the o-cymene – olefin mixture was dripped into the stirred reaction. The addition of this mixture took 30 min, and, while it was occurring, the rest of the acid was added in two aliquots. The reaction temp was kept below 7° throughout the olefin addition and the 1-hr stirring period.

The acid layer (6.7 g) was separated, and the organic layer shaken with Na_2CO_3, filtered, washed with H_2O, and then extracted with ether. Evaporation of the ether yielded 41.2 g of organic material.

The results of gas chromatographic analysis of the reaction mixture are shown in Table IX and Fig. 12.

Sulfuric Acid–Catalyzed Reactions of tert-Butylcymenes With Isobutylene. Run 18a. 2-tert-Butyl-p-cymene (20).—To a 50-ml, 3-necked flask equipped with a thermometer, magnetic bar, and a gas inlet tube were added 4.0 g (0.02 mol) of 20 and 0.8 g of n-dodecane as an internal standard. After cooling the vessel to 5° and introducing 4.0 g H_2SO_4, isobutylene was bubbled through the reaction mixture for 3 hr. Upon washing with a saturated Na_2CO_3 soln, 13.5 g of organic material were obtained.

Gas chromatographic analysis showed the following:

| | ⌜—Ratio of glpc peak areas—⌝ | | |
	n-dodecane	20	4	21
starting material	1.00	2.55	0.0	0.0
final reaction mixture	1.00	0.0	0.63	0.27

Run 18b. 5-*tert*-Butyl-*m*-cymene (36).—In a 100-ml, 3-necked flask

equipped with a thermometer, a gas inlet tube, a magnetic bar, and a

dry-ice condenser were placed 1 ml *n*-dodecane as a internal standard

and 5.0 g of a mixture containing 85% of 36. After cooling to 5°, 5.0

g of H_2SO_4 were added to the vessel, and isobutylene was bubbled into

the reaction mixture for 3.5 hr. The acid layer was separated, and the

organic layer was washed with saturated Na_2CO_3 soln and dried ($CaCl_2$)

giving 34.9 g of organic material. Analysis by gas chromatography

yielded the results shown in Table VI.

Run 18c. 4-*tert*-Butyl-*o*-cymene and 5-*tert*-butyl-*o*-cymene.—The

same apparatus, procedure, and conditions were used as in the reaction

of isobutylene with 20. The quantities used were 2.3 g of approximately

an equal mixture of 51 and 52, 0.6 g *n*-dodecane, and 1.0 g H_2SO_4. Iso-

butylene was passed into the reaction for 3 hr.

Gas chromatographic analysis showed that neither 51 nor 52 had re-

acted.

Acid-Catalyzed Reaction of 1,1,3,3,5-Pentamethylindan (4) With

Isobutylene. Run 19a. Sulfuric acid at 5°.—In a 100-ml, 3-necked

flask equipped with a thermometer, a magnetic bar, and a gas inlet tube

were placed 19.0 g (0.10 mol) of 4 and 1.3 g H_2SO_4. After cooling the

reaction vessel to 5°, isobutylene was passed into the reaction mix-

ture for 7 hr while the temp was maintained below 10°. The reaction

was worked up by the usual method and dried ($MgSO_4$).

Gas chromatographic analysis showed that the ratio of 4 to 21 was

100:9.

Run 19b. Amberlyst-15 at 90°.—The same apparatus was used as in

the reaction of isobutylene with 4 except that the flask was also

equipped with a reflux condenser. To the flask were added 19.0 g (0.10 mol) of 4 and 1.5 g A-15 (dried at 105° for 3 hr at 2.0 mm). The reaction vessel was heated to 90°, and isobutylene was bubbled into the stirred indan - A-15 mixture for 48 hr.

Analysis by glpc showed only a trace of 21 was formed.

The Synthesis of α,m-Dimethylstyrene. A. The preparation of methyl m-toluate.—Using the procedure of Harrison[40] et al., 378 g (2.78 mol) of m-toluic acid (recrystallized, mp 110-112°) was esterified with 1184 g (37 mol) of absolute methanol using 9 ml of H_2SO_4 and 684 g of 4Å molecular sieve.

The reaction took 17 hr, and the reaction product upon distillation yielded 372.1 g (89%) of methyl m-toluate: bp 96° (4.3 mm) [lit.[41] 215° (760 mm)]; ir 1710 (C=O) and 740 cm^{-1}; nmr δ 2.30 (s, 3, $ArCH_3$), 3.78 (s, 3, $-O-CH_3$), 7.12-7.30 (m, 2, ArH), and 7.60-7.88 (m, 2, ArH).

B. The preparation of 2-(m-tolyl)-2-propanol.—To a 6-1., 3-necked, stainless steel reactor equipped with a reflux condenser, 1500-ml dropping funnel, and Vibromix stirrer were added 120 ml methylmagnesium bromide solution (3 molar in ether) while the system was flushed with N_2. A 367-g (2.45 mol) sample of methyl m-toluate was diluted with an equal volume of ether, and the solution was added slowly to the reaction vessel at a rate which kept the reaction mixture at the reflux temp. When the ester addition was complete, the reaction mixture was heated at the reflux temp for 5 hr. An additional 400 ml of methylmagnesium bromide solution (3 molar in ether) was mixed with an equal volume of ether and cautiously added to the reaction mixture, which was then kept at reflux temp for 7 hr.

The reaction was quenched by slowly introducing H_2O and then dilute HCl. The organic layer was separated, and the aqueous layer was extracted twice with ether. The organic fractions were combined, dried ($CaCl_2$) and freed of most of the ether. Glpc analysis showed 90% conversion to the alcohol. Nmr analysis of the crude reaction mixture gave the following data: 1.42 (s, 6, -CH(C$\underline{H}_3$)$_2$), 2.23 (s, 3, ArC$\underline{H}_3$), 3.67-3.80 (broad peak, 1, -O-$\underline{H}$), 6.83-7.27 (m, 4, Ar$\underline{H}$).

When a portion of the crude reaction mixture was distilled at 4.5 mm, approximately 50% of the distillate was the olefin resulting from dehydration of the alcohol.

C. The dehydration of 2-(m-tolyl)-2-propanol.—A trace of p-toluenesulfonic acid was added to 23.4 g of the crude product from the preparation of 2-(m-tolyl)-2-propanol, and the material was distilled yielding 16.3 g of α,m-dimethylstyrene (95% pure): bp 69° (4.5 mm) [lit.[4] 86-89° (25 mm)]; ir 679 (w), 705 (w), 722 (s), 790 (s), and 890 (s) cm^{-1}; nmr δ 2.05 (m, 3, vinylic-C$\underline{H}_3$), 2.23 (s, 3, ArC$\underline{H}_3$), 4.87-5.00 (m, 1, C=C$\underline{H}$), 5.18-5.28 (m, 1, -C=C$\underline{H}$), 6.83-7.17 (m, 4, Ar$\underline{H}$).

The Reaction of α,m-Dimethylstyrene With Diisobutylene.—In a 3-necked, 50-ml flask equipped with a dropping funnel, magnetic bar, and thermometer, were placed 5 ml of n-hexane (H_2SO_4-treated) and 2.0 g H_2SO_4. The reaction mixture was cooled to 10°, and a mixture of 5.0 g (0.035 mol) of α,m-dimethylstyrene and 3.9 g (0.035 mol) of diisobutylene was slowly added dropwise while the mixture was stirred. Stirring was continued for 15 min after the olefin addition was completed, and then the acid layer was separated. The organic layer was washed with a saturated Na_2CO_3 soln, and this aqueous layer extracted with ether. The organic layer and ether extract were combined and concentrated to

7.4 g of crude product.

Analysis by glpc showed in order of increasing retention times 41, 46, 40, and, appearing as one peak, the dimers 2 and 3 in a ratio of of 100:55:12:92. The compounds shown to be 41 and 46 by glpc analysis were purified by preparative glpc. The compound with the same glpc retention time as 41 was found to have nmr and ir specta identical with those of a known sample of 41. The compound identified as 46 gave the following data: ir 788 (s), 764 (s), and 729 (m) cm^{-1}; nmr δ 1.01 (s, 9, C(C$\underline{H}_3$)$_3$), 1.21 (s, 3, geminate C$\underline{H}_3$), 1.30 (s, 3, geminate C$\underline{H}_3$), 1.47 (s, 3, C$\underline{H}_3$ geminate to the neopentyl group), 1.50-2.50 (overlapping m, 4, two C$\underline{H}_2$ groups), 2.39 (s, 3, ArC$\underline{H}_3$), 6.65-7.0 (m, 3, Ar$\underline{H}$).

TABLE XI

MASS SPECTRAL DATA FROM REACTION PRODUCTS

Compd	Molecular ion peak	Fragmentation Peaks					
1	264	249	157	264	251	117	105
4	188	173	188	174	131	128	143
8	216	201	159	216	202	145	157
20	190	175	190	176	133	105	119
21	244	229	230	244	173	157	141
22	244	173	174	143	128	131	157
23	244	201	159	202	145	244	171
27	202	187	202	145	188	141	128
28	202	173	187	202	145	174	128
35	230	173	174	159	230	143	157
36&L	190,188	175	190	176	173	133	105
38	204	175	176	204	173	105	147
39	244	229	230	244	245	173	107
40	300	229	230	300	173	243	213
41	244	173	174	131	143	128	157
A	202	173	174	187	202	143	128
B	216	173	174	216	161	201	159
C	258	173	201	174	187	159	258
D	300	229	173	230	252	255	300
E	300	201	257	202	159	173	300

TABLE XI (Continued)

Compd	Molecular ion peak	Fragmentation Peaks					
F	216	201	159	216	145	202	128
G	216	187	186	145	216	201	111
H	304	289	304	290	137	305	229
I&J	190,204	175	190	176	105	204	133
M	258	173	229	243	174	230	258
N	258	229	243	258	230	173	244
O	272	243	257	173	272	174	187
P	190	175	190	176	105	191	119
Q	190	175	190	176	105	191	145
R	246	175	176	246	105	147	159
S	246	175	176	246	105	159	145
T	246	175	176	246	105	161	119
U	218	175	203	176	204	218	105
V	302	175	176	174	105	302	161
W	302	175	176	174	105	145	302

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