

benzene was added dropwise to discharge the blue color and excess ammonium chloride was added. The ammonia was allowed to evaporate and the product was isolated with ether and purified by short-path distillation, preparative layer chromatography (silica), and short-path distillation (100° at 0.15 mm) to give 49 mg (74%) of ketone **38**:  $\lambda_{\text{max}}^{\text{film}}$  5.83, 6.94, 7.42, 8.18, 8.33, and 9.61  $\mu\text{m}$ ;  $\delta_{\text{TMS}}^{\text{CCl}_4-\text{CDCl}_3}$  2.05 ppm ( $\text{CH}_3\text{CO}$ ).

*Anal.* Calcd for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H, 10.18. Found: C, 80.8; H, 10.2.

**2-(3-Bicyclo[5.3.0]dec-1(7)-enyl)-2-propanol (39).**—To a stirred solution containing 34 mg of ketone **38** in 3 ml of ether at 0° was added 1.0 ml of 1.5 *M* methylolithium. After 3.5 hr at room temperature, the mixture was poured onto ice and the product was isolated with ether. The material thus secured still contained 15% of ketone **38**.<sup>27</sup> The above procedure was thus repeated and the product distilled, affording 35 mg (94%) of alcohol **39**, bp 85° (bath temperature) at 0.2 mm, shown to be 85% pure by gas chromatography:<sup>27</sup>  $\lambda_{\text{max}}^{\text{film}}$  2.97, 6.95, 7.32, 7.67, 8.87, 10.50, 11.02, 11.32, and 11.61  $\mu\text{m}$ ;  $\delta_{\text{TMS}}^{\text{CCl}_4}$  1.10 ppm ( $\text{CH}_3$ ). The analytical sample secured by preparative layer chromatography (silica) and distillation exhibited mp 54–55.5° after sublimation at 25° (0.04 mm).

*Anal.* Calcd for  $\text{C}_{13}\text{H}_{22}\text{O}$ : C, 80.35; H, 11.41. Found: C, 80.4; H, 11.4.

**Registry No.**—2 methyl ester, 29494-06-2; 2 ethyl ester, 29494-34-6; 3 methyl ester, 29494-07-3; 3

ethyl ester, 29494-35-7; 4, 29494-08-4; 5, 29494-09-5; 6, 29494-10-8; 7, 29494-11-9; 8, 29494-12-0; 9, 7125-60-2; 10, 29494-14-2; 11, 29494-15-3; 13 methyl ester, 29494-16-4; 13 ethyl ester, 29494-36-8; 14 methyl ester, 29494-17-5; 14 ethyl ester, 29576-49-6; 15 methyl ester, 29494-18-6; 15 ethyl ester, 29494-37-9; 16, 29494-19-7; 17, 29478-14-6; 18, 29478-15-7; 19, 29478-16-8; 20, 29478-17-9; 21, 29478-18-0; 22, 29478-19-1; 23, 29494-20-0; 26 methyl ester, 29494-21-1; 26 ethyl ester, 7478-39-9; 27 methyl ester, 29494-22-2; 27 ethyl ester, 2088-98-4; desulfurized 27 methyl ester, 29494-24-4; desulfurized 27 ethyl ester, 29494-25-5; 29, 29494-26-6; 30, 29494-27-7; 31, 29478-20-4; 31 mesylate, 29576-48-5; 32, 29478-21-5; 32 monomesylate, 29472-24-0; 33, 29478-22-6; 34, 29494-28-8; 35, 29494-29-9; 36, 29494-30-2; 37, 29494-31-3; 38, 29494-32-4; 39, 29494-33-5.

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## The Acid-Catalyzed Alkylation and Cyclialkylation of the Cymenes with Isobutylene and Related Olefins<sup>1a</sup>

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The acid-catalyzed reactions of *o*-, *m*-, and *p*-cymene with isobutylene, diisobutylene, and triisobutylene give complex mixtures of hydrocarbon products. *o*-Cymene forms only alkylation products, whereas *p*-cymene gives predominantly cyclialkylation products, with only one case of alkylation. *m*-Cymene occupies an intermediate position, providing both alkylation and cyclialkylation products. The reactions of *m*- and *p*-cymene with these olefins afford indans and tetralins as cyclialkylation products. In the cyclialkylation products from *m*-cymene, the point of ring closure (ortho or para position to the methyl group) is strongly influenced by an alkyl group at the 5 position of *m*-cymene. Several acidic materials were used to catalyze the reactions of *p*-cymene with isobutylene, diisobutylene, and triisobutylene, and their effectiveness is compared. Some new hydrocarbons were isolated and identified. These are obtained from alkylation and cyclialkylation of the starting olefin or result from olefins produced in the reaction system *via* polymerization, rearrangement, and fragmentation.

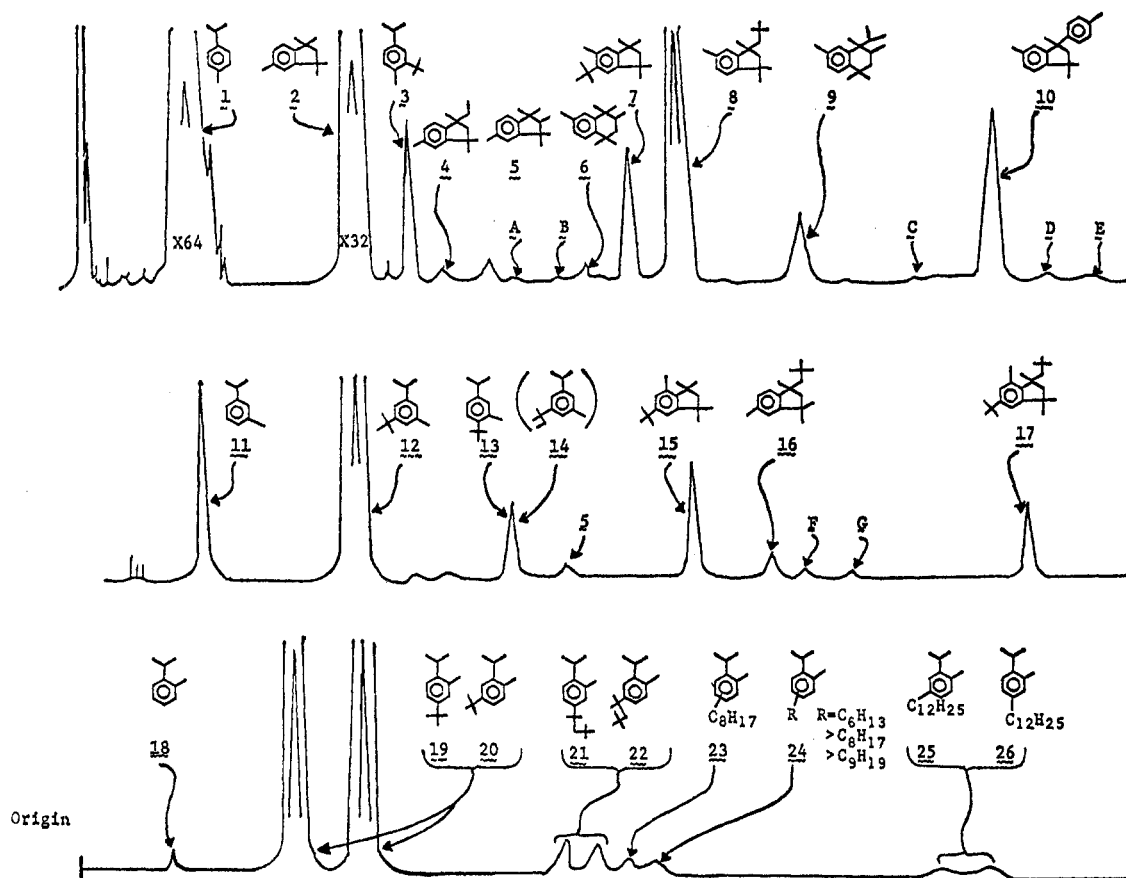
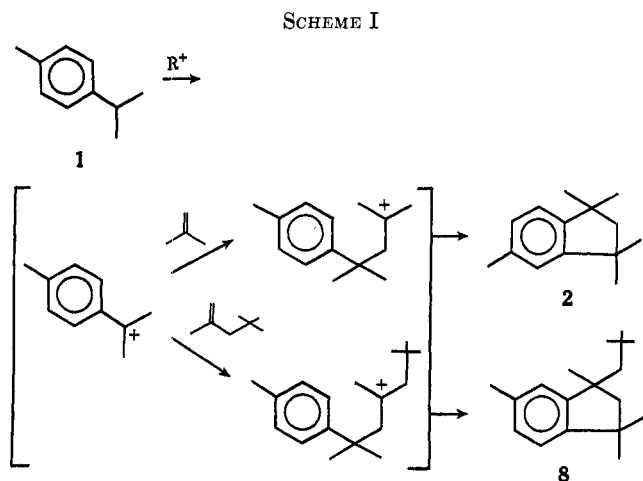
Cyclialkylation reactions initiated by hydride ion abstraction were discovered by Pines and coworkers.<sup>2a</sup> They found that aromatic hydrocarbons having  $\alpha$  tertiary hydrogens may undergo hydride ion abstraction by carbonium ions generated in the reaction medium. Their mechanism<sup>2a</sup> is shown in Scheme I using isobutyl-

ene as the olefin to give 1,1,3,3,5-pentamethylindan (2), first identified by Schlatter.<sup>2b</sup> As pointed out by Barclay,<sup>2c</sup> alkylation competes with cyclialkylation. Alkylation will predominate unless the aromatic hydrocarbons used are substituted so as to sterically hinder alkylation reactions. In addition, branched olefins (or compounds such as branched-chain alcohols which can generate such olefins in acidic media) seem necessary since straight-chain alcohols have been reported<sup>2c,d</sup> to react with *p*-cymene to give only alkylation products.

A variety of substituted indans, hydrindacenes, and tetralins have been prepared<sup>2c</sup> with *p*-cymene, whereas Barclay<sup>2e</sup> used 1,3,5-triisopropylbenzene and diisobutylene to prepare a neopentylindan. Most of the work has been with *p*-cymene, *m*- and *o*-cymene<sup>2c,f</sup> having been used in only a few cases, and no previous studies have dealt extensively with minor products.

(1) (a) D. E. Boone, E. J. Eisenbraun, P. W. Flanagan, and R. D. Grigsby, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, **15**, 77 (1970). (b) American Petroleum Institute Graduate Research Assistant, 1967–1969.

(2) (a) V. N. Ipatieff, H. Pines, and R. C. Olberg, *J. Amer. Chem. Soc.*, **70**, 2123 (1948); (b) M. J. Schlatter, "Symposium on Petrochemicals in the Postwar Years," 124th National Meeting of the American Chemical Society, Chicago, Ill., 1953, p 79; (c) L. R. C. Barclay, "Friedel-Crafts and Related Reactions," Vol. 2, part 2, G. A. Olah, Ed., Interscience, New York, N. Y., 1964, p 785; (d) S. H. Weber, J. Stoffberg, D. B. Spoelstra, and R. J. C. Kleipool, *Recl. Trav. Chim. Pays-Bas*, **75**, 1433 (1956); (e) L. R. C. Barclay, J. W. Hilchie, A. H. Gray, and N. D. Hall, *Can. J. Chem.*, **38**, 94 (1960); (f) H. Pines, D. R. Strehlau, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, **72**, 5521 (1950); (g) Queries regarding samples of hydrocarbons **2**, **8**, and **10** should be directed to A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213.


 Figure 1.—Gas chromatograms of *o*-, *m*-, and *p*-cymene-isobutylene reaction products.


The cyclialkylation reaction has been a valuable source of hydrocarbons for us.<sup>2g</sup> In the current work, *p*-cymene (1) and isobutylene, as well as diisobutylene, provided 1,1,3,3,5-pentamethylindan (2)<sup>2b</sup> and 1,3,3,6-tetramethyl-1-neopentylindan (8) in quantity<sup>2g</sup> as shown in Scheme I. The variety of products found in these reactions and not previously reported prompted us to reexamine the *p*-cymene-isobutylene reaction and to extend the study to other olefins and other cymenes. The cymenes were selected for study since they include the necessary variation in alkyl substitution which permits both extremes of alkylation and cyclialkylation. As previously mentioned, in the absence of steric effects (three or more vicinal hydrogens present), alkylation

is the predominant reaction. Actually, as shown in Figure 1 for the alkylation of *o*-cymene, there were no products due to cyclialkylation. The requirement for cyclialkylation includes a tertiary benzylic hydrogen and an unsubstituted adjacent position on an aromatic ring. With *p*-cymene, eight components were identified as cyclialkylation products but only one, 3, a minor product, is due to alkylation. As expected, *m*-cymene occupies an intermediate position in regard to these reactions and both effects may be summarized as follows: for alkylation, *o*- > *m*- >> *p*-cymene, and for cyclialkylation, *o*- << *m*- < *p*-cymene.

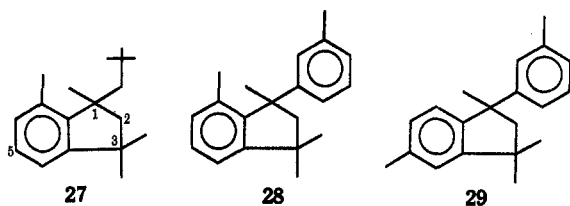
The formation of all hydrocarbons identified in this study may be rationalized through application of existing carbonium ion theories.<sup>3,4</sup> The formation of all the products shown accompanying the top and middle glc curves of Figure 1 except 4, 5, 6, and 14 may be explained by using the mechanism of Scheme I and/or an added alkylation step.<sup>2a-f,3</sup> These four anomalous hydrocarbons cannot be formed directly from isobutylene or diisobutylene and require an olefin fragmentation and/or rearrangement<sup>3a,4</sup> to 2-methyl-1-butene and 2-methyl-2-butene as well as 2,3-dimethyl-1-butene to explain their formation. It should be noted that hydrocarbons 4, 5, 6, and 14 and those unidentified ones having empirical formulas which could not arise from isobutylene or its condensation products also could not arise from impurities in the starting materials since glc

(3) (a) L. Schmerling, ref 2c, p 1075; (b) H. Pines and N. E. Hoffman ref 2c, p 1211.

(4) (a) A. Schneider, *J. Amer. Chem. Soc.*, **174**, 2553 (1952); (b) J. E. Hofmann, *J. Org. Chem.*, **29**, 3627 (1964); (c) G. J. Karabatsos, F. M. Vane, and S. Meyerson, *J. Amer. Chem. Soc.*, **85**, 733 (1963).

analyses ruled out significant amounts of impurities.<sup>5a</sup> In addition, *p*-cymene and diisobutylene were carefully purified by preparative glc<sup>5b</sup> and these purified samples were subjected to sulfuric acid catalyzed condensation. No significant differences in the products from this and conventional runs were observed. While structure **9** represents a C<sub>18</sub> hydrocarbon, its formation cannot be rationalized from diisobutylene except through skeletal rearrangement to 2,3,4-trimethylpentenes and subsequent reaction with *p*-cymene to form the tetralin **9** rather than an indan in a reaction analogous to that described by Wood.<sup>6</sup>

For the most part, the products of the isobutylene and diisobutylene reactions are comparable, although there is some variation in ratios. A notable exception is that diisobutylene and *m*-cymene provide 1,3,3,7-tetramethyl-1-neopentylindan (**27**), which appears to be absent in the reaction products when isobutylene is used. The glc retention time of **27** is the same as that of F in Figure 1; however, **27** and F are not the same. The formation of **27** is of interest because it could be expected to predominate over **16** by



analogy with the fact that in a similar reaction 1,3,3,7-tetramethyl-1-*m*-tolylindan (**28**) and 1,3,3,5-tetramethyl-1-*m*-tolylindan (**29**) were found in a 2:1 ratio.<sup>7a</sup> However, when  $\alpha$ ,*m*-dimethylstyrene is treated with diisobutylene, the ratio of **16**:(**17** + **27**) is 1.4. Since the neopentyl group is bulkier than the *m*-tolyl group, a steric effect may cause the formation of more **16** relative to **17** + **27**. The formation of **17** from **27** is to be expected since position 5 of **27** is unhindered for tertiary butylation. Thus the absence of **27** in the *m*-cymene-isobutylene reaction products is not surprising. The 5 position is also unhindered for other reactions, such as sulfonation, which could influence the combined yield of **17** and **27**. It is of interest that *m*-cymene is readily alkylated by isobutylene to give **12**, which corresponds to reaction at C-5. It would also be expected that diisobutylene should react with *m*-cymene in an analogous manner to form the homolog with an octyl (C<sub>8</sub>H<sub>17</sub>) group at this same position. Our glc and mass spectral data failed to give evidence for its formation and hence initial alkylation is not prerequisite to cyclialkylation when diisobutylene is used.

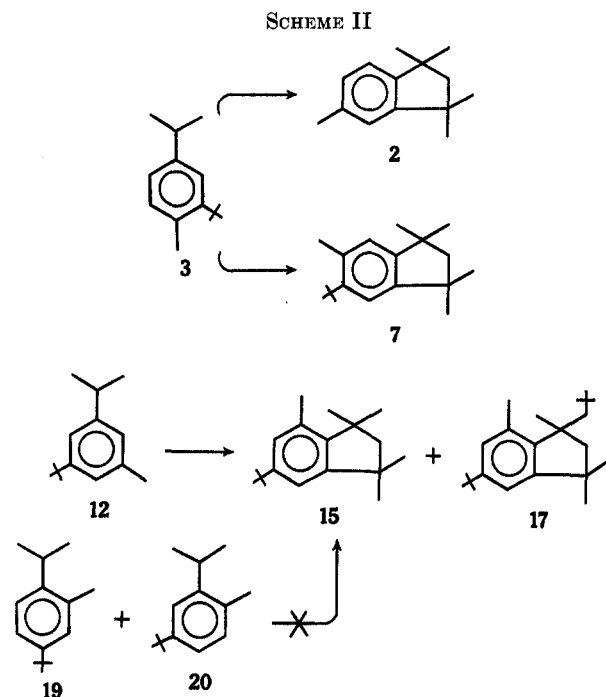
Cyclialkylation is the more important reaction for *p*-cymene. *m*-Cymene may undergo alkylation<sup>2c,f</sup> to **12** followed by cyclialkylation to **15** and **17**. Formation of **15** and **17** may also be explained by cyclialkylation of *m*-cymene with ring closure ortho to the methyl group followed by alkylation at position 5 as discussed above for **27**.

(5) (a) We thank Mr. E. Smith, Analytical Research Section, Continental Oil Co., Ponca City, for helpful assistance with these capillary glc studies. (b) We thank R. E. Laramy, Analytical Research Section, Continental Oil Co., for these separations.

(6) T. F. Wood, W. M. Easter, Jr., M. S. Carpenter, and J. T. Angiolini, *J. Org. Chem.*, **28**, 2248 (1963).

(7) (a) J. C. Petropoulos and J. J. Fisher, *J. Amer. Chem. Soc.*, **80**, 1938 (1958); (b) M. J. Schlatter, U. S. Patent 2,768,982 (1956).

Scheme II shows the products of several experiments devised to probe alkylation *vs.* cyclialkylation. It is



of interest that **3** with isobutylene not only underwent cyclialkylation to form **7** but also suffered de tertiary butylation to form the conventional cyclialkylation product **2**. The sterically and thermodynamically more stable **12** underwent cyclialkylation with no observable dealkylation to give **15** and **17** on treatment with isobutylene and H<sub>2</sub>SO<sub>4</sub>. Significantly, no reaction was observed for a mixture of **19** and **20** on treatment with isobutylene and H<sub>2</sub>SO<sub>4</sub>. It would be expected that **20** would not undergo cyclialkylation because of the steric influence of the *tert*-butyl group. However, it might be expected that **19** could undergo cyclialkylation with isobutylene to form **15**. The lack of reactivity of **19** becomes apparent upon examination of a molecular model which shows the tertiary hydrogen of **19** to be less available for abstraction than the tertiary hydrogens of *m*- or *p*-cymene since the approach of a cation to this site is effectively blocked by the surrounding methyl groups. This argument applies to *o*-cymene and explains the absence of cyclialkylation products.

Several minor or trace products from the cymene-olefin reactions were isolated by preparative glc and analyzed by mass and nmr spectroscopy. However, some of these were contaminated by polymeric hydrocarbons that obscured interpretation of the spectra and consequently their structures remain unknown at this time. These hydrocarbon samples are designated by letters; the available data are presented in Figure 1 as well as in the Experimental Section.

The products obtained are the same whether isobutylene, diisobutylene, triisobutylene, or tetraisobutylene is combined with *p*-cymene. However, the olefin used does affect the product ratios, which are shown in Table I.

When sulfuric acid was used, the best results were obtained with a reaction temperature below 10° (runs 1a, 1b, 5a-c). As the temperature was increased (runs

TABLE I  
 ACID-CATALYZED REACTIONS OF THE CYMENES AND OLEFINS

Run <sup>b</sup>	°C	Moles			2 <sup>c</sup>	Glc ratios of major hydrocarbons <sup>a</sup>					
		Acid	Cymene	Olefin		5	8	9	10	10	
1a <sup>d</sup>	5 <sup>e</sup>	1.14 <sup>f</sup>	12.9 <sup>g</sup>	6 <sup>h</sup>	41		0.15	0.03	0.09		
1b	5 <sup>e</sup>	0.19 <sup>f</sup>	0.25 <sup>g</sup>	3 <sup>h</sup>	42		0.09	0.01	0.10		
2a	10 <sup>e</sup>	0.07 <sup>i</sup>	0.50 <sup>g</sup>	9 <sup>h</sup>	2		0.32	0.53			
2b	115	0.26 <sup>i</sup>	0.34 <sup>g</sup>	6.4 <sup>h</sup>	43	0.03	0.04	0.02	0.02		
3a	25 <sup>e</sup>	7 <sup>i</sup>	0.50 <sup>g</sup>	24 <sup>h</sup>	1		2.00	0.71			
3b	85	5.5 <sup>i</sup>	0.25 <sup>g</sup>	48 <sup>h</sup>	15		0.10	0.03			
3c	130	3.5 <sup>i</sup>	0.25 <sup>g</sup>	39 <sup>h</sup>	33		0.06	0.07	0.05		
4	5 <sup>e</sup>	1.4 <sup>k</sup>	1.07 <sup>g</sup>	2 <sup>h</sup>	12	0.02		0.32	0.03	0.03	
5a	5	0.19 <sup>f</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	9	0.24	0.06	5.04	0.61	0.52	
5b	5	0.76 <sup>f</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	7	0.18	0.08	7.53	1.05	1.46	
5c <sup>d</sup>	5	0.74 <sup>f</sup>	8.20 <sup>g</sup>	13.2 <sup>l</sup>	7	0.19	0.05	7.40	0.74	0.13	
5d	25	0.11 <sup>f</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	8			2.40	0.41	0.14	
5e	25	0.19 <sup>f</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	17	0.07	0.06	2.76	0.53	0.43	
5f	25	0.39 <sup>f</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	10	0.08	0.0	2.22	0.50	0.42	
5g	65	0.10 <sup>f</sup>	0.50 <sup>g</sup>	1.0 <sup>l</sup>	2			1.40	0.47		
6a <sup>m</sup>	70	0.19 <sup>i</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	25	0.12	0.07	0.39	0.19		
6b	70	0.10 <sup>i</sup>	0.09 <sup>g</sup>	0.19 <sup>l</sup>	27	0.15	0.07	0.31	0.16	0.03	
6c	115	0.25 <sup>i</sup>	0.33 <sup>g</sup>	0.67 <sup>l</sup>	43	0.05		0.08	0.05	0.09	
6d	140	0.19 <sup>i</sup>	0.25 <sup>g</sup>	0.50 <sup>l</sup>	35	0.12	0.05	0.19			
7	100	69 <sup>i</sup>	0.29 <sup>g</sup>	0.88 <sup>l</sup>	12			1.20	0.54	0.11	
8a	5	1.0 <sup>k</sup>	0.25 <sup>g</sup>	0.54 <sup>l</sup>	15	0.12	0.0	2.05	0.18	0.04	
8b	5	2.5 <sup>k</sup>	0.25 <sup>g</sup>	0.54 <sup>l</sup>	23	0.15	0.06	1.19	0.16		
9a	5	0.12 <sup>n</sup>	0.25 <sup>g</sup>	0.25 <sup>l</sup>	Trace	0.04		50 <sup>o</sup>			
9b <sup>m</sup>	70	0.12 <sup>n</sup>	0.50 <sup>g</sup>	0.50 <sup>l</sup>	13			2.7	0.17		
10	5	0.10 <sup>f</sup>	0.20 <sup>g</sup>	0.14 <sup>p</sup>	18	0.11	0.108	0.74	0.06	0.13	
11	5	0.07 <sup>n</sup>	0.20 <sup>g</sup>	0.18 <sup>p</sup>	5	0.48		10.2		1.06	
12	5	0.10 <sup>f</sup>	0.50 <sup>g</sup>	0.20 <sup>q</sup>	1.0 <sup>r</sup>	4.6				0.3	
13a <sup>m</sup>	5	0.03 <sup>f</sup>	1.00 <sup>g</sup>	0.10 <sup>q</sup>	1.0 <sup>r</sup>	0.5					
13b	5	0.10 <sup>f</sup>	0.50 <sup>g</sup>	0.25 <sup>q</sup>	1.0 <sup>r</sup>	0.5		6.4	12.5	3.5	
13c	5	0.03 <sup>f</sup>	0.06 <sup>g</sup>	0.13 <sup>q</sup>	1.0 <sup>r</sup>	0.6		1.3	2.0	0.2	
-----											
						5	12	13 + 14	15	16	17
14	10 <sup>e</sup>	0.07 <sup>f</sup>	0.50 <sup>u</sup>	4 <sup>h</sup>		0.01	1.00	0.09	0.21	0.07	0.12
15	5	0.02 <sup>f</sup>	0.07 <sup>u</sup>	0.22 <sup>l</sup>		0.0	1.00	0.97	0.25	2.53	1.14
-----											
						19 + 20	21 + 22	23	24	25 + 26	
16	10 <sup>e</sup>	0.07 <sup>f</sup>	0.50 <sup>w</sup>	6.0 <sup>h</sup>		1.0	0.02	0.002	0.001	0.01	
17	5	0.06 <sup>f</sup>	0.15 <sup>w</sup>	0.30 <sup>l</sup>		1.0	1.06	0.21	0.00	0.00	
18	5	0.06 <sup>f</sup>	0.15 <sup>w</sup>	0.16 <sup>p</sup>		1.0	0.23	0.11	0.03	0.08	

<sup>a</sup> Product normalized to 2 = 1.00. <sup>b</sup> Magnetic stirring except where noted. <sup>c</sup> Values given are per cent yield of 2 based on *p*-cymene except as noted. <sup>d</sup> Vibromixer E-2. <sup>e</sup> °C controlled by flow of isobutylene. <sup>f</sup> H<sub>2</sub>SO<sub>4</sub>. <sup>g</sup> *p*-Cymene. <sup>h</sup> Hours isobutylene flow. <sup>i</sup> Methanesulfonic acid. <sup>j</sup> Amberlyst-15 in grams. <sup>k</sup> HF. <sup>l</sup> Diisobutylene. <sup>m</sup> Motor-driven turbine stirrer. <sup>n</sup> AlCl<sub>3</sub>. <sup>o</sup> Peak ratios are compared to 8 = 1.00; the value for 8 is per cent yield. <sup>p</sup> Triisobutylene. <sup>q</sup> 2-Methyl-2-butene. <sup>r</sup> Ratio only, not a per cent yield. <sup>s</sup> 2,3,4-Trimethyl-2-pentene. <sup>t</sup> Glc ratio of major hydrocarbons normalized to 12 = 1.00. <sup>u</sup> *m*-Cymene. <sup>v</sup> Glc ratio of hydrocarbons normalized to 19 + 20 = 1.00. <sup>w</sup> *o*-Cymene.

5a-f), the yield of low-molecular-weight polyisobutylenes increased until, at 65° (run 5g), only a few per cent of the products resulted from cyclialkylation reactions, and the major product observed on glc was tetraisobutylene.

Within limits, the quantity of sulfuric acid used had little effect on the products formed. When a low molar concentration of sulfuric acid (acid to *p*-cymene ratio of 1:10, run 1a) was used, more tetraisobutylene and other olefinic polymers resulted. Large amounts of sulfuric acid, *i.e.*, acid to *p*-cymene ratio of 2:1 or greater, resulted in loss of material due to sulfonation and consequent emulsion formation during isolation (run 5b).

Anhydrous hydrogen fluoride (runs 4, 8a, and 8b) was effective in catalyzing the cyclialkylation reaction.<sup>7b</sup> In run 4, the isobutylene introduced into the reaction did not approach the stoichiometric amount; therefore, the 12% yield of 2 formed is not a true indication of

this acid's ability to catalyze the reaction. With hydrogen fluoride, the diisobutylene reaction (runs 8a and 8b) gave much less of the cyclialkylation product 8 than with sulfuric acid (runs 5a and 5b) and more fragmentation of diisobutylene occurred. An increased concentration of hydrogen fluoride produced larger yields of fragmentation products.

Methanesulfonic acid (run 2a) gave only olefin polymerization at temperatures below 30°. This catalyst at 70° (runs 6a and 6b) still caused formation of reaction products that were badly contaminated by polymeric material, but it did then yield cyclialkylation products. When the reaction temperature was 115° and above (runs 2b, 6c, and 6d), the amount of polymeric material decreased. The yields of 2 increased while little 8 was formed, indicating that considerable fragmentation of diisobutylene was occurring.

When Amberlyst-15 was the catalyst, it was necessary to use temperatures in excess of 100° (runs 3a-c)

TABLE II

INSTRUMENTAL DATA FOR HYDROCARBONS DERIVED FROM *o*-, *m*-, AND *p*-CYMENE

2 <sup>a</sup>	Bp 42° (0.5 mm) [lit. <sup>6</sup> 153.6° (100 mm)]; ir 815 and 878 cm <sup>-1</sup> ; nmr δ 1.24 (s, 12, -CH <sub>3</sub> β to aromatic ring), 1.86 (s, 2, CH <sub>2</sub> ), 2.27 (s, 3, Ar CH <sub>3</sub> ), 6.81-6.87 (m, 3, Ar H). <i>Anal.</i> Calcd for C <sub>14</sub> H <sub>20</sub> : C, 89.29; H, 10.71. Found: C, 89.27; H, 10.56.		half of doublet from CH(CH <sub>3</sub> ) <sub>2</sub> , 1.28 [s, 12, C(CH <sub>3</sub> ) <sub>3</sub> , also covers the other half of isopropyl doublet], 2.29 (s, 3, Ar CH <sub>3</sub> ), 2.81 (m, 1, Ar H), 6.72 (s, 1, Ar H), and 6.88 (s, 2, Ar H). Comparisons of glc retention times and ir and mass spectra indicate that the minor component is 2.
3 <sup>a</sup>	Ir 812 (s) and 881 cm <sup>-1</sup> (m); nmr δ 1.15 and 1.25 [d, CH(CH <sub>3</sub> ) <sub>2</sub> ], 1.38 [s, 9, C(CH <sub>3</sub> ) <sub>3</sub> ], 2.43 (s, 3, Ar CH <sub>3</sub> ), 2.73 (m, 1, CH), 6.80-7.11 (m, 3, Ar H); mass spectrum M = 190, 175 (M - 15) loss of methyl group, 147 (M - 43) loss of C <sub>3</sub> , 133 (M - 57) loss of C <sub>4</sub> ; see lit. <sup>2b</sup> for preparation.	13 <sup>f</sup>	Ir 712 (m), 823 (s), 857 (m), and 880 cm <sup>-1</sup> (m); mass spectrum, mixture, M = 190 and 204 (intensity ratio ca. 5:1), 175 (M - 15 or M - 29) loss of methyl or ethyl group; nmr δ 1.14 (s), 1.25 (m), 2.37 (s), 2.28 (two s, Ar CH <sub>3</sub> ) in a 1:2 ratio, and 6.70-7.20 (m, Ar H). Comparisons of ir and mass spectra indicate that the major component is 13 and the minor component is 14.
4 <sup>b</sup>	Ir 815 (s) and 878 cm <sup>-1</sup> (m); nmr δ 0.80 (t), 1.02 (s), 1.22 (s), 1.25 (s), 1.58 (m), 1.81 (m), 2.29 (s, 3, Ar CH <sub>3</sub> ), 6.74-6.86 (m, 3, Ar H); mass spectrum M = 202, 187 (M - 15) and 173 (M - 29) loss of methyl and ethyl groups; see lit. <sup>1</sup> for preparation.	14 <sup>g</sup>	Ir 711 (s) and 858 cm <sup>-1</sup> (s); mass spectrum M = 204, 175 (M - 29) loss of ethyl group (s); nmr δ (no integration values are given since the sample was contaminated with polymeric material) 1.17, 1.23, 1.27 (CCH <sub>3</sub> ), 1.40-1.80 (m, CH <sub>2</sub> ), 2.38 (s, Ar CH <sub>3</sub> ), 2.45-2.90 (m, Ar CH), 6.70-6.89 (m, Ar H).
5 <sup>b</sup>	Ir 815 (s) and 879 cm <sup>-1</sup> (m); nmr δ 0.91 (this is half of a doublet CHCH <sub>3</sub> and corresponds to 1.5 protons; the other half is hidden by the 1.04 peak), 1.04 (s, 7.5, geminate dimethyl protons, hides half of the previously listed doublet), 1.26 (s, 6, geminate dimethyl protons), 1.75 (q, 1, CH), 2.30 (s, 3, Ar CH <sub>3</sub> ), 6.83-6.89 (m, 3, Ar H); mass spectrum M = 202, 187 (M - 15) loss of methyl group; see lit. <sup>1</sup> for preparation.	15 <sup>f</sup>	Ir 655 (m), 770 (m), and 872 cm <sup>-1</sup> (s); mass spectrum M = 244, 229 (M - 15) loss of methyl group; nmr δ 1.26 (s, 6, unhindered geminate dimethyl group), 1.28 [s, 9, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.37 (s, 6, hindered geminate dimethyl group), 1.86 (s, 2, CH <sub>2</sub> ), 2.34 (s, 3, Ar CH <sub>3</sub> ), and 6.82 (s, 2, Ar H).
6 <sup>c</sup>	Mp 64-66° (lit. <sup>6</sup> mp 66-67.5°); mass spectrum M = 216, 201 (M - 15) loss of methyl group. Ir, mass, and nmr spectra all agree with those of the known compound. <sup>m</sup>	16 <sup>h</sup>	Ir 815 (s) and 878 cm <sup>-1</sup> (m); mass spectrum M = 244, 173 (M - 71) loss of C <sub>5</sub> group; nmr δ (this sample was contaminated with polymeric material, thus the integration values are not included) 1.00 [s, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.25 and 1.28 (two s, the latter being stronger and having a shoulder), 2.37-2.33 (m, two overlapping AB quartets from two nonequivalent CH <sub>2</sub> groups), 2.28 (s, Ar CH <sub>3</sub> ), and 6.75-6.88 (m, Ar H).
7 <sup>a</sup>	Mp 81-82°; ir (CS <sub>2</sub> ) 880 (s, appears as a shoulder on the next peak) and 887 cm <sup>-1</sup> (s); mass spectrum M = 244, 229 (M - 15) loss of methyl group; <sup>n</sup> nmr δ 1.26 (s, 12, geminate CH <sub>3</sub> ), 1.40 [s, 9, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.86 (s, 2, CH <sub>2</sub> ), 2.49 (s, 3, Ar CH <sub>3</sub> ), 6.70 (s, 1, Ar H), and 6.96 (s, 1, Ar H). <i>Anal.</i> Calcd for C <sub>18</sub> H <sub>28</sub> : C, 88.45; H, 11.55. Found: C, 88.57; H, 11.63.	17 <sup>h</sup>	Ir 653 (m), 774 (w), and 870 cm <sup>-1</sup> (s); mass spectrum M = 300, 229 (M - 71) loss of C <sub>5</sub> group; nmr δ 1.03 [s, 9, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.24 (s, 3, a geminate methyl group), 1.28 [s, 12, Ar C(CH <sub>3</sub> ) <sub>3</sub> 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 <sub>2</sub> appearing as two overlapping AB quartets), 2.37 (s, 3, Ar CH <sub>3</sub> ), and 6.75-6.90 (m, 2, Ar H).
8 <sup>d</sup>	Bp 84-85° (0.5 mm); ir 815 (s) and 878 cm <sup>-1</sup> (m); mass spectrum M = 244, 173 (M - 71) loss of C <sub>5</sub> group; nmr δ 1.03 [s, 9, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.24, 1.28, 1.32 (three s, 3 protons each, CH <sub>3</sub> β to benzene ring), 1.65 (center of AB quartet, 2, CH <sub>2</sub> ), 2.03 (center of AB quartet, 2, CH <sub>2</sub> ), 2.27 (s, 3, Ar CH <sub>3</sub> ), and 6.81-6.87 (m, 3, Ar H). <i>Anal.</i> Calcd for C <sub>18</sub> H <sub>28</sub> : C, 88.45; H, 11.55. Found: C, 88.63; H, 11.39.	19 <sup>i</sup> or 20 <sup>i</sup>	Ir 645 (w), 733 (m), 816 (s), 862 (w), and 888 cm <sup>-1</sup> (m); nmr δ 1.16 [3, half of doublet resulting from the isopropyl methyls, CH(CH <sub>3</sub> ) <sub>2</sub> ; the other half is covered by the next peak mentioned], 1.29 [s, 12, C(CH <sub>3</sub> ) <sub>3</sub> and three protons from CH(CH <sub>3</sub> ) <sub>2</sub> ], 2.25 (s, 3, Ar CH <sub>3</sub> ), 3.08 (m, 1, Ar CH), 6.94 (m, 2, Ar H), 7.14 (m, 1, Ar H).
9 <sup>e</sup>	Bp 87-88° (0.5 mm); ir 758 (w), 816 (s), 887 (m), and 895 (w) appears as a shoulder on the 887 cm <sup>-1</sup> peak; mass spectrum M = 244, 201 (M - 43) loss of C <sub>3</sub> group(s); nmr δ 0.71, 0.82, 0.91, 1.01 (the four preceding peaks account for 18 protons), 1.44 and 1.54 (2 protons), 2.03 (m, 2 protons), 2.22 (s, 3, Ar CH <sub>3</sub> ), 6.73-7.16 (m, 3, Ar H). <i>Anal.</i> Calcd for C <sub>18</sub> H <sub>28</sub> : C, 88.45; H, 11.55. Found: C, 88.24; H, 11.56.	19 <sup>i</sup> or 20 <sup>i</sup>	Ir 825 (s) and 881 cm <sup>-1</sup> (m); nmr δ 1.14 [3, half of the doublet from CH(CH <sub>3</sub> ) <sub>2</sub> ], 1.27 [s, 12, C(CH <sub>3</sub> ) <sub>3</sub> and three protons from CH(CH <sub>3</sub> ) <sub>2</sub> ], 2.29 (s, 3, Ar CH <sub>3</sub> ), 3.07 (m, 1, Ar CH), 7.03 (m, 3, Ar H).
10 <sup>a</sup>	Mp 40-41° (lit. <sup>7a</sup> 37-38°, 40°); ir agrees with published <sup>2a</sup> spectrum; nmr δ 1.03, 1.30, 1.62 (three s, 3 protons each, CH <sub>3</sub> β to the aromatic ring), 2.21 (center of partially hidden AB quartet, 2, CH <sub>2</sub> ), 2.21, 2.28 (two s, 3 protons each, Ar CH <sub>3</sub> ), and 6.71-7.10 (m, 7, Ar H). <sup>o</sup>	21	Mass spectrum M = 246, 175 (M - 71) loss of C <sub>5</sub> group.
12 <sup>f</sup>	Ir 711 (s), 815 (w), 857 (s), and 882 cm <sup>-1</sup> (w); mass spectrum M = 190, 175 (M - 15) loss of methyl group (mass spectral analysis shows a second component with M = 188); intensity ratio of 190 to 188 is 10:1; nmr δ 1.17 [3 H, one-	22	Mass spectrum M = 246, 175 (M - 71) loss of C <sub>5</sub> group.
		23	Mass spectrum M = 246, 175 (M - 71) loss of C <sub>5</sub> group.
		24	Mass spectrum (mixture) M = 218, 246, 260; intensity ratio ca. 3.3:2.2:1.0.
		25	Mass spectrum M = 302, 175 (M - 127) loss of C <sub>9</sub> group.
		26	Mass spectrum M = 302, 175 (M - 127) loss of C <sub>9</sub> group.

TABLE II  
(Continued)

27 <sup>i</sup>	Ir 729 (m), 746 (s), and 788 cm <sup>-1</sup> (s); nmr $\delta$ 1.01 [s, 9, C(CH <sub>3</sub> ) <sub>3</sub> ], 1.21 (s, 3, geminate CH <sub>3</sub> ), 1.30 (s, 3, geminate CH <sub>3</sub> ), 1.47 (s, 3, CH <sub>3</sub> geminate to the neopentyl group), 1.50–2.50 (m, 4, two overlapping AB pattern groups), 2.39 (s, 3, Ar CH <sub>3</sub> ), 6.65–7.0 (m, 3, Ar H); mass spectrum M = 244.2192 (calcd for C <sub>13</sub> H <sub>28</sub> , 244.2191), 229 (M – 15) loss of methyl group, 187 (M – 57) loss of C <sub>4</sub> , 173 (M – 71) loss of C <sub>5</sub> .	(m, 3, Ar H) (integration values are given only when the contaminants did not interfere). This hydrocarbon is thought to be 1-sec-butyl-1,3,3,6-tetramethylindan.
A <sup>a</sup>	Ir spectrum was identical with that of a known sample of 1-isopropyl-1,3,3,6-tetramethylindan; <sup>m</sup> mass spectrum M = 216, 173 (M – 43) loss of C <sub>3</sub> group, in agreement with this structure.	C Mass spectrum = 258, 173 (M – 85) loss of C <sub>6</sub> group(s).
B <sup>a</sup>	Ir 814 (s) and 878 cm <sup>-1</sup> (m); mass spectrum M = 230, 173 (M – 57) loss of C <sub>4</sub> group (s); nmr $\delta$ 0.75–1.25 (m), 1.30 (s, 9, CH <sub>3</sub> $\beta$ to benzene ring), 1.34–2.25 (m), 2.29 (s, 3, Ar CH <sub>3</sub> ), 6.75–6.95	D Mass spectrum M = 300, 229 (M – 71) loss of C <sub>6</sub> group(s).
		E Mass spectrum M = 300, 201 (M – 99) loss of C <sub>7</sub> group(s).
		F <sup>e</sup> Ir 655 (w), 765 (s), 790 (m), 815 (w), and 870 cm <sup>-1</sup> (s); mass spectrum M = 258, 229 (M – 29) and 173 (M – 85) loss of ethyl and C <sub>6</sub> groups, respectively.
		G <sup>e</sup> Ir 653 (m), 769 (m), and 870 cm <sup>-1</sup> (s); mass spectrum M = 258, 243 (M – 15) and 229 (M – 29) loss of methyl and ethyl groups.

Preferred starting materials for synthesis of the above hydrocarbons: <sup>a</sup> *p*-cymene and isobutylene; <sup>b</sup> *p*-cymene and 2-methyl-2-butene; <sup>c</sup> *p*-cymene and 2,3-dimethyl-1-butene; <sup>d</sup> *p*-cymene and diisobutylene; <sup>e</sup> *p*-cymene and 2,3,4-trimethyl-1-pentene; <sup>f</sup> *m*-cymene and isobutylene; <sup>g</sup> *m*-cymene and 2-methyl-2-butene; <sup>h</sup> *m*-cymene and diisobutylene; <sup>i</sup> *o*-cymene and isobutylene; <sup>j</sup>  $\alpha$ ,*m*-dimethylstyrene and diisobutylene. <sup>k</sup> M. J. Schlatter, *Amer. Chem. Soc., Div. Petrol. Chem., Prepr.*, 1, no. 2, 77 (1956). <sup>l</sup> D. B. Spoelstra, S. H. Weber, and R. J. C. Kleipool, *Recl. Trav. Chim. Pays-Bas*, 82, 1100 (1963). <sup>m</sup> We thank Mr. T. F. Wood, Givaudan Corp., for kindly supplying reference samples of 6 and 1-isopropyl-1,3,3,6-tetramethylindan. <sup>n</sup> We thank M. C. Hamming, Analytical Research Section, Continental Oil Co., for the mass spectrum of 7. <sup>o</sup> We thank Dr. R. J. Lee and Amoco Chemicals Corp. for a generous sample of *m*-cymene and hydrocarbon 10.

to minimize the polyisobutylene formation. Comparison of run 6a with run 7 shows that while the yield of 2 is doubled in comparing methanesulfonic acid to Amberlyst-15, the ratio 8:2 is increased in the latter reaction. This shows that even at a higher temperature, Amberlyst-15 gives more intact cyclialkylation products than methanesulfonic acid.

Aluminum chloride (run 9a) at 5° gave essentially no products resulting from cleavage of diisobutylene. A trace of 2 and a large yield of 8 was obtained. When the reaction temperature was increased to 70° (run 9b), indan 2 was formed, but 8 was still the major product. With triisobutylene and aluminum chloride (run 11), a large amount of 8, but no significant amounts of higher molecular-weight cyclialkylation products, was observed.

The ir bands in the regions 815 and 880 cm<sup>-1</sup> corresponding to 1,2,4 trisubstitution on a benzene ring were observed.<sup>8</sup> There were no significant deviations due to structure, e.g., 2 (a 5-methylindan), 3 (a trialkylbenzene), and 9 (a 6-methyltetralin) gave the appropriate bands. In addition, correlations with model hydrocarbons were made as follows: 7 at 880 and 887 cm<sup>-1</sup> with 1,2,4,5-tetramethylbenzene (CS<sub>2</sub>); 12 at 711 and 857 cm<sup>-1</sup> and 14 at 712 and 857 cm<sup>-1</sup> with 1,3,5-trimethylbenzene (neat liquids); 15 at 655, 770, and 872 cm<sup>-1</sup> and 17 at 653, 774, and 870 cm<sup>-1</sup> with an authentic sample of 6-*tert*-butyl-4-ethyl-1,1-dimethylindan (1,2,3,5 tetrasubstitution) at 647, 768, and 872 cm<sup>-1</sup>; and 27 at 729, 764, and 788 cm<sup>-1</sup> with 1,2,3-trimethylbenzene (see Table II).

### Experimental Section<sup>9</sup>

Samples for instrumental analyses were obtained by preparative gas-liquid chromatography (glc) with an F & M Model 700 gas

(8) R. T. Conley, "Infrared Spectroscopy," Allyn & Bacon, Boston, Mass., 1966.

(9) Mass spectra were obtained with a Consolidated Electrodynamics Model 21-110B high-resolution mass spectrometer which was operated under low-resolution conditions using electron energy of 70 eV. Nmr spectra were obtained with a Varian HR-60 and A-60 spectrometers. Peak positions

chromatograph equipped with dual thermal conductivity detectors. A 13 ft  $\times$  0.25 in. column containing 5% silicone rubber UCW-98 on 80–100 mesh, dimethyldichlorosilane- (DMCS) treated, acid-washed Chromosorb G was used with helium as carrier gas.

Hydrocarbons 2 and 8 were purified by preparative glc using an F & M Model 776 gas chromatograph fitted with hydrogen flame detectors. An 8 ft  $\times$  4 in. column containing Carbowax 20M on 80–100 mesh, acid-washed Gas Pac was used with nitrogen as carrier gas.

Qualitative glc analyses were obtained with an F & M Model 5754B apparatus fitted with dual thermal conductivity and hydrogen flame detectors using helium as carrier gas. A 12 ft  $\times$  1/8 in. column containing 10% silicone rubber UCW-98 on 80–100 mesh, DMCS-treated, acid-washed Chromosorb W was used. These data were generally obtained by temperature programming from 130 to 300° at 4°/min.

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

#### Acid-Catalyzed Reactions of *p*-Cymene and Isobutylene.

**Run 1b.**—A 250-ml three-necked Morton flask was equipped with a gas inlet tube, a magnetic bar, and a thermometer and cooled in an ice bath. In the flask were placed 33.5 g (0.25 mol) of *p*-cymene and 19.0 g of H<sub>2</sub>SO<sub>4</sub>. After cooling the reaction vessel to 5°, isobutylene was bubbled into the stirred and cooled reaction mixture for 3 hr at a rate which kept the temperature 10°. The H<sub>2</sub>SO<sub>4</sub> layer was separated and the organic layer was poured over solid Na<sub>2</sub>CO<sub>3</sub>, filtered, washed with saturated Na<sub>2</sub>CO<sub>3</sub> solution, and dried (MgSO<sub>4</sub>) to give 71.4 g of reaction products.

**Hydrogen Fluoride Catalyzed Reaction of *p*-Cymene with Isobutylene.** **Run 4.**—The polyethylene equipment consisted of a 500-ml wide-mouth bottle fitted with a three-holed lid having a sintered gas dispersion tube, a gas exit tube, and a stainless steel sheathed thermocouple. 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 temperature below 10°.

The reaction mixture was poured over ice, and a solution of 40% NaOH was added. The organic layer was separated and dried (CaCl<sub>2</sub>) yielding 165 g of reaction products. The aqueous layer was extracted twice with ether, and after drying (CaCl<sub>2</sub>),

are reported as  $\delta$  parts per million (ppm) downfield from internal tetramethylsilane standard in carbon tetrachloride solvent. Ir spectra were obtained with a Beckman IR-5A spectrometer as films on sodium chloride plates unless otherwise stated. Melting points were measured in degrees centigrade, taken in capillary melting point tubes using a Thomas-Hoover apparatus and are corrected.

the extract was concentrated to yield 10 g more of organic material.

The other reactions catalyzed with HF were run in the same apparatus, with the olefin being added from a polyethylene dropping funnel instead of the gas inlet tube.

#### Acid-Catalyzed Reactions of *p*-Cymene with Diisobutylene.

**Run 5a.**—This run was like run 1b except that the olefin (56 g, 0.50 mol) was added from a pressure-equalizing funnel over a 1-hr period. The yield of products was 77.6 g. The above description, modified as given in Table I, is typical of all the reactions using di-, tri-, and tetraisobutylene.

**Preparation of 1,3,3,6-Tetramethyl-1-neopentylindan (8) from *p*-Cymene and Diisobutylene.** **Run 5c.**—In a 5-l. Morton flask equipped with a 2-l. dropping funnel and a thermocouple were placed 1100 g (8.2 mol) of *p*-cymene. This was cooled to 5° and sulfuric acid, 72 g, was introduced. Diisobutylene, 1480 g (13.2 mol), was added dropwise to the reaction mixture, which was stirred with a large Vibromixer. The temperature was kept below 10° throughout the 2.5 hr required to add the olefin and during the additional 3 hr the mixture was stirred. The mixture was worked up as in run 1b. Glc analysis showed a 43% yield of 8.

A distillation fraction [bp 82–88° (0.5 mm)] from run 5c in which 8 was concentrated was subjected to preparative glc at 150° using the apparatus previously described. The material collected was distilled and then passed through a column of silica gel and acidic and basic alumina to give 92 g of 8 (see Table II).

**Registry No.**—1, 99-87-6; 2, 81-03-8; 3, 29577-13-7; 4, 29641-87-0; 5, 4834-28-0; 7, 29577-15-9; 8, 29577-16-0; 9, 29577-17-1; 10, 1153-36-2; 12, 29577-19-3; 13, 29577-20-6; 14, 29577-21-7; 15, 29577-22-8; 16, 29641-88-1; 17, 29577-23-9; 19, 29577-24-0; 20, 29577-25-1; isobutylene, 115-11-7; *o*-cymene, 527-84-4; *m*-cymene, 535-77-3.

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## Acid-Catalyzed Reactions of Propioloophenone and 2-Ethynyl-2-phenyl-1,3-dioxolane with Ethylene Glycol<sup>1</sup>

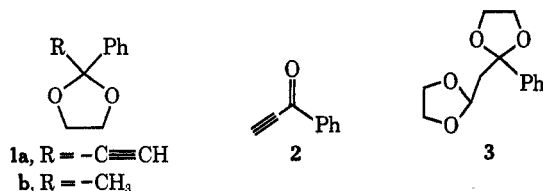
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An attempt to prepare 2-ethynyl-2-phenyl-1,3-dioxolane (1a) from propioloophenone (2), *p*-toluenesulfonic acid, and excess ethylene glycol resulted instead in the formation of 2-phenyl-2,2'-methylenebis-1,3-dioxolane (3) and/or 2-methyl-2-phenyl-1,3-dioxolane (1b). With a small amount of *p*-toluenesulfonic acid the former product predominated, but with equimolar propioloophenone and acid only the latter was formed. It was found that 3 could be converted to 1b with equimolar *p*-toluenesulfonic acid. A synthesis of 1a from 2-(1-bromoethyl)-2-phenyl-1,3-dioxolane (5) is described. Compound 1a was found to be stable to the conditions which converted 2 to 3. This observation and certain spectroscopic evidence indicate that 3 is formed from 2 *via* 1-oxo-1-phenyl-3-(1,3-dioxolane)propane (4).

An attempt to prepare 2-ethynyl-2-phenyl-1,3-dioxolane (1a) from propioloophenone (2), a small amount of anhydrous *p*-toluenesulfonic acid, and excess ethylene glycol in refluxing benzene with constant removal of benzene-water azeotrope yielded instead 2-phenyl-2,2'-methylenebis-1,3-dioxolane (3) (84%). The acetylenic proton of 1a was not observed in the nmr spectrum of the crude product from this reaction, but this spectrum did exhibit a singlet with a chemical shift identical with that of the methyl group of 2-methyl-2-phenyl-1,3-dioxolane (1b). Integration revealed that the 3:1b ratio was 13:1. When an equivalent



amount of 2 and anhydrous *p*-toluenesulfonic acid and excess ethylene glycol were similarly reacted, 1b was the only product that could be isolated (52%). The nmr spectrum of the crude product from this reaction revealed the absence of 1a and 3. Finally, when an equivalent amount of 3 and anhydrous *p*-toluenesulfonic acid and excess ethylene glycol were similarly re-

acted, 1b again was the only product that could be isolated (35%).

When equivalent amounts of 2 and ethylene glycol and a catalytic quantity of anhydrous *p*-toluenesulfonic acid were refluxed in benzene, the product was a multicomponent oil. Its nmr spectrum contained a large multiplet, the chemical shift of which was roughly the same as that previously found for the OCH<sub>2</sub>CH<sub>2</sub>O systems of 3 and 1b. This spectrum also contained the characteristic doublet ( $\tau$  7.79) and triplet ( $\tau$  5.18) of 3, a second doublet ( $\tau$  6.76) and triplet ( $\tau$  4.67), and a signal in the aromatic region. Two components, one an oil and the other a solid, resulted when this mixture was subjected to plc. Nmr analysis revealed the solid to be 2. It was not detected in the nmr of the original oil since its acetylenic proton falls in the same region as the dioxolane ring protons. The new oil exhibited a carbonyl absorption at 5.84  $\mu$ . Further attempts to separate it by plc resulted in small amounts of pure 3, but the carbonyl-containing substituent could not be isolated. The nmr of this oil again exhibited a pair of doublets and a pair of triplets, and aromatic plus dioxolane ring protons. The areas under the signals due to the aromatic and dioxolane ring protons were greater than would be predicted were they to have arisen from 3 alone, but what one would predict if the second component possessed one phenyl group and one dioxolane ring. We feel the spectroscopic evidence strongly implies that the third component was 1-oxo-1-phenyl-3-

(1) Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., April 1971.