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Acid-Catalyzed Reactions of *p*-Alkyl- and *p*-Cycloalkyltoluenes with Olefins. Hydride Transfer Accompanying Cyclialkylation

ASHER ELGAVI*,[1] AND HERMAN PINES†,[2]

**Department of Chemistry, Bar Ilan University, Ramat Gan, Israel, and † The Ipatieff Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201*

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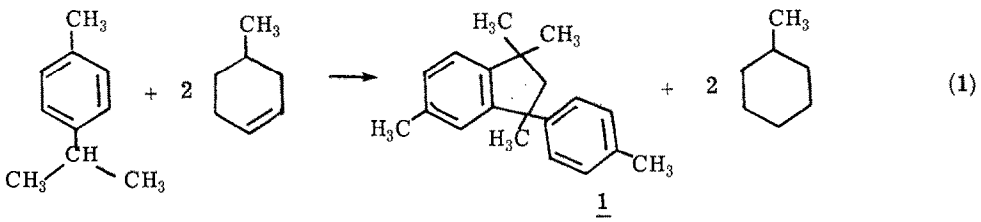
The acid-catalyzed reactions have been studied using arenes such as *p*-cymene, *p*-sec-butylbenzene, and *p*-cyclopentyl- and *p*-cyclohexyltoluene with olefins such as isobutylene, 1-methylcyclopentene, and 1- and 4-methylcyclohexene in the presence of hydrogen fluoride and 96% sulfuric acid as catalysts. The main reaction taking place was cyclialkylation which was accompanied by a hydride transfer from a tertiary benzylic hydrogen to a cation of the olefin. The cyclialkylation was of two types: type 1 in which the product resulted from dehydrodimerization of the aromatic hydrocarbon used in the reaction and type 2 in which the product was derived from the interaction between the aromatic hydrocarbon and the olefin. In the cyclialkylation of *p*-cymene and *p*-sec-butyltoluene with isobutylene, the ratio of products formed via type 2 reaction as compared to type 1 was 25.7 and 32.3, respectively, when sulfuric acid was used as catalyst. In the presence of hydrogen fluoride the ratio of type 2 to type 1 ranged from 2.1 to 5.6 when *p*-cymene was used as the aromatic and 4.2 when *p*-sec-butyltoluene was employed. In the case of *p*-cycloalkyltoluenes with isobutylene, only cyclialkylation of type 2 took place. Type 1 products were the major components resulting from the cyclialkylation of *p*-cymene and *p*-sec-butyltoluene with methylcyclohexenes.

INTRODUCTION

Cyclialkylation reactions accompanied by a hydride transfer was first reported by one of us almost three decades ago (*1–3*). It was observed that *para* and *meta* substituted alkyltoluenes having a tertiary benzylic hydrogen may undergo a hydride abstraction by a tertiary cation generated from an olefin. The identified products of reaction resulting from *p*-cymene and methylcyclohexene catalyzed by either 96% sulfuric acid or anhydrous hydrogen fluoride were methylcyclohexane and 1,1,3,5-tetramethyl-3-*p*-tolylindan, **1**.[3]



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[1] Present address: Shenkar College of Fashion and Textile Technology, Ramat Gan, Israel.
[2] To whom requests for reprints should be sent.
[3] Numbers in boldface correspond to underlined structure numbers in the schemes.

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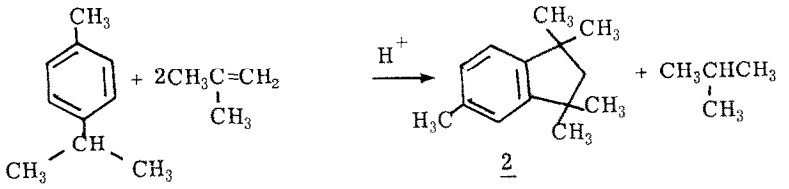
Subsequently it was shown that in the reaction of *p*-cymene with isobutylene the principal product of the reaction was 1,1,3,3,5-pentamethylindan, **2**, formed from the cyclialkylation of the *p*-cymene with the alkene and accompanied by hydride transfer (*4*).



(2)

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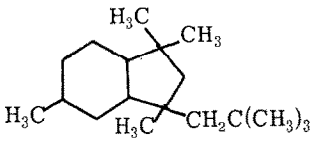
Branched-chain alcohols which can generate a tertiary cation *in situ* can undergo a similar reaction (*5–7*).

A thorough review of the cyclialkylation of aromatic hydrocarbons involving hydride transfer was published by Barclay (*8*).

p-Dialkylbenzenes which contain a secondary instead of a tertiary benzylic hydrogen undergo a hydride transfer reaction with tertiary olefins, but instead of cyclialkylation the product of reaction consisted of diarylalkanes (*9, 10*).

A detailed study of conditions and products of cyclialkylation of *p*-cymene with isobutylene and its dimers and trimers has recently been reported (*11*). These authors have confirmed that the main product of reaction of the tertiary alkenes with *p*-cymene in the presence of either sulfuric acid or hydrogen fluoride catalysts consisted of pentamethylindan, **2**, amounting to 99.3% based on reacted *p*-cymene. The other minor hydrocarbons present, less than 0.4% each, consisted of cyclialkylated compounds **1**, **3**, and **4**.



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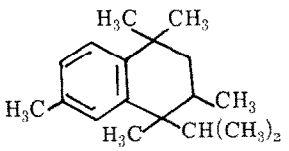

(3)

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Since the two types of cyclialkylation reactions represented by Eqs. (1) and (2), respectively, depend on the olefins used, it was decided to investigate the effect of the structure of olefins upon the course of cyclialkylation. Unlike branched-chain olefins, the interaction of straight-chain olefins and of cyclohexene with *p*-cymene in the presence of acids results in the formation of sec-alkyl- and cyclohexyl-*p*-cymene, respectively.

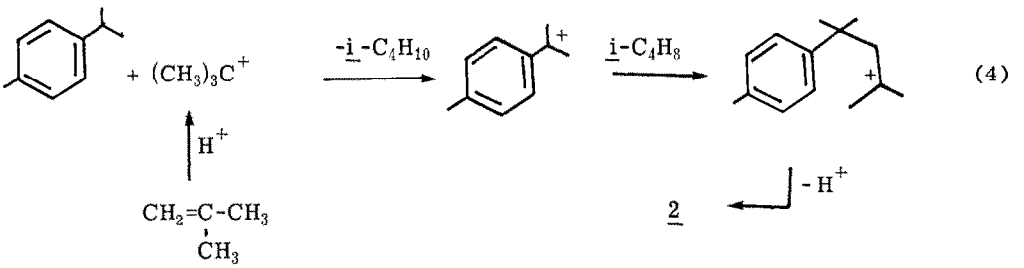
The olefins used in this study were isobutylene, 1-methylcyclopentene, and 4-methylcyclohexene. The aromatic hydrocarbons employed were *p*-cymene and *p*-sec-butyl-, *p*-cyclopentyl-, and *p*-cyclohexyltoluene. The experiments with *p*-cymene and *p*-sec-butyltoluene together with isobutylene were made using hydrogen fluoride and sulfuric acid as catalysts. Both catalysts gave basically the same results. Since, however, the reaction in the presence of hydrogen fluoride was cleaner and the product less complex than in the presence of sulfuric acid, the remainder of the experiments were made with anhydrous hydrogen fluoride as catalyst.

RESULTS

p-Cymene–Isobutylene

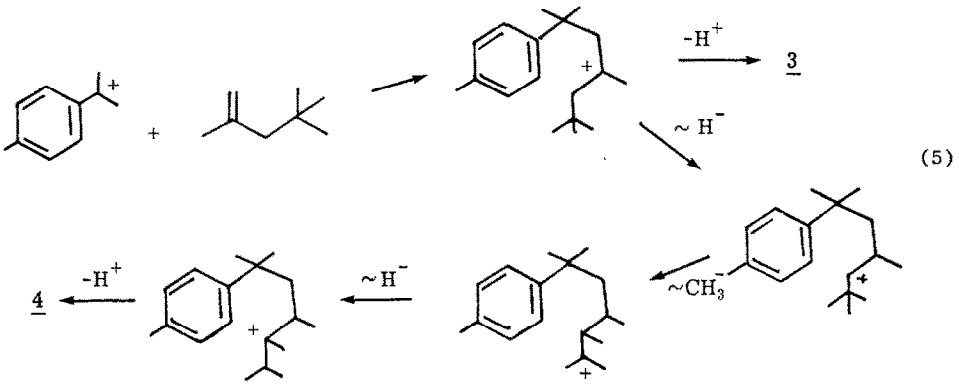
The experiments were made in plastic polyethylene bottles provided with a magnetic stirrer and cooled by an ice bath. The product of the reaction was poured over ice, washed with aqueous potassium carbonate and water, dried, and analyzed. For quantitative composition of the product by glc a measured amount of tert-butylbenzene as an internal standard was added to the organic material. The structure of the individual compounds was determined by NMR and ms.

The experimental conditions and the composition of products obtained are summarized in Table 1. The formation of the cyclialkylated compound **2** can be explained by a mechanism similar to the one proposed previously and in which the first step in the reaction was the transfer of a hydride from the isopropyl group of *p*-cymene to the tertiary butyl cation (*1*).



(4)

The formation of comp ound **3** was explained by the cyclialkylation of *p*-cymene with 2,4,4-trimethyl-1-pentene formed by the dimerization of isobutylene in the presence of the acid catalysts (*11*). Compound **4** is formed by a similar mechanism, however, the cyclialkylation may be accompanied by a skeletal rearrangement involving hydride and methide migrations.



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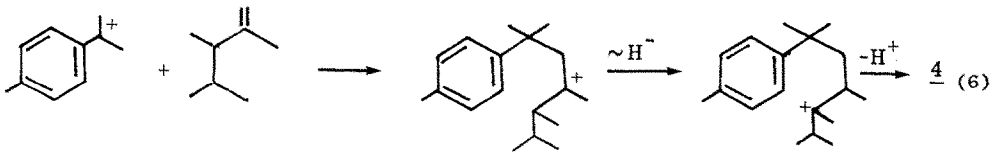
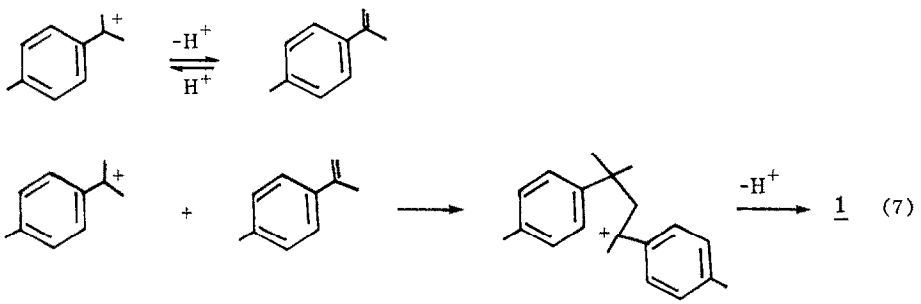
Another route for the formation of compound **4** was suggested as occurring from 2,2,4-trimethylpentenes through skeletal rearrangement to 2,3,4-trimethylpentenes (*12*).



(6)

Compound **1** was produced by a mechanism proposed previously (*1*) and supported recently (*13*) in which *p*-cymyl cation is converted by a proton transfer into *p*-isopropenyltoluene which then reacts with another *p*-cymyl cation to produce a cation adduct. The latter by a subsequent cyclialkylation accompanied by a transfer of a proton to an olefin produces compound **1**.



(7)

The ratio of the cyclialkylated products, **2** to **4**, resulting from the interaction of *p*-cymene with isobutylene or its dimer to the cyclialkylated compound **1** derived from *p*-cymene was in the range of 2.1 to 5.6/1. In the case of sulfuric acid as catalyst the ratio was 25.6/1.

The cyclialkylation reaction between *p*-cymene and isobutylene was also made using $BF_3 \cdot H_3PO_4$ complex as catalyst. The reaction was carried out by bubbling isobutylene into a stirred mixture of *p*-cymene and the catalyst at 50 and 90°C.

At 50°C 34% of *p*-cymene charged underwent reaction and the product obtained consisted of 82% of compound **2** and 11% of **1**. The remainder was composed of small amounts of product consisting of at least 12 compounds.

At 90°C the conversion of *p*-cymene was 38% and the product was composed of 48% of **2** and 32% of **1**, and the remaining product consisted of 14 minor components.

The above results indicate that the temperature at which the reaction is carried out has an effect on the course of the cyclialkylation. At the lower temperature the cyclialkylation of *p*-cymene with isobutylene is more favorable than the dehydrodimerization of *p*-cymene to form compound **1**. At higher temperatures the selectivity of the cyclialkylation reaction is greatly affected.

p-sec-Butyltoluene–Isobutylene

The interaction of the title compounds was made in the presence of 98% sulfuric acid and anhydrous hydrogen fluoride as catalysts. The composition of the cyclialkylated hydrocarbons produced from the reaction is given in Table 2. They were composed of products of condensation of isobutylene and its dimer with *p*-sec-butyltoluene to form 1,1,3,6-tetramethyl-3-ethylindan, **5**, and 1,3,5-trimethyl-1-ethyl-3-neopentylindan, **6**, and of dehydrodimers of butyltoluene, namely, 1,5-dimethyl-1,3-diethyl-3-*p*-tolylindan, **7**, and of 1,2,3,5-tetramethyl-1-ethyl-3-*p*-tolylindan, **8**.

Compounds **7** and **8** were formed from the interaction of *p*-tolyl-sec-butyl cation with the generated olefins, according to the mechanisms given for the formation of compound **1**.

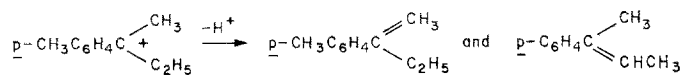


TABLE 1

Reaction of Isobutylene with *p*-Cymene

Expt	*p*-Cymene [g (mol)]	*i*-C_4H_8 [g (mol)]	*p*-Cymene/ *i*-C_4H_8 (molar ratio)	*p*-Cymene reacted (%)	Composition of cyclialkylated product (%)[a]				Molal ratio of compounds 2 + 3 + 4/1
					2	3	4	1	
1[b]	26.8 (0.2)	9 (0.16)	1/0.8	47	71.7	6.6		16	4.9
2[b]	26.8 (0.2)	2.0 (0.36)	1/1.8	53.3	48.3	6.0	6.0	28.6	2.1
3[b]	26.8 (0.2)	23.2 (0.4)	1/2.0	96.2	48.9	7.5	3.2	27	2.2
4[b]	13.4 (0.1)	32 (0.57)	1/5.7	99.1	47.7	2.4	4.3	8.6	5.6
5[c]	6.7 (0.05)	Large excess		83	66.3	12.6	3.5	3.1	25.7

[a] Isobutane was found in the reaction product, but quantitative data are not available.
[b] Catalyst: 15 g of HF.
[c] Catalyst: 3.8 g of 96% H_2SO_4.

As in the case of *p*-cymene, sulfuric acid catalyzes almost exclusively the condensation of *p*-sec-butyltoluene with isobutylene to form cyclialkylated compounds **5** and **6**. Hydrogen fluoride on the other hand produces also dehydrodimers of sec-butyltoluene, namely, **7** and **8**, the concentration of which in the cyclialkylated product amounted to 19.1%.

In order to demonstrate that the dehydrodimers of *p*-sec-butyltoluene are the products of dimerization of the corresponding olefins both 2-*p*-tolyl-1-butene and a mixture of 2-*p*-tolyl-1- and 2-butene were treated with hydrogen fluoride at 0°C. From the 1-butene compound the main dimer had the structure of **7** with an admixture of a compound of similar molecular weight and probably a stereoisomer of **7**. A mixture of the two olefins produced dimer **8** as the main component.

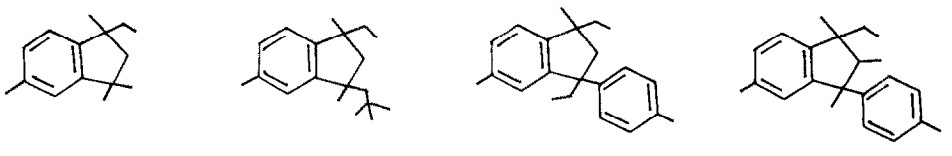
In the presence of sulfuric acid the cyclialkylated product contained 25.6% of a neopentylindan, compound **6**, as against 9.1% in the presence of hydrogen fluoride. The formation of **6** is the result of

TABLE 2

Reaction of Isobutylene with *p*-sec-Butyltoluene[a]

Catalyst (g)	Organic material recovered (g)	*p*-sec-Butyltoluene reacted (%)	Composition of cyclialkylated product (%)[b]				Ratio 5 + 6/7 + 8
			5	6	7	8	
H_2SO_4 (4.3)	7.6	55.9	71.4	25.6	—	3.0	32.3
HF (3.0)	9.0	56.1	71.7	9.1	7.8	11.3	4.2

[a] In each experiment 7.4 g (0.05 *M*) of *p*-sec-butyltoluene and 4.3 g (0.077 *M*) of isobutylene were used.
[b]



(8)

5 6 7 8

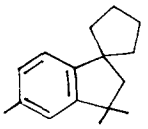
TABLE 3

Reaction of Isobutylene with *p*-Cyclopentyltoluene[a]

Catalyst (g)	Isobutylene [g (mol)]	Organic material recovered (g)	*p*-Cyclopentyltoluene reacted (%)	Composition of cyclialkylated product (%)[b]		
				9	10	11
H_2SO_4 (3.0)	Large excess	13[c]	81.5	55.6	33.5[d]	10.8
HF (5.0)	3.7 (0.07)	6.6	[e]	23.3	60.7[d]	3.9

[a] *p*-Cyclopentyltoluene used in each experiment 5.3 g (0.033 mol).

[b]



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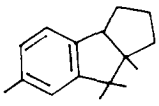

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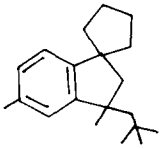

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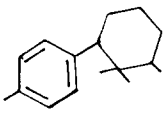


12

(9)

[c] Organic layer contained 1.31 g of diisobutylene.

[d] Contains small amount of compound of M^+ 216, to which structure of 1,2,2-trimethyl-3-*p*-tolylcyclohexane, **12**, was assigned.

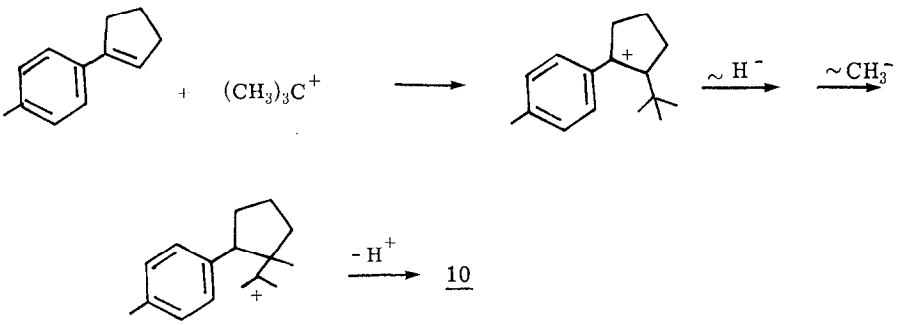
[e] Not determined.

interaction of the sec-butyltoluene with 2,4,4-trimethyl-1-pentene, a dimer of isobutylene.

p-Cyclopentyltoluene–Isobutylene

Cyclialkylation of *p*-cyclopentyltoluene with isobutylene was carried out in the presence of both 96% sulfuric acid and hydrogen fluoride (Table 3). Three cyclialkylated compounds having structures **9**, **10**, and **11** were separated and identified by means of NMR and ms. Compounds **9** (1,1,6-trimethylspiro[cyclopentane-3,3′-indan]) and **11** (1,6-dimethyl-1-neopentylspiro[cyclopentane-3,3′-indan]) are products from the cyclialkylation of *p*-cyclopentyltoluene with isobutylene and 2,4,4-trimethyl-1-pentene, respectively.

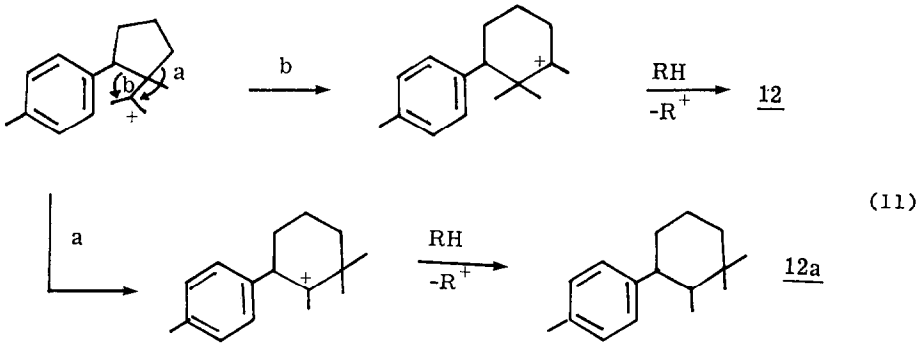
The formation of compound **10**, 3a,4,4,6-tetramethyl-1,2,3,3a,8,8a-hexahydrocyclopent[*a*]indene, could be explained by the initial addition of tertbutyl cation to the generated 1-*p*-tolylcyclopentene, followed by methide migration and cyclialkylation.



(10)

This formation of **10** seems to be the first example whereby an alkyl cation from the original olefin used in the reaction adds to the *p*-tolyl olefin which is generated in the reaction.

According to NMR evidence structure **12**, 1,2,2-trimethyl-3-*p*-tolylcyclohexane, was assigned to the butylated *p*-tolylcyclopentane with mass of 216. This compound was most probably formed from cation **10a** through ring expansion followed by hydride abstraction.

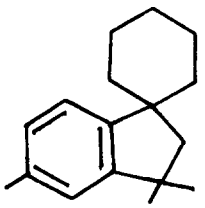


(11)

The nmr spectra indicate the presence of some minor material with M^+ 216 to which structure **12a** was assigned. Ring expansion of a cation from a five- to a six-membered ring in the presence of acids is a common occurrence in hydrocarbon chemistry.

p-Cyclohexyltoluene–Isobutylene

The title compounds were submitted to a cyclialkylation in the presence of hydrogen fluoride under experimental conditions described in Table 3. The cyclialkylated product **13**, 1,1,6-trimethyl-3-spiro[cyclohexane]indan, was the major product identified. It amounted to 75.2% of the 48.3% of *p*-cyclohexyltoluene reacted.

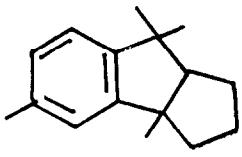


13

p-Cymene, p-sec-Butyltoluene, and p-Cyclopentyltoluene with 1-Methylcyclopentene

The title aromatic hydrocarbons were submitted to a reaction with 1-methylcyclopentene in the presence of hydrogen fluoride as catalyst. In each experiment was used 0.02 mol of the aromatics, 0.04 mol of the olefin, and 2 g of the catalyst.

In the reaction of *p*-cymene with 1-methylcyclopentene it was found that 9.4% of the olefin was converted to methylcyclopentane and 36.5% to two hydrodimers. The hydrodimers with a ratio of 1.0 to 1.78 had a relative retention time of 1334 and 1428 vs tert-butylbenzene of 671 used as an internal standard. The cyclialkylated product **14**, 3a,5,8,8-tetramethyl-1,2,3,3a,8,8a-hexahydrocyclopent-[*a*]indene, was composed of a mixture of *cis* and *trans* isomers. Of the 8.5% of *p*-cymene which underwent reaction the yield of **14** was 84%.



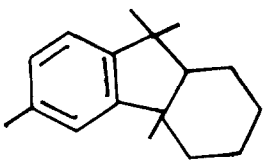
14

p-sec-Butyltoluene on reaction with 1-methylcyclopentene produced mainly dehydrodimers of methylcyclopentene. According to ms and NMR the latter were identical with the dehydrodimers formed in the presence of *p*-cymene. About 97% of the *p*-sec-butyltoluene employed in the reaction was recovered.

1-Methylcyclopentene likewise produced dehydrodimers when allowed to react in the presence of *p*-cyclopentyltoluene and hydrogen fluoride. About 89% of the aromatic used in the reaction was recovered. Some small amounts of product with high retention times were also recovered but owing to their low yields were not examined further.

p-Cymene-1-methylcyclohexene

The cyclialkylation experiments using the title hydrocarbons were first made by one of us in 1948 (*1*) when the analytical tools for separation and identification of products were less refined than at the present. The cyclialkylation reaction was thus repeated at 0 to 7°C using 96% sulfuric acid as the catalyst and a molal ratio of aromatics to olefins of 2:1. The product was separated on a 4-m column composed of 5% SE-30 on Chromosorb G, 60 to 80 mesh, and analyzed by ms and NMR. It consisted of 19.6% of compound **15**, 4a,6,9,9-tetramethyl-1,2,3,4,4a,9,9a-heptahydrocyclohexa[*a*]indene, 71.7% of compound **1**, 4.7% of an unidentified compound, and 4.6% of eight minor products.



15

Results similar to those reported for sulfuric acid were obtained when using hydrogen fluoride as catalyst and a ratio of *p*-cymene to methylcyclohexene of 2 (*1*). The weight composition of compound **1** was 84.1% and that of **15**, 15.9%. When the ratio of *p*-cymene to 1-methylcyclohexene used was changed to 1:1.5 (0.05 *M*:0.075 *M*), the distribution of the products of reaction altered considerably. The cyclialkylated product according to glc was composed of 84% of compound **15** and only 16% of the dehydrodimer of *p*-cymene compound **1**.

In one particular experiment 9.6 g (0.1 mol) of 1-methylcyclohexene and 0.05 mol of *p*-cymene were allowed to react under stirring in the presence of 2 g of hydrogen fluoride at 0 to 6°C. After washing and drying, the recovered organic layer, 15.2 g, was analyzed by glc.

Retention time	Area (%)	Product
138	27.6	Methylcyclohexane
352	19.4	*p*-Cymene
1057	1.8	Dimer of methylcyclohexene (?)
1179	1.7	
1212	2.5	
1751	27.2	Compound **15**
2205	18.9	Compound **1**

All of the methylcyclohexene was consumed. The cyclialkylated product was composed of 59% of compound **15** and 41% of **1**.

p-sec-Butyltoluene–Methylcyclohexenes

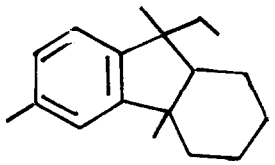
p-sec-Butyltoluene, 0.02 *M*, was allowed to react with 1- and 4-methylcyclohexene in the presence of hydrogen fluoride as catalyst (Table 4). The reaction proceeded according to Eqs. (1) and (2), resulting mainly in the dehydrodimerization of *p*-sec-butylbenzene with the formation of compounds **7** and **8**, the latter being the major product. The interaction of 1-methylcyclohexene with the title aromatic hydrocarbon resulted in the formation of compound **16**, 4a,6,9-trimethyl-9-ethyl-1,2,3,4,4a,9,9a-heptahydrocyclohexa[*a*]indene.

TABLE 4

Reaction of 1- and 4-Methylcyclohexene with *p*-sec-Butyltoluene

HF (g)	*x*-Methyl cyclohexene (mol)	*p*-sec-Butyltoluene		Composition of cyclialkylated product (%)			Molal ratio 16/(7 + 8)
		Charged (mol)	Reacted (%)	16[a]	7	8	
2	1- (0.04)[b]	0.02	51.4	37.2	16.0	46.8	0.59
2.5	4- (0.06)[c]	0.03	33.6	31.9	23.2	44.9	0.47

[a]



16

[b] Of the 1-methylcyclohexene charged 34.4% was converted to methylcyclohexane and 9% to hydrodimers.
[c] Of the 4-methylcyclohexene charged 19% was converted to methylcyclohexane.

4-Methylcyclohexene yielded results similar to those for 1-methylcyclohexene which indicates that isomerization of the 4-isomer to the 1-isomer precedes the cyclialkylation reaction. The ratio of compounds produced via Eq. (2) to those formed via Eq. 1 was either 0.59 or 0.47, depending on the methylcyclohexene employed. In the case when isobutylene was used as olefin, the ratio was 4.2 when HF was used as catalyst and 32 when sulfuric acid was employed.

EXPERIMENTAL

Gas Chromatography

A preparative gas chromatograph (Perkin–Elmer F-21) equipped with a flame ionization detector and a 13 ft × ⅜ in. column containing 10% Apiezon L (grease) on Chromosorb W, 60 to 80 mesh, non-acid-washed with nitrogen as carrier gas, was used for preparative separations. A gas chromatograph (F & M Model 720) equipped with a thermal conductivity detector and a 6 ft × 0.25 in. column, with helium gas as a carrier, was used for product analysis as well as for purification of samples. This gc was connected to an Autolab Computing Integrator for chromatography (Packard). Chromatograms were obtained with temperature programming from 100 to 280°C at 4°C/min.

Hydrogen Fluoride-Catalyzed Reactions—General Procedure

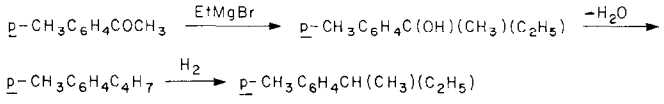
Anhydrous hydrogen fluoride was passed through a spiral 3 ft × ⅛ in. copper tube, cooled in crushed dry ice, and dropped into a polyethylene bottle (50 ml) which contained the aromatic hydrocarbon cooled in an ice–salt bath. The olefin was bubbled or dropped during periods of 10 to 35 min with magnetic stirring. After the addition, stirring was continued for 10 min and a certain amount of tert-butylbenzene was added as internal standard for the yield analysis by glc. The organic phase was separated and washed with a potassium hydroxide solution and then with water until neutral reaction. Chromatograms of such mixtures were taken for determination of the yields of the different products obtained in each reaction.

Sulfuric Acid-Catalyzed Reactions—General Procedure

The olefin was bubbled or dropped slowly into a flask containing a magnetically stirred mixture of the aromatic hydrocarbon and 96 to 98% sulfuric acid, keeping the temperature of reaction at 5 to 10°C.

Synthesis of Aromatic Hydrocarbons

p-sec-Butyltoluene. The title hydrocarbon was prepared by the three-step process from *p*-methylacetophenone (1.0 mol), ethylbromide (1.1 mol), and magnesium (1.06 g) in ether as solvent.



The alcohol produced in the first step was dehydrated to butenyltoluenes by allowing it to reflux in the presence of 30 g of potassium acid sulfate for 2 hr.

The olefins formed in 70% yield, based on the starting *p*-methylacetophenone, were composed of a mixture of three isomers, bp 208–210°C: (a) 2-*p*-tolyl-*cis*-2-butene, 35.6%; (b) 2-*p*-tolyl-1-butene, 7.7%; and (c) 2-*p*-tolyl-*trans*-2-butene, 55.5%. These were separated by preparative gc and analyzed by ms ($M^+ = 146$) and NMR (CCl_4). Isomer (a): 1.6 (3H, d, CH_3CH), 1.91 (3H, s, CH_3–C), 2.25 (3H, s, $ArCH_3$), 5.58–5.65 (1H, q, $CHCH_3$), 6.84–7.22 (4H, q, ArH). Isomer (b): 1.04 (3H, t, ethyl CH_3), 2.28 (3H, s, $ArCH_3$), 2.4 (2H, q, ethyl CH_2), 5.0 (2H, d, CH_2=), 7.1 (4H, q, ArH). Isomer (c): 1.54 (3H, d, CH_3CH), 1.95 (3H, s, CH_3–C), 5.3–5.7 (1H, q, CH–CH_3), 6.98 (4H, s, ArH).

Hydrogenation of the mixture of *p*-sec-butenyl-*p*-toluenes in the presence of 5% Pd/C in absolute ethanol at 30 psi gave *p*-sec-butyltoluene in a 91% yield and two other by-products (9.1 g, 8.8%) which were not analyzed. The title compound was isolated by spinning band distillation (bp 192–194°C). ms ($M^+ = 148$). NMR (CCl_4): 0.8 (3H, t, ethyl CH_3), 1.2 (3H, d, CH–CH_3), 1.5 (2H, q, CH_2), 2.25 (3H,s, $ArCH_3$), 2.45 (1H, m, ArCH), 6.92 (4H, s, ArH).

p-Cyclopentyltoluene. Prepared from *p*-bromotoluene (139 g, 0.825 mol) and cyclopentanone (64 g, 0.76 mol) by the Grignard reaction. The carbinol thus obtained was refluxed for 3 hr with potassium hydrogen sulfate (30 g). The product *p*-(1-cyclopentenyl) toluene, distilled at 155°C (3 cm), solidifies on standing to white plates, mp 66 to 67°C. Yield: 70 g (58%) based on cyclopentanone. NMR (CCl_4): 1.8–2.8 (9H, m, aliphatic H), 2.25 (3H, s, $ArCH_3$), 6.0 (1H, broad s, olefinic H), 7.0 (4H, m, ArH). This olefin was hydrogenated in absolute ethanol on 5% Pd/C at 25 psi overnight. Distillation under atmospheric pressure at 240°C, gave *p*-cyclopentyltoluene (58 g, total yield 48%). ms ($M^+ = 160$). NMR (CCl_4): 1.1–2.1 (8H, m, cyclopentyl hydrogens), 2.25 (3H, s, $ArCH_3$), 2.9 (1H, m, tert-H), 6.94 (4H, s, ArH).

p-Cyclohexyltoluene. Prepared by the Grignard method from *p*-bromotoluene (139 g, 0.825 mol) and cyclohexanone (70 g, 0.715 mol), according to the method described for *p*-cyclopentyltoluene. The intermediate *p*-cyclohexenyltoluene was distilled at 265 to 270°C (116 g, total yield 81%). The olefin was hydrogenated to give *p*-cyclohexyltoluene. NMR (CCl_4): 1.2–1.6 and 1.6–2.1 (9H, 2 m, cyclohexyl H), 2.28 (3H, s, $ArCH_3$), 2.45 (1H, broad d, tert-H), 7.0 (4H, s, ArH).

Identification of the Compounds

1–4 Isolated and analyzed by means of NMR and ms.

5 ms: $M^+ = 202$, 187 ($M-CH_3$), 173 ($M-C_2H_5$). NMR (CCl_4): 0.8 (3H, t, CH_2CH_3), 1.20 (3H, s, CH_3 gem to ethyl), 1.24 (6H, s, gem CH_3), 1.52 (2H, q, CH_2CH_3), 1.86 (2H, m, cyclic CH_2), 2.27 (3H, s, $ArCH_3$), 6.75, 6.81 (3H, two s, ArH).

6 ms: $M^+ = 258$, 243 ($M-CH_3$), 229 (M-Et), 187 ($M-C_5H_{11}$). NMR (CCl_4): 0.8 (3H, t, CH_3–CH_2), 1.0 (9H, s, tert-Bu), 1.2 (3H, s, CH_3 gem to Et), 1.3 (3H, s, CH_3 gem to neopentyl), 1.35–1.65 (4H, m, two CH_2 groups), 1.7 (2H, s, cyclic CH_2), 2.27 (3H, s, $ArCH_3$), 6.75, 6.81 (3H, d, ArH).

7 ms: $M^+ = 292$, 263 (M-Et). NMR (CCl_4): 0.8 (6H, partly hidden triplet, $2CH_3$), 1.24 (3H, s, CH_3), 2.0 (6H, two overlapping quartets and a singlet, $3CH_2$), 2.25, 2.35 (6H, 2 s, $ArCH_3$), 6.92 (7H, broad s, ArH). This compound was also obtained by dimerization of 2-*p*-tolyl-1-butene in hydrogen fluoride.

8 ms: $M^+ = 292$, 277 ($M-CH_3$), 263 ($M-CH_2CH_3$). NMR (CCl_4): 0.8 (3H, t, CH_3–CH_2), 1.1 (3H, s, CH_3 gem to ethyl), 1.4 (3H, s, CH_3 β to aromatic ring), 1.6 (2H, q, CH_2–CH_3), 2.1 (3H, d, CH_3–CH), 2.3 (1H, q, tert-H, partly hidden), 2.2–2.3 (6H, two s, $ArCH_3$), 6.7–7.1 (7H, m, ArH). This compound was also obtained by dimerization of a mixture of 2-*p*-tolyl-*cis*- and *trans*-2-butene.

9 ms: $M^+ = 214$, 199 ($M-CH_3$), 185 ($M-C_2H_5$), 171 ($M-C_3H_7$), 157 ($M-C_4H_9$), 143 ($M-C_5H_{11}$), 129 ($M-C_6H_{13}$), and 128 (M-86); loss of $2CH_3$ and $4CH_2$ groups. NMR (CCl_4): 1.0–1.8 (8H, m, $(CH_2)_4$), 1.25 (6H, s, gem CH_3 β to aromatic ring), 1.85 (2H, s, CH_2 β to aromatic ring), 2.3 (3H, s, $ArCH_3$), 6.7–6.9 (3H, m, ArH).

10 ms: $M^+ = 214$, 199 ($M-CH_3$), 185 ($M-C_2H_5$), 171 ($M-C_3H_9$), 157 ($M-C_4H_9$). NMR (CCl_4): 1.04–1.05 (6H, 2 s, gem CH_3), 1.2 (3H, s, β to aromatic ring), 2.3 (3H, s, $ArCH_3$), 3.01–3.09 (1H, d, tert-H).

11 ms: $M^+ = 270$, 255 ($M-CH_3$), 199 ($M-C_5H_{11}$). NMR (CCl_4): 1.0 (9H, s, tert-Bu), 1.2 (3H, s, gem CH_3), 1.4 (2H, s, $-CH_2-$), 1.6–2.0 (10H, broad peak, $4CH_2$), 2.28 (3H, s, $ArCH_3$), 6.8 (3H, m, ArH).

12 ms: $M^+ = 216$, 201 ($M-CH_3$), 173 ($M-CH_3$ and $2CH_2$), 171 ($M-3CH_3$), 157 ($M-3CH_3$ and CH_2), 143 ($M-3CH_3$ and $2CH_2$), 131 ($M-CH_3$, $2CH_2$, and $C(CH_3)_2$), 118 ($M-C_7H_{14}$). NMR (CCl_4): 0.51, 0.58 (3H, d, CH_3 far from aromatic ring), 0.87, 0.95 (6H, 2 s, gem CH_3), 1.25–1.90 (8H, m, aliphatic hydrogens), 2.30 (3H, s, $ArCH_3$), 7.04 (4H, s, ArH).

13 ms: $M^+ = 228$, 213 ($M-CH_3$), 185 ($M-C_3H_7$), 171 ($M-C_4H_9$), 157 ($M-C_5H_{11}$), 143 ($M-C_6H_{13}$), 131 ($M-C_7H_{13}$). NMR (CCl_4): 1.3–1.8 (10H, broad band, cyclohexyl H), 1.9 (2H, s, CH_2), 2.28 (3H, s, $ArCH_3$), 6.8, 1.9 (3H, two s, ratio 1:2, ArH).

14 ms: $M^+ = 214$, 199 ($M-CH_3$), 185 ($M-C_2H_5$), 171 ($M-C_3H_7$), 143 ($M-C_5H_{11}$). NMR (CCl_4): 1.18 (9H, s, $3CH_3$), 2.28 (3H, s, $ArCH_3$), 6.8 (3H, 2 s, ArH); small signals, concentrated in the region 0.8–1.9 ppm, account for the aliphatic hydrogens.

15 ms: $M^+ = 228$, 213 ($M-CH_3$), 199 ($M-C_2H_5$), 185 ($M-C_3H_7$), 171 ($M-C_4H_9$), 157 ($M-C_5H_{11}$). NMR (CCl_4): 1.0–2.0 (9H, m, cyclohexyl H), 1.24 (9H, s, $3CH_3$), 2.28 (3H, s, $ArCH_3$), 6.7–6.9 (3H, m, ArH).

16 ms: $M^+ = 242$, 226 ($M-CH_3$), 213 ($M-C_2H_5$). NMR (CCl_4): 0.78 (3H, t, CH_3–CH_2), 1.18 (6H, s, $2CH_3$), 1.3–2.0 (11H, m, cyclohexyl hydrogens and the ethyl CH_2 quartet half-hidden),

2.28 (3H, s, $ArCH_3$), 6.78, 6.82 (3H, two partly overlapping singlets, ArH).

CONCLUSION

The cyclialkylation of *p*-sec-alkyl- and cycloalkyltoluenes with isobutylene, 1-methylcyclopentene, and 1- and 4-methylcyclohexene in the presence of either 96% sulfuric acid or anhydrous hydrogen fluoride results in two types of reaction which are exemplified by Eqs. (1) and (2) in the text.

Type 2 reaction was predominant in the cyclialkylation of the aromatic hydrocarbons with isobutylene. Sulfuric acid as compared with hydrogen fluoride as catalyst favors type 2 reaction.

Products of type 1 reaction were the major components of the cyclialkylation of *p*-cymene and *p*-sec-butylbenzene with methylcyclohexenes when an excess of aromatics over the olefins were used.

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