

same two compounds as are obtained with 1-methylcyclohexene. The monoalkylation product is 1-methyl-1-phenylcyclohexane, and the dialkyla-

tion product is believed to be 1,4-di-(1'-methylcyclohexyl)-benzene.

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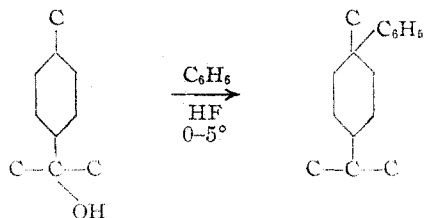
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[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Studies in the Terpene Series. IX.¹ Isomerization Accompanying Cycloalkylation of Benzene²

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It was observed that the products from the reaction of benzene with dihydrolimonene (1-methyl-4-isopropylcyclohexene) and a mixture of *p*-menthenes, in the presence of hydrogen fluoride at 0–5°, consisted of the same compound, 1-methyl-1-phenyl-4-isopropylcyclohexane.⁵ A hydrogen shift had occurred so that reaction always took place at the carbon atom holding the methyl group.⁶ Further work showed that the reaction of benzene with menthol (2-isopropyl-5-methylcyclohexanol) and dihydroterpineol [dimethyl-(4-methylcyclohexyl)-carbinol] under the same conditions also yielded the same product as formed previously (Equation I).



The main product was always accompanied by a small amount of crystalline material, melting at 145°, which corresponded to the dicycloalkylated benzene, presumably *p*-di-(1-methyl-4-isopropylcyclohexyl)-benzene.

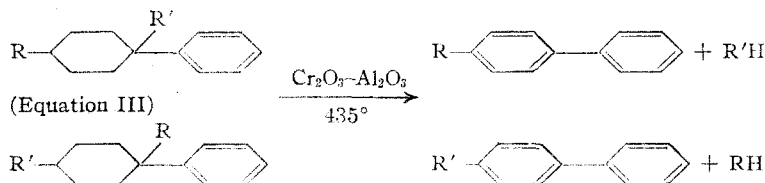
In order to gain additional evidence regarding the scope of the reaction, cyclohexanols with an ethyl and methyl group and with an ethyl and isopropyl group were used to cycloalkylate benzene.

The results obtained from the reactions of benzene with 1-ethyl-4-methylcyclohexanol, 1-ethyl-4-methylcyclohexene and 1-methyl-4-ethylcyclo-

hexanol produced a mixture of isomers. The greater amount of reaction had occurred at the carbon atom holding the methyl group, but a substantial amount had also occurred at the carbon atom holding the ethyl group.

The results from the reactions of benzene with 1-ethyl-4-isopropylcyclohexanol and 1-isopropyl-4-ethylcyclohexanol were somewhat inconclusive because of the difficulty of analyzing the reaction product. It appeared, however, that the greater amount of reaction had occurred at the carbon atom holding the ethyl group.

The structures of the cycloalkylated benzenes were determined by means of dehydrogenation. Naphthenes having a geminal alkyl group may be dehydrogenated under suitable conditions to yield aromatics with the elimination of alkyl groups.⁷ The gaseous product obtained from the dehydrogenation was analyzed on a mass spectrometer.⁸ Identification of the gaseous products thus produced made it possible to determine the position of the quaternary carbon atom. From the ratio of alkanes RH and R'H, produced from the dehydrogenation it was possible to establish the amount of each isomer, as exemplified by the following equations:



Dehydrogenation of known mixtures, given in Table II indicate the reliability of the method. Ethyl groups are cleaved more readily than methyl, making it imperative to have dehydrogenation as complete as possible. Dehydrogenation of hydrocarbons which may have an isopropyl group attached to the quaternary carbon atom, given in Table III, give inconclusive results, probably due to side reactions occurring during dehydrogenation.

In order to determine the behavior of hydrocarbons containing an isopropyl group attached to a

(1) For paper VIII of this series see H. Pines, R. C. Olberg and V. N. Ipatieff, *THIS JOURNAL*, **70**, 533 (1948).

(2) Taken from the dissertation submitted by H. R. Appell to the Graduate Faculty of Northwestern University in partial fulfillment of the requirements for the Ph.D. degree.

(3) Universal Oil Products Company Predoctorate Fellow (1947–1949).

(4) Universal Oil Products Company, Riverside, Illinois.

(5) This compound was also obtained by W. W. Thompson of our laboratories from the sulfuric acid catalyzed reaction of benzene with dihydrolimonene (unpublished work).

(6) It has previously been shown that if a tertiary carbon atom is part of the ring, reaction will occur at that position; V. N. Ipatieff, E. E. Meisinger and H. Pines, *THIS JOURNAL*, **72**, 2772 (1950).

(7) V. N. Ipatieff, H. Pines and R. C. Olberg, *THIS JOURNAL*, **68**, 1709 (1946).

(8) Mass spectrometer analyses were made by J. B. Grutka, Universal Oil Products Company, Riverside, Illinois.

TABLE I
COMPOUNDS OBTAINED BY THE CYCLOALKYLATION OF BENZENE

Cycloalkylating agent	Products formed	Yield, ^a %	°C.	B. p., mm.	n_D^{20}	Formula	Analyses, %	
							Carbon	Hydrogen
							Calcd.	Found
1-Methyl-4-isopropylcyclohexene (I)	1-Methyl-1-phenyl-4-isopropylcyclohexane	60	112-116	3.2	1.5128	C ₁₆ H ₂₄	88.81	88.70
Menthol (II)	1-Methyl-1-phenyl-4-isopropylcyclohexane	65	107-114	2.6	1.5133	C ₁₆ H ₂₄	88.81	88.70
Dimethyl-(4-methylcyclohexyl)-carbinol (III)	1-Methyl-1-phenyl-4-isopropylcyclohexane	77	108-115	2.8	1.5158	C ₁₆ H ₂₄	88.81	88.70
<i>p</i> -Menthene-(x) (IV)	1-Methyl-1-phenyl-4-isopropylcyclohexane	75	110-114	3.0	1.5151	C ₁₆ H ₂₄	88.81	88.70
1-Ethyl-4-methylcyclohexanol (V)	40% 1-ethyl-1-phenyl-4-methylcyclohexane, 60% 1-methyl-1-phenyl-4-ethylcyclohexane	68	103	2.6	1.5181	C ₁₆ H ₂₂	89.06	89.44
1-Ethyl-4-methylcyclohexene (VI)	40% 1-ethyl-1-phenyl-4-methylcyclohexane, 60% 1-methyl-1-phenyl-4-ethylcyclohexane	68	104	3	1.5176	C ₁₆ H ₂₂	89.06	89.44
1-Methyl-4-ethylcyclohexanol (VII)	20% 1-ethyl-1-phenyl-4-methylcyclohexane, 80% 1-methyl-1-phenyl-4-ethylcyclohexane	70	115	4	1.5171	C ₁₆ H ₂₂	89.06	89.44
1-Ethyl-4-isopropylcyclohexanol (VIII)	1-Ethyl-1-phenyl-4-isopropylcyclohexane, 1-isopropyl-1-phenyl-4-ethylcyclohexane	80	137	4.5	1.5145	C ₁₇ H ₂₆	88.62	88.37
1-Isopropyl-4-ethylcyclohexanol (IX)	1-Ethyl-1-phenyl-4-isopropylcyclohexane, 1-isopropyl-1-phenyl-4-ethylcyclohexane	57	118	3.5	1.5129	C ₁₆ H ₂₂	88.62	88.64
<i>x</i> -Isopropylcyclohexene (X)	1-Isopropyl-1-phenylcyclohexane ^b	70	150	16	1.5211	C ₁₅ H ₂₂	89.06	89.36

^a The yield is expressed in moles based on the cycloalkylating agent used. ^b The structure of this compound has not been conclusively established.

TABLE II

DEHYDROGENATION OF KNOWN COMPOUNDS

Compound	Dehydrogenated, %	Gaseous products and their ratios		
		CH ₄	C ₂ H ₆	H ₂
1-Methyl-1-phenylcyclohexane (XI)	85	26	..	74
1-Ethyl-1-(<i>p</i> -tolyl)-cyclohexane (XII)	98	1	27	72
1:1 mole mixture of (XI) and (XII)	50	11	15	74
1:1 mole mixture of (XI) and (XII)	95	14	15	71

TABLE III

DEHYDROGENATION OF BENZENE CYCLOALKYLATES

Cycloalkylating agents	Liquid	Dehydrogenation products—Gaseous products and their ratios			
		CH ₄	C ₂ H ₆	C ₃ H ₈	H ₂
I	4-Isopropylbiphenyl	21	3	5	71
II	4-Isopropylbiphenyl	24	1	2	73
III	4-Isopropylbiphenyl	26	1	1	72
V	4-Methylbiphenyl	15	11	..	74
VI	4-Ethylbiphenyl	23	17	..	60
VII	4-Ethylbiphenyl	22	6	1	71
VIII	4-Ethylbiphenyl	7	12	4	77
IX	4-Isopropylbiphenyl	7	13	4	76
X	Unknown mixture	5	1	3	91

quaternary carbon atom toward dehydrogenation, benzene was cycloalkylated with *x*-isopropylcyclohexene. From previous observations,^{8,9} the sole product should be 1-isopropyl-1-phenylcyclohexane. This material gave considerable amounts of methane, ethane and propane upon dehydrogenation and yielded a liquid product from which no pure compound could be isolated. Such unusual behavior would not be expected from any other theoretically possible cycloalkylate.

Experimental

Cycloalkylating Agents

1-Methyl-4-isopropylcyclohexene (I).—Prepared by the hydrogenation of 136 g. (1 mole) of *d*-limonene using 15 g. of nickel on kieselguhr¹⁰ at 30° under 50 atmospheres of hydrogen; yield 128 g. (93%), b. p. 170°, n_D^{20} 1.4540.

Menthol (II).—Prepared by the hydrogenation of 490 g. (3.26 M) of thymol using 70 g. of nickel on kieselguhr at 115° under 100 atmospheres of hydrogen; yield 426 g. (91%), b. p. 140° (41 mm.).

Dimethyl-(4-methylcyclohexyl)-carbinol (III).—Prepared by the hydrogenation of α -terpineol using nickel on kieselguhr at 50° under 100 atmospheres of hydrogen, b. p. 97° (14 mm.), n_D^{20} 1.4663.

***p*-Menthene-(x) (IV).**—Ninety grams of menthol was passed over 100 ml. of Harshaw alumina pills at 450° and an hourly space velocity of 0.75; yield 71.6 g. (90%), b. p. 170°, n_D^{20} 1.4552.

1-Ethyl-4-methylcyclohexene (VI).—Seventy-five grams of 1-ethyl-4-methylcyclohexanol was passed over 100 ml. of Harshaw alumina pills at 350° and an hourly space velocity of 0.75; yield, 58 g. (89%), b. p. 149°, n_D^{20} 1.4526.

The remaining cycloalkylating agents, listed in Table

(9) It has repeatedly been observed that reaction takes place in the cyclohexene ring at a tertiary carbon atom.

(10) V. N. Ipatieff and B. B. Corson, *Ind. Eng. Chem.*, **30**, 1039 (1938).

TABLE IV
 CYCLOALKYLATING AGENTS (NEW COMPOUNDS*)

Compound	Yield, %	B. p., °C.	mm.	d_{20}^{20}	n_D^{20}	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
1-Ethyl-4-methylcyclohexanol	78	186-190		0.9064	1.4598				
1-Methyl-4-ethylcyclohexanol*	80	58-59	4	.9037	1.4582	75.98	76.15	12.77	12.61
1-Ethyl-4-isopropylcyclohexanol*	50	165	96	.9055	1.4654	77.58	77.26	13.03	13.34
1-Isopropyl-4-ethylcyclohexanol*	10	163	103	.9087	1.4667	77.58	77.32	13.03	13.05

IV, were prepared by the action of an alkyl magnesium halide upon the appropriate ketone.¹¹

Cycloalkylations

These reactions were carried out by a procedure described previously.¹² Usually, 0.1 to 0.5 mol of cycloalkylating agent was used, with 2 mols of benzene and 10 mols of hydrogen fluoride for each mol of cycloalkylating agent. The excess benzene was removed at atmospheric pressure and the cycloalkylate vacuum distilled through a five plate column. The first 5% was discarded and then the product collected until the vapor temperature began to rise rapidly.

The dicycloalkylated product resulting from the reactions in which *p*-menthenes or their progenitors were used crystallized from the distillations bottoms. Recrystallization from 1:1 ethanol-chloroform gave needle-like crystals believed to be [*p*-di-(1-methyl-4-isopropylcyclohexyl)-benzene]. The yield was 5-8%, based on the cycloalkylating agent; m. p. 143-144°.

Anal. Calcd. for $C_{26}H_{42}$: C, 88.04; H, 11.96. Found: C, 88.07; H, 11.84.

Hydrogenation of 20 g. of the dicycloalkylate using 4 g. of nickel on kieselguhr at 120° and 100 atm. of hydrogen gave the completely saturated compound, corresponding to [1,4-di-(1-methyl-4-isopropylcyclohexyl)-cyclohexane] and melting at 81-85°.

Anal. Calcd. for $C_{26}H_{48}$: C, 86.68; H, 13.32. Found: C, 86.37; H, 13.36.

None of the other cycloalkylating agents yielded a crystallizable dicycloalkylate.

Dehydrogenations

The dehydrogenations were conducted in a vertical furnace with a chromia on alumina catalyst, promoted with cerium and potassium,¹⁸ at 435° and an hourly space velocity of 0.03. The exit gas was analyzed by a mass spectrometer. A 10% pentane solution of the liquid product was prepared and passed through a 3-foot, 8-mm. glass tube filled three-quarters full with through-200 Davison silica gel.¹⁴ The aromatic portion was eluted with alcohol and then distilled under vacuum. If the presence of more than one compound was suspected, three cuts were taken and derivatives of all cuts prepared.

Oxidation of 0.2 g. of the dehydrogenated material by refluxing with 2 g. of chromic oxide, in 20 ml. of 50% acetic acid, for four hours produced *p*-phenylbenzoic acid in all cases. The sublimed acid melted at 220-222°, and a mixed melting point with an authentic specimen was not dispersed. The methyl ester melted at 114-115°.

Derivatives

Derivatives of the hydrocarbons were prepared by acety-

(11) P. Sabatier and A. Mailhe, *Ann. chim. phys.*, [8] **10**, 527 (1927).

(12) V. N. Ipatieff, H. Pines and R. C. Olberg, *THIS JOURNAL*, **70**, 2123 (1948).

(13) R. C. Archibald and B. S. Greenfelder, *Ind. Eng. Chem.*, **37**, 356 (1945).

(14) B. J. Mair and A. F. Forziati, *J. Research Natl. Bureau of Standards*, **52**, 151, 165 (1944).

lation followed by preparation of the 2,4-dinitrophenylhydrazones.¹⁶

If more than one isomer was present in the cycloalkylation products, a pure derivative could not be isolated. The derivatives resulting from the dehydrogenation products of cycloalkylates consisting of more than one isomer had to be purified by passing a benzene solution through a column of Harshaw activated alumina, 80-200 mesh. The first and last portions of the eluent were discarded and the pure derivative crystallized from the central portion.

TABLE V

DINITROPHENYLHYDRAZONES OF ACETYLATED HYDROCARBONS

Hydrocarbon	M. p. of der., °C.	Formula	Nitrogen, %	
			Calcd.	Found
1-Methyl-1-phenyl-4-isopropylcyclohexane	202-203	$C_{24}H_{30}N_4O_4$	12.79	13.00
4-Methylbiphenyl	230-232	$C_{21}H_{18}N_4O_4$	14.35	14.22
4-Ethylbiphenyl	227-229	$C_{22}H_{20}N_4O_4$	13.58	13.21
4-Isopropylbiphenylphenylcyclohexane	156-157	$C_{23}H_{28}N_4O_4$	13.19	13.41

The derivatives of 4-methylbiphenyl and 4-ethylbiphenyl were prepared from known compounds. Because their melting points are so close and because they do not depress each other's melting point, analytical data were obtained for the derivatives from the dehydrogenation product of the 1-ethyl-4-methylcyclohexanol cycloalkylate.

Anal. Calcd. for $C_{21}H_{18}N_4O_4$: N, 14.35. Found: 14.62. Calcd. for $C_{22}H_{20}N_4O_4$: N, 13.58. Found: N, 13.37.

Summary

The reaction of benzene with disubstituted cyclohexenes in the presence of hydrogen fluoride was accompanied by a hydrogen shift. Dihydrolimonene, *p*-menthene-(x), menthol and dihydroterpeneol yielded 1-methyl-1-phenyl-4-isopropylcyclohexane. 1-Methyl-4-ethyl-, 1-ethyl-4-methyl-, 1-ethyl-4-isopropyl- and 1-isopropyl-4-ethylcyclohexanol on reaction with benzene formed a mixture of hydrocarbons. The phenyl group was attached predominantly to the carbon atom on the cyclohexyl ring holding the smallest alkyl group.

The following new compounds have been prepared: 1-methyl-4-ethyl-, 1-ethyl-4-isopropyl-, and 1-isopropyl-4-ethylcyclohexanol.

EVANSTON, ILLINOIS

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(15) H. Pines, A. Weizmann and V. N. Ipatieff, *THIS JOURNAL*, **70**, 3859 (1948).