Aerograph) with a 20-ft. Versamid column at 165°. The purified product contained 98.3% *o*-, 0.9% *m*-, and 0.8% *p*-diethylbenzene.

Gas-Liquid Chromatographic Analysis.—Gas-liquid chromatographic analyses were carried out on a Perkin-Elmer Model 226 vapor fractometer equipped with a 150-ft. *m*-bis(*m*-phenoxyphenoxy)benzene-coated (modified by 20% Apiezon L grease) capillary column and hydrogen flame ionization detector. Column temperature was at 80° with He carrier gas pressure of 20 p.s.i. Peak areas were directly determined by the use of a high speed electronic Infotronics Model CRS-1 integrator. Characteristic retention times are shown in Table VI.

TABLE VI

RETENTION TIMES OF ETHYLBENZENE, DIETHYLBENZENES, AND 1,3,5-TRIETHYLBENZENE

Compound	Retention time, min.
Ethylbenzene	7.3
o-Diethylbenzene	23.9
m-Diethylbenzene	20.6
p-Diethylbenzene	21.8
1,3,5-Triethylbenzene	38.6[a]

[a] At 110°; He, 30 p.s.i.

Friedel-Crafts Isomerization. IX.[1a] Aluminum Chloride Catalyzed Isomerization of the Diisopropylbenzenes

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The isomerization of *o*-, *m*-, and *p*-diisopropylbenzene with water-promoted aluminum chloride was investigated. The isomer distributions were established by gas-liquid chromatography. The equilibrium isomer mixture starting from any of the isomers contains about 68% *m*- and 32% *p*-diisopropylbenzene, with no *ortho* isomer present. The isomerizations proceed by a predominant 1,2-shift mechanism, although they are accompanied by substantial disproportionation to cumene and 1,3,5-triisopropylbenzene.

The aluminum chloride catalyzed isomerization of cymenes was investigated by Allen, Alfrey, and Yats.[2] No investigation of the acid-catalyzed isomerization of diisopropylbenzenes was reported.

Results and Discussion

The isomerization of *o*-, *m*-, and *p*-diisopropylbenzene with water-promoted aluminum chloride was investigated and the isomer distribution at equilibrium was established using gas-liquid chromatography.

Results are presented in Tables I-III. The equilibrium mixture contains about 68% *m*- and 32% *p*-diisopropylbenzene, with no *ortho* isomer present. There were always formed products of disproportionation (transalkylation), among which cumene and 1,3,5-triisopropylbenzene are the main ones. Cumene and 1,3,5-triisopropylbenzene at equilibrium amounted to about 40 mole % of total aromatic present. Later peaks in the gas chromatograms indicated the presence of higher boiling materials. These materials were present in small amounts only, and no attempts were made at

TABLE I

ISOMERIZATION OF *p*-DIISOPROPYLBENZENE WITH WATER-PROMOTED ALUMINUM CHLORIDE

Time	% *ortho*	% *meta*	% *para*	% cumene	% 1,3,5-triisopropylbenzene
1 min.	0	1	99	<0.5	
15	0	4	96	2	
1 hr.	0	17	83	8	
1.5	0	42	58	15	14
4.5	0	59	41	18	18
5.5	0	64	36	18	19
6	0	66	34	18	21
65	0	65	35	26	25
71	0	66	34	22	26
88	0	64	36	20	27
95	0	67	33	22	23

TABLE II

ISOMERIZATION OF *m*-DIISOPROPYLBENZENE WITH WATER-PROMOTED ALUMINUM CHLORIDE

Time	% *ortho*	% *meta*	% *para*	% cumene	% triisopropylbenzene
1 min.	0	>99	<1	<1	
10	0	99	1	2	
15	0	97	3	5	2
25	0	89	11	9	4
40	0	79	21	13	9
1 hr.	0	74	26	19	13
2	0	69	31	25	19
3	0	67	33	24	22
60	0	66	34	25	27
65	0	65	35	23	21
71	0	66	34	19	25
88	0	67	33	21	24
95	0	66	34	22	20

TABLE III

ISOMERIZATION OF *o*-DIISOPROPYLBENZENE WITH WATER-PROMOTED ALUMINUM CHLORIDE IN THE PRESENCE OF BENZENE

Time, min.	% *ortho*[a]	% *meta*[a]	% *para*[a]	% cumene	% 1,3,5-triisopropylbenzene
1	92	8	Trace	7	~0.5
2	79	18	3	15	~0.5
4	57	37	6	24	~0.5
6	11	74	15	39	3.5
10	Trace	82	18	47	2.0
75	0	78	22	51	1.5
25	0	74	26	56	1.5
40	0	72	28	61	1.5
60	0	71	29	69	2.0
90	0	69	31	73	<1.0
120	0	69	31	78	<1.0
150	0	68	32	80	<1.0
180	0	68	32	81	<1.0

[a] Normalized.

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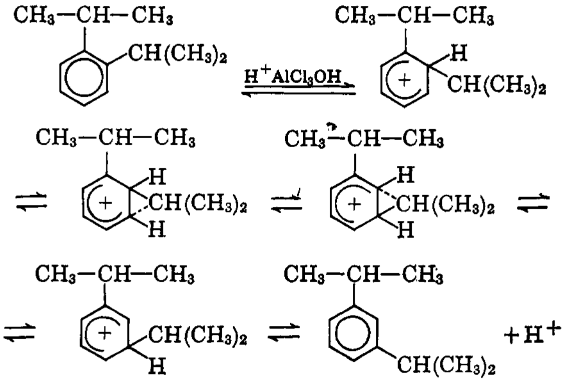
(2) R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 42 (1959).

SCHEME I

1,2-SHIFT MECHANISM OF THE ISOMERIZATION of DIISOPROPYLBENZENES



identification. The absence of *o*-diisopropylbenzene from the equilibrium mixture can be understood for steric reasons, as in the case of the previously investigated terphenyls[3] and *t*-butylbenzenes.[4] The isomerization of neat *o*-diisopropylbenzene was too fast to follow conveniently; therefore, the isomerization of *o*-diisopropylbenzene was investigated in the presence of an equal weight of benzene at 0° (see Table IV).

TABLE IV

ISOMERIZATION OF *o*-DIISOPROPYLBENZENE IN THE PRESENCE OF BENZENE AT 0° WITH WATER-PROMOTED ALUMINUM CHLORIDE

Time, min.	% *ortho*[a]	% *meta*[a]	% *para*[a]	% cumene
0.5	98	2	0	1
2.5	97	3	0	2
3	96	4	0	1
4	96	4	0	2
4.5	94	6	0	2
5	92	8	Trace	4
5.5	91	9	Trace	4
6	88	11	<1	6
6.5	85	14	<1	4
7	83	16	<1	7
7.5	79	20	<1	10
8	73	26	1	12
8.5	68	30	2	11
9	59	39	2	14
9.5	41	55	4	17

[a] Normalized.

Following the isomer distribution with time shows that a considerable amount of *meta* isomer forms before the *para* isomer shows any increase. It seems, therefore, that the diisopropylbenzenes isomerize with aluminum chloride under heterogeneous conditions predominantly by a 1,2-shift mechanism, as do the xylenes, diethylbenzenes,[1] terphenyls,[3] and fluorobiphenyls.[6] At the same time, the intramolecular isomerization is accompanied by substantial disproportionation to cumene and 1,3,5-triisopropylbenzene. Disproportion in all probability results through transalkylation of diisopropylbenzene by the intermediate σ-complex, a substantially bulky alkylating agent not capable of alkylation *ortho* to an isopropyl group and thus helping, besides consecutive isomerization, the preferential formation of 1,3,5-triisopropylbenzene.

Experimental

Starting Materials.—The isomeric diisopropylbenzenes were obtained from The Dow Chemical Company, Midland, Mich. *o*-Diisopropylbenzene contained 93% *ortho* isomer, 98% after purification by gas chromatography; *m*-diisopropylbenzene contained 98% *meta*, 1.5% *ortho*, and 0.5% *para* isomer; and *p*-diisopropylbenzene contained 99% *para* and 1% *meta* isomer.

General Process of Isomerizations.—Reactions were carried out in stoppered vessels with magnetic stirring. The amounts used were 0.2 mole of aluminum chloride/mole of diisopropylbenzenes; 1 ml. of water was added as a promoter. Samples were drawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. The dried ether extracts were analyzed by gas–liquid chromatography. All isomerization were carried out, if not otherwise indicated, at ~25°.

Results are given in normalized % of *ortho*, *meta*, and *para* isomer. Numbers given for other materials represent mole % of total aromatic present.

Gas–Liquid Chromatographic Analysis.—Gas–liquid chromatographic analyses were carried out on Perkin-Elmer Model 154-D and Model 226 vapor fractometers equipped with Golay-type capillary columns and hydrogen flame ionization detectors. Peak areas were directly obtained by the use of a high speed electronic Infotronics Model CRS-1 integrator. Columns used were 150 ft. and coated with polypropylene glycol (PPG) and *m*-bis(*m*-phenoxyphenoxy)benzene (MBMA) modified with 20% Apiezeon L grease, respectively. The PPG column was operated at 105° with a He carrier gas pressure of 15 p.s.i., whereas the MBMA column was operated at 100° with a He carrier gas pressure of 20 p.s.i. Characteristic retention times are given in Table V.

TABLE V

RETENTION TIMES OF CUMENE, DIISOPROPYLBENZENES, AND 1,3,5-TRIISOPROPYLBENZENE[a]

Compound	PPG column	MBMA column
Cumene	9	6.7
o-Diisopropylbenzene	24.2	20.7
m-Diisopropylbenzene	21.5	18.1
p-Diisopropylbenzene	25.8	22.5
1,3,5-Triisopropylbenzene	49.7	45.5

[a] In minutes.

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