Friedel–Crafts Isomerization. VIII.[1a] Aluminum Chloride Catalyzed Isomerization of the Diethylbenzenes

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The isomerization of *o*-, *m*-, and *p*-diethylbenzene with water-promoted aluminum chloride was investigated. The isomer distributions were established using gas–liquid chromatography. The equilibrium isomer mixture starting from any of the isomers contains about 3% *o*-, 69% *m*-, and 28% *p*-diethylbenzene. The isomerizations proceed by a predominant 1,2-shift mechanism, although they are accompanied by substantial disproportionation to ethylbenzene and triethylbenzene.

Despite the importance of diethylbenzenes as byproducts in the ethylation of benzene and starting materials for the production of divinylbenzenes, no data have been published on the isomerization of diethylbenzenes or the equilibrium mixture of the isomers.

Results and Discussion

The isomerization of neat *o*-, *m*-, and *p*-diethylbenzene with water-promoted aluminum chloride was investigated and the isomer distribution at equilibrium was established using gas–liquid chromatography. In nitromethane solution the isomerization was too slow to be conveniently followed.

Results are presented in Table I to V. Starting with any one of the isomers, an equilibrium mixture containing about 3% *ortho*, 69% *meta*, and 28% *para* isomer was obtained. There are always formed products of disproportionation (transalkylation) among which chiefly are ethylbenzene and 1,3,5-triethylbenzene. The sum of ethylbenzene and 1,3,5-triethylbenzene at equilibrium amounts to about 40 mole % of total aromatic. Later peaks in the gas chromatogram indicated the presence of higher boiling materials. They never amounted, however, to more than about 5 mole % and no attempts at identification were made.

TABLE I

ISOMERIZATION OF *o*-DIETHYLBENZENE WITH WATER-PROMOTED ALUMINUM CHLORIDE

Time	% *ortho*[a]	% *meta*[a]	% *para*[a]	% ethylbenzene	% triethylbenzene
1 min.	92	7	1	2	
2	88	11	1	3	
4	86	13	1	5	
6	83	15	2	9	
10	82	16	2	6	
15	73	23	4	10	<1
25	35	57	8	19	3
40	16	63	21	21	6
1 hr.	8	65	27	21	11
2	4	65	31	20	22
3	3	67	30	19	20
5	3	68	29	16	21
6	3	69	28	15	21
48	3	69	28	19	16
100	3	71	26	17	22
140	2	69	29	15	19

[a] Normalized.

TABLE II

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

Time	% *ortho*[a]	% *meta*[a]	% *para*[a]	% ethylbenzene	% triethylbenzene
1 min.	0	100	0	0	0
6	Trace	>99	<1	4	1
15	<1	99	<1	9	6
25	<1	99	1	13	9
40	1	92	7	16	11
1 hr.	1	90	9	18	17
1.5	2	83	15	21	18
2	3	78	19	20	17
3	2	76	22	21	19
5	3	70	27	18	18
6	2	71	27	20	21
8	3	70	27	21	20
32	2	69	29	23	20
52	2	70	28	20	22
72	3	69	28	21	19

[a] Normalized.

TABLE III

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

Time	% *ortho*[a]	% *meta*[a]	% *para*[a]	% ethylbenzene	% triethylbenzene
1 min.	0	<1	99	1	
10	0	1	99	4	
15	<1	1	98	4	
25	<1	3	97	6	
40	<1	4	96	10	1
1 hr.	1	7	93	12	2
1.5	1	10	89	17	3
2	2	13	85	17	5
2.5	2	18	80	18	6
3.5	2	24	74	19	9
4.5	2	29	69	20	12
5.5	3	32	65	14	16
6.5	2	35	63	17	18
9	3	43	54	14	21
22	3	47	50	16	18
55	3	58	39	19	19
75	3	68	29	18	23
96	3	68	29	20	22

[a] Normalized.

Table I indicates that, in the isomerization of *o*-diethylbenzene at room temperature, the *para* isomer appears only after a significant amount of *meta* isomer has formed, indicating the 1,2-shift mechanism predominated. Starting with the *para* isomer (Table III), the data do not suggest a fast *para–ortho* conversion, and a 1,2-shift mechanism can again be assumed despite

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[1] (a) Part VII: *J. Org. Chem.*, **29**, 2310 (1964). (b) To whom correspondence should be addressed at The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

TABLE IV

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

Time	% *ortho*[a]	% *meta*[a]	% *para*[a]	% ethylbenzene	% triethylbenzene
1 min.	93	6	1	1	0
10	88	11	1	9	0
15	85	14	1	13	<1
25	74	24	2	23	<1
40	66	31	3	24	1
1 hr.	56	40	4	39	2
1.5	47	47	6	41	3
2	41	52	7	46	6
2.5	34	52	9	47	5
3	35	55	9	44	5
4	32	58	10	48	5
5	24	64	12	53	5
6	19	67	14	56	5
7	16	68	16	58	5
8	9	71	20	63	3
9	5	72	23	71	2
22	3	70	27	79	<1
25	3	70	27		<1
28	3	70	27	78	<1
46	3	69	28		

[a] Normalized.

TABLE V

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

Time, min.	% *ortho*[a]	% *meta*[a]	% *para*[a]	% ethylbenzene
0	98.3	0.9	0.8	*b*
6	98	1.3	0.7	1
10	97.2	2.1	0.7	2
12	96.5	2.9	0.6	3
14	95.6	4.0	0.4	4
16	94.1	5.2	0.7	6
18	93.1	6.3	0.6	6
20	91.2	8.0	0.8	8
22	89.6	9.8	0.6	9
24	87.6	11.8	0.6	10.9
26	85.3	13.7	1.0	19
28	80.3	18.8	0.9	35
30	76.7	22.1	1.2	15

[a] Normalized. [b] Starting materials, see Experimental section.

the fact that the evidence is less convincing owing to the small amount of *ortho* isomer present at equilibrium.

Certain similarities can be expected to exist between the isomerization of the xylenes and the diethylbenzenes with aluminum chloride. The isomerization of xylenes with aluminum chloride was studied kinetically by Allen and Yats[2] as a three-compound equilibration involving six rate constants.

It was found that in toluene solution the rate constants of the *ortho–para* as well as those of the *para–ortho* conversion are equal to zero, indicating that the isomerization of xylenes takes place through a 1,2-shift mechanism exclusively. Similar conclusions were reached by Brown and Jungk.[3]

In the absence of rate constants for the isomerization of diethylbenzenes, a qualitative picture as to the extent to which the intra- and intermolecular mechanisms operate may be gained by carrying out the isomerization in added aromatic. In the presence of added aromatic, transalkylation products will be present in higher concentrations and, if the transalkylation mechanism contributes to the isomerization, an increase in rate should result.

Conversely, if the isomerization takes place predominantly by a 1,2-shift mechanism, the added aromatic would act as a diluent only and a decrease in rate might result.

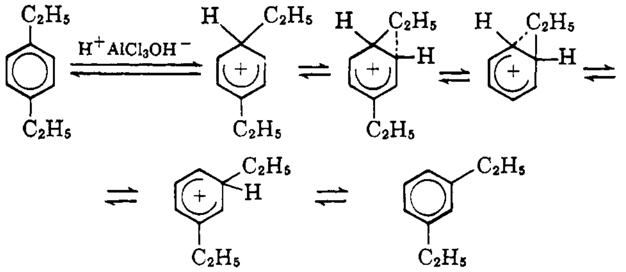
To test this possibility, the isomerization of *o*-diethylbenzene was carried out in the presence of an equal weight of benzene.

Equilibrium was reached in about 20 hr. (Table IV) compared with 3 hr. in the absence of benzene (Table I). The latter, therefore, acts largely as a diluent. Further evidence for the intramolecular rearrangement is presented in Table V, where *o*-diethylbenzene was isomerized in the presence of benzene at 0°. In 30 min., the normalized % *o*-diethylbenzene decreased to 77%, 22% *meta* isomer appeared, while the *para* isomer did not increase in that time.

The mechanism of the isomerization of the diethylbenzenes in accordance with the experimental data of time–composition studies can be best explained by a sequence of 1,2-shifts, as shown in Scheme I in the case of *p*-diethylbenzene.

SCHEME I

1,2-SHIFT MECHANISM OF THE ISOMERIZATION OF DIETHYLBENZENE



Disproportionation results *via* transalkylation of diethylbenzene by the intermediate σ-complex. Thus, a substantially bulky alkylating agent is involved which contributes, besides the possibility of consecutive isomerization, to the formation of 1,3,5-triethylbenzene.

Experimental

Materials.—Diethylbenzenes were obtained from the Aldrich Chemical Co., Milwaukee, Wis. *o*-Diethylbenzene contained 93% *ortho*, 6% *meta*, and 1% *para* isomer; *m*-diethylbenzene contained 99.9% *meta* isomer; and *p*-diethylbenzene contained 99.9% *para* isomer.

General Process of Isomerization.—Reactions were carried out in stoppered flasks with magnetic stirring. The amounts used were 0.2 mole of aluminum chloride/mole of diethylbenzene, and 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 the isomerizations 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.

o-Diethylbenzene used for the run described in Table V was purified using a preparative gas–liquid chromatograph (Wilkins

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(2) R. H. Allen and L. D. Yats, *J. Am. Chem. Soc.*, **81**, 5289 (1959).

(3) H. C. Brown and J. Jungk, *ibid.*, **77**, 5579 (1955).

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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(1) (a) Part VIII: *J. Org. Chem.*, **29**, 2313 (1964). (b) To whom correspondence should be addressed at The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

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