outlined by Cason and Prout.[18] A solution of 3-(*p*-tolyl)butyryl chloride (3.1 g., 0.015 mole) in benzene (30 ml.) was added dropwise to the cadmium reagent and resulting mixture was refluxed for 5 hr. The usual work-up followed by fractional distillation gave 1.4 g. (28%) of ketone, b.p. 151–155° (1.1 mm.), $n^{25}\text{D}$ 1.4843, $[\alpha]^{25}\text{D}$ +4.38° (*c* 1.5860, chloroform).

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.40; H, 11.16. Found: C, 83.45; H, 10.95.

The infrared spectrum, gas chromatogram, and n.m.r. spectrum of this ketone were found to be identical with those of the ketone obtained from dehydrogenation of the unsaturated ether.

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[18] J. Cason and F. S. Prout, *J. Am. Chem. Soc.*, **66**, 46 (1944).

Friedel–Crafts Isomerization. VII.[1a] Aluminum Chloride Catalyzed Isomerization of the *t*-Butyltoluenes

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The isomerization of *o*-, *m*-, and *p*-*t*-butyltoluene with water-promoted aluminum chloride in excess of the *t*-butyltoluenes (heterogeneous system) and in nitromethane solution (homogenous system) was investigated. The isomer distributions were established using gas–liquid chromatography. The equilibrium isomer mixture starting from any of the isomers contains about 64% of the *m*- and 36% of the *p*-*t*-butyltoluene isomer.

Acid-catalyzed isomerization of the isomeric xylenes,[2] ethyltoluenes,[3] and cymenes[4] was investigated in considerable detail. Particularly the work of Allen established rate and equilibrium data of these three compound equilibrations.

The problem of aluminum chloride catalyzed isomerization of *t*-butyltoluenes was considered by Allen in the case of *p*-*t*-butyltoluene.[5]

This work was mainly concerned with the demonstration that intermolecular isomerization of neat *p*-*t*-butyltoluene is not possible and that the isomerization in aromatic hydrocarbon solvent (*o*-xylene), consequently, is entirely a dealkylation–alkylation process. It was concluded by Allen that the process is entirely intermolecular and involves only *t*-butylation of formed toluene, as *p*-*t*-butyltoluene can not be butylated.

Previous investigations have not considered the isomerization of *m*- and *o*-*t*-butyltoluene; neither was the equilibrium composition of the *t*-butyltoluenes established.

Results and Discussion

The isomerization of *o*-, *m*-, and *p*-*t*-butyltoluene with water-promoted aluminum chloride (heterogeneous system) and with aluminum chloride in nitromethane (homogeneous system) was investigated at room-temperature (~25°). The isomer distributions were established using gas–liquid chromatography.

Results of the rearrangement of *p*- and *m*-*t*-butyltoluene are presented in Tables I to IV. The equilibrium mixture contains about 63–64% *m*- and 36–37% *p*-*t*-butyltoluene with no *ortho* isomer present. Rearrangements in nitromethane solution are much slower than those of the neat compounds. Neat *p*-*t*-butyltoluene, for example, when isomerized with water-promoted aluminum chloride, reached equilibrium in about 60 min. (Table I), but over 20 hr. was needed in nitromethane solution (Table III). In the isomerization of the undiluted, neat isomers as well as in nitromethane solution, the main disproportionation products are toluene and di-*t*-butyltoluenes which are found in very roughly the same molecular amounts. The total of disproportionation products increased with time and at equilibrium amounted to about 30–50 mole % of total aromatic.

TABLE I

ISOMERIZATION OF *p*-*t*-BUTYLTOLUENE WITH WATER-PROMOTED ALUMINUM CHLORIDE (HETEROGENEOUS)

Time, min.	% *meta*	% *para*	% toluene	% 3,5-di-*t*-butyltoluene
1	14	86	6	5
2	21	79	8	7
4	37	63	12	8
6	44	56	13	9
10	54	46	13	10
15	61	39	15	11
25	60	40	17	12
40	59	41	17	11
60	63	37	18	12
90	62	38	22	15
150	64	36	20	15

TABLE II

ISOMERIZATION OF *m*-*t*-BUTYLTOLUENE WITH WATER-PROMOTED ALUMINUM CHLORIDE (HETEROGENEOUS)

Time, min.	% *meta*	% *para*	% *toluene*	% 3,5-di-*t*-butyltoluene
1	88	12	6	7
2	80	20	10	15
4	74	26	11	16
6	70	30	14	20
10	66	34	15	21
15	64	36	16	21
25	64	36	18	18
40	64	36	22	20
60	64	36	25	23
120	64	36	29	22
180	64	36	35	28

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[1] (a) Part VI: *J. Org. Chem.*, **28**, 1912 (1963). (b) To whom correspondence should be addressed at The Dow Chemical Co., Eastern Research Laboratory, Framingham, Mass.

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

[3] R. H. Allen, L. D. Yats, and D. S. Erley, *ibid.*, **82**, 4853 (1960).

[4] R. H. Allen, T. Alfrey, Jr., and L. D. Yats, *ibid.*, **81**, 42 (1959).

[5] R. H. Allen, *ibid.*, **82**, 4856 (1960).

TABLE III

ISOMERIZATION OF *p*-*t*-BUTYLTOLUENE WITH ALUMINUM CHLORIDE IN NITROMETHANE SOLUTION

Time, hr.	% *meta*[a]	% *para*[a]	% toluene	% 3,5-di-*t*-butyltoluene
1	3	97	4	6
2	5	95	7	7
3	13	87	11	16
4	24	76	15	20
5	33	67	15	17
6	41	59	17	18
7	48	52	18	22
8	53	47	14	20
23	63	37	15	23
27	64	36	14	22
73	65	35	17	24
79	64	36	18	22
96	64	36	19	20

[a] Normalized.

TABLE IV

ISOMERIZATION OF *m*-*t*-BUTYLTOLUENE WITH ALUMINUM CHLORIDE IN NITROMETHANE SOLUTION

Time, hr.	% *meta*[a]	% *para*[a]	% toluene	% 3,5-di-*t*-butyltoluene
3	94	6	3	5
6	85	15	6	8
30	64	36	7	12
49	64	36	13	20
71	63	37	12	21
95	64	36	13	18
118	64	36	19	20

[a] Normalized.

There were always present varying amounts of further products of disproportionation (transalkylation), among which benzene, *t*-butylbenzene, and *p*-di-*t*-butylbenzene were identified. Benzene and *p*-di-*t*-butylbenzene obviously originate from the acid-catalyzed disproportionation of *t*-butylbenzene. The presence of *t*-butylbenzene indicates that under the present conditions the methyl group also displays some migratory ability. However, the relative amount of *t*-butylbenzene found at any time before equilibrium was reached was always below 5% of total aromatic present, with less than 1% benzene and 2% *p*-di-*t*-butylbenzene also present.

Allen found[5] that, in *o*-xylene solution at 0° employing *o*-xylene and *p*-*t*-butyltoluene in a ratio of 9:1 and total aromatic and aluminum chloride in a ratio of 100:1, the *t*-butyl group could be transferred to *o*-xylene without isomerizing *p*-*t*-butyltoluene. Transalkylation was orders of magnitude faster than isomerization.

Furthermore, treatment of *p*-*t*-butyltoluene with anhydrous HCl and 1 mole of aluminum chloride at 0° showed that it alkylates chloride ion more readily than it undergoes isomerization intramolecularly. The toluene formed then permits intermolecular isomerization. This led to the conclusion that *p*-*t*-butyltoluene isomerizes exclusively through the intermolecular mechanism.

It might be expected that in replacing *o*-xylene (or toluene) by benzene, as the added aromatic, a slowing down of transalkylation will be observed since benzene is a weaker nucleophile than either *o*-xylene or toluene. The primary products would be toluene and *t*-butylbenzene. Toluene could react in a further transalkylation reaction with both the σ-complexes of the starting isomer and the σ-complex of *t*-butylbenzene to form the products.

Taking *p*-*t*-butyltoluene and benzene in a molar ratio of 1:2 using 0.01 mole of aluminum chloride per mole of *t*-butyltoluene, equilibrium was reached in about 30 min. The products of transalkylation, toluene, and *t*-butylbenzene, were found to be present in a molar ratio of about 1:1 and at equilibrium accounted for 75–80 mole % of the original amount of *p*-*t*-butyltoluene used (Table V). Some *p*-di-*t*-butylbenzene and 1,3,5-di-*t*-butylbenzene was also detected. In the absence of benzene, using the same alkylbenzene–catalyst ratio, equilibrium was reached in about 60 min., with toluene at equilibrium accounting for about 10% of total aromatic. It appears, therefore, that, at room temperature in the presence of a small amount of catalyst under heterogeneous conditions, the rates of isomerization of *p*-*t*-butyltoluene with and without added benzene are, while still different, of comparable magnitude, in contrast to the reaction as carried out by Allen.

TABLE V

ISOMERIZATION OF *p*-*t*-BUTYLTOLUENE WITH WATER-PROMOTED ALUMINUM CHLORIDE IN THE PRESENCE OF BENZENE[a]

Time, min.	% *meta*[b]	% *para*[b]	% toluene	% *t*-butylbenzene	% *p*-di-*t*-butylbenzene
1	5	95	5	3	
2	6	94	8	6	
4	11	89	16	12	1
6	22	78	21	15	1
10	29	71	31	23	3
15	59	41	34	38	3
25	61	39	41	39	3
40	63	37	41	39	2
60	63	37	37	39	3

[a] 0.01 mole of aluminum chloride/mole of *p*-*t*-butyltoluene.
[b] Normalized.

The absence of *o*-*t*-butyltoluene from the equilibrium mixture can be understood for steric reasons, and the results of the isomerization of the *meta* and *para* isomers show that the isomerization of the *ortho* isomer is an irreversible process.

As the isomerization of *o*-*t*-butyltoluene proved too fast for measurement under conditions where the isomerization of the *meta* and *para* isomers could easily be followed, the rearrangement was investigated in a more dilute solution containing 50 moles of nitromethane and 0.8 mole of aluminum chloride per mole of *o*-*t*-butyltoluene (Table VI). *o*-*t*-Butyltoluene disappeared in 13 min., forming a mixture of *meta* and *para* isomers. During isomerization, the ratio of the normalized per cent of *meta* and *para* isomer remained practically constant (2.5:3), leading to the kinetically controlled formation of 25% *meta* and 75% *para*. Subsequent isomerization to the final (thermodynamic) equilibrium of about 64% *meta* and 36% *para* is much slower. Equilibrium was reached in about 20 hr. Similar results were obtained at 0°.

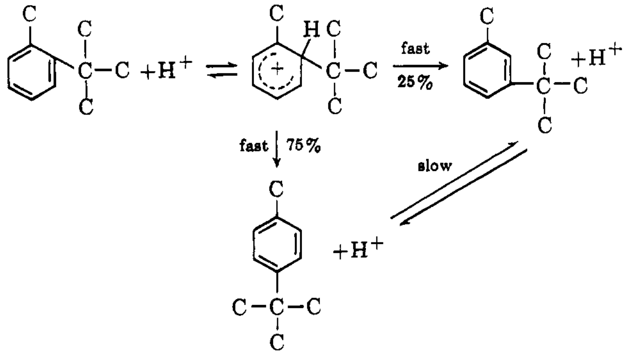
In the over-all isomerization of *o*-*t*-butyltoluene, the concentration of *para* isomer goes through a maximum. The mainly kinetically controlled part of the isomerization can be described by the following scheme.

TABLE VI

ISOMERIZATION OF *o-t*-BUTYLTOLUENE WITH ALUMINUM CHLORIDE IN NITROMETHANE SOLUTION

Time, min.	% *ortho*[a]	% *meta*[a]	% *para*[a]
2	96	Trace	4
3	69	8	23
4	58	11	31
5	41	16	43
6	26	20	54
7	14	23	63
8	10	24	66
9	5	25	70
10	2	25	73
11	1	28	71
12	1	24	75
13	Trace	25	75
15	0	25	75
75	0	27	73
135	0	30	70
210	0	36	64
255	0	40	60
315	0	45	55
375	0	48	52
495	0	56	44
21 hr.	0	61	39
30 hr.	0	61	39
57 hr.	0	62	38
71 hr.	0	63	37

[a] Normalized.



The situation is reminiscent of the isomerization of *o*-bromotoluene[6] where a fast *ortho–para* conversion was found indicating the possibility of complete detachment of the moving entity from the aromatic ring. A π-type intermediate might however also be postulated as it was demonstrated to play a role in the Friedel–Crafts *t*-butylation of toluene.[7] As the isomerization is fast, it is reasonable to suggest that the *t*-butyl group is not completely detached from the aromatic ring, but stays in interaction through a π-type of intermediate. Complete detachment with a real dealkylation–alkylation mechanism would be expected to be a much slower process, owing to the low concentration of the alkylable aromatic present in the system.

In the absence of rate data, no decision can be reached as to the contribution of the 1,2-shift mechanism to the isomerization of the undiluted isomers at low catalyst concentration. However, the formation of substantial amounts of *meta* isomer in the fast first stage of the isomerization seems to indicate that a concurrent 1,2-shift mechanism contributes to the reaction. Friedel–Crafts *t*-butylation of toluene under kinetic conditions generally yields only 6% of the *meta* isomer.[7]

Experimental

Starting Materials.—*p-t*-Butyltoluene used was Eastman White Label, containing 97% *para* and 3% *meta* isomer. *m-t*-Butyltoluene was American Petroleum Institute standard sample. *o-t*-Butyltoluene was obtained from Dr. B. S. Friedman, Sinclair Research Inc., Harvey, Ill., containing 95% *ortho* and 3% *para* isomer, and 2% unknown material.

General Process of Isomerization.—Reactions were carried out in stoppered flasks, in the case of heterogeneous reaction, with magnetic stirring. Unless indicated otherwise, 0.2 mole of aluminum chloride was used per mole of *t*-butyltoluene, and 1 ml. of water was added as a promoter. Isomerizations of *m*- and *p-t*-butyltoluene in nitromethane solution were carried out using equal weights of aromatic and solvent. Samples were drawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. Dried ether extracts were analyzed by gas–liquid chromatography. Only a small quantity of *o-t*-butyltoluene was available. It was used in quantities of 50 mg. in any one run, and the reactions were carried out in capped vials. All isomerizations were carried out at ~52°.

In the tables the amounts of *o*-, *m*- and *p-t*-butyltoluene are given as normalized %. Per cent given for other materials represent mole % of total aromatic present.

Gas–Liquid Chromatographic Analysis.—The 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 Infotronics Model CRS-1 integrator. Columns used were 150 ft. and were coated with polypropylene glycol (PPG) and *m*-bis(*m*-phenoxyphenoxy)-benzene (MBMA) modified with 20% Apiezon L grease, respectively. The polypropyleneglycol column was operated at 105° with a carrier He gas pressure of 10 p.s.i., whereas the MBMA column was operated at 100° with a carrier He gas pressure of 20 p.s.i. Characteristic retention times of *t*-butyltoluenes, toluene and di-*t*-butyltoluene observed are summarized in Table VII following.

TABLE VII

RETENTION TIMES OF TOLUENE, *t*-BUTYLTOLUENES, AND 3,5-DI-*t*-BUTYLTOLUENE[a]

Compound	PPG column	MBMA column
Toluene	9.1	4.3
o-t-Butyltoluene	33.2	24.1
m-t-Butyltoluene	25.4	18.6
p-t-Butyltoluene	26.7	17.7
3,5-di-*t*-Butyltoluene	76.1	43.6

[a] Values are given in minutes.

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[6] G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962).

[7] G. A. Olah, S. H. Flood, and M. E. Moffatt, *J. Am. Chem. Soc.*, **86**, 1060 (1964).