D. *o*-**Bromo-*t*-butylbenzene.**—Starting from 41 g (0.17 mole) of α,α-dimethyl-*o*-bromobenzyl chloride and 65 ml of an approximately 3 *M* solution of methylmagnesium bromide in ether (0.2 mole, *ca.* 15% excess), a yield of 14.9 g of crude *o*-bromo-*t*-butylbenzene boiling at 100–105° (40 mm) was obtained. Glpc analysis showed that it was only about 40% pure (*ca.* 15% yield based on olefin), the main impurity being *o*-bromoisopropenylbenzene. It was purified by bromination and redistillation under vacuum. As during vacuum distillation even at 0.5 mm pressure some debromination of the 2,α,β-tribromocumene takes place, yielding olefin, preparative-scale gas chromatography using an F and M Model 770 gas chromatograph with a polypropylene glycol packed column was necessary to obtain the *o*-bromo-*t*-butylbenzene in 99.8% purity.

Anal. Calcd for $C_{10}H_{13}Br$: C, 56.35; H, 6.15; Br, 37.50. Found: C, 56.29; H, 6.11; Br, 37.60.

General Procedure of Isomerization.—The ratio of substrate and catalyst in all isomerizations was 0.15 mole of aluminum chloride/mole of halo-*t*-butylbenzene. One milliliter of water was added as promoter. All isomerizations were carried out in stoppered reaction flasks, magnetically stirred and thermostated at 25 ± 0.5°. Samples were withdrawn periodically; the reaction was stopped by quenching with water. The organic material was extracted with ether. The extracts were dried with anhydrous magnesium sulfate and analyzed by gas-liquid partition chromatography.

Gas-Liquid Partition Chromatographic Analysis.—All analyses were carried out on a Perkin-Elmer Model 226 Fractometer equipped with a 150-ft polypropylene glycol coated open-tubular (Golay) column, using a hydrogen flame-ionization detector. Helium carrier gas pressure of 30 psi was used, columns being operated at 85–100°. Peak areas were directly determined by the use of a high-speed Infotronics Model CRS-1 electronic integrator. Characteristic retention times and column conditions used are summarized in Table XI.

Table XI

Retention Times of Halo-*t*-butylbenzenes

Compound	Column temp, °C	Time, min
o-Fluoro-*t*-butylbenzene	85	12.8
m-Fluoro-*t*-butylbenzene		14.0
p-Fluoro-*t*-butylbenzene		14.4
o-Chloro-*t*-butylbenzene	100	14.4
m-Chloro-*t*-butylbenzene		13.5
p-Chloro-*t*-butylbenzene		14.8
o-Bromo-*t*-butylbenzene	100	26.5
m-Bromo-*t*-butylbenzene		24.0
p-Bromo-*t*-butylbenzene		28.8

The accuracy of the gas-liquid partition chromatographic analytical method, as established from the analysis of isomer mixtures of known composition, was better than ±5 relative % for all isomers.

Acknowledgment.—Dr. Christoph Rüchardt (Organic Chemical Institute, University of Munich) is thanked for samples of pure isomeric halo-*t*-butylbenzenes.

Notes

Friedel-Crafts Isomerization. XII.[1a] Aluminum Chloride Catalyzed Isomerization of the Methylbiphenyls

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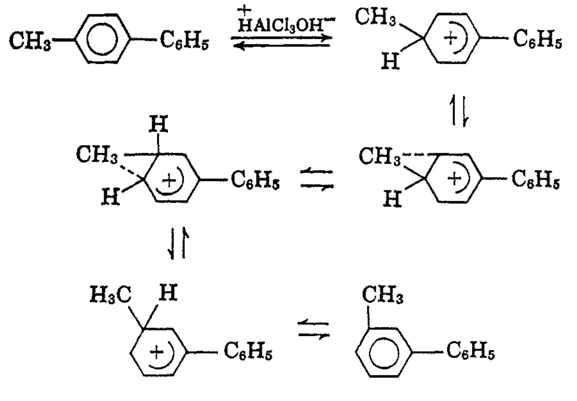
In previous work we reported on the aluminum chloride catalyzed isomerization of terphenyls[2] and fluorobiphenyls.[3] We felt that it would be of interest to extend the investigation to the isomerization of methylbiphenyls, which was so far not reported in the literature.

Isomerization of *o*-, *m*-, and *p*-methylbiphenyls with water-promoted aluminum chloride was carried out at 50°. The results are summarized in Table I.

The equilibrium mixture obtained starting with any one of the isomers contained about 16% *o*-, 58% *m*-, and 26% *p*-methylbiphenyl. The mixtures also contained smaller amounts of products of disproportionation, biphenyl and dimethylbiphenyls. The compositions of the latter were, however, not investigated. There was little variation in the composition of the final mixtures with temperature or time.

The relatively low temperatures needed for the isomerization of methylbiphenyls (50°), as compared with those needed for terphenyls (140–210°) and fluorobiphenyls (140–200°) where phenyl migration takes place, and the observed products (even if in small amounts) of intermolecular methyl group migration (disproportionation) point to the preferential migration of the methyl and not of the phenyl group. The mechanism of the migration is considered in accordance with experimental data to be predominantly that of intramolecular 1,2-methyl shifts. (See Scheme I.)

Scheme I



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[1] (a) Part XI: G. A. Olah, J. C. Lapierre, and C. G. Carlson, *J. Org. Chem.*, **30**, 541 (1965). (b) To whom inquires should be sent: Western Reserve University.

[2] G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3682 (1962).

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TABLE I

ISOMERIZATION OF METHYLBIPHENYLS WITH WATER-PROMOTED ALUMINUM CHLORIDE AT 50°

Reaction time	% methylbiphenyl isomer distribution (normalized) *ortho*	*meta*	*para*
	2-Methylbiphenyl		
0 min	99.7	0.3	0
5 min	98.9	1.1	0
10 min	89.2	10.6	0.2
15 min	77.2	22.6	0.2
20 min	65.4	34.4	0.2
25 min	59.5	40.3	0.2
30 min	56.1	42.7	1.2
40 min	50.3	46.5	3.2
1 hr	37.1	54.6	8.3
2.5 hr	15.1	75.6	9.3
4.5 hr	15.3	72.1	12.6
6.5 hr	15.2	70.4	14.4
24 hr	15.6	65.3	19.1
72 hr	15.8	58.1	26.1
	3-Methylbiphenyl		
0 min	0	95.4	4.7
5 min	0.7	95.4	4.1
15 min	0.3	92.7	7.0
20 min	0.4	91.8	7.8
45 min	1.1	89.8	9.1
1 hr	0.8	82.0	17.2
1.5 hr	0.7	78.2	21.1
2 hr	1.2	75.4	23.4
2.5 hr	1.8	73.6	24.6
3 hr	2.3	72.3	25.4
4 hr	3.6	71.2	25.3
5 hr	4.5	70.3	25.2
6 hr	5.9	68.2	25.9
8 hr	8.1	64.4	27.5
24 hr	15.1	58.0	26.9
48 hr	15.3	57.8	26.9
72 hr	15.8	57.8	26.4
	4-Methylbiphenyl		
0 min	0.3	0	99.7
5 min	0.3	2.1	97.6
10 min	0.3	8.3	91.4
20 min	0.3	23.5	76.2
30 min	0.4	37.0	62.6
40 min	0.5	47.0	52.5
50 min	0.5	52.1	47.4
1 hr	0.5	54.9	44.6
2 hr	0.6	63.9	35.5
2.5 hr	0.8	64.5	34.7
3 hr	0.8	70.4	28.8
4 hr	1.1	71.2	27.7
5 hr	1.3	70.5	28.6
6 hr	2.4	68.7	28.9
8 hr	3.3	67.6	29.1
24 hr	6.3	66.6	27.1
48 hr	15.2	57.8	27.0
72 hr	15.7	56.3	28.0

Experimental Section

Materials.—*o*-, *m*-, and *p*-methylbiphenyl were obtained from Chemical Procurement Laboratories, College Point, N. Y., and were used without further purification.

Isomerization Procedure.—Isomerizations were carried out in stoppered glass flasks, magnetically stirred and thermostated at 50 ± 0.5°. The amounts of substrate and catalyst in each experiment were 0.2 mole of aluminum chloride/mole of methylbiphenyl. To this mixture 1 ml of water was added as a promoter. Samples were withdrawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. The dried ether extracts were analyzed by gas-liquid partition chromatography (glpc).

Glpc Analysis.—The analyses were carried out by glpc on a Perkin-Elmer Model 226 Vapor Fractometer using a 150-ft, 0.01-in. diameter open-tubular column coated with Apiezon L and a hydrogen flame-ionization detector. At a column temperature of 165° and He carrier gas pressure of 30 psi the isomeric methylbiphenyls had the following retention times: *o*-methylbiphenyl, 16.0 min; *m*-methylbiphenyl, 24.7 min; and *p*-methylbiphenyl, 26.0 min. Biphenyl under the same conditions has a retention time of 15.6 min and the isomeric dimethylbiphenyls (not further identified concerning isomeric distribution) between 30.9 and 41 min (at 200° column temperature). Peak areas were determined by the use of an Infotronics Model CRS-1 high-speed electronic integrator.

The accuracy of the glpc analytical method, as established from the analysis of isomer mixtures of known composition was better than ±5 relative % for all isomers.

Reactions Catalyzed by Potassium Fluoride.
V. The Kinetics of the Knoevenagel Reaction

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There are numerous examples of exchange reactions reported for the preparation of fluorinated organic compounds in which sodium or potassium fluorides are refluxed with chloro compounds.[1-3] In an attempt to prepare trifluoroacetic acid from trichloroacetic acid and potassium fluoride, Nesmeyanov[4] discovered that, rather than the expected exchange, the fluoride served to catalyze decarboxylation to afford chloroform, a procedure ordinarily requiring bases such as hydroxide or amines. This apparent basic property of potassium fluoride was further exemplified by Midorikawa and co-workers[5] who reported examples of catalysis of the Knoevenagel reaction, and by LeGoff[6] in preparing dihydrohexaphenylpentalene *via* a Michael-Knoevenagel sequence from 1,2,3-triphenylcyclopentadiene and 1,2,3-triphenylpropenone. It was further demonstrated[7] that rubidium and cesium fluorides were more effective as catalysts than potassium fluoride for the Knoevenagel reaction in both polar and nonpolar solvents.

The kinetics and mechanism of the uncatalyzed reaction of ethyl cyanoacetate with aromatic aldehydes in various solvent mixtures have been determined by Patai and Zabicky.[8] Their data indicate that the reaction sequence is governed by a initial dissociation of the active methylene, although this dissociation is not the rate-determining step for the over-all reaction whose steps are given in Chart I.

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