Friedel–Crafts Isomerization. XIV.[1] Aluminum Chloride Catalyzed Isomerization of the Halo-*t*-butylbenzenes

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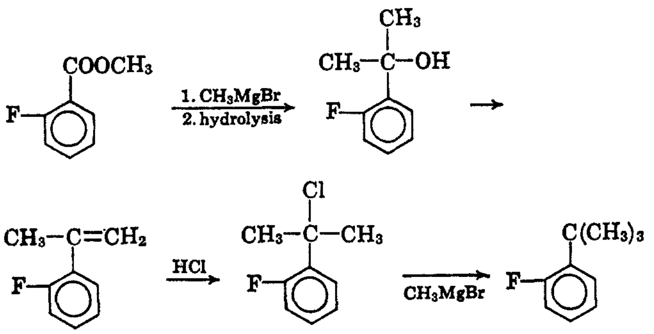
The water-promoted aluminum chloride catalyzed isomerization of the isomeric *o*-, *m*- and *p*-fluoro-, chloro-, and bromo-*t*-butylbenzenes was investigated. Fluoro- and chloro-*t*-butylbenzenes isomerize by migration of the *t*-butyl group, whereas in the case of bromo-*t*-butylbenzenes both the *t*-butyl group and the bromine atom migrates. The equilibrium isomer distributions consist in the case of fluoro-*t*-butylbenzenes of about 3.5% *ortho*, 78.5% *meta*, and 18.0% *para* isomer, in the case of chloro-*t*-butylbenzenes of 75% *meta* and 25% *para* isomer, and in the case of bromo-*t*-butylbenzenes of about 68% *meta* and 32% *para* isomer. The preparation or pure isomeric halo-*t*-butylbenzenes, as well as the mechanism of their Friedel–Crafts isomerization, was investigated.

No previous reports exist on the Friedel–Crafts isomerization of halo-*t*-butylbenzenes. In the continued investigation of the Friedel–Crafts isomerization of disubstituted benzenes[3] we now investigated the aluminum chloride catalyzed isomerization of the isomeric *fluoro*-, *chloro*-, and *bromo*-*t*-butylbenzenes.

Results and Discussion

Preparation of Halo-*t*-butylbenzenes—*p*- and *m*-*t*-butylfluorobenzenes were known from the literature, having been prepared from the corresponding *t*-butylanilines by the Schiemann reaction.[4] The preparation of the diazonium tetrafluoroborate of *o*-*t*-butylaniline, however, represents serious difficulties and could not be affected under usual conditions. It was necessary therefore to synthesize *o*-fluoro-*t*-butylbenzene through another synthetic route.

Methyl *o*-fluorobenzoate was allowed to react with methylmagnesium bromide and was hydrolyzed to give dimethyl-*o*-fluorophenylcarbinol which was then dehydrated to *o*-fluoroisopropenylbenzene. Anhydrous hydrogen chloride was then added to yield α-chloro-*o*-fluorocumene, which was then treated with methylmagnesium bromide.



The isomeric chloro-*t*-butylbenzenes were all reported in the literature and were recently synthesized by Rüchardt and Eichler.[4] So were the *m*- and *p*-bromo-*t*-butylbenzenes. *o*-Bromo-*t*-butylbenzene was prepared by us from methyl *o*-bromobenzoate under similar conditions as the *o*-fluoro-*t*-butylbenzene.

Isomerization.—The isomerization of *o*-, *m*-, and *p*-fluoro-, chloro-, and bromo-*t*-butylbenzenes was investigated using water-promoted aluminum chloride as catalyst at 25°. Experimental conditions are given in the Experimental Section. The molar ratio of halo-*t*-butylbenzenes to aluminum chloride was 1:0.15, with the exception of *o*-chloro- and bromo-*t*-butylbenzene, which isomerized faster than the other isomers, and therefore a 1:0.07 ratio gave sufficiently fast isomerization.

Fluoro-*t*-butylbenzenes.—Tables I–III show the data of the isomerization of the three isomeric fluoro-*t*-butylbenzenes. The equilibrium mixtures contain

TABLE I

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *o*-FLUORO-*t*-BUTYLBENZENE

	—Normalized % of fluoro-*t*-butylbenzenes—		
Time	*ortho*	*meta*	*para*
0 min	99.7	0.1	0.2
1 min	30.6	44.2	25.2
2 min	15.2	58.2	26.6
5 min	7.1	64.7	28.2
10 min	4.4	73.9	21.7
20 min	3.4	77.4	17.2
30 min	3.5	77.8	18.7
1 hr	3.4	77.7	18.9
2 hr	3.5	78.1	18.4
5 hr	3.2	78.3	18.5
24 hr	3.7	79.0	17.3
48 hr	3.4	78.4	18.2
72 hr	3.3	78.5	18.2

TABLE II

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-FLUORO-*t*-BUTYLBENZENES

	—Normalized % of fluoro-*t*-butylbenzenes—		
Time	*ortho*	*meta*	*para*
0 min	0.2	99.7	0.1
2 min	1.0	98.7	0.3
3 min	2.7	96.3	1.0
4 min	3.2	94.0	2.8
5 min	3.3	92.0	4.7
10 min	3.4	83.5	13.1
15 min	3.3	80.2	16.4
20 min	3.7	78.7	17.6
30 min	3.6	79.3	17.1
1 hr	3.8	79.1	17.3
2 hr	3.5	78.9	17.6
8 hr	3.6	78.5	17.9
24 hr	3.6	79.5	16.9
48 hr	3.4	78.7	17.9

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[1] Part XIII: G. A. Olah, J. C. Lapierre, and G. J. McDonald, *J. Org. Chem.*, **31**, 1262 (1966).

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[3] Parts II–XIII of this series.

[4] C. Rüchardt and S. Eichler, *Chem. Ber.*, **95**, 1922 (1962).

Table III
Aluminum Chloride Catalyzed Isomerization of *p*-Fluoro-*t*-butylbenzene

Time	Normalized % of fluoro-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	0.8	1.0	98.2
1 min	2.7	4.2	93.1
2 min	4.1	28.1	67.8
3 min	4.2	49.2	46.6
4 min	4.3	61.8	33.9
5 min	3.8	69.8	26.4
10 min	3.7	77.3	19.0
20 min	3.8	77.6	18.6
30 min	3.3	76.8	19.9
45 min	3.5	78.4	18.1
1 hr	3.4	78.7	17.9
1.5 hr	3.6	78.2	18.2
2 hr	3.2	78.3	18.5
8 hr	3.3	76.8	19.9
24 hr	3.6	77.4	19.0
96 hr	3.8	77.3	18.9

about 3.5% *o*-, 78.5% *m*-, and 18.5% *p*-fluoro-*t*-butylbenzene. There were always formed products of disproportionation, among which fluorobenzene and 3,5-di-*t*-butylfluorobenzene are the main ones (besides nonidentified higher boiling products). At equilibrium these amount to as much as 50% of total aromatics present. The absence of *t*-butylbenzene from the products indicates that the isomerization proceeds by migration of the *t*-butyl group and no fluorine migration is involved. Halogen exchange with the catalyst giving *t*-butylchlorobenzenes is also observed, but at the temperature of our investigations (25°) its importance is limited.

Chloro-*t*-butylbenzenes.—Tables IV–VI summarize data of the isomerization of the isomeric chloro-*t*-butylbenzenes. The equilibrium mixtures contain about 75% *m*- and 25% *p*-chloro-*t*-butylbenzene. Products of the isomerizations always contained chlorobenzene and 3,5-di-*t*-butylchlorobenzene (besides other nonidentified higher boiling materials). No *t*-butylbenzene was, however, detected in any of the samples, indicating that the *t*-butyl group and not the chlorine atom is the migrating entity.

Table IV
Aluminum Chloride Catalyzed Isomerization of *o*-Chloro-*t*-butylbenzene

Time	Normalized % of chloro-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	100	0	0
1 min	85.9	7.5	6.6
2 min	50.3	38.5	11.1
5 min	32.5	46.8	20.7
10 min	0	64.1	35.9
15 min	0	72.1	27.9
30 min	0	71.5	28.5
1 hr	0	79.0	21.0
1.5 hr	0	73.9	26.1
2 hr	0	73.8	26.2
8 hr	0	73.9	26.1
24 hr	0	74.4	25.6

Bromo-*t*-butylbenzenes.—The isomerization of the isomeric bromo-*t*-butylbenzenes yields an equilibrium mixture of about 68% *m*- and 32% *p*-bromo-*t*-butylbenzene. Tables VII–IX summarize data of the isomerizations. The reaction products include bromobenzene and benzene, as well as higher disproportionation products (di-*t*-butylbenzenes, 1,3,5-tri-*t*-butylbenzene, 3,5-di-*t*-butylbromobenzene, and unidentified products). Data indicate that, although the *t*-butyl group is preferred as the migrating group, bromine migration followed by the disproportionation of the formed *t*-butylbenzene is also to be considered.

Table V
Aluminum Chloride Catalyzed Isomerization of *m*-Chloro-*t*-butylbenzene

Time	Normalized % of chloro-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	0	100	0
1 min	0	100	0
2 min	0	99.8	0.2
5 min	0	97.8	2.2
10 min	0	86.7	13.3
15 min	0	83.7	16.3
20 min	0	77.0	23.0
30 min	0	74.8	25.2
40 min	0	74.0	26.0
1 hr	0	74.5	25.5
1.5 hr	0	75.1	24.9
0 hr	0	73.3	26.7
24 hr	0	75.3	24.7

Table VI
Aluminum Chloride Catalyzed Isomerization of *p*-Chloro-*t*-butylbenzene

Time	Normalized % of chloro-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	1.0	0	99.0
1 min	0	4.4	95.6
2 min	0	8.2	91.8
3 min	0	12.2	87.8
4 min	0	29.2	70.8
10 min	0	33.7	66.3
15 min	0	46.1	53.9
30 min	0	55.9	44.1
45 min	0	61.8	38.2
1 hr	0	70.1	29.9
1.5 hr	0	71.6	28.4
2 hr	0	73.4	26.6
24 hr	0	73.0	27.0
48 hr	0	74.8	25.2
96 hr	0	74.8	25.2
168 hr	0	75.0	25.0

Table VII
Aluminum Chloride Catalyzed Isomerization of *o*-Bromo-*t*-butylbenzene

Time	Normalized % of bromo-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	99.8	0.1	0.1
1 min	99.1	0.8	0.1
2 min	77.1	10.6	12.3
5 min	0	59.4	40.6
10 min	0	63.7	26.3
15 min	0	64.5	35.5
30 min	0	67.8	32.2
40 min	0	68.4	31.6
1 hr	0	69.4	30.6
2 hr	0	70.4	29.6
3 hr	0	67.8	32.2
5 hr	0	68.6	31.4
24 hr	0	67.8	32.2
48 hr	0	68.6	31.3

TABLE VIII

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *m*-BROMO-*t*-BUTYLBENZENE

Time	Normalized % of bromo-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	0	100	0
5 min	0	99.7	0.3
15 min	0	99.3	0.7
25 min	0	97.3	2.7
30 min	0	94.8	5.2
40 min	0	91.0	9.0
50 min	0	81.6	18.4
1 hr	0	80.0	20.0
1.5 hr	0	68.5	31.5
2 hr	0	70.8	29.2
3 hr	0	71.9	28.1
5 hr	0	69.7	30.3
24 hr	0	68.7	31.3
48 hr	0	69.3	30.7

TABLE IX

ALUMINUM CHLORIDE CATALYZED ISOMERIZATION OF *p*-BROMO-*t*-BUTYLBENZENE

Time	Normalized % of bromo-*t*-butylbenzenes		
	ortho	*meta*	*para*
0 min	0	1.8	98.2
5 min	0	3.3	96.7
10 min	0	5.9	94.1
20 min	0	12.6	87.4
30 min	0	26.9	73.1
45 min	0	50.9	49.1
1 hr	0	58.9	41.1
1.5 hr	0	67.3	32.7
2 hr	0	69.1	30.9
3 hr	0	69.8	30.2
24 hr	0	68.8	31.2

The migration of the *t*-butyl group in the halo-*t*-butylbenzenes follows the same pattern as previously observed in the isomerization of *t*-butyltoluenes[5] and di-*t*-butylbenzenes.[6] In the isomerization of the *o*-halo-*t*-butylbenzenes the concentration of *para* isomers goes through a maximum. This is in good agreement with our previous observations and supports the suggestion of a similar mechanism involving preferential *t*-butyl group migration.

TABLE X

EQUILIBRIUM COMPOSITION OF HALOALKYLBENZENES

	% isomer			
	ortho	*meta*	*para*	Reference
Fluorotoluenes	31	56	13	*a*
Fluoroethylbenzenes	36	52	12	*b*
Fluorocumenes	22	62	16	*c*
Fluoro-*t*-butylbenzenes	3.5	78.5	18	*d*
Chlorocumenes	31	44	25	*a*
Chloroethylbenzenes	28	52	20	*b*
Chlorocumenes	10	66	24	*c*
Chloro-*t*-butylbenzenes	0	75	25	*d*
Bromotoluenes	38	44	18	*a*
Bromoethylbenzenes	24	56	20	*b*
Bromocumenes	9	66	25	*c*
Bromo-*t*-butylbenzenes	0	68	32	*d*

[a] G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962). [b] G. A. Olah, J. C. Lapierre, and C. G. Carlson, *ibid.*, **30**, 541 (1965). [c] Reference 1. [d] Present work.

The effect of increasing bulkiness of substituen (both alkyl groups and halogen atoms) on the isomer distributions of alkylhalobenzenes can be well established from summarized data in Table X.

Experimental Section

Halo-*t*-butylbenzenes, with the exception of *o*-fluoro- and *o*-bromo-*t*-butylbenzene, were prepared according to Rüchardt and Eichler.[4]

***o*-Fluoro-*t*-butylbenzene. A. Dimethyl-*o*-fluorophenylcarbinol.**—While cooling with an ice bath 46.5 g (0.3 mole) of methyl *o*-fluorobenzoate dissolved in 60 ml of ether was added over 20 min to 250 ml of an approximately 3 *M* solution of methylmagnesium bromide in ether (0.75 mole, 25% excess). After stirring at room temperature for 0.25 hr and refluxing for 1 hr, the reaction was quenched with 30 g of crushed ice and 100 ml of 40% sulfuric acid. To complete the hydrolysis the mixture was stirred overnight. The organic layer was then separated, washed with saturated potassium bicarbonate solution and water, and dried over anhydrous magnesium sulfate. After pumping off the solvent, 42.6 g of dimethyl *o*-fluorophenylcarbinol was collected as a red oil which was not further purified.

B. *o*-Fluoroisopropenylbenzene.—A mixture of 42.6 g of the carbinol, 7 g of potassium bisulfate, and 2 g of phosphorus pentoxide was heated to 130° for 15 min. Then the reaction mixture was distilled at reduced pressure (70° at *ca.* 40 mm). After drying the distillate over anhydrous magnesium sulfate, 28.3 g (69% over-all yield) of the colorless *o*-fluoroisopropenylbenzene (α-methyl-*o*-fluorostyrene) was obtained.

C. α,α-Dimethyl-*o*-fluorobenzyl Chloride.—Dry hydrogen chloride was passed through 28.3 g of *o*-fluoroisopropenylbenzene during 2 hr. The excessive hydrogen chloride was pumped off, yielding 34.1 g of α,α-dimethyl-*o*-fluorobenzyl chloride which was not further purified.

D. *o*-Fluoro-*t*-butylbenzene.—The neat chloride (34.1 g, 0.21 mole) was added over 30 min to 85 ml of a 3 *M* solution of methylmagnesium bromide in ether (0.26 mole, 25% excess). After about $^5/_6$ of the chloride had been added, the reaction mixture was diluted with 50 ml of ether because of the formation of a heavy precipitate. It was stirred at room temperature for 1 hr and refluxed for another hour. Then the reaction mixture was quenched with 20 g of crushed ice and 100 ml of 40% sulfuric acid. After stirring for 1 hr, the organic layer was separated, washed, and dried. Finally, the solvent was pumped off and the resulting liquid was distilled under reduced pressure. A colorless liquid (14.1 g) was obtained, which boiled at 68–72° (40 mm). Glpc analysis showed that the product was only about 50% pure (22% over-all yield based on olefin), the main byproduct being *o*-fluoroisopropenylbenzene.

The impure *o*-fluoro-*t*-butylbenzene was dissolved in carbon tetrachloride, and to this solution bromine was added dropwise until the red color caused by excess bromine remained. The excessive bromine was then washed out with a solution of sodium thiosulfate. The organic layer was washed, separated, dried over anhydrous magnesium sulfate, and, after removing the solvent, was distilled under reduced pressure to give 3.94 g of *o*-fluoro-*t*-butylbenzene [bp 96° (40 mm)].

Anal. Calcd for $C_{10}H_{13}F$: C, 78.95; H, 8.55; F, 12.5. Found: C, 78.92; H, 8.52; F, 12.56.

Isomeric purity by gas chromatography was 99.7%.

***o*-Bromo-*t*-butylbenzene.**—In general, the same procedure as for the preparation of *o*-fluoro-*t*-butylbenzene was followed.

A. Dimethyl-*o*-bromophenylcarbinol.—Starting from 64.5 g (0.3 mole) of methyl *o*-bromobenzoate and 250 ml of an approximately 3 *M* solution of methylmagnesium bromide in ether (0.75 mole, 25% excess), a yield of 68.5 g of crude diemethyl-*o*-bromophenylcarbinol was obtained which was not further purified.

B. *o*-Bromoisopropenylbenzene.—Dehydration of 68.5 g of the crude carbinol with 7 g of potassium bisulfate and 2 g of phosphorus pentoxide gave a yield of 52.6 g (89% based on benzoate) of *o*-bromoisopropenylbenzene [bp 90–95° (40 mm)].

C. α,α-Dimethyl-*o*-bromobenzyl Chloride.—Dry hydrogen chloride was introduced into 35 g of *o*-bromoisopropenylbenzene while cooling with a Dry Ice–acetone bath. Then the excess HCl was pumped off at room temperature. A yield of 41 g of the α,α-dimethyl-*o*-bromobenzyl chloride was obtained.

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(5) G. A. Olah, M. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2310 (1964).

(6) G. A. Olah, C. G. Carlson, and J. C. Lapierre, *ibid.*, **29**, 2687 (1964).

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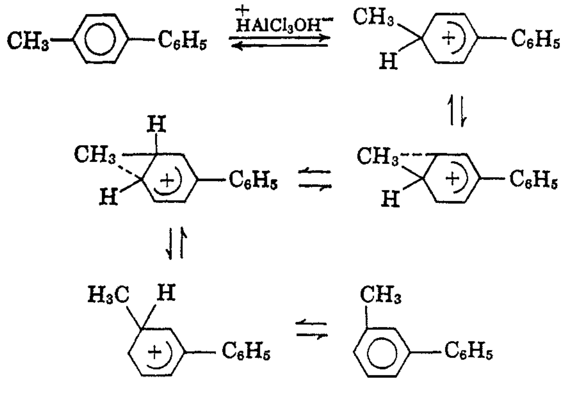
In previous work we reported on the aluminum chloride catalyzed isomerization of terphenyls[2] and fluorobiphenyls.[3] We felt that it would be of interest to extend the investigation to the isomerization of methylbiphenyls, which was so far not reported in the literature.

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).

[3] G. A. Olah and M. W. Meyer, *ibid.*, **28**, 1912 (1963).