[CONTRIBUTION FROM THE PURDUE RESEARCH FOUNDATION AND DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Reactions of 1-Heptafluoropropylmagnesium Bromide. II.[1] The Synthesis of Fluorine-containing Olefins and of 1-Heptafluoropropylbenzene

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RECEIVED JULY 5, 1956

A new synthesis for (perfluoroalkyl)-benzenes has been developed by the use of perfluoroalkyl Grignard reagents. 2-(1-Heptafluoropropyl)-1,3-cyclohexadiene obtained from the dehydration of an adduct from 1-heptafluoropropylmagnesium bromide and 2-cyclohexanone was converted to 1-heptafluoropropylbenzene using N-bromosuccinimide and subsequent dehydrobromination. The exchange reaction between a Grignard reagent and a perfluoroalkyl iodide was found to be most successful with aryl Grignard reagents.

Discussion

Few (perfluoroalkyl)-benzenes other than trifluoromethylbenzene have been synthesized.[3] In an attempt to synthesize 1-heptafluoropropylbenzene, heptafluoro-1-iodopropane was treated with phenylmagnesium bromide, phenyllithium,[4] phenylsodium and phenylcalcium iodide. However, no evidence of coupling was observed, the predominant reaction in each case being an exchange. 1-Heptafluoropropylbenzene was synthesized by a series of reactions starting with the 1-heptafluoropropyl Grignard reagent and 2-cyclohexenone. The adduct, which was thermally unstable, was dehydrated to 2-(1-heptafluoropropyl)-1,3-cyclohexadiene. Treatment of the latter substance with N-bromosuccinimide and subsequent dehydrobromination gave 1-heptafluoropropylbenzene.[5]

The 1-heptafluoropropyl Grignard reagent was prepared by an exchange reaction between heptafluoro-1-iodopropane and phenylmagnesium bromide.[1] This exchange has been shown to be rapid and quantitative even at Dry Ice temperatures.[6] Phenylmagnesium bromide has been found to react similarly with pentafluoroethyl iodide to provide the first reported synthesis of the perfluoroethyl Grignard reagent. This type of rapid exchange, although common in the organolithium series, is without parallel in the field of Grignard reagents. Gilman and Jones[7] and Kharasch and Fuchs[8] observed no functional exchange between various Grignard reagent–halide mixtures.[9] Various Grignard reagents have been investigated in this new exchange reaction, but the aryl Grignard reagents appear to be the most useful. As indicated in Table I, the 1-heptafluoropropyl Grignard reagent reacts with ketones to give good yields of the corresponding alcohols.

TABLE I

THE EXCHANGE REACTIONS WITH HEPTAFLUORO-1-IODOPROPANE

Grignard reagent	3,3,4,4,5,5,5-Heptafluoro-2-methyl-2-pentanol from acetone, %[a]	1-(1-Heptafluoropropyl)-cyclohexanol from cyclohexanone, %[a]
Phenylmagnesium bromide	85	90
α-Naphthylmagnesium bromide	40	58
o-Tolylmagnesium bromide	. .	87
Methylmagnesium iodide	19	. .
2-Propylmagnesium bromide	. .	12
t-Butylmagnesium chloride	. .	32

[a] Yield and conversion based on heptafluoro-1-iodopropane.

Experimental[10]

Typical reactions are given both where known and new compounds are reaction products. The 1-heptafluoropropyl Grignard reagent was prepared by the exchange reaction[1] and its reactions with the carbonyl compounds were run as indicated.

3,3,4,4,5,5,5-Heptafluoro-2-pentanol.—Phenylmagnesium bromide was prepared from 2.7 g. (0.11 g.-atom) of magnesium shavings and 17.3 g. (0.11 mole) of bromobenzene in 100 ml. of anhydrous ether under a nitrogen atmosphere. The mixture was cooled in a Dry Ice-bath and 29.6 g. (0.10 mole) of heptafluoro-1-iodopropane[11] in an equal volume of anhydrous ether was added during 15 min. While the temperature was maintained at −40 to −50°, 15 g. (0.34 mole) of freshly distilled acetaldehyde in an equal volume of ether was added. The reaction mixture was allowed to come to room temperature, cooled by ice-water, and hydrolyzed with a cold 10% aqueous solution of sulfuric acid. The ether layer was separated, the aqueous acid layer was

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[1] Paper I, O. R. Pierce, A. F. Meiners and E. T. McBee, THIS JOURNAL, **75**, 2516 (1953).

[2] This paper represents part of a thesis submitted by A. F. Meiners to the Graduate School, Purdue University, in partial fulfillment for the degree of Doctor of Philosophy, June, 1956.

[3] J. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., 1954, p. 399, summarized the difficulty in preparing these compounds and mentions the obvious need for new methods of synthesis.

[4] O. R. Pierce, E. T. McBee and G. F. Judd, THIS JOURNAL, **76**, 474 (1954).

[5] The ultraviolet spectrum of 1-heptafluoropropylbenzene indicated characteristic substituted benzene maxima (E. Braude, *Ann. Repts. Progress Chem.*, **42**, 105 (1945)) at 254 mμ (log ε 2.67), 261 mμ (log ε 2.85) and at 267 mμ (log ε 2.76). The spectrum was very similar to the spectrum of benzotrifluoride, American Petroleum Institute Research Project 44, "Ultraviolet Spectral Data," Carnegie Institute of Technology, Pittsburgh, Penna., No. 299; also, C. Miller and H. Thompson, *J. Chem. Phys.*, **17**, 845 (1949).

[6] E. T. McBee, A. F. Meiners and C. W. Roberts, *Proc. Indiana Acad. Sci.*, **64**, 112 (1955).

[7] H. Gilman and R. Jones, THIS JOURNAL, **51**, 2840 (1929).

[8] M. Kharasch and O. Fuchs, *J. Org. Chem.*, **10**, 292 (1945).

[9] M. Kharasch and O. Reinmuth ("Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 1062) suggest that Grignard reagent–halide exchange occurs only when the halogen atom of the halide has replaced an "active" hydrogen atom. Thus, the treatment of α-haloketones with Grignard reagents produces enolates that behave like Grignard reagents (A. Umnowa, *J. Russ. Phys. Chem. Soc.*, **45**, 881 (1913); *Chem. Zentr.*, **84**, **II**, 1478 (1913); C. Fisher, H. Snyder and R. Fuson, THIS JOURNAL, **54**, 3665 (1932); B. Howk and S. McElvain, *ibid.*, **55**, 3372 (1933); 1-haloethynes react with Grignard reagents to give acetylenic Grignard reagents (M. Kharasch, F. Lambert and W. Urry, *J. Org. Chem.*, **10**, 298 (1945)); some heterocyclic halides react in an analogous manner (C. Hurd and K. Wilkinson, THIS JOURNAL, **70**, 739 (1948). That the iodine atom in heptafluoro-1-iodopropane has not replaced an "active" hydrogen was shown by the inertness of heptafluoropropane to methylmagnesium iodide (see Experimental).

[10] Analyses were performed by Dr. C. T. Yeh, Purdue University, and the Clark Micro-analytical Laboratory; ultraviolet spectra were measured by Mr. E. Copelin using a Cary spectrophotometer; melting points are uncorrected.

[11] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 2461 (1951).

extracted three times and the combined ether layers were washed with water and dried over Drierite. The ether solution was distilled through a Todd column (8-mm. barrel, Heli-pak packing) to give 14.0 g. (30%) of 3,3,4,4,5,5,5-heptafluoro-2-pentanol, b.p. 98.5–101°, $n^{20}\text{D}$ 1.3157.[12]

1,1,1,2,2,3,3-Heptafluoro-4-heptanol.—The 1-heptafluoropropyl Grignard reagent, prepared from 29.6 g. (0.10 mole) of heptafluoro-1-iodopropane in 100 ml. of anhydrous ether and 100 ml. of 1 molar phenylmagnesium bromide, was treated with an ether solution of 7.2 g. (0.10 mole) of butyraldehyde during 15 min. The cooling bath was removed and the reaction mixture was allowed to come to room temperature; the mixture was hydrolyzed with a 10% aqueous solution of hydrochloric acid and the ether layer separated and dried over Drierite. The ether was distilled and the residue rectified through a Todd column to give 11.0 g. (45.5%) of 1,1,1,2,2,3,3-heptafluoro-4-heptanol, b.p. 128–130°, $n^{20}\text{D}$ 1.3376.[13]

1,1,1,2,2,3,3-Heptafluoro-4-heptene.—The 1,1,1,2,2,3,3-heptafluoro-4-heptanol (9 g., 0.037 mole) was heated with 15 g. of phosphorus pentoxide at gentle reflux for 8 hours. The liquid was distilled and subsequently rectified to give 6.4 g. (78%) of 1,1,1,2,2,3,3-heptafluoro-4-heptene, b.p. 84°, $n^{19}\text{D}$ 1.3181–1.3185, d^{20}_4 1.257.

Anal. Calcd. for $C_7H_7F_7$: C, 37.51; H, 3.15; *MR*D, 35.05. Found: C, 37.35; H, 3.20; *MR*D, 35.16.

3,3,4,4,5,5,5-Heptafluoro-2-phenyl-2-pentanol.—From the 1-heptafluoropropyl Grignard reagent (0.15 mole in 250 ml. of anhydrous ether) and 18 g. (0.15 mole) of acetophenone in 50 ml. of anhydrous ether there was obtained 34 g. (77.4%) of 3,3,4,4,5,5,5-heptafluoro-2-phenyl-2-pentanol, b.p. 102–104° (22 mm.), $n^{20}\text{D}$ 1.4219–1.4215, d^{20}_4 1.411.

Anal. Calcd. for $C_{11}H_9F_7O$: C, 45.53; H, 3.13; *MR*D, 51.91. Found: C, 45.83; H, 3.28; *MR*D, 52.21.

The urethan of 3,3,4,4,5,5,5-heptafluoro-2-phenyl-2-pentanol (2 ml.) was prepared at 135–140° in a sealed Pyrex tube from an equal volume of phenyl isocyanate and three drops of pyridine. After two days, the residue was extracted with petroleum ether (b.p. 90–100°) and the extract was evaporated and the residue recrystallized four times from petroleum ether (b.p. 90–100°) to give a white crystalline product, m.p. 131–131.5°.

Anal. Calcd. for $C_{18}H_{14}F_7NO_2$: C, 52.82; H, 3.45. Found: C, 53.05; H, 3.22.

3,3,4,4,5,5,5-Heptafluoro-2-phenyl-2-pentene.—The 3,3,-4,4,5,5,5-heptafluoro-2-phenyl-2-pentanol (34 g., 0.117 mole) was heated at gentle reflux for 12 hours with 40 g. of phosphorus pentoxide. The resulting mixture was distilled and rectified to give 26 g. (81%) of 3,3,4,4,5,5,5-heptafluoro-2-phenyl-2-pentene, b.p. 164–165°, $n^{20}\text{D}$ 1.4160–1.4166, d^{20}_4 1.349.

Anal. Calcd. for $C_{11}H_7F_7$: C, 48.53; H, 2.58; *MR*D, 49.92. Found: C, 48.65; H, 2.80; *MR*D, 50.65.

2,2,3,3,4,4,4-Heptafluoro-1,1-diphenyl-1-butanol.—From the 1-heptafluoropropyl Grignard reagent (0.1 mole in 200 ml. of anhydrous ether) and 17.7 g. (0.1 mole) of benzophenone in 50 ml. of anhydrous ether, there was obtained 43.4 g. (62%) of product, b.p. 143–144° (10 mm.), $n^{20}\text{D}$ 1.4831–1.4839, d^{20}_4 1.334.

Anal. Calcd. for $C_{16}H_{11}F_7O$: C, 54.55; H, 3.15; F, 37.76; *MR*D, 71.40. Found: C, 54.53; H, 3.10; F, 37.48; *MR*D, 71.76.

1-(1-Heptafluoropropyl)-cyclohexanol.—The 1-heptafluoropropyl Grignard reagent (0.5 mole in 800 ml. of anhydrous ether) was treated with 49 g. (0.5 mole) of cyclohexanone in 100 ml. of anhydrous ether during 1 hour. The cooling bath was removed and the contents of the flask were allowed to come to room temperature during 4 hours. The reaction mixture was hydrolyzed with a 10% aqueous solution of hydrochloric acid and the ether layer was separated and dried over Drierite. Distillation gave 130 g. of crude product, b.p. 160–170°, which upon rectification gave 121 g. (90%) of pure 1-(1-heptafluoropropyl)-cyclohexanol, b.p. 167–168°, $n^{20}\text{D}$ 1.3858, d^{20}_4 1.354.

Anal. Calcd. for $C_9H_{11}F_7O$: C, 40.31; H, 4.14; *MR*D, 44.08. Found: C, 40.18; H, 4.04; *MR*D, 46.50.

The *p*-toluenesulfonate was prepared by refluxing 1.0 g. of sodium sand in anhydrous ether and 10.1 g. (0.037 mole) of 1-(1-heptafluoropropyl)-cyclohexanol for 10 hours and then adding 7.19 g. (0.037 mole) of *p*-toluenesulfonyl chloride in 30 ml. of anhydrous ether. The mixture was refluxed for an additional hour, the precipitate filtered and the filtrate evaporated to give 9.5 g. (61%) of the crude ester, m.p. 70–71.5°. After four recrystallizations from petroleum ether the m.p. was found to be 72.5–73°.

Anal. Calcd. for $C_{16}H_{17}F_7O_3S$: C, 45.46; H, 4.07. Found: C, 45.71; H, 4.36.

The 3,5-dinitrobenzoate was prepared at reflux temperature from 1.0 g. (0.04 g.-atom) of sodium in 50 ml. of anhydrous ether and 12 g. (0.045 mole) of 1-(1-heptafluoropropyl)-cyclohexanol. The reaction mixture was allowed to reflux for 15 hours, during which time the sodium was completely consumed. An ether solution of 3,5-dinitrobenzoyl chloride (9.2 g., 0.4 mole) was added to the mixture and refluxing was continued for 2 hours. The mixture was filtered, the filtrate evaporated under reduced pressure, and the residue recrystallized four times from petroleum ether (b.p. 60–70°) to give the product, m.p. 85.5–86.5°.

Anal. Calcd. for $C_{16}H_{13}F_7N_2O_6$: C, 41.57; H, 2.83. Found: C, 41.51; H, 3.14.

1-(1-Heptafluoropropyl)-cyclohexene.—1-(1-Heptafluoropropyl)-cyclohexanol (57 g., 0.21 mole) was mixed with 60–65 g. of phosphorus pentoxide and refluxed gently for 4 hours, then heated strongly to distil 54 g. of crude product which was rectified to give 44 g. (83%) of 1-(1-heptafluoropropyl)-cyclohexene, b.p. 134–135°, $n^{20}\text{D}$ 1.3629, d^{20}_4 1.326.

Anal. Calcd. for $C_9H_9F_7$: C, 43.21; H, 3.63; *MR*D, 42.08. Found: C, 43.40; H, 3.91; *MR*D, 41.91.

2-(1-Heptafluoropropyl)-1,3-cyclohexadiene.—The 1-heptafluoropropyl Grignard reagent (0.144 mole in 250 ml. of anhydrous ether) was treated with 13.8 g. (0.144 mole) of 2-cyclohexenone[14] in 100 ml. of anhydrous ether during 30 min. The reaction mixture was allowed to come to room temperature during 6 hours and hydrolyzed with a 10% aqueous solution of hydrochloric acid; the ether layer was separated, washed with water and dried over Drierite. The ether was distilled through a 1′ glass-helices packed column[15] and the residue was rectified to give 52 g. of a mixture of iodobenzene and crude 1-(heptafluoropropyl)-2-cyclohexen-1-ol, b.p. 67–70° (17 mm.). This mixture reacted vigorously with 20 g. of phosphorus pentoxide and rectification gave 15.0 g. (43%) of 2-(1-heptafluoropropyl)-1,3-cyclohexadiene, b.p. 130–131°, $n^{20}\text{D}$ 1.3749–1.3752, d^{20}_4 1.334.

Anal. Calcd. for $C_9H_7F_7$: C, 43.56; H, 2.85; F, 53.60; *MR*D, 41.62. Found: C, 43.97; H, 2.52; F, 53.67; *MR*D, 41.67.

2-(1-Heptafluoropropyl)-bicyclo[2.2.2]-2-octene-5,6-dicarboxylic Acid Anhydride.—2-(1-Heptafluoropropyl)-1,3-cyclohexadiene (2 g.) and an excess of maleic anhydride were heated in a sealed tube for 12 hours at 180–185°. The cooled tube was opened, the contents dissolved in a 10% solution of ethanolic sodium hydroxide, and the solution warmed on a steam-plate for 6 hours. The hot solution was filtered, the filtrate acidified with concentrated hydrochloric acid, and the precipitate air dried and sublimed at about 50° *in vacuo* to give 2-(1-heptafluoropropyl)-bicyclo[2.2.2]-2-octene-5,6-dicarboxylic acid anhydride, m.p. 100–103° with sublimation.

Anal. Calcd. for $C_{13}H_9F_7O_3$: C, 45.10; H, 2.62. Found: C, 45.26; H, 2.72.

(1-Heptafluoropropyl)-benzene.—2-(1-Heptafluoropropyl)-1,3-cyclohexadiene (9.4 g., 0.038 mole) was treated with 6.8 g. (0.038 mole) of N-bromosuccinimide and 0.1 g. of benzoyl peroxide in 25 ml. of refluxing carbon tetrachloride for 8 hours. The cooled reaction mixture was filtered and the filtrate was distilled with the evolution of hydrogen

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[12] R. N. Haszeldine, *J. Chem. Soc.*, 3423 (1952).

[13] E. T. McBee, O. R. Pierce and M. C. Chen, This Journal, **75**, 2324 (1953).

[14] F. C. Whitmore and G. Pedlow, *ibid.*, **63**, 758 (1941).

[15] A portion of the residue gave neither a bisulfite addition compound nor a positive 2,4-dinitrophenylhydrazine test. This was unexpected because of the tendency for 2-cyclohexenone to give 1,4-addition products with Grignard reagents (see M. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, p. 455).

bromide. The distillate was dissolved in 10 ml. of carbon tetrachloride and washed with a 5% aqueous solution of sodium carbonate and with water. The solution was treated with an excess of 5% potassium permanganate in acetone–water and heated on a steam-plate until the violet color remained. The solution was filtered, washed with water until the solution was colorless, dried by passing it through a column of calcium chloride, and rectified to give 4.9 g. (53%) of (1-heptafluoropropyl)-benzene, b.p. 127–128°, $n^{20}D$ 1.3875, d^{20}_4 1.384.

Anal. Calcd. for $C_9H_5F_7$: C, 43.92; H, 2.04; *MR*D, 41.09. Found: C, 43.57; H, 2.01; *MR*D, 41.91.

The Preparation of Pentafluoroethyl Grignard Reagent: Reaction with Acetone.—A 500-ml., round-bottomed flask was equipped with a stirrer and two closed-circuit addition funnels. The system was flamed out in a stream of dry nitrogen and cooled in a Dry Ice-bath prior to the addition of 75 ml. of anhydrous ether and 49 g. (0.2 mole) of pentafluoroethyl iodide.[11] In one funnel was placed 200 ml. (0.21 mole) of 1.07 molar phenylmagnesium bromide in ether and in the other 12 g. (0.2 mole) of acetone in 100 ml. of anhydrous ether. The contents of the funnels were simultaneously added to the flask during 3 hours while the reaction mixture was held at Dry Ice temperature. The reaction mixture was allowed to come to room temperature and cooled in ice-water and hydrolyzed with 150 ml. of a 10% aqueous solution of hydrochloric acid. Very little evolution of gas was observed throughout the experiment. The ether solution was separated, the acid layer was washed three times with ether and the combined ether portions were dried over Drierite. The ether was distilled through a glass-helices packed column and the residue rectified to give 13.1 g. (38%) of 3,3,4,4,4-pentafluoro-2-methyl-2-butanol, b.p. 94–97°, $n^{20}D$ 1.3325–1.3335.[16]

The Treatment of Heptafluoropropane with Methylmagnesium Iodide.—Methylmagnesium iodide was prepared from 2.4 g. (0.1 g.-atom) of magnesium shavings and 14.2 g. (0.1 mole) of methyl iodide in 75 ml. of anhydrous ether. The reagent was transferred to a Carius tube and the tube was cooled in Dry Ice (a nitrogen atmosphere was maintained.) Heptafluoropropane (12 g., 0.07 mole, b.p. −14 to −15°) was distilled into the tube and the tube was sealed. The tube was allowed to warm to room temperature and to stand, with occasional shaking, for 24 hours. It was then cooled in a liquid nitrogen bath, opened and quickly connected to a system consisting of a Dry Ice trap and an inverted bottle filled with water which could be filled with gas by displacement of the water. The tube was removed from the liquid nitrogen bath, allowed to warm slightly and placed in a Dry Ice-bath. There was a 100-ml. evolution of a non-flammable gas within a few minutes that would correspond to no more than that caused by thermal expansion. On removing the tube from the Dry Ice-bath and warming to 30° no further gas evolution was observed, but 7 g. (58%) of heptafluoropropane was recovered. Since no methane was formed, it was concluded that heptafluoropropane does not react at room temperature with methylmagnesium iodide.

Acknowledgment.—The authors are indebted to Westinghouse Electric Corporation for financial support of this work.

WEST LAFAYETTE, INDIANA

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[16] E. T. McBee, J. F. Higgins and O. R. Pierce, THIS JOURNAL **74**, 1387 (1952).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO.]

The Synthesis of Alkylhaloboranes[1,2]

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RECEIVED AUGUST 15, 1956

Alkylchloroboranes and alkylfluoroboranes have been prepared by a high temperature reaction of a trialkylborane with the appropriate trihaloborane. Attempts to isolate compounds containing both chlorine and fluorine attached to boron were not successful. However, an equimolar mixture of butyldichloroborane and butyldifluoroborane reacts with alcohols in a manner that would be expected of the compound $C_4H_9B(F)Cl$.

The alkylhaloboranes are versatile intermediates which can be utilized for the preparation of many organic boron compounds containing one or two boron–carbon bonds. The halides, except the fluorides, are very reactive. They readily undergo reactions in which the halogen is replaced without affecting the boron–carbon bonds. Alkylhaloboranes have been prepared by a number of different reactions. These include the dealkylation of trialkylboranes with hydrogen chloride or chlorine or bromine,[3–5] the addition of acetylene to trichloroborane[6] and the reaction of alkylboryl oxides with trifluoroborane.[7] The reaction of aliphatic Grignard reagents with trihaloboranes gives excellent yields of trialkylboranes, but attempts to prepare alkylhaloboranes in this manner have not been successful. Only trialkylboranes are recovered despite low temperatures and an excess of trihalide. Arylhaloboranes have, however, been prepared using aryl Grignard reagents[8] or diaryl mercury.[9] A mixture of trimethylborane, dichloromethylborane and chlorodimethylborane has been reported from the reaction of trichloroborane with zinc dimethyl.[10]

The present investigation has developed a synthesis of alkylhaloboranes which consists of heating a trialkylborane with a trihaloborane under pressure, thus effecting a redistribution of alkyl and halogen groups

$$R_3B + BX_3 \rightleftarrows R_2BX + RBX_2$$

The reaction is reversible, the rate depending upon the nature of the substituent groups. Thus dichloromethylborane and chlorodimethylborane are said to undergo complete disproportionation to trichloroborane and methylborane on attempted distillation.[10] Analogous reactions are known in other fields of organometallic chemistry. Kocheshkov[11] prepared the three butyltin chlorides by heating tetrabutyltin with the appropriate amounts of an-

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[1] This paper reports work done under contract with the Chemical Corps. U. S. Army, Washington 25, D. C.

[2] Recommendations of an American Chemical Society Nomenclature Committee have been followed in naming these compounds; see *Chem. Eng. News*, **34**, 560 (1956).

[3] E. Frankland, *Ann.*, **124**, 137 (1862).

[4] J. R. Johnson, H. R. Snyder and M. G. Van Campen, Jr., THIS JOURNAL, **60**, 115 (1938).

[5] R. B. Booth and C. A. Kraus, *ibid.*, **74**, 1415 (1952).

[6] H. R. Arnold, U. S. Patent 2,402,589, June 25, 1946.

[7] A. B. Burg, THIS JOURNAL, **62**, 2228 (1940).

[8] E. Krause and R. Nitsche, *Ber.*, **55B**, 1261 (1922).

[9] A. Michaelis and P. Becker, *ibid.*, **13**, 58 (1880).

[10] E. Wiberg and W. Ruschmann, *ibid.*, **70B**, 1583 (1937).

[11] K. A. Kocheshkov, *J. Gen. Chem. USSR*, **5**, 211 (1935).