[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Preparation of Substituted Tricyclohexylgermanes

BY O. H. JOHNSON AND W. H. NEBERGALL

Generally the use of an excess of Grignard reagent on germanium tetrachloride yields tetrasubstituted germanium compounds. Bauer and Burschkies,[1] using the conventional Grignard reaction, found that the action of an excess of cyclohexylmagnesium bromide on germanium tetrachloride resulted solely in bromotricyclohexylgermane, apparently according to the reaction

$$3C_6H_{11}MgBr + GeCl_4 \longrightarrow (C_6H_{11})_3GeBr + MgBr_2 + 2MgCl_2$$

The results reported by Bauer and Burschkies led us to determine whether other groups could be substituted for bromine in the tricyclohexylgermanium compound. Accordingly we have prepared a number of new compounds by means of the reaction of bromotricyclohexylgermane with various Grignard reagents and with sodium metal.

Bromotricyclohexylgermane was prepared from cyclohexyl bromide and germanium tetrachloride[2] by the method of Bauer and Burschkies. The substituent groups for the bromine atom in the bromotricyclohexylgermane were introduced by forming Grignard reagents in the usual manner with the appropriate alkyl or aryl halide and adding the bromotricyclohexylgermane in dry benzene

$$RMgBr + (C_6H_{11})_3GeBr \longrightarrow (C_6H_{11})_3GeR + MgBr_2$$

The reaction between bromotricyclohexylgermane and methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl-, and benzylmagnesium bromides proceeded smoothly. It was found that the isopropyl, the phenyl and the cyclohexylmagnesium bromides did not react under the conditions that gave good yields of the *n*-alkyl and benzyl compounds. Failure to introduce the isopropyl, phenyl and cyclohexyl groups may be due to possible steric effects.

Formation of hexacyclohexyldigermane by the Wurtz synthesis using sodium metal and bromotricyclohexylgermane was successful.

Experimental

Substituted Germanes.—Grignard reagent was prepared by treating 0.264 mole of alkyl bromide with 0.270 mole of magnesium in 200 ml. of absolute ether. To this mixture was added 0.032 mole of bromotricyclohexylgermane dissolved in 100 ml. of dry benzene. The ether was removed by distillation and the reaction mixture refluxed on the steam-bath for three hours. The excess Grignard was destroyed by dilute acetic acid. The aqueous and the organic layers were separated and the aqueous layer extracted twice with 50 ml. of benzene. The benzene solution was dried over anhydrous calcium chloride and the benzene removed by distillation, leaving an oily liquid. This residual oily liquid was dissolved in boiling absolute ethanol and upon cooling the substituted tricyclohexylgermane precipitated as fine white crystals. The product was purified by recrystallizing four times from absolute ethanol.

Substituted Digermane.—An excess of sodium was added to a solution of 5.5 g. of bromotricyclohexylgermane in 75 ml. of dry toluene and refluxed for two hours. The hot mixture was filtered, allowed to cool and about one-half of the toluene removed by air evaporation by an electric fan. The cooling and the evaporation of the solvent were accompanied by the precipitation of white crystals. These crystals were filtered off, washed with dry toluene, and dried in a pistol for two hours using toluene for a refluxing agent. The analysis indicated that it was hexacyclohexyldigermane, m. p., d. *ca.* 316°; yield, 85%.

Anal. Calcd.: C, 67.31; H, 10.33; Ge, 22.54. Found: C, 67.15; H, 10.59; Ge, 22.49.

Comments on Analytical Procedure.—The standard microcombustion method for determining carbon and hydrogen gave consistently low values for carbon. The cause of these low results is believed to be the formation of germanium carbides which resisted oxidation. To minimize this factor the procedure was modified[3] by increasing the volume of oxygen to 150 ml. for a period of thirty minutes followed by a current of air for another thirty minutes, the heating being continued for twenty minutes after the oxygen was discontinued. The platinum boat was placed as close to the furnace as possible to limit the area to be heated.

Germanium was determined as the dioxide by an adaptation of the method of Bauer and Burschkies.[1] A sample of 0.05 to 0.07 g. weight was heated in a platinum crucible over a steam bath for an hour with a mixture of three parts fuming nitric acid and one part concentrated sulfuric acid. The crucible and mixture were then heated on an electric hot-plate until a brown color appeared. More fuming nitric acid was added from time to time and the process repeated several times until a white residue remained upon evaporation. The residue was ignited and weighed as germanium dioxide.

TABLE I

SUBSTITUENT TRICYCLOHEXYLGERMANES

Substituent	M. p., °C.	Yield, %	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Germanium, % Calcd.	Germanium, % Found
CH_3	48.0–48.5	65	67.71	67.25	10.72	11.00	21.55	21.59
C_2H_5	38.5–39.0	56	68.41	68.46	10.91	11.31	20.68	20.58
n-C_3H_7	124–125	70	69.08	69.10	11.04	11.55	19.88	19.77
n-C_4H_9	152.5–153.5	61	69.68	69.16	11.17	11.60	19.15	19.20
n-C_5H_{11}	78–79	71	70.25	69.27	11.27	11.27	18.47	18.52
$C_6H_5CH_2$	54–54.5	69	72.66	72.03	9.76	10.26	17.57	17.52

Results.—Table I gives the results of the analyses and the melting points of the compounds prepared.

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[1] Bauer and Burschkies, *Ber.*, **65B**, 956 (1932).

[2] Obtained from Research Department, Eagle-Picher Co., Joplin, Mo.

[3] As suggested by R. W. Amidon who made the analyses for carbon and hydrogen.

Solubility.—The compounds prepared were found to be insoluble in water, slightly soluble in acetone and cold ethanol and soluble in ether, benzene, toluene, chloroform, petroleum ether and hot ethanol.

Summary

1. Seven new compounds of germanium, methyl-, ethyl-, *n*-propyl-, *n*-butyl-, *n*-amyl- and benzyltricyclohexylgermane, and hexacyclohexyldigermane have been prepared and some properties described.

2. Possible steric effects were encountered in attempts to introduce the isopropyl, the phenyl and the cyclohexyl group as the fourth group into tricyclohexylgermane.

3. Hexacyclohexyldigermane was prepared from bromotricyclohexylgermane by the Wurtz synthesis.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXII. Conductance of Some Long Chain Salts in Ethylene Chloride and Nitrobenzene at 25°[1]

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I. Introduction

Conductance measurements with aqueous solutions[3] of salts containing hydrocarbon chains of progressively increasing length indicate that the characteristic effect—ascribed to micelle formation—first becomes noticeable with the *n*-nonyl group. In order to determine whether similar effects occur in solutions of such electrolytes in nonaqueous solvents, measurements were carried out with several salts in ethylene chloride and nitrobenzene. At the time that this investigation was initiated, no data were available on the conductance of long chain salts in solvents other than water; in the meantime, however, results of measurements by several investigators have appeared.[4]

The following salts have been studied: octadecyltrimethylammonium and octadecyltributylammonium nitrates in ethylene chloride and dioctadecyldimethylammonium, octadecyltributylammonium and octadecylpyridonium nitrates in nitrobenzene. The octadecyl salts are well adapted to the purpose of the present investigation since octadecyl alcohol of high purity is readily available and the quaternary salts are readily crystallized from a variety of solvents.

II. Experimental

Apparatus and Procedure.—These have been fully described in earlier papers of this series. Bright platinum electrodes were used.

Materials.—Ethylene chloride was purified according to the method described by Mead.[5] The specific conductance was always less than 5×10^{-11}, making solvent corrections unnecessary.

Nitrobenzene was purified as described by Witschonke.[6] The specific conductance of the material was less than 5×10^{-10} so that corrections were unnecessary.

n-Octadecyl alcohol served as the starting material in the preparation of the salts used in this investigation. One recrystallization of the alcohol from nitromethane gave a product which melted at 57.5–58.5°.

n-Octadecyl iodide was obtained by heating the alcohol with iodine and red phosphorus in a sealed tube at 180° for one hour according to the method of Levene, West and van der Scheer.[7] The resulting mixture was extracted with hexane, in which the iodide is very soluble; the excess phosphorus was separated by filtration. The *n*-octadecyl iodide was recrystallized from hexane by slow cooling to 0° in a refrigerator; m. p., 34–35°.

n-Octadecyltri-*n*-butylammonium iodide was prepared by heating *n*-octadecyl iodide with tri-*n*-butylamine (10% excess) in a stoppered flask at 60° for from four to six days. The salt was recrystallized from hexane containing a trace of alcohol; m. p., 97–98°.

n-Octadecyltrimethylammonium iodide was prepared by heating *n*-octadecyl iodide with trimethylamine (20% excess) in a water–alcohol solution in a sealed tube at 60° for from a week to ten days. The salt was recrystallized from hexane containing 3–5% of alcohol; m. p., 234.5–236°.

n-Octadecylpyridonium iodide was prepared by heating *n*-octadecyl iodide with excess pyridine for from twelve to eighteen hours at 60° in a stoppered flask. The excess pyridine was evaporated and the salt was recrystallized from hexane containing a trace of alcohol; m. p., 101.5–103°.

Di-*n*-octadecyldimethylammonium iodide was prepared by Dr. E. C. Evers by heating *n*-octadecyl iodide with excess dimethylamine in water–alcohol solution. The product was recrystallized from hexane containing a trace of alcohol; m. p., 154°.

The corresponding nitrates were obtained from the iodides by metathesis with silver nitrate in an alcohol–water mixture containing 75% alcohol. As a rule, several hours of digestion at 60° were required to coagulate the colloidal silver iodide. Care was exercised to avoid peptization of the coagulated silver iodide on filtration. The solutions were evaporated to dryness and the salts redissolved and crystallized from suitable solvents.

Di-*n*-octadecyldimethylammonium nitrate is very soluble in pure hexane but crystallizes on cooling to Dry Ice temperatures; m. p., 79–81°.

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[1] This paper is based on a portion of a thesis presented by Harold E. Weaver in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, May, 1940.

[2] University Fellow at Brown University, 1938–1939; Metcalf Fellow, Brown University, 1939–1940.

[3] E. L. McBain, Dye and Johnson, THIS JOURNAL, **61**, 3210 (1939).

[4] Ward, *J. Chem. Soc.*, I, 522 (1939); *Proc. Roy. Soc.* (*London*), **176A**, 512 (1940); Ralston and Hoerr, THIS JOURNAL, **68**, 2460 (1946); Thompson and Kraus, *ibid.*, **69**, 1016 (1947).

[5] Mead, Fuoss and Kraus, *Trans. Faraday Soc.*, **32**, 594 (1936).

[6] Witschonke and Kraus, THIS JOURNAL, **69**, 2472 (1947).

[7] Levene, West and van der Scheer, *J. Biol. Chem.*, **20**, 525 (1915).