[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Studies Relating to Organic Germanium Derivatives. VI. Reactions of Sodium Triphenylgermanide with Organic Polyhalides in Liquid Ammonia and Diethyl Ether[1]

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The reaction of sodium triphenylgermanide with certain aliphatic polyhalides in liquid ammonia and in ether solution has been investigated as has, also, the reaction of this compound with aromatic halides in liquid ammonia. When the two halogen atoms of an aliphatic dihalide occur on adjacent carbon atoms, one halogen atom is largely substituted by the triphenylgermanyl group; the second is largely replaced by hydrogen. Triphenylgermanylamine is formed in amount equivalent to the hydrogen so bound. The amine is recovered as triphenylgermanyl oxide as a result of hydrolysis in its separation. When one or more carbon atoms intervene between the halogens, both the latter are largely substituted by germanyl groups. In ether, the reactions with the aliphatic halogens follow much the same course as in liquid ammonia. The germanyl groups that fail to substitute for halogens are recovered as hexaphenyldigermane. With aromatic halides, the germanyl group does not substitute for the halogen. Instead, the aromatic nucleus is hydrogenated and the germanium is recovered as triphenylgermanyl oxide. Sodium triphenylgermanide reacts with boron trichloride in ether solution. The halogens are split off as sodium halide and the germanyl groups appear to couple with boron.

I. Introduction

Although sodium triphenylgermanide reacts quantitatively with aliphatic monohalides in liquid ammonia to form the corresponding monoalkyltriphenylgermanes[3,4] with polyhalogenated methanes, side reactions occur involving the solvent. Kraus and Nutting[4] found that with methylene chloride, in addition to simple coupling yielding bistriphenylgermanylmethane, there was concomitant reaction with ammonia yielding triphenylgermanylamine and triphenylgermanylmethane. Chloroform gave the same products as methylene chloride, but in different proportions, showing that only one of the three chlorine atoms is quantitatively replaced by the triphenylgermanyl group; a second chlorine is largely substituted while the third is completely replaced by hydrogen. The reaction with carbon tetrachloride is similar to that with chloroform, although, apparently, more complex.

It seemed of interest to extend this study to aliphatic dihalides in which the halogens are located on different carbon atoms. With chlorine on adjacent carbon atoms, the reaction is complex, much like that with chloroform and there is no evidence that both the chlorine atoms are replaced by the triphenylgermanyl group. However, when the chlorines are separated by one or more carbon atoms, the principal reaction is substitution, although partial replacement of halogen by hydrogen is indicated since triphenylgermanyl oxide may be isolated from the reaction mixture. Thus, bistriphenylgermanylpropane and bistriphenylgermanylpentane were prepared from tri- and pentamethylene bromide, respectively.

In view of the above, it seemed of interest to carry out similar reactions in an inert solvent such as diethyl ether with the thought of avoiding reactions with the solvent. Reactions were carried out with carbon tetrachloride, chloroform, acetylene dichloride, ethylene dibromide, β-butylene bromide and trimethylene bromide. The evidence indicates that, on the average, not more than one chlorine atom in carbon tetrachloride is replaced by the triphenylgermanyl group and that not more than two are replaced in chloroform. The principal reaction here is probably not too different from that in ammonia. However, rather than entering into reaction with the solvent, two triphenylgermanyl groups combine and the main product is hexaphenyldigermane. With carbon tetrachloride, an oil was obtained from which triphenylgermanyl oxide was isolated during attempted purification; this may have resulted from a highly reactive substitution product. Chloroform gave a small yield of bistriphenylgermanylmethane. As in ammonia, the reaction with dihalogen compounds in ether is dependent on the relative position of the halogen atoms. When on adjacent carbon atoms, the halogens are not replaced by the triphenylgermanyl group. Two triphenylgermanyl groups combine and the residual hydrocarbon groups are apparently reduced to the corresponding unsaturated compounds. When the halogens are separated, as in trimethylene bromide, both halogens are replaced by triphenylgermanyl groups to some extent.

Coupling fails to occur when aromatic mono- or dihalides are treated with sodium triphenylgermanide in liquid ammonia. Here, the aromatic group is invariably hydrogenated and triphenylgermanylamine is formed. Because of the ease with which the amine is hydrolyzed, the metallo-organic group is ordinarily recovered as the oxide. Thus, α-bromonaphthalene gives naphthalene and triphenylgermanyl oxide; similar reactions occur with β-bromonaphthalene, *p*-bromoaniline, *p*-bromoanisole, *p*-bromodiphenyl ether, *p*-bromodiphenyl, 4,4'-dibromodiphenyl and *p*-dibromobenzene. As might be expected, the compound *p*-bromobenzyl chloride combines the reactions of the aromatic and aliphatic monohalides. Hydrogen replaces the halogen on the aromatic nucleus, while the triphenylgermanyl group replaces the halogen of the aliphatic group.

Finally, boron has been coupled to germanium through the reaction of sodium triphenylgermanide with boron trichloride in diethyl ether. The resulting compound, tristriphenylgermanylborane was obtained as a yellow oil, presumably as the monoetherate.

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[3] C. A. Kraus and C. S. Sherman, THIS JOURNAL, **55**, 4694 (1933).

[4] C. A. Kraus and H. S. Nutting, *ibid.*, **54**, 1622 (1932).

II. Materials, Apparatus and Procedure

Hexaphenyldigermane.—This compound was prepared by the method of Morgan and Drew[5] by the reduction of triphenylgermanyl bromide with sodium in boiling xylene. Oxygen and moisture were excluded by an atmosphere of nitrogen. The compound was recrystallized several times from ether.

Ether.—C.P. grade diethyl ether, after first drying with calcium chloride, was refluxed over sodium-lead alloy (NaPb) and distilled. Final traces of moisture and oxygen were eliminated by treating with metallic sodium and benzophenone in a closed glass container. The ether was distilled directly from the container into the reaction vessel as needed.

Carbon Tetrachloride.—Carbon tetrachloride was dried by refluxing over phosphorus pentoxide and then distilled. The fraction boiling between 75.8–76.0° was stored over phosphorus pentoxide and distilled into weighed, fragile glass bulbs.

Chloroform.—Treatment was similar to that given the carbon tetrachloride; the fraction boiling between 61.0–61.8° was employed.

Other Organic Halides.—All were Eastman Kodak Co. C.P. products which were used without purification.

Boron Trichloride.—This was prepared in this Laboratory according to the method of Smith[6] by treating calcium boride with chlorine at 550°.

Apparatus and Procedure.—Reactions in liquid ammonia were carried out in an apparatus very similar to that described by Kraus and Nutting.[4] Sodium triphenylgermanide was prepared by the method of Kraus and Foster,[7] by treating carefully purified hexaphenyldigermane with sodium in liquid ammonia under exclusion of air and moisture. After preparing the germanide, an equivalent amount of halide, dissolved in dioxane, was added from a dropping funnel which was attached to a side arm of the reaction tube. The dioxane solution was added slowly and the liquid ammonia solution was stirred vigorously with a stream of ammonia vapor. The reaction was adjudged complete when the yellow color of the solution had been discharged. After removing ammonia, the organic products were extracted with hot dioxane and purified by various means, depending upon the nature of the compounds.

A somewhat different procedure was employed when reactions were carried out in ether solution. A two-legged reaction vessel was used. A fragile glass bulb containing the halogen compound was placed in one leg of the vessel and sodium, also in a fragile glass bulb, and hexaphenyldigermane were placed in the second. The bulb containing sodium was broken with a bulb crusher and ammonia was condensed in the reaction tube. Sodium triphenylgermanide comes out of solution as the tri-ammoniate. Ammonia of crystallization was removed by heating the tube to 120° while exhausting with a mercury diffusion pump.

The reaction tube was then surrounded by a cooling bath of liquid ammonia and dry ether was distilled onto the sodium salt. The tube was detached from the system, and the bulb containing the halogen compound was broken by shaking. A small amount of ether was distilled onto the halide to dissolve it, and the resulting solution was poured slowly into the solution of sodium triphenylgermanide. Reaction in most instances was vigorous and exothermic, and sodium halide precipitated immediately. To ensure complete reaction, the tube was heated for several days at 40–45°. After removing the ether, the sodium halide was dissolved with water, and organic products were recovered by leaching with hot benzene. These were separated and purified by various means.

Analyses.—Two methods were employed to determine the extent and course of the reaction. The extent of reaction or "conversion" was found by taking the ratio of the atoms of sodium recovered as sodium halide to the atoms of sodium used in the preparation of the sodium triphenylgermanide. The ratio was taken in this way since usually the other reactants were employed in slight excess. The percentage yield of the various products containing germanium was taken as the ratio of atoms of germanium recovered to the total number of atoms initially introduced as hexaphenyldigermane. Germanium was determined by oxidizing the organic compounds with fuming nitric and sulfuric acids and weighing the germanium as GeO_2, which is a method commonly employed in this Laboratory.[8] Sodium halide was determined by precipitating the halogen with silver nitrate and weighing as silver halide.

Boron was determined by the method of Booth.[9] Molecular weights were determined by the cryoscopic method using benzene as solvent.

III. Reaction with Aliphatic Dihalides in Liquid Ammonia

1. **Trimethylene Bromide.**—The reaction of trimethylene bromide and sodium triphenylgermanide resulted in a conversion of 94.7%, calculated as indicated above. A 27.0% yield of triphenylgermanium oxide was obtained and 60.5% of the germanium was recovered as bistriphenylgermanylpropane, m.p. 132.5–133°. Apparently, the principal reaction occurs according to the equation

$$Br(CH_2)_3Br + 2NaGePh_3 = Ph_3Ge(CH_2)_3GePh_3 + 2NaCl \quad (1)$$

It seems not unlikely that the presence of triphenylgermanium oxide in the product may be accounted for by side reaction with solvent leading to the production of hydrocarbon and triphenylgermanylamine. As reference to Section V will show, this is the only reaction which occurs in the case of the aromatic halides.

Bistriphenylgermanylpropane.—Mol. wt.: wt. benzene, g., 12.928 g.; wt. subst., 0.0976, 0.1957 g.; Δt, 0.065°, 0.131°; found: mol. wt., 582, 579; calcd. for $C_{39}H_{36}Ge_2$: mol. wt., 649.2. *Anal.* wt. subst., 0.1476, 0.1517 g.; GeO_2, 0.0475, 0.0489; found: Ge, 22.34, 22.31; calcd. for $C_{39}H_{36}Ge_2$: Ge, 22.37.

2. **Pentamethylene Bromide.**—Reaction of sodium triphenylgermanide with pentamethylene bromide proceeds in the same fashion as with trimethylene bromide. Per cent. conversion, 95.9; % yield of triphenylgermanium oxide, 16.05; bistriphenylgermanylpentane, 59.5.

Bistriphenylgermanylpentane.—Mol. wt.: wt. benzene 12.171 g.; wt. subst., 0.1005, 0.2006 g.; Δt, 0.065°, 0.130°; found: mol. wt., 636, 635; calcd. for $C_{41}H_{40}Ge_2$: mol. wt., 677.2. *Anal.* wt. subst., 0.1480, 0.1338 g.; GeO_2, 0.0457, 0.0413; found: Ge, 21.43, 21.43; calcd. for $C_{41}H_{40}Ge_2$: Ge, 21.44.

3. **β-Butylene Bromide.**—Conversion in the case of this compound was 96%, and 82.1% of the germanium was recovered as triphenylgermanyl oxide. Apparently, the main reaction is one involving solvent; no other compounds were recovered to indicate that substitution had occurred. However, the possibility does exist that an unstable substitution compound may have been formed which was hydrolyzed or oxidized during subsequent operations.

IV. Reaction with Aliphatic Polyhalides in Ether

1. **Carbon Tetrachloride.**—Carbon tetrachloride and sodium triphenylgermanide reacted in ether solution according to the procedure outlined above. After removing the solvent, the residue was washed thoroughly with water to remove sodium chloride. The yield of sodium chloride was then determined and these data were used to calculate the per cent. conversion.

The product remaining was dissolved in hot benzene. This was concentrated and cooled, whereupon crystals of hexaphenyldigermane were obtained. The mother liquor

TABLE I

REACTION OF CARBON TETRACHLORIDE AND SODIUM TRIPHENYLGERMANIDE IN ETHER

Hexaphenyldigermane, % Used	Recovered	Yield, %	Conversion, %
2.3417	1.839	78.5	83.7
2.9600	2.410	81.6	88.7
12.673	10.265	81.0	87.7
11.419	9.072	79.5	91.0
14.041	11.395	81.2	89.3
13.485	10.977	81.4	85.4

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[5] G. T. Morgan and D. K. Drew, *J. Chem. Soc.*, **127**, 531 (1925).

[6] J. E. Smith and C. A. Kraus, THIS JOURNAL, **73**, 2751 (1951).

[7] C. A. Kraus and L. S. Foster, *ibid.*, **47**, 457 (1927).

[8] C. A. Kraus and C. L. Brown, *ibid.*, **52**, 3693 (1930).

[9] R. B. Booth, *ibid.*, **74**, 1415 (1952).

was decanted and the benzene was evaporated. This left an oil and produced an additional crop of hexaphenyldigermane crystals. The mixture was treated with low-boiling petroleum ether (40–60°) which dissolved the oil, leaving the hexaphenyldigermane. The two fractions of hexaphenyldigermane were combined and recrystallized several times from benzene and weighed. The results of several experiments are given in Table I.

Since somewhat more than three-fourths of the germanium was recovered as hexaphenyldigermane, it is evident that, at best, only one triphenylgermanium group combines with each carbon atom. Attempts to isolate a substitution compound were unsuccessful as described below.

The petroleum ether solution of the oil, referred to above, was evaporated to dryness, and final traces of solvent were removed at reduced pressures. A small portion of the oil was distilled *in vacuo*. At 140–180°, a white crystalline solid was obtained, which was identified as triphenylgermanyl oxide by its melting point. The residue was black and glassy in appearance. and was found to contain germanium.

The oil was analyzed for germanium and its molecular weight was determined: mol. wt.: wt. benzene, 13.031 g.; wt. subst., 0.0762, 0.1704 g.; Δt, 0.76, 0.162; found: mol. wt., 385, 404. *Anal.* wt. subst., 0.1385, 0.1270 g.; GeO_2, 0.0427, 0.0392; found; Ge, 21.42, 21.45. The percentage of germanium found corresponds fairly closely to that calculated for triphenylgermanium oxide (22.72), but the molecular weight is only approximately one-half that of the oxide (623.2). The oil was found to contain only a trace of chloride. When dissolved in ethyl acetate and allowed to stand for several months. crystals of triphenylgermanium oxide separated.

2. **Chloroform.**—The reaction with chloroform is similar to that with carbon tetrachloride. In a typical experiment, the conversion was 92.3 and 61.5% of the germanium was recovered as hexaphenyldigermane. The remaining product was an oil from which there was recovered an 8.74% yield of bistriphenylgermanylmethane. This substance was identified by comparing it with a sample of material prepared by Nutting.[4] Since somewhat more than one-half of the hexaphenyldigermane was recovered, it seems safe to assume that not more than two triphenylgermanyl groups combine with carbon and probably only one chlorine is substituted quantitatively. The source of the second hydrogen in bistriphenylgermanylmethane remains unaccounted for.

3. **Acetylene Dichloride, Ethylene Dibromide and β-butylene Bromide.**—These three dihalides react quite similarly. The recovery of hexaphenyldigermane was 62.5, 87 and 91.1% in the order named. In the case of acetylene dichloride, the yields of triphenylgermanium oxide was 15.6%, the remaining product being an oil. Only very small amounts of oxide were recovered in the products of reaction with the other two substances. In view of the high recovery of the digermane, it seems likely that the dihalides may be reduced to the corresponding unsaturated hydrocarbons, although this has not been established. The presence of triphenylgermanium oxide may indicate that substitution does occur to some extent to yield unstable compounds that decompose during handling.

4. **Trimethylene Bromide.**—Reaction with trimethylene bromide gave hexaphenyldigermane (62.4% yield) together with a small amount of bistriphenylgermanylpropane, which was identified by comparing it with the same substance prepared by a similar reaction in liquid ammonia.

V. Reaction with Aromatic Halides in Liquid Ammonia

The reaction of sodium triphenylgermanide with aromatic halides was carried out in liquid ammonia as described above. In the examples studied, the germanium was recovered practically quantitatively in the form of triphenylgermanium oxide, which indicates that the germanium is converted to triphenylgermanylamine and that the aromatic nucleus is hydrogenated. As an example, a 95% conversion was obtained with β-bromonaphthalene and 91% of the germanium was recovered as triphenylgermanium oxide. Another solid product, remaining after triphenylgermanium oxide was removed, was purified by steam distillation, and identified as naphthalene by its melting point. The reaction evidently takes place according to the equation

$$C_{10}H_7Br + Ph_3GeNa + NH_3 = NaBr + C_{10}H_8 + Ph_3GeNH_2 \quad (2)$$

The amine is hydrolyzed to oxide in the course of separation.

Results with other aromatic halides are presented in Table II. Judging by the yield of oxide, it is apparent that reaction in each case takes place in the sense of equation (2) even though the resulting hydrocarbons have not always been isolated.

TABLE II

REACTION OF SODIUM TRIPHENYLGERMANIDE AND AROMATIC HALIDES

Halide	Conversion, %	Yield, % $(Ph_3Ge)_2O$	Other products
β-Bromonaphthalene	97.6	95.7	Naphthalene
p-Bromoaniline	90.2	88.7	Aniline
p-Bromoanisole	98.0	91.9	....
p-Bromodiphenyl ether	99.2	92.4	....
p-Bromodiphenyl	97.4	93.8	Diphenyl
4,4′-Dibromodiphenyl	98.4	93.3	Diphenyl
p-Dibromobenzene	..	95.0	....

On treating *p*-bromobenzyl chloride with sodium triphenylgermanide, there was obtained a yield of 52% of triphenylgermanyl oxide and 37% of triphenylbenzylgermane. The latter product was identical with an earlier preparation of Kraus and Sherman.[10]

VI. Sodium Triphenylgermanide and Boron Trichloride

Boron trichloride and sodium triphenylgermanide react very readily in ether solution. The products of reaction are sodium chloride and a viscous oil which contains all the original boron and germanium. No hexaphenyldigermane or other germanium compounds appear to be formed. Analysis of the oil for boron and germanium indicated approximately three germanium atoms per atom of boron. Molecular weight determinations indicated the presence of one molecule of ether. There can be little doubt that the germanium and boron atoms were coupled.

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[10] C. A. Kraus and C. S. Sherman, THIS JOURNAL, **55**, 4694 (1933).