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The Reaction of Potassium Germyl with Organic Halides

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Received January 15, 1971

Many organic halides react with potassium germyl in diglyme to give the corresponding organogermanes. However, halides for which nucleophilic substitutions are slow react with potassium germyl to give principally the corresponding hydrocarbons. Data relevant to the mechanism of the latter type of reaction are presented. A method for the preparation and standardization of stock solutions of potassium germyl is described. A new compound, digermylmethane (1,3-digermapropane), is reported, and its nmr, mass, and infrared spectra are discussed.

Introduction

The germyl anion, GeH_3^-, was first prepared by Kraus and Carney by the reaction of germane, GeH_4, with sodium–ammonia solutions.[1] Teal and Kraus found the germyl anion to be an excellent nucleophile, capable of converting primary alkyl halides to the corresponding alkylgermanes.[2] However, simple displacement did not occur with all organic halides. Sodium germyl and bromobenzene did not yield the expected phenylgermane but rather benzene and GeH_2[3]

$$NaGeH_3 + C_6H_5Br \longrightarrow NaBr + C_6H_6 + GeH_2$$

Methylene bromide also did not react to give simple germyl anion substitution. The reported products were methylgermane and aminogermane[2]

$$2NaGeH_3 + CH_2Br_2 + NH_3 \longrightarrow CH_3GeH_3 + GeH_3NH_2 + 2NaBr$$

In each of these reactions, a hydrogen atom replaced a halogen atom. It was the aim of this study to determine the types of halides for which this type of reaction occurs and to investigate the reaction mechanism. Reactions were carried out in diglyme (bis(methoxyethyl) ether) because of the ease of preparation of potassium germyl in this solvent and because of the hope that diglyme might prove to be a more favorable medium than liquid ammonia for germyl anion substitutions and that it might enable us to prepare the elusive compound digermylmethane.

Experimental Section

Reagents.—Germane was obtained from the Matheson Co.; its purity was checked by infrared and mass spectrometry and by vapor pressure measurements at −111.6° (180 Torr as compared to the literature value[4] 181 Torr). Diglyme (Ansul Ether 141) was purified by distillation from potassium hydroxide followed by vacuum distillation from lithium aluminum hydride at approximately 40°. Organic halides of reagent grade were used without purification; lower grade materials were purified by distillation from phosphorus pentoxide or by gas chromatography. The identity and purity of volatile substances were determined by infrared spectrometry with Perkin-Elmer Infracord spectrometers (Models 137 and 137B), by mass spectrometry with a Consolidated Engineering Corp. mass spectrometer (Model 21-103C) or a Varian M-66 mass spectrometer, and by gas chromatography with a Varian Aerograph, Model A-90-P.

Preparation and Standardization of Potassium Germyl.—Potassium germyl was prepared in the apparatus shown in Figure 1. A magnetic stir bar and 20 g of powdered reagent grade potassium hydroxide were placed in flask A. Sixty or seventy milliliters of diglyme was then pipetted into the flask. The diglyme was degassed at −78° by pumping through stopcock B; stopcock B was then closed. The diglyme slurry was stirred while holding it at 0°, and stopcock B was opened to a section of the vacuum line containing 30 mmol of germane. Stirring was continued for about 1 hr, during which essentially all the germane was absorbed by the slurry; the remainder was condensed into a −196° trap.

The apparatus was then inverted, a tube leading to a tank of dry nitrogen was attached at stopcock B, and an atmosphere of dry nitrogen was introduced. (The tube was alternately flushed with nitrogen and evacuated several times to ensure the absence of air.) The solution was filtered by gravity flow through the medium-porosity filter C into the long-necked erlenmeyer flask E. When the filtration was complete, dry nitrogen at atmospheric pressure was introduced through stopcock D, using the same precautions noted above. A and C were removed from E, and E was stoppered with a ground-glass sleeve joint attached to an open stopcock. After a few minutes of flushing, the latter stopcock and stopcock D were almost simultaneously closed.

This procedure yielded a clear, colorless solution of potassium germyl which could be stored at 0° without apparent decomposition. The solution was standardized as follows. Using the precautions described above, dry nitrogen at atmospheric pressure was again introduced at stopcock D. When the pressure in the flask slightly exceeded 1 atm, the flask was unstoppered and seated into a sleeve joint sheath with a side arm as shown in Figure 2. Dry nitrogen was flushed through the side arm; this nitrogen and the nitrogen simultaneously flushing the flask vented through the narrow top of the sheath. A long glass pipet was clamped over the solution as shown in Figure 2 and was flushed by drawing in nitrogen with a greased syringe, followed by expulsion of the nitrogen through the side arm of the three-way stopcock. When the system was completely purged of air, the pipet was lowered and potassium germyl solution was sucked up to one of several calibrated marks on the pipet. The pipet was then redrawn into the sheath, and the stock solution flask was removed and restoppered as before. An identical flask, previously evacuated, was then opened with nitrogen flushing and was fitted to the sheath. After the system had been purged, the potassium germyl in the pipet was transferred to the new flask. The flask was restoppered as before, cooled to −196°, and evacuated.

An excess of degassed water was then distilled onto the frozen potassium germyl solution; the mixture was warmed to room temperature, and the evolved germane was distilled, with pumping, through a −111.6° trap into a −196° trap. The germane was quantitatively measured by *PVT* measurements, and its purity was checked by vapor pressure and infrared measurements. A known excess of 0.1 *M* HCl was added to the residue, and the solution was titrated with 0.1 *M* NaOH to the phenolphthalein end point. In accordance with the hydrolysis reaction $GeH_3^- + H_2O \rightarrow GeH_4 + OH^-$, the germane produced equalled the titrated hydroxide within ±1%.

Qualitative Aryl Halide Experiments.—An aliquot of 0.2 *M* $KGeH_3$ was transferred to a long-necked erlenmeyer flask as described in the standardization procedure. Excess bromobenzene was condensed onto the frozen solution at −196°, and the mixture was allowed to warm to room temperature. Immediately a white precipitate formed which soon developed a yellow color; after 0.5 hr, the reaction mixture was orange. The solution was then pumped to dryness through traps at −45, −160, and −196°. The first trap contained diglyme and benzene, the second, benzene and digermane, and the third, ger-

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[1] C. A. Kraus and E. S. Carney, *J. Amer. Chem. Soc.*, **56**, 765 (1934).

[2] G. K. Teal and C. A. Kraus, *ibid.*, **72**, 4706 (1950).

[3] S. N. Glarum and C. A. Kraus, *ibid.*, **72**, 5398 (1950).

[4] W. L. Jolly and J. E. Drake, *Inorg. Syn.*, **7**, 34 (1963).

TABLE I

REACTIONS OF POTASSIUM GERMYL WITH ARYL HALIDES

Halide	Reaction time, min	Amt, mmol					Hydrocarbon/ $KGeH_3$
		$KGeH_3$	GeH_4 formed	Ge_2H_6 formed	Nonvolatile Ge	Hydrocarbon formed[a]	
Bromobenzene	5	1.33	0.597	0	0.72	0.85	0.64
	90	1.33	0.589	Trace	0.74	0.81	0.61
	1200	1.33	0.602	Trace	0.66	0.85	0.64
Iodobenzene	90	1.36	0.247	0.058	0.60	0.90	0.66
	90	1.36	0.202	0.073	0.63	0.91	0.67
	90	1.36	0.188	0.073	0.65	0.91	0.67
	90	1.57	0.326	0.082	0.65	1.01	0.64
4-Bromo-*m*-xylene	90	1.57	0.521	0.017	0.90	0.82	0.52
2-Bromo-*m*-xylene	90	1.57	0.490	0.013	0.88	0.50	0.38

[a] Benzene formed in the reactions of the halobenzenes; *m*-xylene formed in the runs with the bromo-*m*-xylenes.

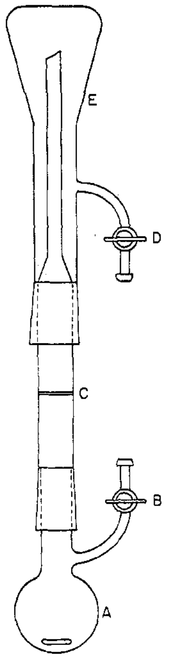

Figure 1.—Apparatus for the preparation and filtration of $KGeH_3$ solutions.

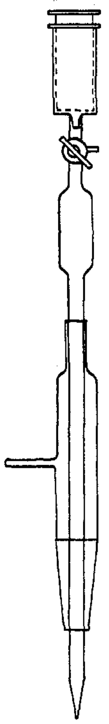

Figure 2.—Apparatus for pipetting $KGeH_3$ solutions.

mane, as indicated by infrared and mass spectra. No trace of any compound containing a carbon–germanium bond was detected in these samples. A similar experiment using iodobenzene also showed benzene, germane, and digermane to be the only volatile products.

Adding the potassium germyl solution dropwise to bromobenzene or iodobenzene in other experiments gave identical results. In an attempt to detect biphenyl formation, the contents of the −45° trap were analyzed by gas chromatography. The retention time of biphenyl was determined using a 4-ft × 1/4-in. 20% silicone GE SF-96 on firebrick column[5] at 230°. Under these conditions, an aliquot of the unknown showed no evidence of biphenyl.

Quantitative Aryl Halide Experiments.—Excess chlorobenzene was condensed onto a diglyme solution containing 1.33 mmol of potassium germyl. After 2 hr at room temperature, a faint yellow cloudiness had appeared. The mixture was then distilled, with pumping, for 15 min; the volatile products were collected in traps at −95 and −196°. A total of 0.132 mmol of germanium (as germane and digermane) was found in the −196° trap. (The digermane was separated by fractional condensation in a −160° trap.) Water was then distilled into the solution, and germane and digermane (1.10 mmol of germanium) were produced. To the contents of the −95° trap was added 10 ml of a solution of toluene in diglyme which contained 1.0 ml of toluene (9.41 mmol)/100 ml of solution. The mixture was analyzed gas chromatographically for benzene using the GE SF-96 column at 65°; less than 0.01 mmol was found.

The results of experiments in which excesses of bromobenzene, 4-bromo-*m*-xylene, and 2-bromo-*m*-xylene were condensed onto potassium germyl solutions are presented in Table I. After the indicated reaction times, the volatile materials were collected in traps at −95 and −196°. The germane and digermane in the −196° traps were separated and identified, and the respective amounts were measured. The −95° traps were analyzed for benzene or xylene as described above. The solid residues were dissolved by boiling in a slightly basic 3% H_2O_2 solution. Excess peroxide was destroyed by acidification and further boiling, and the resulting solution was then analyzed volumetrically for germanium by the method of Tchakirian.[6] We have no explanation for the low total germanium analyses in the iodobenzene experiments.

Reaction of Bromobenzene with Potassium Germyl-d_3.—Germane-d_4 was prepared from $GeCl_4$ and $LiAlD_4$ according to a standard method.[7] A small portion was pyrolyzed, and the hydrogen was analyzed by mass spectrometry; 92 atom % of the hydrogen in the sample was deuterium.

Reagent grade potassium was distilled from a side arm into a reaction vessel equipped with a break-off seal and an outlet to the vacuum line. About 0.5 ml of diglyme was distilled from lithium aluminum hydride onto the potassium mirror. Germane-d_4 (0.366 mmol) was condensed in, the vessel was sealed off, and the mixture was allowed to react for 3 days at −20°. At the end of this time, the solution was warmed to 0°, the vessel

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(5) Materials available from Varian Aerograph, Walnut Creek, Calif.

(6) R. Belcher and C. L. Wilson, "New Methods in Analytical Chemistry," 2nd ed, Chapman and Hall, London, 1956, p 232.

(7) A. D. Norman, J. R. Webster, and W. L. Jolly, *Inorg. Syn.*, **11**, 170 (1968).

was attached to the vacuum line, and the break-off seal was opened. The solution was pumped on through two liquid nitrogen traps with a Toepler pump; 0.98 mmol of hydrogen (of which 85 atom % was deuterium) was collected.

An excess of bromobenzene was condensed onto the potassium germyl, and the solution was allowed to react 0.5 hr at room temperature. The volatiles were then passed through a −95° trap and a −196° trap. The fraction in the −95° trap was analyzed by mass spectrometry and was found to have peaks at *m/e* 78, 79, and 80, with relative intensities 30.2:100:5.7, respectively. A sample of ordinary benezene was shown to have *m/e* 77, 78, and 79 peaks with relative intensities 19.8:100:7.1; from these data we calculate that 87% of the benzene produced in the above reaction contained one deuterium atom.

Reaction of Phenylsodium with Germyl Bromide in Diglyme.—Germyl bromide was prepared from GeH_4 and AgBr;[8] its infrared spectrum agreed with the literature,[9] and its mass spectrum showed no peaks other than those due to GeH_xBr^+, GeH_x^+, Br^+, and the double charged species. A dispersion of sodium (2.42 mg-atoms) was converted to phenylsodium by reaction with chlorobenzene in *p*-xylene[10] (100% yield corresponds to 1.21 mmol of NaC_6H_5). The stirred slurry of phenylsodium was degassed by pumping, after which a solution of 1.29 mmol of GeH_3Br in 10 ml of diglyme was added quickly. Effervescence began at once and continued for 0.5 hr. The mixture was then cooled to −196° and Toepler-pumped; 0.082 mmol of hydrogen was collected. Water was then condensed onto the reaction mixture and the mixture was warmed to room temperature and Toepler-pumped through cold traps; this time 0.256 mmol of hydrogen was collected. The other volatile products of the reaction (identified by infrared[11] and mass spectrometry) were germane (isolated by distillation through a −160° trap), a mixture of digermane and methyl vinyl ether (isolated by distillation through a −95° trap), and a mixture of trigermane and benzene (isolated by distillation through a −12° trap). No phenylgermane was detected. The hydrogen produced in the reaction presumably was a result of unreacted sodium metal in the slurry.

Neopentyl and Neophyl Halides.—About 1.5 mmol of neopentyl chloride (1-chloro-2,2-dimethylpropane), obtained from Matheson Coleman and Bell and purified by gas chromatography, was condensed onto an equal number of millimoles of potassium germyl solution. A slight cloudiness appeared after several hours at room temperature, but analysis of the volatiles showed that essentially no reaction had taken place.

About 1.5 mmol of neopentyl bromide, obtained from K & K Laboratories and purified by gas chromatography, was condensed onto an equal number of millimoles of potassium germyl solution. A white cloudiness formed within a few minutes at room temperature; this soon became slightly yellow. After 2 hr, the volatile products were analyzed and were found to consist of germane, digermane, and an approximately 1:1 mixture of neopentane and an alkylgermane, probably neopentylgermane. An attempt was made to separate the latter two compounds using the silicone GE SF-96 chromatograph column at room temperature. The neopentane was isolated as the pure compound (identified by comparison of its ir spectrum with that of a known sample of the material); the alkylgermane had an ir spectrum with the most intense bands at 845 and 2100 cm^{-1}, typical of alkylgermanes.[12] However, the bands found in neopentane were also present; therefore there is some doubt as to the purity of the isolated alkylgermane. The mass spectrum of this material contained an envelope of peaks at *m/e* 141–147 and a much more intense envelope at *m/e* 120–135. The first band could be due to ions of formula $C_5GeH_x^+$, while the second could be due to $C_4GeH_x^+$, the most stable carbonium ion formed by fragmentation of neopentylgermane.[13]

Neophyl chloride (1-chloro-2-methyl-2-phenylpropane) was obtained from Fluka A.G. It did not react with potassium germyl. Neophyl bromide was prepared by bromination of the chloride Grignard reagent. In separate experiments, potassium germyl solutions (0.2 and 0.01 *M*) were added dropwise to equivalent amounts of neophyl bromide. The reaction was allowed to proceed 2 hr, during which time a yellow-white precipitate formed. The volatiles were analyzed by gas chromatography using a 20-ft × $^3/_8$-in. silicone SE-30 on Chromosorb W column[5] at 110°. Some *tert*-butylbenzene, but no isobutylbenzene, could be detected.

Haloalkane Experiments.—Bromomethane (1.62 mmol) was condensed onto a frozen solution of 1.12 mmol of potassium germyl. The reaction vessel was warmed, with shaking, to room temperature. After 5 min a white precipitate had formed. The volatile materials were Toepler-pumped for 2 hr through a −78° trap and two −196° traps. No noncondensable gas was found. The contents of the −196° traps were pumped through a −160° trap; 0.034 mmol of germane was isolated. The contents of the −160° trap were passed through a −111.6° trap, and 1.07 mmol of methylgermane was obtained (vapor pressure 47 mm at −83°, lit.[14] value 46.3 Torr). A trace of dimethylgermane and 0.40 mmol of bromomethane were found in the residue.

The same experiment was carried out using iodomethane. Again, an essentially quantitative formation of methylgermane was found (1.12 mmol of $KGeH_3$ yielded 1.10 mmol of CH_3GeH_3). However, about 0.01 mmol of methane was found.

The results of several experiments with di- and trihalomethanes are summarized in Table II. In most cases the halide was distilled from phosphorus pentoxide onto the frozen potassium germyl solution at −196°, and the reactants were allowed to warm to room temperature. In other cases, potassium germyl solution was added dropwise through a dropping funnel to the pure halide, and in one case, a 1% solution of the dihalide in diglyme was added dropwise to the germyl solution. After reaction had proceeded for the stated period of time, the volatile materials were fractionally condensed using −45, −111.6, −160, and −196° traps. Infrared spectra of the contents of the −45° trap indicated solvent and traces of organogermanes which were then discarded. The −196° trap contained germane and the −160° trap methylgermane; these were identified by their ir spectra and vapor pressures, and were quantitatively measured. The −111.6° trap contained digermylmethane, dihalomethane, digermane, digermylmethane, and digermylpropane, as indicated by mass and ir spectrometry. The latter mixture was treated in either of two ways to effect isolation of pure digermylmethane. Digermane and dibromomethane could be removed by hydrolysis overnight with a saturated aqueous solution of potassium hydroxide (the water being subsequently removed by passing through magnesium perchlorate) or by gas chromatography. Either method is effective; however hydrolysis is easier for greater than 0.2 mmol of product. Dichloromethane proved impossible to separate from digermylmethane; using the 20-ft × $^3/_8$ in. silicone SE-30 column a 1-min difference in retention times was obtained after 20 min. Even then the peaks over-

TABLE II

REACTIONS OF POTASSIUM GERMYL WITH DI- AND TRIHALOMETHANES

Organic halide	Time, hr	$KGeH_3$/halide	GeH_4/$KGeH_3$	CH_3GeH_3/$KGeH_3$	$CH_2(GeH_3)_2$/$KGeH_3$[d]
CH_2Br_2[a]	2	0.25	0.034	0.20	0.025
CH_2Br_2[a]	12	0.45	0.060	0.25	...
CH_2Br_2[a]	2	1.0	0.038	0.27	0.06
CH_2Br_2[a]	4	2.0	0.076	0.37	0.06
CH_2Br_2[b,e]	2	0.06	0.18	0.23	...
CH_2Br_2[c]	0.2	2.0	0.17	0.14	0.04
CH_2Cl_2[a]	2	3.5	0.12	0.081	0.05
CH_2Cl_2[a]	4	2.0	0.16	0.061	0.07
CH_2Cl_2[a]	0.5	2.0	0.13	0.032	...
CH_2Cl_2[b]	0.6	2.0	0.072	0.045	0.05
$CHCl_3$[a]	2	1.0	0.41	0.028	0.07[f]

[a] Halide condensed onto potassium germyl. [b] Germyl added dropwise to halide. [c] Halide solution added dropwise to potassium germyl. [d] These values are only approximate; they are estimates of yield of 90% pure compound. [e] A trace of methyl bromide could be detected by ir as a product of this reaction. [f] A significant amount of dichloromethane was formed in this reaction.

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[8] K. M. Mackay, P. Robinson, E. J. Spanier, and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **28**, 1377 (1966).

[9] D. E. Freeman, K. H. Rhee, and M. K. Wilson, *J. Chem. Phys.*, **39**, 2908 (1963).

[10] W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1970, p 476.

[11] Y. Mikawa, *Bull. Chem. Soc. Jap.*, **29**, 110 (1956).

[12] K. A. Hooton, *Prep. Inorg. React.*, **4**, 165 (1968).

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lapped to a small extent. The other germylalkanes were not detected chromatographically, yet they were detected by mass spectrometry.

Digermylmethane Mass Spectrum.—The mass spectrum was obtained with a Varian M-66 mass spectrometer. The sample pressure was 5×10^{-7} Torr; sample temperature was 90° at the inlet and 125° at the analyzer. The electron energy was 70 eV, and the electron current was 30 μA. The m/e values and relative intensities follow: 169 (4.2), 168 (2.1), 167 (23), 166 (21), 165 (52), 164 (55), 163 (87), 162 (83), 161 (100), 160 (87), 159 (85), 158 (58), 157 (47), 156 (23), 155 (16), 154 (2.8), 153 (3.5), 152 (1.4), 151 (2.1), 150 (6.3), 149 (10), 148 (18), 147 (16), 146 (20), 145 (10), 144 (15), 143 (3.5), 142 (4.2), 141 (3.5), 140 (3.5), 93 (2.8), 92 (2.1), 91 (31), 90 (31), 89 (42), 88 (24), 87 (27), 86 (16), 85 (6.3), 84 (1.4), 80 (1.4), 79 (1.4), 78 (1.4), 77 (2.8), 76 (2.8), 75 (5.6), 74 (16), 73 (5.6), 72 (9.9), 71 (2.8), 70 (5.6). The peaks may be grouped into envelopes corresponding to the ions GeH_x^+ (m/e 82–96), $Ge_2H_x^+$ (m/e 140–156), and $Ge_2CH_x^+$ (m/e 152–172). The reported spectrum of disilylmethane shows analogous envelopes, including one corresponding to the anomalous ion $Si_2H_x^+$.[15]

Digermylmethane Nmr Spectrum.—The spectrum of a neat sample prepared from dichloromethane was recorded on a Varian A-60 spectrometer and consisted of a 1:2:1 triplet and a 1:6:15:20:15:6:1 septet, 3.84 and 0.33 ppm downfield from external tetramethylsilane, respectively; $J_{H-C-Ge-H}$ was 4.00 Hz. Three tiny peaks could be detected under the expanded septet; these may have been part of a quartet, of which one peak was hidden by the digermylmethane peaks. Such a feature would be expected for contamination by digermylethane. The spectrum of digermylmethane is entirely analogous to that reported for disilylmethane.[16]

Digermylmethane Infrared Spectrum.—The infrared spectrum of digermylmethane was recorded on Perkin-Elmer Infracord spectrometers (Models 137 and 137B). A 10-cm NaCl cell with a sample pressure of 10 mm was used, and the spectrum was recorded from 4000 to 650 cm^{-1}. The sample was then transferred to a KBr cell, and the spectrum was recorded from 800 to 400 cm^{-1}. The observed bands (in cm^{-1}), intensities, and tentative assignments are as follows: 3000 (w, CH_2 str), 2160 (sh), 2100 (vs, GeH_3 str), 2030 (sh), 1380 (w, br, CH_2 scissor), 1140 (w, CH_2 twist), 1060, 1050 (mw, CH_2 wag), 960 (br, sh, GeH_3 asym def), 880 (br, m, GeH_3 asym def), 840 (vs, GeH_3 sym def), 755 (br, m, CH_2 rock), 680 (s, Ge–C asym str).

The assignments were made by analogy with previous assignments for related compounds, notably disilylmethane[17] and methylgermane.[18] In digermylmethane, the Ge–C asymmetric stretch has a high frequency, 680 cm^{-1}, compared to Ge–C stretches in methylgermane, 601.6 cm^{-1}, and in ethylgermane,[19] 610 cm^{-1}. However, this shift is consistent with that observed for the silyl analogs. In disilylmethane the C–Si asymmetric stretch frequency is 773 cm^{-1} whereas in methylsilane[20] it is 701 cm^{-1}.

Results and Discussion

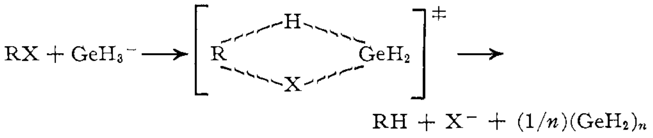
Potassium germyl reacts with organic halides in two different ways. The reaction which produces an organogermane undoubtedly involves nucleophilic attack by a germyl anion on a carbon atom, with simultaneous halide ion displacement. The reaction which produces a hydrocarbon and GeH_2 polymer probably involves nucleophilic attack by a germyl anion on a halogen atom, with simultaneous or subsequent formation of a C–H bond and cleavage of a Ge–H bond. A possible mechanism for the latter, hydrogen-substitution, reaction is

$$RX + GeH_3^- \longrightarrow R^- + XGeH_3 \longrightarrow RH + X^- + (1/n)(GeH_2)_n$$

Halogen atom attack mechanisms have been proposed for many reactions of organophosphines[21,22] and for the reaction of organic halides with potassium triphenylsilyl[23] and sodium triphenylgermyl.[24]

The hydrogen-substitution reaction predominates in cases where one would expect halide ion displacement by the germyl anion to be slow. Consequently, high yields of the hydrogen-substituted products are obtained in the reactions with aromatic halides,[25] neopentyl and neophyl halides,[26] and dihalomethanes.[27] However, even in the case of iodomethane, a trace of the hydrogen-substituted product, methane, is obtained; It appears that the two types of reaction always occur simultaneously.

In the reaction of potassium germyl-d_3 with bromobenzene, it was observed that the hydrogen atom that replaced the bromine atom was originally bonded to germanium. This means that a phenyl anion, if it is formed, deprotonates the nascent bromogermane in preference to the solvent, diglyme. However, we have observed that when sodium phenyl is introduced to diglyme containing excess bromogermane, the principal reaction is the cleavage of the diglyme.[28] Hence we conclude that no free phenyl anion is formed in the reaction of the germyl anion with bromobenzene. For a carbanion-type mechanism to be valid, a concerted reaction, in which germyl anion deprotonation occurs almost simultaneously with bromine cation removal, must be assumed. Perhaps a four-center activated complex[29] is formed; such a mechanism is almost equivalent to a cage reaction[30] in which the phenyl anion reacts with bromogermane before it can be dispersed and react with the solvent. This type of mechanism is



$$RX + GeH_3^- \longrightarrow \left[R \cdots H \cdots GeH_2 \cdots X \cdots R \right]^{\ddagger} \longrightarrow RH + X^- + (1/n)(GeH_2)_n$$

Both the hydrogen-substitution reaction and the germyl-substitution reaction accelerate as one goes from a chloride to a bromide to an iodide but the acceleration is more pronounced in the former than in the latter reaction. Thus much more benzene is obtained from bromobenzene than from chlorobenzene, more methylgermane is obtained from dibromomethane than from chlorobenzene, more methylgermane is obtained from dibromomethane than from dichloromethane, and a detectable amount of methane is obtained from iodomethane but not from bromomethane. The trends in rates may be explained by considering the activated complexes in the two types of reaction. Nucleophilic attack by germyl anion at either carbon or halogen results in an activated complex in which the carbon–halogen bond is partially broken. The carbon–iodine

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(28) W. H. Snyder, J. Parascandola, and M. Wolfinger, *J. Org. Chem.*, **31**, 2027 (1966).

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(30) See ref 26, p 475.

bond is weaker than the carbon–chlorine bond; therefore both types of reaction are enhanced when a carbon–iodine, rather than a carbon–chlorine, bond is involved. However, there are further effects (which do not apply to the nucleophilic attack on carbon) that enhance nucleophilic attack on halogen when one goes from a chloride to an iodide. Because iodine is less electronegative than chlorine, a bonded iodine atom is more susceptible to attack by an anion than is a bonded chlorine atom. Furthermore, iodine is "softer" than chlorine and therefore might be expected to react more readily with the soft germyl anion. Thus one would expect that the overall accelerative effect of going from a chloride to a bromide to an iodide would be more pronounced for the hydrogen-substitution reaction than for the germyl-substitution reaction.

It should be pointed out that a free-radical mechanism, analogous to that proposed for the reaction of organic halides with organotin hydrides,[31] will account for most of the experimental results. However, in the reaction of neophyl bromide, the intermediate neophyl radical would be expected to rearrange to yield isobutylbenzene;[32,33] only *tert*-butylbenzene was formed. Also, one might expect phenyl radicals to cleave the diglyme in the reaction of bromobenzene with potassium germyl-d_3; however, no such cleavage products were found. These two negative observations are consistent with a radical mechanism if one assumes that abstraction of a germanium-bonded hydrogen by the intermediate radical is so fast that all other reactions, including rearrangement, are precluded.

Certain mechanisms for the hydrogen-substitution reaction can be ruled out. The aromatic halide sugstitutions cannot be explained by a benzyne[34] intermediate because of the observed reactivity of 2-bromo-*m*-xylene toward potassium germyl. Organogermane formation and subsequent decomposition to GeH_2 and hydrocarbon is ruled out because phenylgermane[35] and digermylmethane[36] are known to be stable compounds, even in basic solution. Finally, nucleophilic attack on carbon by a hydrogen atom of the germyl anion is ruled out by the following argument. It has been shown[37] that, in substitution reactions of ambident nucleophiles, if the substrate is changed so as to increase the "SN1 character" of the reaction, attack by the most electronegative atom of the nucleophile is favored. An effect of this type would be expected to be small in the case of GeH_3^- because germanium and hydrogen have similar electronegativities. Furthermore, neither the potassium germyl–bromobenzene reaction nor the potassium germyl–methyl bromide reaction would be expected to have significant SN1 character; therefore one would expect little difference in the relative rates of attack by the hydrogen atom and germanium atom in these reactions, and one would expect the same relative yields of hydrocarbon and organogermane. This result was not found.

In addition to undergoing the germyl and hydrogen substitutions, dihalo- and trihalomethanes react in yet another way with potassium germyl, *i.e.*, to form digermylethane and digermylpropane. The latter products can be explained by the deprotonation of the halomethanes by potassium germyl. Indeed, the yield of GeH_4 increases on going from dibromomethane to dichloromethane to trichloromethane, in accord with the expected acid strengths of the halomethanes. The carbanions formed can go on to attack unreacted halomethane, forming haloethanes, halopropanes, etc., which then react with the germyl anion to form the corresponding digermylalkanes

$$CH_2X_2 + GeH_3^- \longrightarrow GeH_4 + CHX_2^-$$

$$CHX_2^- + CH_2X_2 \longrightarrow CH_2XCHX_2 + X^-$$

$$CH_2XCHX_2 + 3GeH_3^- \longrightarrow GeH_3CH_2CH_2GeH_3 + (1/n)(GeH_2) + 3X^-, \text{etc}$$

Acknowledgment.—This research was supported by the U. S. Atomic Energy Commission.

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