Alkylgermanium Isothiocyanates and Cyanides

By Herbert H. Anderson

All three ethylgermanium isocyanates are stable,[1] and their existence suggested that alkylgermanium isothiocyanates might exist. Exploratory work showed that trialkylgermanium oxide(s) reacted with formic acid or mercaptoacetic acid to yield the corresponding ester[2]; moreover, the organogermanium oxide and sulfuric acid gave an organogermanium sulfate.[3] In light of this work, the use of an organogermanium oxide and the pseudohalogen acids isocyanic, isothiocyanic and hydrocyanic acids have now been examined; the results indicate that the strength of the acid[2] is not important for reaction, since isocyanic acid does not react. Isothiocyanic acid reacts with trialkylgermanium or dialkylgermanium oxides, while hydrocyanic acid reacts with trialkylgermanium oxides only. A different approach consists of treating an organogermanium iodide—or possibly a bromide—with silver isothiocyanate or silver cyanide; in this method impure, unanalyzed $EtGe(CN)_3$ and $EtGe(NCS)_3$ were observed.

Recently Eaborn[4] has reported a "conversion series" for organosilicon halides, pseudohalides and sulfides, which has now in part been extended to organogermanium chemistry. Any "conversion series" covers a rather limited scope and must apply only to the type of process specified—in these instances the use of silver salts. It is possible to proceed in a different direction from that in the "conversion series" or that in a previous interpretation[5] by employing a different type of process, such as replacing oxygen by iodine, when $(Et_3Ge)_2O$ and HI form Et_3GeI[6]; or replacing nitrogen by iodine when $EtSi(HNC_6H_5)_3$ and HI form $EtSiI_3$ and insoluble $C_6H_5NH_3I$[7]; or replacing fluorine by iodine when Et_3SiF and AlI_3 form Et_3SiI and insoluble AlF_3.[8]

In a few special instances it is difficult to convert a highly volatile organogermanium halide into the corresponding oxide and obtain a fair yield of the oxide; perhaps treatment with silver carbonate will prove a good method, since aqueous solutions are not needed, and the oxide remains in whatever solvent chosen.

Preparation of New Compounds. Isothiocyanates.—Starting materials consisted of $(Et_3Ge)_2O$, Et_2GeO polymer, $(n\text{-}Pr_3Ge)_2O$ and $(n\text{-}Bu_3Ge)_2O$; the first two are known, while the latter two are made from bromine and either $n\text{-}Pr_4Ge$ or $n\text{-}Bu_4Ge$, followed by treatment with excess alkali. The latter two (new) oxides boil at 305 and 353°, respectively. Professor Eugene G. Rochow, of this Laboratory, kindly contributed some diethylgermanium dichloride—which was later converted into oxide. In the preparation of ethereal isothiocyanic acid, 5.0 g. of NH_4SCN was dissolved in 5.5 ml. of water and then 2.50 ml. of 60% sulfuric acid was added; two extractions with 8-ml. portions of diethyl ether then yielded 2.1 *M* isothiocyanic acid.

In a typical preparation of a trialkylgermanium isothiocyanate, 4.70 g. of $(Et_3Ge)_2O$ and 16 ml. of 2.1 *M* isothiocyanic acid in ether produced a temperature rise of 7° and a cloudiness due to water formed; after two hours 0.27 ml. of water was removed by a transfer pipet. The ether solution was dried for several hours using Na_2SO_4 and then the solution separated by pipet, with several washings of the solid. After distillation of the ether, the remaining liquid was allowed five minutes of free reflux, wherein the isothiocyanic acid polymerized into insoluble yellow thiocyanuric acid; it was advantageous to remove the bulk of the liquid organogermanium isothiocyanate by transfer pipet, and then to filter through a fritted Pyrex glass disc, using a unit which fitted into the top of the distillation unit (equipped with ground joints). Yields were at least 80%, consisting of quantitative reactions, followed by mechanical losses of 20%. Table I lists the conditions of distillation and the properties of the four isothiocyanates.

Table I

Compounds distilled under lowest pressures specified. Isothiocyanate analyzed by titration with base; see H. H. Anderson, This Journal, 71, 1801 (1949). Cyanide analyzed by addition of $AgNO_3$ in methanol–H_2O to a solution of the compound in methanol, with later titration of liberated nitric acid using methyl red indicator. All mol. wts. by freezing point lowering of camphor.

Compound	B.p., °C.	Mm.	M.p., °C.	n^{20}	R	d^{20}_4	NCS or CN, % Calcd.	Found	Mol. wt. Calcd.	Found
$n\text{-}Bu_3Ge(NCS)$	319	760	..	1.5039	84.3	1.071	19.2	19.1, 19.2	303.0	300
	135–136	2								
$n\text{-}Pr_3Ge(NCS)$	287	760	−56	1.5063	69.8	1.105	22.3	22.3, 22.6	256.0	269
	143–144	9								
$Et_2Ge(NCS)_2$	298	760	16	....	..	1.356	47.1	46.4, 46.7	246.9	236
	113–116	1								
$Et_3Ge(NCS)$	252	760	−46	1.517	55.7	1.184	26.7	26.9, 26.9	217.9	222
	113–114	8								
$n\text{-}Pr_3Ge(CN)$	253	760	−13	1.4544	59.4	1.041	11.4	11.6, 10.7	227.9	238
	115–117	10						10.9		
$Et_3Ge(CN)$	213	760	18	1.4509	45.0	1.111	14.0	14.2, 14.0	185.8	197

Seven grams of $Et_3Ge(NCS)$ resulted when 5.40 g. of the oxide $(Et_3Ge)_2O$ and 20 ml. of 2.8 *M* isothiocyanic acid in ether reacted; after mechanical removal of most of the water, phosphorus pentoxide was used overnight as a dryer, followed by a process like that above.

Similarly, 4.0 g. of $(Et_2GeO)_{3\text{ or }4}$ and 24 ml. of 2.8 *M* isothiocyanic acid in ether reacted easily; after removal of 0.5 ml. of water, the solution was dried overnight using phosphorus pentoxide, which is added carefully. After removal of solvent and polymerization of the free acid, approximately 5.7 g. of a diisothiocyanate of 99% purity—based upon available thiocyanate and m.p. range of 0.5° resulted.

Likewise, 5.3 g. of $(n\text{-}Bu_3Ge)_2O$ and 16 ml. of 2 *M* isothiocyanic acid in ether, using the Na_2SO_4 process, ultimately yielded 5 g. of the corresponding isothiocyanate, in which, however, a trace of thiocyanuric acid persisted.

Throughout this work micro transfer methods and equipment bearing ground joints have been advantageous.

Cyanides (this word is without structural implication).—Essentially anhydrous hydrogen cyanide resulted when 50%

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[1] H. H. Anderson, This Journal, **71**, 1799 (1949).

[2] H. H. Anderson, *ibid.*, **72**, 2089 (1950).

[3] H. H. Anderson, *ibid.*, **72**, 194 (1950).

[4] C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

[5] H. H. Anderson, This Journal, **72**, 2761 (1950).

[6] C. A. Kraus and E. A. Flood, *ibid.*, **54**, 1637 (1932).

[7] H. H. Anderson, D. L. Seaton and R. P. T. Rudnicki, *ibid.*, **73**, 2144 (1951).

[8] C. Eaborn, *J. Chem. Soc.*, 2755 (1949).

sulfuric acid dropped gradually onto potassium cyanide. Nearly all the cyanide work was done inside a good hood.

When the hydrogen cyanide gas obtained from 6 g. of KCN and 9 ml. of 50% H_2SO_4 bubbled into 5.15 g. of ice-cold $(n\text{-}Pr_3Ge)_2O$ over a period of 40 minutes, a whitish emulsion resulted; after transfer and then drying for two hours with Na_2SO_4, approximately 5.3 g. of product resulted.

Similarly, 7 g. of $(Et_3Ge)_2O$ and the hydrogen cyanide from 7 g. of KCN and 11 ml. of 50% H_2SO_4 reacted to furnish a whitish emulsion, later dried and distilled at atmospheric pressure.

Both trialkylgermanium cyanides are colorless liquids with odors like that of hydrogen cyanide.

All six new alkylgermanium isothiocyanates and cyanides are mobile liquids and are easily soluble in 95% ethanol, acetone and (30–60°) petroleum ether.

Other Reactions and Conversions.—Diethylgermanium oxide and hydrogen cyanide did not react, and unchanged oxide remained; no cloudiness formed and the reaction did not go even when phosphorus pentoxide was present.

Bis-(triethylgermanium) oxide did not react with isocyanic acid, either when heated in the same tube with cyanuric acid, or when HNCO gas, generated from diphenylsilicon diisocyanate and water, was passed in. Carbon dioxide and $(Et_3Ge)_2O$ did not react, since the carbon dioxide did not dissolve in the germanium compound; at 25°, 5.40 g. of $(Et_3Ge)_2O$ gained 1.70 g. of SO_2 within 22 minutes, but the SO_2 escaped completely upon warming to 110°. A loose compound such as $(Et_3Ge)_2O \cdot SO_2$ may exist in the cold, but no stable sulfite or carbonate forms under these conditions.

Six grams of Et_3GeBr and 15 g. of Ag_2CO_3 when suspended in 25 ml. of dry benzene reacted with a considerable evolution of gas bubbles; after 20 minutes on the steam-bath, the solid was filtered and washed. A test for AgBr by dissolving Ag_2CO_3 in nitric acid and then weighing the insoluble residue, which was 3.6 g., indicated approximately 80% reaction; when the benzene was distilled, the residue evolved no carbon dioxide upon addition of concentrated HBr. Thus $(Et_3Ge)_2O$ was the product.

Nine grams of Et_3GeBr and 14 g. of $AgNO_3$ in 40 ml. of benzene showed no reaction in the cold, but the solution turned a reddish-brown upon 30 minutes of reflux on a steam-bath; undoubtedly N_2O_4 was being formed. However, $Et_3Ge(NO_3)$ may be moderately stable—especially if the reaction be done in a *truly inert* solvent.

Seven grams of $EtGeI_3$ and 14 g. of AgNCS in 30 ml. of benzene, after the usual half-hour reflux, filtration and washing, yielded about 5 g. of a liquid which still contained a little iodine in the least volatile fraction collected at 130–132° under one mm. At 760 mm. the boiling point was 308°, with decomposition. A comparable reaction with $EtGeBr_3$ should go better, at least regarding separations.

Ten grams of $EtGeI_3$ and 14 g. of AgCN in 75 ml. of dry benzene showed no heat of reaction, although the silver salt turned yellow at once; after an hour of reflux, the solution was filtered, but an extra three washings with boiling 75-ml. portions of benzene were necessary to extract 7.5 g. of product. After two crystallizations from benzene the supposed $EtGe(CN)_3$ was a white solid melting at 127° and boiling at about 255°—but the whole sample polymerized during a check determination of boiling point, a black solid being formed.

A reaction between $GeBr_4$ and AgNCS in isopropylbenzene gave evidence of proceeding, although no unpolymerized $Ge(NCS)_4$ was ever isolated.

In the Eaborn fashion, using a silver salt without any solvent,[4] 2.94 g. of AgNCO and 1.60 g. of $Et_3Ge(NCS)$ upon reflux for five minutes yielded, after distillation, a product which was essentially pure $Et_3Ge(NCO)$ and had a b.p. of 200°, no NCS content, n^{20} 1.454; yield 1.46 g. or 90% of the theoretical amount.

When 1.0 g. of $Et_3Ge(CN)$ and 1.8 g. of AgNCS were given ten minutes of reflux, followed by distillation of the liquid, then the resulting liquid boiled at 227°, had a neutralization equivalent of 340 (by direct titration using ethanolic NaOH and phenolphthalein), and also had n^{20} 1.483; reconstruction of this information, plus a strong qualitative test with ferric ion, indicates the composition 65% $Et_3Ge(NCS)$ and 35% unchanged $Et_3Ge(CN)$. It is obviously more difficult to ensure complete mixing and reaction in the Eaborn modification[4] than in the older style of reaction using a solvent such as benzene.

Several preliminary experiments have shown that SbF_3 reacted with either $Ge(NCO)_4$ or $Et_3Ge(NCS)$.

Germanium is a transitional element, and its reactions fall between those of silicon and those of the relatively electropositive tin; many organogermanium pseudohalides are volatile liquids, but polymerization is also a problem.

Thus a "conversion series" essentially I → Br → CN → NCS → Cl → NCO → F exists in trialkylgermanium derivatives when a silver salt is used; a silver salt should convert any compound to one on its right, but not to one on its left.

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Tri-*n*-propylgermanium Halides, Isocyanate and Oxide

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The interaction of tetra-*n*-propylgermanium and bromine yields primarily tri-*n*-propylgermanium bromide, which upon alkaline hydrolysis furnishes bis-(tri-*n*-propylgermanium) oxide, a liquid boiling at 305°, which reacts with halogen acids to produce four new tri-*n*-propylgermanium halides. Silver isocyanate converts the chloride into the isocyanate.

Tri-*n*-propylgermanium halides and isocyanate tend to retain small amounts of free hydrogen halide or isocyanic acid, most of which can be removed by boiling with small pieces of sodium hydroxide.

Table I lists the properties of the six new compounds.

Experimental

Preparation of New Compounds.—The methods used for preparing the oxide and the halides follow the method of Kraus and Flood,[2] while the conversion of chloride to isocyanate is our own process.[3]

Bis-(tri-*n*-propylgermanium) Oxide.—Over a five-hour period, with occasional cooling, 107 g. of pure tetra-*n*-propylgermanium, b.p. 225–227°, was treated with small portions of bromine in the presence of a half-gram of pure iron powder, until 78 g. of bromine was added; after 40 hours at 45°, only a gram of free bromine remained. At this point the liquid contained tri-*n*-propylgermanium bromide, *n*-propyl bromide, bromine, di-*n*-propylgermanium dibromide or bromine substitution products, as well as some dibromopropane. Shaking with an excess of 25% aqueous sodium hydroxide solution converted the crude tri-*n*-propylgermanium bromide into the oxide, which was finally extracted nearly quantitatively using repeated large portions of (30–60°) petroleum ether. After drying overnight with calcium oxide, then distillation of solvent, there remained 89 g. of product, at least 67 g. of which was bis-(tri-*n*-propylgermanium) oxide, or a yield of 66% based on bromine; the 48-g. center fraction boiled at 175° under 14 mm. pressure, and another 14 g. boiled at 175–177°, while 21 g. boiling above this was either an azeotrope of bis-(tri-*n*-propylgermanium) oxide and trimeric di-*n*-propylgermanium oxide (the latter new compound will be reported separately) or an altered bis-(tri-*n*-propylgermanium) oxide in which bromine has replaced a hydrogen. Material from the center fraction served for all measurements and analyses, as in Table I. (This 21-g. fraction does not yield pure di-*n*-propylgermanium dichloride with hydrochloric acid.)

Fluoride.—Repeated agitation of 5.8 g. of bis-(tri-*n*-propylgermanium) oxide with 12 ml. of 48% hydrofluoric acid in a transparent plastic tube furnished a rise of 10° in temperature, and then the two layers stood covered for two hours, whereupon (30–60°) petroleum ether extracted the germanium halide in four treatments. After drying over-

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(1) 1932 Commonwealth Ave. Auburndale 66, Mass.

(2) C. A. Kraus and E. A. Flood, THIS JOURNAL, **54**, 1635 (1932).

(3) G. S. Forbes and H. H. Anderson, *ibid.*, **62**, 761 (1940); **65**, 2271 (1943).