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.

CHEMICAL LABORATORY OF HARVARD UNIVERSITY
CAMBRIDGE 38, MASS. RECEIVED JUNE 15, 1951

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

BY HERBERT H. ANDERSON[1]

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-

---

[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).

TABLE I

Compound	B.p., °C.	Mm.	M.p., °C.	d^{20}_4	n^{20}	R	Halide, % Calcd.	Halide, % Found	Mol. wt. Calcd.	Mol. wt. Found
$(n\text{-}Pr_3Ge)_2O$	305	760	−55	1.068	1.4648	108.1	34.6[a]	34.5[a]	419.7	405
	175	14								
n-Pr_3GeF	203	760	−27.5	1.074	1.4340	53.6	8.60	9.0, 9.0	220.9	217
n-Pr_3GeCl	227	760	−70	1.100	1.4641	59.5	15.0	15.1, 15.2	237.2	235
	98–99	11								
n-Pr_3GeBr	242	760	−47	1.282	1.4832	62.7	28.4	28.4, 28.4	281.8	278
	112–113	12								
n-Pr_3GeI	259	760	−38	1.443	1.5144	68.7	38.5	38.6, 38.9	328.8	318
	122–123	10								
n-PrGe(NCO)	247	760	−19	1.055	1.4575	61.4	17.3	17.5, 17.6	234.9	230
	114	10								

[a] Per cent. germanium. All indices of refraction in white light. R for Ge, oxide to iodide, 8.4, 8.0 (if R_F is 1.0), 8.3, 9.0, 9.9 by n^2-1 formula.

night with anhydrous sodium sulfate, the solvent was distilled, leaving 6.05 g. of tri-*n*-propylgermanium fluoride; after three distillations 0.40% free hydrogen fluoride still remained in the product, the properties of which are in Table I. Distillation from sodium fluoride would have been ideal.

Chloride.—Vigorous shaking of 12.8 g. of oxide and 25 ml. of 12 *M* hydrochloric acid gave a temperature rise of 17°; after standing overnight, there followed extraction with light petroleum ether, drying with calcium chloride and then distillation. A yield of 14.2 g. was essentially quantitative; the first center fraction contained 16.2% chlorine, but boiling for ten minutes with a half-gram of barium carbonate lowered the value to 15.14%. Table I lists the properties.

Bromide and Iodide.—Upon shaking 9.6 g. of oxide and 25 ml. of 48% hydrobromic acid the temperature rose 12°; after extraction and then drying with anhydrous sodium sulfate, the solvent was distilled, leaving 11.9 g. of tri-*n*-propylgermanium bromide or a yield of 93%. Before using 0.15 g. of sodium hydroxide the analysis was 29.1% bromine; afterwards, 28.4%. Nine grams of oxide and 29 ml. of 45% aqueous hydriodic acid when shaken rose 7.3°; after extraction, without drying, the solvent was distilled and then 11.1 g. of iodide remained—a yield of 85%, lowered by slight mechanical losses. Before using 0.10 g. of sodium hydroxide in seven pieces, the iodine content was 39.5%; afterwards, 38.8%. Table I lists the distillations at reduced pressure and the properties of center fractions.

Isocyanate.—Sixteen grams of silver isocyanate and 12 g. of tri-*n*-propylgermanium chloride in 30 ml. of pure benzene rose 13° in temperature; the usual one-hour reflux[4] also included presence of 3 ml. of nitromethane. After purification, the 12 g. of product contained no chlorine, but had 17.9% isocyanate; after boiling 5 g. with 0.10 g. of sodium hydroxide, the analysis was better. Table I lists the properties of the purer sample.

Properties and Analysis.—All six compounds are colorless, mobile liquids easily soluble in organic solvents; the melting points, good to a degree in all cases, indicate fairly pure compounds, sometimes bearing a few tenths of a per cent. of hydrogen halide. Because of low solubility in water, the compounds do not hydrolyze easily in pure water; overnight heating of 1.9 g. of tri-*n*-propylgermanium bromide with 0.22 g. of water at 100° gave an aqueous layer 0.70 *M* in hydrobromic acid—or 2.2% of the bromine was in the aqueous layer. Ethanolic sodium hydroxide and micropipets served in titrations of acidity, while the germanium content of the oxide relied upon fuming nitric acid and sulfuric acid in oxidation; the results are in Table I. All molecular weights are by freezing point of camphor.

Throughout the investigation all transfers were by pipet, not by pouring; all the distillation units bore interchangeable ground joints. Bis-(tri-*n*-propylgermanium) oxide had a weak aromatic odor, while the fluoride and chloride were penetrating and camphoraceous; the bromide and isocyanate were penetrating in odor, while the iodide had little odor.

CHEMICAL LABORATORY OF HARVARD UNIVERSITY
CAMBRIDGE 38, MASS.
RECEIVED JULY 5, 1951

The Reaction of Methylmagnesium Iodide with β-(1-Hydroxy-3,4-dihydro-2-naphthyl)-butyric Acid Lactone[1]

BY B. BELLEAU[2]

In another communication,[3] we reported the synthesis of 1-methyl-3-keto-1,2,3,9,10,10a-hexahydrophenanthrene (XI) as an intermediate in a projected synthesis of doisynolic acid analogs. This paper deals with an improved synthesis of this phenanthroid ketone together with an original synthesis of 1,3-dimethylphenanthrene.

Attempted applications of the technique of Wilds and Johnson[4] to the synthesis of the diketone II from the ketoacid I[3] were fruitless because of the spontaneous lactonization to III that the acid chloride of I underwent. In view of this result, a method for the preparation of the diketone II from the enol lactone III was desirable, and in this respect, the reaction of an equimolar amount of methylmagnesium iodide with the latter was attempted. This led to an oily reaction mixture which was hydrolyzed with hydrochloric acid to give a 15% yield of the ketone XI identified by means of mixed melting point determination with an authentic sample[3] and a 30% yield of a hydrocarbon of empirical formula $C_{16}H_{18}$. Dehydrogenation of the latter produced 1,3-dimethylphenanthrene identical with a sample prepared from the ketone XI.[3]

The hydrocarbon exhibited absorption bands at 274, 280, 290, 307, 314 and 322 mμ with respective molar extinction coefficients (log *e*) of 3.73, 3.76, 3.64, 2.98, 2.80 and 2.88; these values are characteristic of a naphthalenoid conjugated system and the spectrum is superimposable to that reported for 1,2,3,4-tetrahydrophenanthrene.[5] Since the hydrocarbon $C_{16}H_{18}$ also formed a picrate, the presence in it of a naphthalenoid ring system is unquestionable and provisionally, the compound can best be formulated as 1,3-dimethyl-1,2,3,4-tetrahydrophenanthrene (X). The latter has previously been prepared by Haworth, Mavin and Sheldrick,[6]

---

[1] Abstracted from the Ph.D. thesis of B. Belleau presented to the Department of Biochemistry, McGill University, 1950.

[2] The Sloan-Kettering Institute for Cancer Research, New York, N. Y.

[3] B. Belleau, THIS JOURNAL, **73**, 5149 (1951).

[4] A. L. Wilds and T. L. Johnson, *ibid.*, **70**, 1166 (1948).

[5] F. A. Askew, *J. Chem. Soc.*, 512 (1935).

[6] R. D. Haworth, C. R. Mavin and G. Sheldrick, *ibid.*, 454 (1934).