***p*-(Tri-1-naphthylsilyl)-benzyl Bromide (Attempted).**—The procedure for obtaining *p*-(triphenylsilyl)-benzyl bromide from triphenyl-(*p*-tolyl)-silane and N-bromosuccinimide was employed. Fifteen grams (0.03 mole) of tri-1-naphthyl-(*p*-tolyl)-silane was dissolved in 600 ml. of carbon tetrachloride, 5.35 g. (0.03 mole) of finely powdered N-bromosuccinimide was added, and the mixture was refluxed, with stirring, for 30 minutes while irradiating the reaction flask with a mercury vapor lamp. The N-bromosuccinimide had disappeared from the bottom of the flask and a test for active bromine was negative. After cooling and filtering off the succinimide, the solvent was removed from the filtrate to give a yellow oil. Digestion of this oil with about 200 ml. of petroleum ether (b.p. 90–110°), followed by filtration, gave 14.0 g. of yellow solid melting over the range 150–155°. Even after several recrystallizations from ethanol, ethyl acetate and petroleum ether (b.p. 90–110°), the melting point range could not be raised above 160–165°.

This experiment was repeated twice with essentially the same negative results.

***p*-(Tri-1-naphthylsilyl)-benzoic Acid (Attempted).**—Several attempts were made to oxidize tri-1-naphthyl-(*p*-tolyl)-silane with chromium trioxide by the same procedure that was used to prepare *p*-(triphenylsilyl)-benzoic acid from triphenyl-(*p*-tolyl)-silane. A typical experiment is described. Ten grams (0.02 mole) of tri-1-naphthyl-(*p*-tolyl)-silane was suspended in 400 ml. of glacial acetic acid and 6.0 g. (0.06 mole) of chromium trioxide was added in small portions to the stirred mixture. After stirring for an additional hour, the green solution was poured onto crushed ice and filtered. There resulted an 80% recovery of tri-1-naphthyl-(*p*-tolyl)-silane as evidenced by the mixed melting point method.

In a similar experiment the mixture was refluxed for 15 minutes and a 15% recovery of the starting organosilicon compound was obtained. Extraction of the organic material with potassium and ammonium hydroxide followed by neutralization of the aqueous layer did not reveal any acid. (It was expected that some benzoic or phthalic acid might be formed from oxidation of cleavage products.)

Three runs were made in which 1, 3 and 10 ml. of concd. sulfuric acid were added to the respective mixtures which were all stirred at room temperature throughout the reaction. Tri-1-naphthyl-(*p*-tolyl)-silane was not isolated from these attempts but the resulting oils and tars resisted purification. These latter substances apparently were not acidic. Essentially the same negative results were obtained by using sulfuric acid at 50 and 100° except that some charring occurred at 100°

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DREXEL INSTITUTE OF TECHNOLOGY]

Esters in Organogermanium "Conversion Series"

BY HERBERT H. ANDERSON

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A systematic investigation of the ester group in the organogermanium "conversion series" for reactions using silver salts, together with other reactions, now makes available a single conversion series for germanium including esters. The properties of eleven new diisopropylgermanium derivatives, chiefly esters, are reported.

Conversion series, in which the appropriate silver salt converts an organometallic compound to any other organometallic compound to the right of it in the series, are available for silicon,[1] tin,[2] germanium[3] and phosphorus.[4] Previous results showed conversion of organogermanium iodide, bromide or chloride to the acetate, cyanide to isothiocyanate and isothiocyanate to isocyanate.[3] Recent papers on organosilicon and organotin compounds demonstrated the conversion of cyanides, isothiocyanates, isocyanates and sulfides to esters.[1,2]

In the present paper there is presented an investigation of the ester group in the organogermanium conversion series. An organogermanium ester forms almost quantitatively from silver acetate and the organogermanium iodide, sulfide, bromide, hydride, cyanide, chloride, isothiocyanate or isocyanate; the oxide gives the ester in approximately 60% yield; the ester does not form from the fluoride. On the basis of this and previously published work,[3] the single conversion series for organogermanium compounds, using silver salts, is as follows: I → S → Br → CN → (NCS and Cl) → NCO → (O and OCOR) → F. Here the isothiocyanate and chloride are paired, although the mixture at equal mole fractions contains 20% organogermanium isothiocyanate and 80% chloride; oxide and ester are paired since neither replaces the other completely; hydride is omitted since silver hydride is so unstable.

There is no adequate explanation for these conversion series. As Eaborn[5] points out, the relative positions of organosilicon oxide and sulfide in the organosilicon conversion series are inconsistent with the relative solubilities of silver oxide and silver sulfide, compared with those of the silver halides. Moreover, all series should be identical if the solubilities of the silver salts were the only factor; however, no two of the four known series[1,2,4] are identical.

Experimental

I. **Preparation of New Esters.**—Table I lists the properties of the new compounds prepared, and also the temperatures of distillations.

Equipment included distilling units with 10/30 standard taper ground joints on all units and accessories, micropipets for the measurement of a liquid and the subsequent titration of the available acidity,[6] and transfer micropipets.

Starting Materials.—The slow addition of 1100 ml. of 1.3 *M* isopropylmagnesium chloride to 67 g. of germanium tetrachloride was followed by decomposition with water, two hours after the final addition of the Grignard reagent. After washing the reaction mixture with water to remove magnesium salts, the organometallic layer was shaken with excess aqueous sodium hydroxide and extracted with hexane, which was later removed by distillation. Further distillation under 9 mm. pressure yielded 15 g. of $(i\text{-}C_3H_7)_3GeOH$, b.p. 90–92°; subsequent distillation under 1 mm. pressure furnished a 10-g. mixture boiling as high as 126°, and finally

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TABLE I

NEW COMPOUNDS

Compound	B.p., °C.	d^{20}_4	n^{20}	MR	Mol. wt. Calcd.	Mol. wt. Found	Neut. equiv. Calcd.	Neut. equiv. Found	Distilled at °C. (1 mm.)
$(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$	236	1.193	1.445	61.8	276.8	257	138.4	138, 137	79–80
$(i\text{-}C_3H_7)_2Ge(OCOC_2H_5)_2$	255	1.146	1.447	71.0	304.9	..	152.5	151, 152	94–95
$(i\text{-}C_3H_7)_2Ge(OCO\text{-}n\text{-}C_3H_7)_2$	274	1.112	1.452	80.6	332.9	..	166.5	167, 168	106–108
$(i\text{-}C_3H_7)_2Ge(OCOCH_2Cl)_2$	298	1.372	1.480	71.6	345.8	..	172.9	172, 172	136–138
$(i\text{-}C_3H_7)_2Ge(OCOCH_2CH_2Cl)_2$	..	1.294	1.474	81.2	373.8	..	186.9	183, 183	140–142
$(i\text{-}C_3H_7)_2Ge(OCO_6H_5)_2$[a]	385	Solid	...	..	401.0	..	200.5	198, 197	186–188
$[(i\text{-}C_3H_7)_2GeSO_4]_2$[b]	..	Solid	...	..	509.7	..	254.9	254	.....
$(i\text{-}C_3H_7)_2Ge(NCO)_2$	239	1.225	1.464	54.7	242.8	237	121.4	121, 121	72–73
$(i\text{-}C_3H_7)_2Ge(NCS)_2$	296	1.234	1.558	..	274.9	260	137.5	133, 133	105–107
$[(i\text{-}C_3H_7)_2GeS]_2$	312	1.327	1.551	..	381.8	380	(16.8	16.6%S)	117–121
$(i\text{-}C_3H_7)_2GeH_2$[c]	110	0.982	1.432	42.5	160.8	..	...	.....	110–111[d]

[a] M.p. 54°. [b] M.p. approximately 115°; the crystals darkened during the determination. [c] Calcd. for $(i\text{-}C_3H_7)_2GeH_2$: C, 44.81; H, 10.03. Found: C, 44.44; H, 9.89. [d] Distilled at 760 mm.

TABLE II

REACTIONS IN THE "CONVERSION SERIES"

One hour of reflux with a 30–40% excess of the silver salt.

Reagents		Germanium product	B.p., °C.	Yield, %
$[(C_2H_5)_3Ge]_2O$	AgF	$(C_2H_5)_3GeF$	149.5	60
$(C_2H_5)_3GeOCOCH_3$	AgF	$(C_2H_5)_3GeF$	149.4	80
$(i\text{-}C_3H_7)_2Ge(NCO)_2$	$AgOCO\text{-}n\text{-}C_3H_7$	$(i\text{-}C_3H_7)_2Ge(OCO\text{-}n\text{-}C_3H_7)_2$	272	78[a]
$(n\text{-}C_3H_7)_3GeCN$	$AgOCOC_2H_5$	$(n\text{-}C_3H_7)_3GeOCOC_2H_5$	..	80[b]
$(i\text{-}C_3H_7)_2Ge(NCS)_2$	$AgOCOCH_3$	$(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$	239	80[c]
$(i\text{-}C_3H_7)_3GeBr$	AgCN	$(i\text{-}C_3H_7)_3GeCN$	..	..[b]
$(i\text{-}C_3H_7)_3GeBr$	AgNCS	$(i\text{-}C_3H_7)_3Ge(NCS)$	277	..
$[(i\text{-}C_3H_7)_2GeS]_2$	$AgOCOCH_3$	$(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$	228	..
$[(i\text{-}C_3H_7)_2GeS]_2$	AgCN	$(i\text{-}C_3H_7)_2Ge(CN)_2$	..	..[b]
$[(i\text{-}C_3H_7)_2GeS]_2$	AgBr	$(i\text{-}C_3H_7)_2GeBr_2$	..	..[a,b]
$(i\text{-}C_3H_7)_2GeH_2$	$AgOCOCH_3$	$(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$	244	..[d]

[a] The reverse reaction did not occur. [b] Identity established by qualitative tests for S, Br or CN. [c] A very small amount of NCS present. [d] About 16% $[(i\text{-}C_3H_7)_2GeO]_3$ present as a decomposition product.

24 g. of nearly pure $[(i\text{-}C_3H_7)_2GeO]_3$ which was later converted to $(i\text{-}C_3H_7)_2GeCl_2$ or $(i\text{-}C_3H_7)_2GeI_2$.[3]

Diisopropylgermanium Diacetate, Dipropionate, Di-*n*-butyrate and Dibenzoate.—A 30% excess of the appropriate silver salt and a final yield of organogermanium ester at least 80% of the calculated amount were typical. Refluxing of 4.44 g. of $(i\text{-}C_3H_7)_2GeCl_2$ and 9.3 g. of silver propionate in 25 ml. of hexane for 30 minutes was followed by filtration and washing of the silver salts. Distillation of hexane left 5.75 g. of $(i\text{-}C_3H_7)_2Ge(OCOC_2H_5)_2$, then distilled under 1 mm. pressure. Table I lists the center fraction of the ester.

Diisopropylgermanium Bis-(monochloroacetate), Bis-(β-chloropropionate) and Sulfate.—Five minutes of gentle reflux of 3.50 g. of $(i\text{-}C_3H_7)_2Ge(OCOCH_3)_2$ and 2.45 g. of chloroacetic acid, equivalent amounts, furnished 1.50 g. of acetic acid (collected as it distilled in the five minutes) and 4.45 g. of $(i\text{-}C_3H_7)_2Ge(OCOCH_2Cl)_2$, a yield of 98%. Table I lists the viscous center fraction. During measurement of the b.p. under 760 mm. the monochloroacetate turned dark red while much hydrolyzable chloride formed.

Similarly, 4.10 g. of $(i\text{-}C_3H_7)_2Ge(OCOC_2H_5)_2$ and 2.80 g. of β-chloropropionic acid furnished propionic acid and the desired bis-(β-chloropropionate), which decomposed too rapidly to allow measurement of a b.p. under 760 mm. pressure.

The reaction of 4.45 g. of $(i\text{-}C_3H_7)_2Ge(OCO\text{-}n\text{-}C_3H_7)_2$ and 1.19 g. of 100% sulfuric acid at 80 mm. pressure furnished approximately 3.7 g. of crude dimeric organogermanium sulfate, later recrystallized once from hexane and then twice from carbon tetrachloride, which dissolves 60 g. of the sulfate per liter of solvent at 23°.

Diisopropylgermanium Diisocyanate and Diisothiocyanate.—A nearly quantitative yield of $(i\text{-}C_3H_7)_2Ge(NCO)_2$ resulted from a reaction between 4.0 g. of $(i\text{-}C_3H_7)_2GeCl_2$ and 6.7 g. of silver cyanate, refluxed for 15 minutes under 72 mm. pressure without a solvent, followed by distillation of the organogermanium isocyanate. After centrifuging to remove some cyanuric acid, the isocyanate was redistilled and the highest-boiling 80% collected for measurements.

Fifteen ml. of 2.8 *M* isothiocyanic acid in ether and 2.50 g. of $[(i\text{-}C_3H_7)_2GeO]_3$ were allowed to stand for 3 hours; after removal of a small amount of water, the solution was dried overnight over sodium sulfate. After distillation of the ether, the iso-thiocyanic acid was polymerized by heating, and the diisothiocyanate distilled; the compound was a moderately viscous, pale-yellow liquid, yield 80%.

Diisopropylgermanium Sulfide and Dihydride.—Thirty minutes reflux of 10 g. each of silver sulfide and of $(i\text{-}C_3H_7)_2GeI_2$, followed by total distillation and then fractional distillation, yielded a center fraction of $[(i\text{-}C_3H_7)_2GeS]_2$, which smelled like dilute hydrogen sulfide; yield approximately 3.5 g.

Lithium iodide and aluminum iodide precipitated during a two-hour reflux of 8.55 g. of $(i\text{-}C_3H_7)_2GeI_2$ and 2.2 g. of lithium aluminum hydride in 40 ml. of dry ether. Water was added dropwise to the cooled solution. Afterwards, the ether layer was shaken briefly with dilute sulfuric acid and then with water, next dried with sodium sulfate and then distilled to obtain 1.80 g. of crude, halogen-free $(i\text{-}C_3H_7)_2GeH_2$, a yield of 54%. Air slowly oxidized the dihydride to the corresponding oxide $[(i\text{-}C_3H_7)_2GeO]_3$.

II. **Reactions in the Conversion Series.**—These results furnished evidence for the organogermanium conversion series presented in the discussion.

In Table II are presented the results of eleven successful complete conversions which did not yield mixtures; a 30–40% excess of the silver salt was present in each one-hour reaction. For example, 1.70 g. of $(i\text{-}C_3H_7)_2Ge(NCO)_2$ and 3.1 g. of silver *n*-butyrate yielded 1.80 g. of isocyanate-free $(i\text{-}C_3H_7)_2Ge(OCO\text{-}n\text{-}C_3H_7)_2$, b.p. 272°, n^{20} 1.450, d^{20}_4 1.109. No reaction occurred in the following cases: $(n\text{-}C_3H_7)_3GeF$ with $AgOCOCH_3$, Ag_2O, Ag_2CO_3, AgCN or AgNCS; $[(n\text{-}C_3H_7)_3Ge]_2O$ with AgCN, AgNCS or AgNCO[7]; $(n\text{-}C_3H_7)_3GeOCOCH_3$ with AgCN, Ag_2S or AgNCS or AgNCS. In the last case a small amount of $(n\text{-}C_3H_7)_3GeNCS$ was ignored.

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(7) A small acidity, due to the decomposition of silver cyanate, was ignored.

since a complete reaction between $(i\text{-}C_3H_7)_2Ge(NCS)_2$ and silver acetate occurs. The two systems below yield mixtures of organogermanium compounds (Table II).

$[(C_2H_5)_3Ge]_2O + 2\ AgOCOCH_3 \leftrightarrows 2\ (C_2H_5)_3GeOCOCH_3 + Ag_2O$.—One hour of reflux of 0.742 g. of $[(C_2H_5)_3Ge]_2O$ and 0.732 g. of silver acetate followed by distillation under low pressure yielded a mixture containing 16.3% $-OCOCH_3$; similarly, 1.122 g. of $(C_2H_5)_3GeOCOCH_3$ and 0.595 g. of silver oxide yielded a liquid mixture containing 16.6% $-OCOCH_3$. Distillation of a combination of the two mixtures showed 33% $[(C_2H_5)_3Ge]_2O$ and 67% $(C_2H_5)_3GeOCOCH_3$ to be present by weight. This confirmed the composition obtained by titration, which averaged 3.12 mole of $(C_2H_5)_3GeOCOCH_3$ per mole of $[(C_2H_5)_3Ge]_2O$.

$(i\text{-}C_3H_7)_3GeCl + AgNCS \leftrightarrows (i\text{-}C_3H_7)_3Ge(NCS) + AgCl$.—Study of this reaction from both sides, with fractional distillation of each product and with tests or the isothiocyanate contents, showed that the system required 80% $(i\text{-}C_3H_7)_3GeCl$ and 20% $(i\text{-}C_3H_7)_3Ge(NCS)$.

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[CONTRIBUTION NO. 1336 FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

Chromate Esters. I. Solvolysis of Di-(2,4-dimethyl-4-hexyl) Chromate[1]

BY HAROLD H. ZEISS[2] AND CLIFFORD N. MATTHEWS

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Chromate esters of simple tertiary alcohols are isolable by freeze-drying technique. A new method of preparation of such esters using chromyl chloride is described. The solvolysis of the chromate ester of optically active 2,4-dimethyl-4-hexanol in methanol yields only the parent alcohol with essentially unchanged optical activity. The general occurrence of chromium–oxygen bond formation and fission in these reactions implied by this optical result and product is related to the oxidizing power of hexavalent chromium.

The appearance of a red, crystalline compound, decomposing to menthone at 53°, was observed by Beckmann[3] in 1889 during the chromic acid oxidation of menthol and is the earliest reported indication of the existence of chromate esters. Such intermediates have been observed since, during similar oxidations of a few other alicyclic alcohols[4-6] such as cholesterol,[6] but as a rule oxidation proceeds too rapidly to allow either the observation or isolation of chromate esters. If, however, chromic anhydride is shaken with a solution of a secondary alcohol in benzene[7] or petroleum ether[8] a yellow color often forms which must be due to the formation of the chromate ester, since chromic anhydride itself is insoluble in these solvents. Decomposition to a brown solid usually occurs rapidly, within one-half hour, the one exception being the ester of borneol[9] which was isolated as a fairly stable, red liquid. The chromate esters of tertiary alcohols, however, have been isolated as solids or liquids, ranging from yellow to orange to red in color and are, in general, more stable than those derived from oxidizable alcohols.[10] All esters so far isolated have been diesters of the oxyacid, $(HO)_2CrO_2$, although monoesters have been proposed as transient oxidation intermediates.

In a remarkable series of papers Westheimer and his colleagues[11] have presented compelling evidence for the participation of chromate ester in the oxidation of isopropyl alcohol and have shown further that the elimination of the secondary hydrogen atom of this alcohol after esterification is the rate-determining process. The lack of stability of secondary chromates is undoubtedly related to the ease of elimination of the secondary hydrogen atom. Since tertiary alcohols possess no α-hydrogen atoms, the Westheimer mechanism is inoperable; hence their esters are more stable and must decompose by a different path requiring a greater activation energy.[12]

Since Gomberg isolated the chromate of triphenylcarbinol by treating silver chromate with triphenylmethyl chloride in benzene,[13] other chromate esters have been obtained by treating tertiary alcohols with chromic acid in suitable solvents. Thus Wienhaus and Treibs have systematically prepared a series of such chromates by this method in petroleum ether, benzene, hydrogen sulfide and carbon tetrachloride.[8-10] Alternatively, chromic anhydride can be treated directly with the carbinol,[14] the ester then being dissolved in solvent to remove it from the aqueous phase formed by the elimination of water during reaction. For several carbinols Fieser and Ourisson[15] found that the esters resulted from shaking the alcohols with sodium dichromate dihydrate in glacial acetic acid or with chromic anhydride in acetic anhydride. Stable esters such as di-2-methylfenchyl chromate[16] can be prepared by all known methods, and these esters have been prepared for the purpose of purifying tertiary alcohols[9] such as tricyclohexylcarbinol[17] and 9-deca-

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