

ORGANOGERMANIUM COMPOUNDS. XII.*

SYNTHESIS OF SOME TRIMETHYLGERMYL-SUBSTITUTED ALCOHOLS

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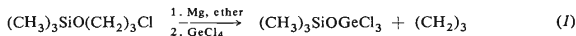
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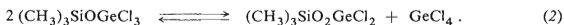
In preparing (3-hydroxypropyl)trimethylgermane from (3-trimethylsiloxypropyl)trichlorogermane an anomalous course of the reaction was found, leading to (trimethylsiloxy)trichlorogermane, bis(trimethylsiloxy)dichlorogermane and cyclopropane as products. The synthesis of (3-hydroxypropyl)trimethylgermane was accomplished using addition of trichlorogermane to allyl chloride and (4-hydroxybutyl)trimethylgermane was prepared from (4-trimethylsiloxybutyl)-trichlorogermane.

Trimethylgermyl-substituted alcohols are suitable model compounds for studying the effect of the germyl group on the properties of the hydroxy group. The synthesis of some of these compounds was reported, but, when attempting to repeat the reported synthesis of (2-hydroxyethyl)trimethylgermane¹, we found some differences from the literature data².

In the present work we prepared (acetoxymethyl)trimethylgermane³ from (chloromethyl)trimethylgermane using a modified procedure⁴. The reaction was carried out under higher pressure, which made it possible to substantially increase the yield of the product.

The synthesis of (3-hydroxypropyl)trimethylgermane⁵ by the procedure starting from uncatalyzed addition of trichlorogermane to allyl acetate has not been successful. All attempts to modify the original procedure (*e.g.* by using a catalyst, or by changing reaction time, temperature, or the ratio of the starting compounds) led to a viscous, apparently high molecular weight material. For this reason we decided to use another route, *via* (3-trimethylsiloxypropyl)trichlorogermane. Reaction of (3-chloropropoxy)trimethylsilane⁶ with magnesium in ether, followed by treatment of the mixture with tetrachlorogermane afforded, however, (trimethylsiloxy)trichlorogermane which disproportionated to tetrachlorogermane and bis(trimethylsiloxy)dichlorogermane:

* Part XI: Synth. Inorg. Metalorg. Chem. *J.*, 51 (1971).



This reaction is comparatively fast; the products of disproportionation can be detected by gas chromatography already after 24 hours at ambient temperature.

A detailed investigation of the first reaction showed that cyclopropane is quantitatively evolved already during the preparation of the Grignard reagent from (3-chloropropoxy)trimethylsilane, probably under the formation of trimethylsiloxymagnesium chloride, which further reacts with tetrachlorogermane, giving (trimethylsiloxy)-trichlorogermane. We finally succeeded in preparing (3-hydroxypropyl)trimethylgermane by addition of trichlorogermane to allyl chloride, followed by methylation of the (3-chloropropyl)trichlorogermane formed and oxidation of the Grignard reagent prepared from the methylated product—(3-chloropropyl)trimethylgermane.

When attempting to prepare (2-hydroxyethyl)trimethylgermane from (3-hydroxypropyl)trimethylgermane we were able to realize only the first step — oxidation of (3-hydroxypropyl)trimethylgermane to (2-carboxyethyl)trimethylgermane. The second step, Hundsdiecker degradation of the silver salt of the carboxyderivative, has failed.

TABLE I
Physical Properties and Elemental Analyses of Organogermanium Compounds

Compound	n_D^{20} (lit.)	d_4^{20} (lit.)	Calculated/Found		
			% C	% H	% Cl
$\text{CH}_3\text{COOCH}_2\text{Ge}(\text{CH}_3)_3$	1.4288 (1.4283) ³	1.1149 (1.1403) ³	—	—	—
$\text{HOCH}_2\text{Ge}(\text{CH}_3)_3$	1.4465 (1.4424) ³	1.1811 (1.1710) ³	—	—	—
$(\text{CH}_3)_3\text{SiOGeCl}_3$	1.4339	—	13.4	3.4	36.7
	—	—	13.1	3.2	37.1
$[(\text{CH}_3)_3\text{SiO}]_2\text{GeCl}_2$	1.4212	—	22.4	5.6	22.0
	—	—	22.2	5.5	22.4
$\text{Cl}(\text{CH}_2)_3\text{GeCl}_3$	1.5064 (1.5065) ⁷	—	—	—	—
$\text{Cl}(\text{CH}_2)_3\text{Ge}(\text{CH}_3)_3$	1.4514 (1.4520) ⁷	—	—	—	—
$\text{HO}(\text{CH}_2)_3\text{Ge}(\text{CH}_3)_3$	1.4502 (1.4513) ¹	1.1031 ^a (1.1042) ¹	40.8 40.6	9.1 9.2	—
$\text{HOOC}(\text{CH}_2)_2\text{Ge}(\text{CH}_3)_3$	1.4485	—	37.8 37.6	7.4 7.4	—
$\text{Cl}_3\text{Ge}(\text{CH}_2)_4\text{OSi}(\text{CH}_3)_3$	1.4877	1.4168	25.9 25.7	5.3 5.2	32.8 33.2
$\text{HO}(\text{CH}_2)_4\text{Ge}(\text{CH}_3)_3$	1.4528	1.0837	44.1 44.1	9.5 9.5	—

^a d_4^{25} .

The last model alcohol, (4-hydroxybutyl)trimethylgermane, was prepared in the following way: a reaction of tetrachlorogermane with (4-chlorobutoxy)trimethylsilane⁶ gave (4-trimethylsiloxybutyl)trichlorogermane which was then by methylation with methylmagnesium chloride and subsequent hydrolysis converted into the desired (4-hydroxybutyl)trimethylgermane. Physical properties of all the compounds prepared are given in Table I.

EXPERIMENTAL

(*Acetoxymethyl*)trimethylgermane³. The reported procedure was modified in that the reaction of (chloromethyl)trimethylgermane with potassium acetate was carried in an autoclave. Heating the reaction mixture for 18 hours at 200°C afforded (acetoxymethyl)trimethylgermane in 73% yield (instead of 37%)³. (*Hydroxymethyl*)trimethylgermane was prepared by methylation of (acetoxymethyl)trimethylgermane with Grignard reagent and subsequent hydrolysis in 77% yield (b.p. 136–138°C, lit. 50–51°C/21 Torr). *Attempted preparation of (3-hydroxypropyl)trimethylgermane from tetrachlorogermane and (3-chloropropoxy)trimethylsilane*⁶. With the use of dibromomethane as an initiator of the reaction, 114 g of (3-chloropropoxy)trimethylsilane were added dropwise to 17 g of magnesium turnings in 1 l of ether. After refluxing for 16 hours, the filtered reagent was added dropwise to a mixture of 214.4 g of tetrachlorogermane in 500 ml of ether, and the reaction was completed by heating the reaction mixture for 2 hours. Fractionation of the ethereal extract afforded (trimethylsiloxy)trichlorogermane, b.p. 64°C/48 Torr, and bis(trimethylsiloxy)dichlorogermane, b.p. 97–98°C/48 Torr. The structure of these compounds was inferred from their NMR and IR spectra.

(*3-Chloropropyl*)trichlorogermane. To 125 g of allyl chloride were added dropwise 420 g of trichlorogermane at such a rate to keep the reaction mixture boiling. Fractionation afforded 268 g of (3-chloropropyl)trichlorogermane (64% yield), b.p. 106°C/20 Torr (lit.⁷ 78–80°C/8 Torr).

(*3-Chloropropyl*)trimethylgermane⁷ was obtained by methylation of (3-chloropropyl)trichlorogermane with methylmagnesium chloride in 92% yield (b.p. 82.5°C/51 Torr, lit.⁷ 161°C/1753 Torr).

(*3-Hydroxypropyl*)trimethylgermane. Dry oxygen was passed through a solution of the Grignard reagent prepared from 160 g of (3-chloropropyl)trimethylgermane for 2 hours. The reaction was completed by refluxing the mixture for 1 hour. The reaction mixture after hydrolysis was worked-up in the usual manner and then rectified to give 134 g (92%) of (3-hydroxypropyl)trimethylgermane, b.p. 182°C (lit.¹ 79–80°C/14 Torr).

(*2-Carboxyethyl*)trimethylgermane. Into a mixture of 10 g of (3-hydroxypropyl)trimethylgermane, 20 g of concentrated sulphuric acid, and 100 ml of water were added 12.2 g of solid potassium permanganate in small portions so as to avoid warming-up the reaction mixture. Then, the suspension was shaken for 12 hours at room temperature. Rectification of the ethereal extract afforded 7.4 g of (2-carboxyethyl)trimethylgermane (69% yield), b.p. 110–115°C/4 Torr.

Attempted degradation of the silver salt of (2-carboxyethyl) trimethylgermane. A solution of 6.6 g of silver nitrate in 35 ml of water was added dropwise to a suspension of 7.4 g of (2-carboxyethyl)trimethylgermane in a solution of 2.19 g of potassium hydroxide in 25 ml of water, giving 9.3 g of the silver salt (79% yield). Into a suspension of the salt in 150 ml of tetrachloromethane a solution of 2.28 g of chlorine in 20 ml of tetrachloromethane was added dropwise at 40°C and the reaction was completed by boiling the reaction mixture for 1 hour. The reaction product did not contain the desired (2-chloroethyl)trimethylgermane.

(4-Trimethylsiloxybutyl)trichlorogermane. Grignard reagent, prepared from 110 g of (4-chlorobutoxy)trimethylsilane⁶, was added dropwise to a solution of 214 g of tetrachlorogermane in 500 ml of ether. The reaction was completed by refluxing the mixture for 1 hour. Fractionation of the ethereal extract afforded 99 g of (4-trimethylsiloxybutyl)trichlorogermane (51% yield), b.p. 106–108°C/1 Torr.

(4-Hydroxybutyl)trimethylgermane was prepared by methylation of (4-trimethylsiloxybutyl)trichlorogermane with methylmagnesium chloride, followed by hydrolysis, in 49% yield. B.p. 115.5°C/40 Torr.

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