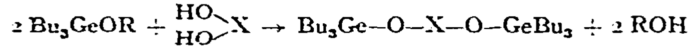
Organic derivatives of germanium

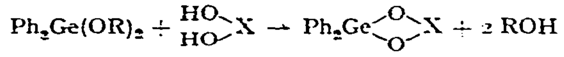
V. Glycol derivatives of tri-n-butyl- and diphenylgermanium alkoxides

In recent communications we have reported the syntheses of a number of di-n-butylglycoxygermanes from di-n-butyldialkoxygermanes[1] and dibutylgermanium oxide[2]. Two glycol derivatives of triethylgermanes had been reported by Lesbre and Satge[3] in 1962, but there appears to be no reference of such derivatives of diphenylgermanes. We have already synthesised a few typical bis(tributylgermanium) glycolates and diphenylgermanium glycolates from their oxides[2] and it was considered of interest to study these syntheses starting from the appropriate alkoxygermanes. Reactions of glycols with alkoxides of a number of elements (Ge[4], Sn[5-6], B[7], Ti[8], V[9], Nb[10], Ta[11], Se[12], Fe[13], Al[14], Pr[15], La[16], Nd[16], Sb[17]) have been studied in these laboratories in recent years.

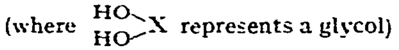
The reactions of glycols with tri-n-butylalkoxygermanes and diphenyldialkoxygermanes can be represented by the following general equations:



$$2\,Bu_3GeOR + \begin{matrix}HO\\HO\end{matrix}\!>\!X \rightarrow Bu_3Ge{-}O{-}X{-}O{-}GeBu_3 + 2\,ROH$$



$$Ph_2Ge(OR)_2 + \begin{matrix}HO\\HO\end{matrix}\!>\!X \rightarrow Ph_2Ge\!<\!\begin{matrix}O\\O\end{matrix}\!>\!X + 2\,ROH$$



(where $\begin{matrix}HO\\HO\end{matrix}\!>\!X$ represents a glycol)

The reactions were carried out in benzene in the presence of *p*-toluenesulfonic acid as a catalyst. The ethanol produced was fractionated out azeotropically, and the catalyst was destroyed with a few drops of triethylamine. The products were found to be stable to heat and could be distilled under reduced pressure in high yields. All the bis(tributylgermanium) glycolates are colourless viscous liquids, while the diphenyl derivatives are colourless, and either highly viscous liquids or white solids. Molecular weight determinations in boiling benzene show that they are monomeric Refractive indices have been measured by use of Abbe refractometer.

Experimental

Methods for drying the reagents and analytical procedures have been described in an earlier communication[18]. Tri-n-butylethoxygermane and diphenyldiethoxygermane were prepared by the ammonia method[19]. The glycols were distilled before use.

Reaction between tri-n-butylethoxygermane and ethylene glycol. Tri-n-butylethoxygermane (1.55 g) was mixed with ethylene glycol (0.17 g) and benzene (45 g) and the clear reaction mixture was refluxed for 4–5 hours in the presence of *p*-toluenesulfonic acid as a catalyst (0.02 g). The azeotrope (benzene/ethanol) was slowly collected. After the reaction was over, the catalyst was destroyed with a few drops of triethylamine. Excess of solvent was removed under reduced pressure, and the residue distilled at 180°/0.4 mm to give a colourless, slightly viscous liquid (yield 84 %). (Found: C, 56.37; H, 10.83. $C_{26}H_{58}Ge_2O_2$ calcd.: C, 57.00; H, 10.95 %.)

The details of other glycolysis reactions are given in Table 1.

TABLE I

PREPARATION AND PROPERTIES OF BIS(TRI-n-BUTYLGERMANIUM) GLYCOLATES AND OF DIPHENYLGERMANIUM GLYCOLATES

Ethoxide (g)	*Glycol* (g)	*Product b.p.* (°C/mm)	*Yield* (%)	*EtOH liberated*		*Mol. wt.*		n_D^{20}	*Found %*		*Calcd. %*	
				Found	*Calcd.*	*Found*	*Calcd.*		*C*	*H*	*C*	*H*
Tri-n-butylgermanium glycolates												
1.55	Ethylene glycol (0.17)	180/0.4	84	0.20	0.24	550	547.8	1.4625	56.37	10.83	57.00	10.66
1.33	1,2-propanediol (0.17)	165/0.1	65	0.19	0.21	558	561.9	1.4685	57.95	11.30	57.71	10.76
1.32	1,3-propanediol (0.17)	180/0.3	85	0.18	0.21	562	561.9	1.4630	56.58	10.74	57.71	10.76
1.46	1,3-butanediol (0.23)	175/0.2	93	0.18	0.23	579	575.9	1.4635	57.14	10.85	58.38	10.58
1.36	1,4-butanediol (0.22)	187/0.25	85	0.18	0.21	564	575.9	1.4650	58.16	10.67	58.38	10.58
1.48	2,3-butanediol (0.24)	165/0.2	88	0.19	0.23	583	575.9	1.4625	57.42	10.76	58.38	10.58
1.38	Diethylene glycol (0.26)	185/0.1	94	0.19	0.22	589	591.9	1.4650	56.69	10.76	56.79	10.55
1.24	1,5-Pentanediol (0.21)	186/0.2	70	0.20	0.24	597	589.9	1.4660	57.85	10.79	58.38	10.58
1.34	Pinacol (0.27)	141/0.2	60	0.19	0.21	592	604	1.4625	56.24	10.56	59.65	11.02
1.46	Hexylene glycol (0.30)	184/0.5	81	0.20	0.23	604	604	1.4605	58.68	10.55	59.65	10.01
Diphenylgermanium glycolates												
1.21	Ethylene glycol (0.24)	140/0.6	80	0.30	0.34	288	286.8		58.37	5.33	58.60	4.92
1.36	1,2-Propanediol (0.33)	127/0.6	78	0.34	0.39	320	300.8		60.05	5.52	59.85	5.35
1.29	Trimethylene glycol (0.31)	150/0.6	85	0.36	0.37		300.8		57.84	5.56	59.85	5.35
1.29	1,3-Butanediol (0.30)	135/0.8	81	0.31	0.33	332	314.9	1.5665	60.72	5.76	61.19	5.76
1.31	1,4-Butanediol (0.39)	142/0.2	85	0.38	0.38	320	314.9		60.50	5.52	61.19	5.76
1.19	2,3-Butanediol (0.33)	127/0.6	74	0.30	0.33	310	314.9	1.5680	61.30	6.13	61.19	5.76
1.21	Pinacol (0.46)	133/0.3	85	0.31	0.35	347	342.9	1.5595	63.16	6.44	63.04	6.46
1.20	Diethylene glycol (0.35)	155/0.2	70	0.34	0.34	335	330.9		56.58	5.59	58.05	5.48
1.36	1,5-Pentanediol (0.43)	138/0.2	78	0.38	0.39				61.87	6.05	62.07	6.13
1.37	Hexylene glycol (0.52)	129/0.2	82	0.34	0.39	342	343	1.5570	62.59	6.60	63.04	6.46

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Eine einfache Synthese von Methyltrichlorgerman

Für präparative Studien benötigten wir grössere Mengen an Methyltrichlorgerman, CH_3GeCl_3. Nach den bisher beschriebenen Umsetzungen von Methylhalogeniden mit Germanium bildet sich diese Verbindung nur in Gemischen mit anderen Methylchlorgermanen, aus denen sie, wenn überhaupt, nur in recht mässigen Ausbeuten rein isolierbar ist[1,2,3].

Wir haben deshalb die Umsetzung von Methylchlorid mit fein gepulvertem Germanium ohne Zusatz von Kupfer bei höheren Temperaturen untersucht. Dabei zeigte sich, dass oberhalb von *ca.* 450° praktisch nur Methyltrichlorgerman gebildet wird. Um optimale Bedingungen für die Synthese zu finden (höchstmögliche Ausbeute in einem erträglichen Zeitraum) wurde die Temperatur systematisch zwischen 460° und 550° variiert. Die Reaktionsdauer betrug jeweils 72 Stunden. Wie aus der Tabelle 1 ersichtlich ist, liegt die günstigste Temperatur für die Reaktion bei 505–520°. Unterhalb dieser Temperatur läuft die Umsetzung zu langsam ab, oberhalb wird durch unkontrollierbare Zerfallsreaktionen an der Metalloberfläche die Ausbeute wieder erniedrigt.

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