520. *Reactions of Orthoesters of Germanium. Part II.*[1] *Reactions of Tetraethoxygermanium with Glycols.*

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Reactions between tetraethoxygermanium and various glycols in different stoicheiometric ratios have led to alkylenedioxydiethoxy- and bisalkylenedioxy-germanium. Hexane-1,6-diol has yielded the tris-compound also.

RECENTLY, the alcohol-interchange technique has been extensively employed for the preparation of orthoesters of a number of elements, including cyclic orthoesters of titanium,[2] zirconium,[3] boron,[4] and aluminium.[5] Preparation of similar derivatives of germanium has been achieved by the reaction between tetraethoxygermanium and various glycols. Bradley, Kay, and Wardlaw[6] were the first to synthesise higher-alkyl orthogermanates by the alcoholysis of methyl, ethyl, or isopropyl derivatives.

The reaction between tetraethoxygermanium and glycols in equimolar ratio was carried out in benzene. Ethanol produced was removed azeotropically and its amount

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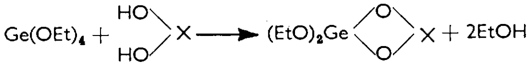
[1] Part I, Mehrotra and Chandra, *J. Indian Chem. Soc.*, 1962, **39**, 235.
[2] Mehrotra and Puri, *J. Indian Chem. Soc.*, 1963, in the press.
[3] Mehrotra, private communication.
[4] Mehrotra and Srivastava, *J.*, 1961, 4045; 1962, 1032.
[5] Mehrotra and Mehrotra, *J. Indian Chem. Soc.*, 1962, **39**, 635.
[6] Bradley, Kay, and Wardlaw, *J.*, 1956, 4916.

could be used to check the progress of the reaction. The alkylenedioxydiethoxygermanium was isolated.



These mixed cyclic orthogermanates are colourless viscous liquids, miscible with benzene, the only insoluble derivative being that of hexane-1,6-diol. They generally disproportionate into the symmetrical esters on pyrolysis.

The thermal stability of these compounds, however, increases with the steric hindrance of the cyclic group. Thus the corresponding derivatives with pinacol and 2-methylpentane-2,4-diol could be distilled unchanged. 1,2-Dimethylethylenedioxy-diethoxygermanium could not be prepared from butane-2,3-diol.

The reactions of tetraethoxygermanium with the above glycols in 1 : 2 molar ratio in benzene yielded the bisalkylenedioxy-compound quantitatively as a white solid. Bisethylenedioxy-, bistetramethylenedioxy-, and bishexamethylenedioxy-germanium are insoluble and undistillable, whereas bis-derivatives from other glycols are soluble in benzene and can be purified by sublimation or distillation.

The reaction of tetraethoxygermanium with excess of hexane-1,6-diol (molar ratio 1 : 4) afforded the tris-derivative, which when heated disproportionated into the bis-derivative and the glycol.

The distillable derivatives prepared are listed in Table 1.

TABLE 1.

Compound	B. p./mm.	Molecular weight Found	Molecular weight Reqd.
Diethyl 1,1,3-trimethyltrimethylene orthogermanate	114—118°/7	282·0	278·8
Diethyl tetramethylethylene orthogermanate	100—110°/5·5—6·5	276·0	278·8
Bis(propylene) orthogermanate	140°/1·0	233·6	220·7
Bis-(1-methyltrimethylene) orthogermanate	93°/0·4	—	248·8
Bis-(1,2-dimethylethylene) orthogermanate	Sublimes at 130—140°/0·1	253·1	248·8
Bis-(2,2-dimethyltrimethylene) orthogermanate	90—95°/0·8—0·9	291·3	276·8
Bis(tetramethylethylene) orthogermanate	Sublimes at 90—100°/0·3	294·0	304·9
Bis-(1,1,3-trimethyltrimethylene) orthogermanate	78°/0·05	312·0	304·9

The molecular weights indicate that these soluble derivatives, therefore, have the simplest structures, $(EtO)_2Ge(O_2X)$ or $Ge(O_2X)_2$. The insoluble non-volatile products with 2 mol. of ethylene, tetramethylene, and hexamethylene are in sharp contrast. Similar observations have been made with glycol derivatives of titanium[2] and zirconium.[3] Further work to elucidate the above difference is in progress.

EXPERIMENTAL

Apparatus and Chemicals.—All-glass apparatus was used, and special precautions were taken to exclude moisture. All fractionations were carried out in a column packed with Raschig rings and fitted to a total-condensation variable take-off stillhead.

Molecular weights were determined ebullioscopically in boiling benzene. Benzene was stored over sodium wire for 2 days, refluxed (Na), and distilled. Finally it was dehydrated azeotropically with ethanol. Tetraethoxygermanium was prepared by the ammonia method.[6] The various glycols were purified by distillation before use. 2,2-Dimethylpropane-1,2-diol was dried at 60°/1·0 mm. for 2 hours.

Analytical Method.—The compounds were moistened with few ml. of aqueous ammonia containing a few drops of ethanol, evaporated to dryness at low temperature, and then ignited to the dioxide at 900°. This method gave slightly low results with some compounds owing to incomplete hydrolysis; germanium was then estimated by titrating the mannitol–germanic acid complex with sodium hydroxide.

TABLE 2.

$Ge(OEt)_4$ (g.)	Glycol (mol.)	Product yield (g.)	Ethanol (g.)		Molecular formula	Ge (%)	
			Found	Calc.		Found	Reqd.
2·34	Propane-1,2-diol (1)	2·0	0·82	0·86	$(EtO)_2Ge(O_2C_3H_6)$	30·5	30·5
2·72	,, ,, (2)	2·3	1·90	1·97	$Ge(O_2C_3H_6)_2$	32·9	32·9
1·40	Butane-1,3-diol (1)	1·24	0·50	0·51	$(EtO)_2Ge(O_2C_4H_8)$	28·8	28·9
1·74	,, ,, (2)	1·71	1·21	1·27	$Ge(O_2C_4H_8)_2$	29·2	29·2
3·55	Butane-2,3-diol (1)	2·0	1·22	1·22	$Ge(O_2C_4H_8)_2$	29·0	29·2
1·72	,, ,, (2)	1·72	1·20	1·25	$Ge(O_2C_4H_8)_2$	29·2	29·2
1·99	Butane-1,4-diol (1)	1·96	0·71	0·72	$(EtO)_2Ge(O_2C_4H_8)$	28·5	29·0
1·50	,, ,, (2)	1·46	1·06	1·09	$Ge(O_2C_4H_8)_2$	28·8	29·2
1·24	2,2-Dimethylpropane-1,3-diol (1)	1·26	0·46	0·46	$(EtO)_2Ge(O_2C_5H_{10})$	27·6	27·4
1·04	,, ,, (2)	1·16	0·70	0·75	$Ge(O_2C_5H_{10})_2$	26·1	26·2
1·12	2-Methylpentane-2,4-diol (1)	1·20	0·40	0·41	$(EtO)_2Ge(O_2C_6H_{12})$	26·1	26·1
1·40	,, ,, (2)	1·68	0·98	1·01	$Ge(O_2C_6H_{12})_2$	23·7	23·8
1·32	2,3-Dimethylbutane-2,3-diol (1)	1·33	0·44	0·48	$(EtO)_2Ge(O_2C_6H_{12})$	26·2	26·2
2·50	,, ,, (2)	2·9	1·72	1·82	$Ge(O_2C_6H_{12})_2$	23·9	23·8
1·44	Hexane-1,6-diol (1)	1·47	0·52	0·52	$(EtO)_2Ge(O_2C_6H_{12})$	26·5	26·0
1·88	,, ,, (2)	2·30	2·30	2·39	$Ge(O_2C_6H_{12})_2$	23·5	23·8
1·21	,, ,, (4)	2·18	0·84	0·88	$Ge(O_2C_6H_{12})_2,C_6H_{14}O_2$	17·0	17·1

Diethoxyethylenegermanium.—A white crystalline precipitate began to form when ethylene glycol (0·52 g.; 1 mol.) was added to tetraethoxygermanium (2·12 g.). Benzene (30 c.c.) was added and the mixture was refluxed at 110—115° for about 2 hr. The ethanol produced was removed azeotropically. The remaining solvent was removed under reduced pressure and the product dried at 35°/0·5 mm. for 2·5 hr. A colourless, moisture-sensitive viscous liquid (1·54 g.) was obtained; 0·73 g. of ethanol was formed (complete reaction requires 0·77 g.) (Found: Ge, 32·6. $C_6H_{14}GeO_4$ requires Ge, 32·6%).

The above *compound* (1·2 g.) was heated under reduced pressure. A few drops of tetraethoxygermanium were collected at 86°/12 mm.; the residue (0·50 g.) contained Ge, 46·5%.

Bisethylenedioxygermanium.—(*a*) Ethylene glycol (0·53 g.; 1 mol.), diethoxyethylenedioxygermanium (1·91 g.), and benzene (35 c.c.) were refluxed for 2 hr. The benzene–ethanol azeotrope was distilled off, the remaining solvent was removed under reduced pressure, and the product was dried at 50°/2 mm. for 1½ hr. A white solid (1·70 g.), insoluble in benzene, was obtained. The azeotrope contained 0·71 g. of ethanol (reaction requires 0·79 g.) (Found: Ge, 37·6. $C_4H_8GeO_4$ requires Ge, 37·7%).

(*b*) Ethylene glycol (1·10 g.; 2 mol.), tetraethoxygermanium (2·30 g.), and benzene (40 c.c.) were refluxed for about 3 hr., and the benzene–ethanol azeotrope was collected very slowly. The remaining benzene was evaporated under reduced pressure and the product was dried at 35°/1 mm. for about 2 hr. A white solid (1·76 g.), insoluble in benzene, ether, and chloroform but soluble in cold water without immediate precipitation of germanium dioxide, was obtained. The azeotrope contained 1·63 g. of ethanol (required 1·68 g.) (Found: Ge, 37·7%).

The reactions of tetraethoxygermanium with other glycols were carried out at different stoicheiometric ratios; the results are tabulated (Table 2).

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