ORGANIC DERIVATIVES OF GERMANIUM

I. SYNTHESIS AND REACTIONS OF DIALKOXYDI-*n*-BUTYLGERMANES

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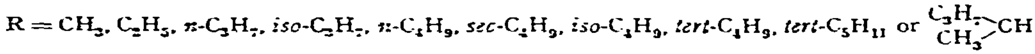
In view of the non-reactivity[1] of germanium tetrachloride with alcohols, the tetraalkoxygermanes have been prepared by treating the tetrachlorogermane with alcohols in the presence of hydrogen chloride acceptors like sodium[2], ammonia[3], pyridine[4] or by alcohol interchange technique[3]. Alkylchlorogermanes have also been shown to react with sodium alkoxides, and a few alkoxyalkylgermanes have been prepared by this method[5–7]. Recently Lesbre and Satge[8–9] have prepared alkoxyalkylgermanes by refluxing alkylgermanium hydrides with an alcohol, aldehyde or ketone in the presence of copper powder.

The advantage of using ammonia as a proton acceptor have already been discussed[10] in an earlier communication dealing with corresponding silicon derivatives. In the present communication is described the synthesis of a number of new dialkoxydibutylgermanes by allowing dibutyldichlorogermanes to react with alcohols in the presence of ammonia gas:

$$(Bu)_2GeCl_2 + 2ROH + 2NH_3 \xrightarrow{C_6H_6} (Bu)_2Ge(OR)_2 + 2NH_4Cl$$



$$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ iso\text{-}C_3H_7,\ n\text{-}C_4H_9,\ sec\text{-}C_4H_9,\ iso\text{-}C_4H_9,\ tert\text{-}C_4H_9,\ tert\text{-}C_5H_{11}\ \text{or}\ \begin{matrix}C_3H_7\\CH_3\end{matrix}\!\!>\!CH$$

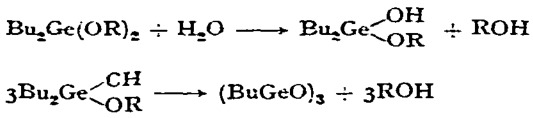
In the case of tertiary alkoxy derivatives, the butylchlorogermane was added dropwise, with constant shaking, to a mixture of pyridine (> 2 moles/mole of Bu_2GeCl_2) and tertiary alcohol in benzene and the reaction was completed by treatment with ammonia. The dialkoxydibutylgermanes isolated are colourless, monomeric, slightly viscous liquids, susceptible to hydrolysis, which can be purified by distillation under reduced pressure.

Since Ge–OR linkages in tetraalkoxygermanes are more reactive than Ge–Cl linkages in tetrachlorogermane, it was of interest to study the hydrolysis and other reactions of these mixed alkoxyalkylgermanes.

RESULTS

(i) *Hydrolysis*

Di-*n*- and -*sec*-alkoxydibutylgermanes are readily and almost quantitatively hydrolysed to trimeric dibutylgermanium oxide by water (1 or 2 moles) in the parent alcohol at room temperature:



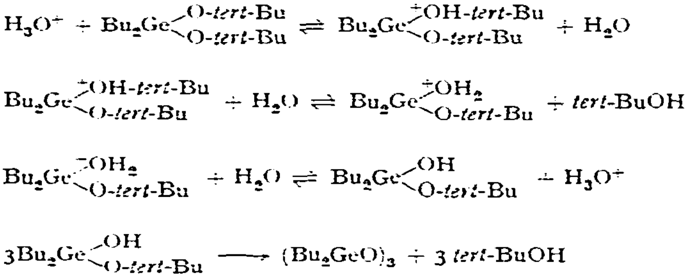
$$Bu_2Ge(OR)_2 + H_2O \longrightarrow Bu_2Ge{<}\begin{smallmatrix}OH\\OR\end{smallmatrix} + ROH$$

$$3Bu_2Ge{<}\begin{smallmatrix}CH\\OR\end{smallmatrix} \longrightarrow (BuGeO)_3 + 3ROH$$

$(R = C_2H_5 \text{ or iso-}C_3H_7)$

The hydrolysis does not proceed in benzene, probably because of the immiscibility of water; thus, diethoxydibutylgermane was recovered unchanged after refluxing (2 hours) with equimolecular proportions of water in benzene solution. Dibutylgermanium oxide was first isolated by Anderson[11] by the hydrolysis of dibutyldichlorogermane with warm caustic soda, and the alkoxide thus seems to be much the more readily hydrolysable. Dibutylgermanium oxide is immiscible with water whereas dimethylgermanium oxide has been reported to be soluble[12].

Di-*tert*-butoxydi-*n*-butylgermane showed a remarkable stability towards hydrolysis as it was recovered unchanged after it had been refluxed with two molar proportions of water in *tert*-butanol. But in the presence of *p*-toluenesulphonic acid, treatment with one mole of water in *tert*-butanol gave the trimeric organogermanium oxide, $(Bu_2GeO)_3$, even at room temperature. Presumably, nucleophilic attack by water on germanium is preceded by protonation of the oxygen atom, as in the case with silicon[13]:



$$H_3O^+ + Bu_2Ge{<}\begin{smallmatrix}O\text{-}tert\text{-}Bu\\O\text{-}tert\text{-}Bu\end{smallmatrix} \rightleftharpoons Bu_2Ge{<}\begin{smallmatrix}\overset{+}{O}H\text{-}tert\text{-}Bu\\O\text{-}tert\text{-}Bu\end{smallmatrix} + H_2O$$

$$Bu_2Ge{<}\begin{smallmatrix}\overset{+}{O}H\text{-}tert\text{-}Bu\\O\text{-}tert\text{-}Bu\end{smallmatrix} + H_2O \rightleftharpoons Bu_2Ge{<}\begin{smallmatrix}\overset{+}{O}H_2\\O\text{-}tert\text{-}Bu\end{smallmatrix} + tert\text{-}BuOH$$

$$Bu_2Ge{<}\begin{smallmatrix}\overset{+}{O}H_2\\O\text{-}tert\text{-}Bu\end{smallmatrix} + H_2O \rightleftharpoons Bu_2Ge{<}\begin{smallmatrix}OH\\O\text{-}tert\text{-}Bu\end{smallmatrix} + H_3O^+$$

$$3Bu_2Ge{<}\begin{smallmatrix}OH\\O\text{-}tert\text{-}Bu\end{smallmatrix} \longrightarrow (Bu_2GeO)_3 + 3\ tert\text{-}BuOH$$

The same catalyst has also been used successfully in the alcoholysis and glycolysis reactions of the dialkoxydibutylgermanes (Part II of this series, in press).

(*ii*) *Reaction with hydrogen sulphide*

Dimeric dibutylgermanium sulphide has been obtained by passing anhydrous hydrogen sulphide gas into a solution of di-*n*- and -*sec*-alkoxydibutylgermanes in the parent alcohol:

$$Bu_2Ge(OR)_2 + 2H_2S \longrightarrow Bu_2Ge(SH)_2 + 2ROH$$

$$2Bu_2Ge(SH)_2 \longrightarrow (Bu_2GeS)_2 + 2H_2S$$

In the case of di-*tert*-butoxydibutylgermane the reaction proceeds only in the presence of *p*-toluenesulphonic acid. The dimethyl- and diisopropylgermanium sulphides are the only compounds of the series reported, and have been shown to be trimeric[12] and dimeric[14] respectively in benzene.

TABLE 1

REACTIONS OF DIBUTYLDICHLOROGERMANES WITH ALCOHOLS

No	*R in* $Bu_2Ge(OR)_2$	*ROH* (*g*)	Bu_2GeCl_2 (*g*)	*B.p.* $Bu_2Ge(OR)_2$ (°*C/mm*)	*Yield* (%)	*Molecular weight*		*Refractive index*	*Analyses*							
									Found %				*Calculated %*			
						Found	*Calcd.*		*C*	*H*	*Ge*	*OR*	*C*	*H*	*Ge*	*OR*
1	CH_3	15	8.00	113–116/13.0	84	255	249	1.4365	46.50	9.42	28.72	—	48.23	9.71	29.17	—
2	C_2H_5	13	14.90	106/5.9	82	286	277	1.4357	51.40	10.11	26.08	34.90	52.05	9.50	26.21	32.5
3	iso-C_3H_7	20	11.76	103–108/5.0	84	290	305	1.4350	55·35	10.45	23.30	38.4	55.13	10.58	23.83	38.7
4	*n*-C_3H_7	8	5.00	127/4.8	80	281	305	1.4357	55·50	10.52	—	—	55.13	10.58	—	—
5	*n*-C_4H_9	15	8.58	106–108/0.5	75	330	333	1.4388	57·50	10.99	—	—	57·71	10.90	—	—
6	*sec*-C_4H_9	14	6.12	110/2.4	50	320	333	1.4373	55·14	10.43	—	—	57·71	10.90	—	—
7	iso-C_4H_9	7	4·17	114–116/2.0	62	326	333	1.4390	56.87	10.62	—	—	57·71	10.90	—	—
8	*tert*-C_4H_9	20	10.55	105–108/2.5	70	325	333	1.4355	58.89	11.15	—	—	57·71	10.90	—	—
9	*tert*-C_5H_{11}	15	7·29	141/4.7	52	347	361	1.4452	57·90	10.68	—	—	59.87	11.17	—	—
10	$\begin{smallmatrix}H_7C_3\\H_3C\end{smallmatrix}\!>\!CH$	7	4·78	142–145/4.0	97	353	361	1.4400	59·77	10.98	—	—	59.87	11.17	—	—

(*iii*) *Reaction with acetyl bromide*

The reaction of acetyl bromide with dialkoxydibutylgermanes in 1:1 and 1:2 molar ratios has led to the synthesis of alkoxybromo- and dibromodibutylgermanes, respectively:

$$Bu_2Ge(OR)_2 + CH_3COBr \longrightarrow Bu_2Ge\begin{matrix}\diagup Br\\ \diagdown OR\end{matrix} + CH_3COOR$$

$$Bu_2Ge(OR)_2 + 2CH_3COBr \longrightarrow Bu_2GeBr_2 + 2CH_3COOR$$

$(R = C_2H_5$, iso-C_3H_7 or *tert*-$C_4H_9)$

The analytical data (Table 4) suggest that the monobromo derivatives undergo some disproportionation during distillation.

EXPERIMENTAL

All-glass apparatus with interchangeable joints was used throughout, and special precautions were taken to exclude moisture. Benzene (B.D.H.) was stored over sodium wire and finally dried azeotropically with ethanol. Alcohols were dried by usual procedures and were finally purified by careful fractionation. Ammonia and hydrogen sulphide gases were dried by passing through towers packed with aluminium isopropoxide or anhydrous calcium chloride (in the case of H_2S only) and finally through a battery of benzene solutions of aluminium isopropoxide. Dibutyl dichlorogermane, b.p. 112°/8 mm, was distilled before use.

Molecular weights were measured with a Mechrolab Vapour Pressure Osmometer, and refractive indices with an Abbe Refractometer.

A few derivatives of germanium, $Bu_2Ge(OR)_2$ $(R = CH_3$, C_2H_5 and iso-$C_3H_7)$, were analysed by hydrolysing the samples with a little aqueous parent alcohol, evaporating slowly in an electric oven at 80° and then heating to 110–120° for about two hours. Germanium was then weighed as organogermanium oxide $(Bu_2GeO)_x$. Ethoxy and isopropoxy contents were estimated by a back-titration method[15].

General method of synthesis

Ammonia gas was slowly bubbled into a mixture of dibutyldichlorogermane, alcohol and benzene (30–50 cc). The reaction appeared to start with a very slow formation of ammonium chloride. After a few minutes, an exothermic reaction progressed at a more rapid rate as was observed from the precipitation of ammonium chloride. It has been found that in presence of benzene, the precipitated ammonium chloride separates out more readily. The flow of ammonia gas was discontinued when the reaction mixture cooled down. The precipitated ammonium chloride was filtered out after allowing the reaction mixture to stand overnight. The filtrate was concentrated, and the dialkoxydibutylgermanes were purified by distillation under reduced pressure. Data for ten new dialkoxydibutylgermanes are given in Table 1. Further data on the reactions of the dialkyldialkoxygermanes with water, hydrogen sulphide and acetyl bromide are given in Tables 2, 3 and 4 respectively.

TABLE 2

HYDROLYSIS OF DIBUTYLDIBUTOXYGERMANES

No.	Reactants			Conditions	B.p. of the product (°C/mm)	Yield (g)	Analyses						
	$Bu_2Ge(OR)_2$ (*g*)	*H_2O* (*g*)	*Solvent* (*ml*)				*Found (%)* *C*	*H*	*Mol. wt.*	*Suggested formula*	*Calculated (%)* *C*	*H*	*Mol. wt.*
1	$Bu_2Ge(OEt)_2$ (1.57)	0.12	C_6H_6 (60)	Refluxed 2 h	102–105/6.5	1.5				$Bu_2Ge(OEt)_2$[a]			
2	$Bu_2Ge(OEt)_2$ (1.65)	0.108	EtOH (6)	Room temp. 3 h	180/0.8	0.82	47.17	9.07	607	$(Bu_2GeO)_3$	47.39	8.94	202.8
3	$Bu_2Ge(OEt)_2$ (1.31)	0.16	EtOH (10)	Room temp. ½ h	167/0.6	0.40	47.2	8.82	622	$(Bu_2GeO)_3$	47.39	8.94	202.8
4	$Bu_2Ge(O\text{-iso-}Pr)_2$ (2.11)	0.12	iso-PrOH (4)	Room temp. overnight	180–182/1	1.20	47.17	9.07	600	$(Bu_2GeO)_3$	47.39	8.94	202.8
5	$Bu_2Ge(O\text{-iso-}Pr)_2$ (2.00)	0.24	iso-PrOH (5)	Room temp. 2 h	184/1.1	1.01	47.38	9.10	622	$(Bu_2GeO)_3$	47.39	8.94	202.8
6	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (1.67)	0.18	*tert*-BuOH (18)	Refluxed 3 h	84–86°/0.7	0.78	55.61	10.51	332	$Bu_2Ge(tert\text{-}O\text{-}Bu)_2$[b]	57.71	10.90	333
7	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (1.37)	0.06	*tert*-BuOH (7)	Room temp. Catalyst[c] 5 h	189–192/0.9	0.80	47.40	8.83	609	$(Bu_2GeO)_3$	47.39	8.94	202.8
8	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (1.78)	0.10	*tert*-BuOH (5)	Refluxed Catalyst[c] 1 h	162–164/0.3	0.86	47.30	8.85	605	$(Bu_2GeO)_3$	47.39	8.94	202.8
9	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (1.24)	0.13	*tert*-BuOH (8)	Refluxed Catalyst[c] 1 h	157/0.1	0.60	47.20	8.82	600	$(Bu_2GeO)_3$	47.39	8.94	202.8

[a] No hydrolysis took place in the presence of benzene in $Bu_2Ge(OEt)_2$. Found: Ge, 26.17; C_2H_5O, 32.61. Calcd.: Ge, 26.21; C_2H_5O, 32.54%. [b] No hydrolysis took place in the case of $Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ in the absence of p-toluenesulphonic acid. [c] In each case 0.002 g of *p*-toluenesulphonic acid was neutralised with triethylamine before the distillation of the product.

TABLE 3

REACTIONS OF DIALKYLDIALKOXYGERMANES WITH HYDROGEN SULPHIDE

No.	*$Bu_2Ge(OR)_2$* (*g*)	*Solvent ROH added* (*g*)	*H_2S passed* (*h*)	*B.p. of product* (°*C/mm*)	*Yield Bu_2GeS* (*g*)	*Analysis*						*Molecular weight*	
						Found %			*Calculated %*			*Found*	*Calcd.*
						C	*H*	*S*	*C*	*H*	*S*		
1	$Bu_2Ge(OEt)_2$ (1.80)	EtOH (65)	6	176–180/0.8	0.64	43.97	8.27	14.90	43.91	8.28	14.62	438	219
2	$Bu_2Ge(O\text{-iso-}Pr)_2$ (1.80)	iso-PrOH (70)	6	193–198/1.0	0.65	43.83	8.17	14.50	43.91	8.28	14.62	436	219
3	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (2.13)	*tert*-BuOH (50)	6	106–110/2.9	—^{a}	56.18	10.27	—	57.71^{a}	10.90^{a}	—	331^{a}	333^{a}
4	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$^{b} (1.81)	*tert*-BuOH (35)	8	175–182/0.3	0.82	43.83	8.31	13.10	43.91	8.28	14.62	457	219

[a] Product was 1.20 g of unreacted $Bu_2Ge(O\text{-}tert\text{-}Bu)_2$. [b] Reaction in presence of *p*-toluenesulphonic acid.

TABLE 4

REACTIONS OF DIALKYLDIALKOXYGERMANES WITH ACETYL BROMIDE

No.	*$Bu_2Ge(OR)_2$ (g)*	*Acetyl bromide (g)*	*Molar ratio*	*Bromine % in undistilled product*	*B.p. of product (°C/mm)*	*Analysis of the distilled product*						*Molecular weight*	
						Found %			*Calculated %*			*Found*	*Calcd.*
						C	*H*	*Br*	*C*	*H*	*Br*		
1	$Bu_2Ge(OEt)_2$ (2.56)	1.15	1:1	25.67	104–110/4.0	32.44	6.09	26.15	38.51	7.43	25.67	322	312
2	$Bu_2Ge(OEt)_2$ (2.88)	2.76	1:2	47.87	101–103/2.5	27.35	4.09	47.80	27.71	5.23	46.13	340	347
3	$Bu_2Ge(O\text{-iso-}Pr)_2$ (1.74)	0.70	1:1	25.26	104–120/5.0	35.17	6.63	26.17	40.53	7.73	24.54	—	—
4	$Bu_2Ge(O\text{-iso-}Pr)_2$ (1.40)	1.20	1:2	45.43	118/4.5	27.58	5.13	45.66	27.71	5.23	46.13	—	—
5	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (1.34)	0.51	1:1	22.7	112–116/3.5	39.58	7.45	23.62	42.39	8.02	23.54	—	—
6	$Bu_2Ge(O\text{-}tert\text{-}Bu)_2$ (1.37)	1.03	1:2	42.55	130/9.0	27.75	5.17	45.25	27.71	5.23	46.13	—	—

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SUMMARY

The preparation of a number of new di-*n*-butyldialkoxygermanes, $Bu_2Ge(OR)_2$, with R = CH_3, C_2H_5, iso-C_3H_7, *n*-C_4H_9, *sec*-C_4H_9, iso-C_4H_9, *tert*-C_4H_9, *tert*-C_5H_{11} or *sec*-C_5H_{11} has been described, and their hydrolyses have been studied. Di-*n*-butylgermanium sulphide and di-*n*-butylgermanium bromide derivatives have been synthesized for the first time by the reactions of the alkoxides with hydrogen sulphide and acetyl bromide respectively.

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