ORGANIC DERIVATIVES OF GERMANIUM

II. REACTIONS OF DIALKOXYDI-*n*-BUTYLGERMANES WITH ALCOHOLS AND GLYCOLS

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In a recent communication[1], the authors have described the synthesis and reactions of dialkoxydi-*n*-butyl germanes. Alcoholysis[2-3] and glycolysis[4] reactions have been extensively employed in these laboratories for the preparation of a large number of organic derivatives of germanium, and it was considered of interest to study the reactions of dialkoxydi-*n*-butyl germanes, $Bu_2Ge(OR)_2$ (R = Et and iso-Pr), with higher alcohols and various glycols.

Diethoxy- and diisopropoxydibutylgermanes were found to interchange their alkoxy groups quantitatively in benzene with higher alcohols:

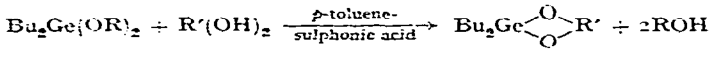
$$(Bu)_2Ge(OR)_2 + 2R'OH\ (\text{excess}) \xrightarrow{\text{benzene}} (Bu)_2Ge(OR')_2 + 2ROH$$

(R=*n*-Bu, *sec*-Bu or *tert*-C_5H_{11})

The reactivity of these alcohols gradually decreases with the branching of the alkyl chain in the alcohol molecule. The reaction in the case of *n*-butanol was completed within a short period of time. Treatment of diethoxydibutylgermane with *sec*-butanol in the presence of benzene was found to give mainly ethoxy-*sec*-butoxydibutylgermane, and further interchange was very slow and could only be completed by the addition of an acid catalyst such as *p*-toluenesulphonic acid.

With tertiary alcohols, the reaction did not appear to proceed at all without the catalyst.

Cyclic products are formed in the reactions between dialkoxydibutylgermanes and various glycols in the presence of *p*-toluenesulphonic acid. In the case of ethylene glycol the reaction proceeds even in the absence of the catalyst.



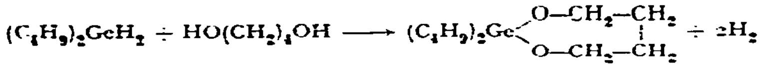
$$Bu_2Ge(OR)_2 + R'(OH)_2 \xrightarrow[\text{sulphonic acid}]{p\text{-toluene-}} Bu_2Ge\genfrac{}{}{0pt}{}{\diagup O \diagdown}{\diagdown O \diagup}R' + 2ROH$$

R = Et or iso-Pr; R' = $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, $-CH_2CH_2CH_2CH_2-$,

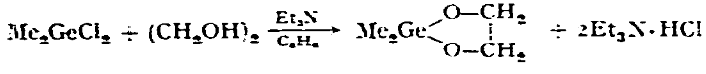
$-CH_2CH_2CH(CH_3)-$, $-CH(CH_3)CH(CH_3)-$, $-CH_2CH_2OCH_2CH_2-$,

$-CH(CH_3)CH_2C(CH_3)_2-$.

The only other glycol derivatives of dialkylgermanium reported in the literature appear to be $(C_4H_9)_2Ge(O_2C_4H_8)$[5] and $(CH_3)_2Ge(O_2C_2H_4)$[6], prepared by the following reactions:



$$(C_4H_9)_2GeH_2 + HO(CH_2)_4OH \longrightarrow (C_4H_9)_2Ge\begin{matrix}O-CH_2-CH_2\\ |\\ O-CH_2-CH_2\end{matrix} + 2H_2$$



$$Me_2GeCl_2 + (CH_2OH)_2 \xrightarrow[C_6H_6]{Et_3N} Me_2Ge\begin{matrix}O-CH_2\\ |\\ O-CH_2\end{matrix} + 2Et_3N\cdot HCl$$

EXPERIMENTAL

Analytical procedures and methods for drying the reagents have been described earlier[1].

Diethoxy- and diisopropoxydibutylgermanes were prepared by ammonia method[1]. The glycols were distilled before use.

Reaction between diisopropoxydibutylgermane and n-butanol

A mixture of diisopropoxydibutylgermane (1.51 g), *n*-butanol (4.0 g) and benzene (40.0 g) was refluxed for 3 h and then fractionated. After removal of the excess of benzene, the residue (1.67 g) was distilled under reduced pressure to give di-*n*-butoxydibutylgermane (88 %), a colourless liquid, b.p. 106–108°/0.5 mm. (Found: C, 56.80; H, 10.70. $C_{16}H_{36}O_2Ge$ calcd.: C, 57.71; H, 10.90 %.)

Reaction between diethoxydibutylgermane and trimethylene glycol in molar ratio 1:1

Trimethylene glycol (0.40 g) was distilled in a solution of diethoxydibutylgermane (1.46 g) in benzene (50 g). The reaction mixture was refluxed for about 2 h and the benzene–ethanol azeotrope was collected. On analysis, the azeotrope was found to contain only 0.066 g of alcohol against 0.485 g for complete reaction. *p*-Toluenesulphonic acid (0.002 g) and benzene (20 g) were added and the reaction mixture was again refluxed for about an hour and the benzene–ethanol azeotrope was fractionated off, 0.413 g ethanol being present in the azeotrope. After the reaction was over, the solution was neutralised with a few drops of triethylamine. After removal of the volatile fractions, the residue was distilled under reduced pressure to give a colourless, slightly viscous liquid (1.51 g, 81 %), b.p. 104–108°/3.8 mm. (Found: C, 50.55; H, 9.47. $C_{11}H_{24}O_2Ge$ calcd.: C, 50.65; H, 9.27 %.) The total ethanol liberated was 0.48 g as against 0.485 g for the replacement of two moles.

Results of the other alcoholysis and glycolysis reactions are tabulated in Tables 1 and 2 respectively.

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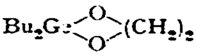
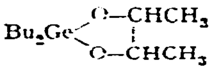
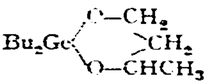
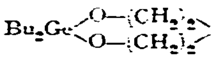
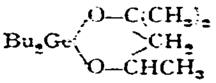
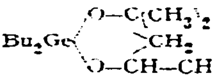
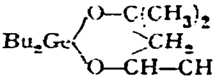
TABLE 1

REACTIONS OF DIBUTYLDIALKOXYGERMANES WITH ALCOHOLS

No.	*$Bu_2Ge(OR)_2$ (g)*	*Alcohol added (g)*	*Hours of refluxing*	*Product DI*	*B.p. (°C/mm)*	*Yield (%)*	*Analysis*			
							Found %		*Calculated %*	
							C	*H*	*C*	*H*
1	$Bu_2Ge(O\text{-}iso\text{-}Pr)_2$ (1.51)	*n*-butanol (4.0)	3	$Bu_2Ge(O\text{-}n\text{-}Bu)_2$	100/0.5	88	56.80	10.70	57.71	10.90
2	$Bu_2Ge(OEt)_2$ (1.46)	*sec*-butanol (5.0)	3	$Bu_2Ge(O\text{-}sec\text{-}Bu)_2$	112/2.0	81	56.50	10.64	57.71	10.90
3	$Bu_2Ge(OEt)_2$ (1.30)	*tert*-pentanol (2.0)	4	$Bu_2Ge(O\text{-}tert\text{-}C_5H_{11})_2$	108/0.8	65	57.57	10.96	59.87	11.17

TABLE 2

REACTIONS OF DIBUTYLDIALKOXY GERMANES WITH GLYCOLS

No.	$Bu_2Ge(OR)_2$ (g)		Glycol added (g)		Hours of refluxing	Product formed
1	$Bu_2Ge(OEt)_2$	(2.46)	$HOCH_2CH_2OH$	(0.56)	2	
2	$Bu_2Ge(O\text{-iso-}Pr)_2$	(1.58)	$HOCH_2CH_2OH$	(0.34)	4	
3	$Bu_2Ge(OEt)_2$	(1.46)	$HOCH_2CH_2CH_2OH$	(0.40)	3.5	
4	$Bu_2Ge(OEt)_2$	(1.12)	$HOCH_2CH_2CH_2CH_2OH$	(0.36)	4	
5	$Bu_2Ge(OEt)_2$	(1.31)	$HOCH_2CH_2CHOHCH_3$	(0.43)	2	
6	$Bu_2Ge(O\text{-iso-}Pr)_2$	(1.31)	$CH_3CHOHCHOHCH_3$	(0.43)	2	
7	$Bu_2Ge(OEt)_2$	(1.21)	$HOCH_2CH_2OCH_2CH_2OH$	(0.46)	2	
8	$Bu_2Ge(OCH_3)_2$	(1.74)	$CH_3CHOHCH_2C(CH_3)_2OH$	(0.84)	4	
9	$Bu_2Ge(OEt)_2$	(1.40)	$CH_3CHOHCH_2C(CH_3)_2OH$	(0.61)	4	
10	$Bu_2Ge(O\text{-iso-}Pr)_2$	(1.35)	$CH_3CHOHCH_2C(CH_3)_2OH$	(0.66)	3.5	

m)	*Yield* (%)	*Molecular weight*		*Refractive index*	*Analysis*				*Alcohol liberated* (*moles*)
		Found	*Calcd.*		*Found %*		*Calculated %*		
					C	*H*	*C*	*H*	
06/3.5	73	333	247	—	47.60	9.03	48.66	8.98	1.81
..0	76	—	—	1.4712	47.70	9.04	48.66	8.98	1.90
108/4.0	81	270	261	1.4705	50.55	9.58	50.65	9.27	1.91
111/3.5	81	267	275	1.4725	51.95	9.69	52.42	9.53	1.82
94/1.5	85	258	275	1.4555	51.30	9.80	52.42	9.53	1.84
105/3.0	86	279	275	1.4550	51.34	9.92	52.42	9.53	1.80
122/2.7	66	306	291	1.4695	47.88	9.57	49.55	9.01	1.70
108/2.5	88	303	303	1.4500	54.90	10.04	55.50	9.98	1.81
107/2.0	85	—	—	—	54.70	10.19	55.50	9.98	1.77
118/4.0	82	301	303	—	54.81	10.05	55.50	9.98	1.82

SUMMARY

The reactions of diethoxy- and diisopropoxydi-*n*-butylgermanes with higher alcohols and glycols have been studied. An acid catalyst like *p*-toluenesulphonic acid is necessary in the cases of branched alcohols and most of the glycols. A number of new alkoxy and glycoxy derivatives have been characterised.

REFERENCES

1 S. Mathur, G. Chandra, A. K. Rai and R. C. Mehrotra, *J. Organometal. Chem.*, 4 (1965) 294.
2 D. C. Bradley, L. Kay and W. Wardlaw, *Chem. Ind. (London)*, (1953) 746; *J. Chem. Soc.*, (1956) 4916.
3 R. C. Mehrotra and G. Chandra, *J. Indian Chem. Soc.*, 39 (1962) 235.
4 R. C. Mehrotra and G. Chandra, *J. Chem. Soc.*, (1963) 2804.
5 H. Lesbre and J. Satge, *Compt. Rend.*, 254 (1962) 4051.
6 M. Wieberg and M. Schmidt, *Z. Naturforsch.*, 18b (1963) 847.