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ORGANIC DERIVATIVES OF GERMANIUM

PART III. SYNTHESIS OF ALKOXYGERMANES FROM ORGANOGERMANIUM OXIDES

R. C. MEHROTRA AND S. MATHUR
The Chemical Laboratories, University of Rajasthan, Jaipur (India)

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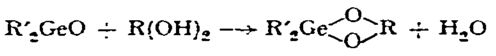
Alkoxides of boron[1], vanadium[2] and selenium[3] have been prepared, by refluxing their oxides with an excess of alcohol. Recently, alkyltin alkoxides[4] have also been prepared from their oxides by this method. Water formed in these reactions is removed azeotropically with benzene. The corresponding reactions of oxide derivatives of germanium have not been utilised for the preparation of alkoxygermanes. The preparation of a number of dibutyl-[5], diphenyl-[6] and tributyl-[6] alkoxygermanes has already been carried out in these laboratories by the reaction of organogermanium chlorides with alcohols in the presence of dry ammonia, and ethylenedioxygermanes[7] have been synthesised by the reaction of these alkoxygermanes with glycols.

In the present investigations, we have synthesised a number of dibutyl-, tributyl- and diphenyl-alkoxygermanes as well as their derivatives with glycols, acetylacetone and substituted amines directly from their oxides for the first time. The oxide is refluxed with the ligand in benzene and the water which is formed removed azeotropically. *p*-Toluenesulphonic acid was generally used as a catalyst in these reactions. The present method appears to be the most convenient of all the methods reported so far for the preparation of these alkoxides, as well as other organic derivatives, and the general utility of the method is demonstrated by the synthesis of a large number of new derivatives. These reactions are summarised by the following equations:

$$R'_2GeO + 2\,ROH \longrightarrow R'_2Ge(OR)_2 + H_2O$$

R′ = Bu; R = Me, Et, Pr, iso-Pr, Bu, *sec*-Bu, *tert*-Bu
R′ = Ph; R = Et, iso-Pr, *tert*-Bu

$$(Bu_3Ge)_2O + 2\,ROH \longrightarrow 2\,Bu_3GeOR + H_2O$$ R = Et, iso-Pr, *tert*-Bu



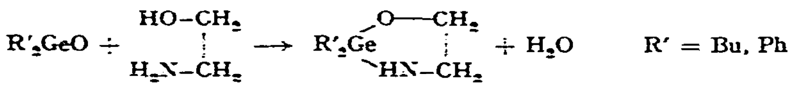
$$R'_2GeO + R(OH)_2 \longrightarrow R'_2Ge{<}^{O}_{O}{>}R + H_2O$$

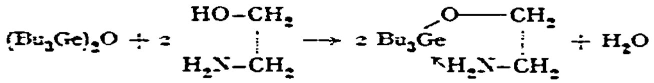
R = CH_2CH_2; R′ = Bu, Ph
R = CH_2CHMe; R′ = Bu

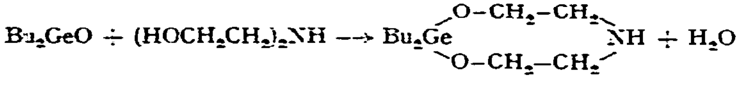
$$(Bu_3Ge)_2O + R(OH)_2 \longrightarrow (Bu_3GeO)_2R + H_2O$$ R = CH_2CH_2, CH_3CHMe

$$R'_2GeO + 2\,Hacac \longrightarrow R'_2Ge(acac)_2 + H_2O$$ R′ = Bu, Ph

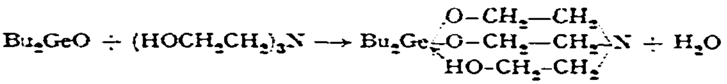
$$(Bu_3Ge)_2O + 2\,Hacac \longrightarrow 2\,Bu_3Ge(acac) + H_2O$$







$$(Bu_3Ge)_2O + (HOCH_2CH_2)_2NH \longrightarrow (Bu_3Ge{-}O{-}CH_2CH_2)_2NH + H_2O$$



The reactions with *n*- and *sec*-butanols were carried out in an excess of the alcohol, whereas all other reactions were carried out in benzene. With normal alcohols the reactions could be completed even in the absence of any catalyst, which appeared to be essential in the cases of secondary alcohols. Yields were almost quantitative except with methanol and *tert*-butanol when the yields were poor despite longer reflux times. With methanol the slowness appears to be due to the non-formation of a ternary azeotrope, formation of which facilitates the removal of water in other cases, but with *tert*-butanol the effect is probably due to steric factors. When the reaction of dibutylgermanium oxide and *tert*-butanol was carried out in the presence of ethanol the product obtained on refluxing for about forty hours was dibutylethoxy-*tert*-butoxygermane but dibutyldi-*tert*-butoxygermane was obtained in good yield after a further twenty hours reflux time.

Reactions of alkylgermanium oxides with glycols, acetylacetone and substituted amines are quite facile; the water formed in these reactions was fractionated out azeotropically with benzene. (Catalyst was added wherever necessary.)

Dibutylgermanium bis(acetylacetonate) is an orange-red liquid, the tributyl derivative is yellow liquid and the diphenyl derivative is a light-yellow, low-melting solid. The glycol derivatives in all cases are colourless liquids except in the case of diphenyl derivative which is a highly viscous compound (white semi-solid). Molecular weight determinations show that they are all monomeric.

The dibutyl- and diphenylgermanium oxides react with ethanolamine in equimolar amounts, and both the hydroxyl and the amino groups appear to take part in the reaction. [With bis(tributylgermanium) oxide only the hydroxyl group appears to take part in the reaction.] The yields of the products were lower than with the hydroxy compounds, probably due to high sensitivity of germanium–nitrogen bond to hydrolysis. The diphenyl derivative, with its higher boiling point, could not be distilled out without decomposition. Diethanolamine derivatives obtained from di- and tributylgermanium oxides are colourless viscous liquids.

The germanium in the acetylacetone and the ethanolamine derivatives of bis(tributyl)germanium oxide may be five-coordinate and it would be interesting to study these compounds further.

TABLE 1

PREPARATION OF DIBUTYLDIALKOXYGERMANES FROM DIBUTYLGERMANIUM OXIDE

No.	*Bu_2GeO*	*ROH (g)*	*Hours of refluxing*	*b.p. [°C (mm)] $Bu_2Ge(OR)_2$*	*Yield (%)*	*Mol. wt. found (calcd.)*	*n_D^{20}*	*Analyses found (calcd.) (%)*	
								Ge	*OR*
1	2.0	MeOH (5)	6	103–106 (7.5)	25	255 (248.8)	1.4365	28.77 (29.17)	24.60 (24.96)
2	2.4	EtOH (20)	2	103–106 (6.0)	78	286 (276.9)	1.4330	26.30 (26.21)	32.96 (32.54)
3	10.45	iso-PrOH (20)	6	72 (0.5) without catalyst	5	299 (305.0)	1.4345	23.60 (23.83)	38.49 (38.70)
4	5.07	iso–PrOH (18)	18	106–109 (4.5)	70	300 (305.0)	1.4340	23.50 (23.83)	38.61 (38.70)
5	2.1	PrOH (9)	4	117–120 (3.8)	78	295 (305.0)	1.4355	23.77 (23.83)	
6	2.33	BuOH (45)	4	92–95 (0.01)	80	331 (333.0)	1.4380	22.03 (21.78)	
7	2.46	*sec*-BuOH (27)	6	116–121 (3.1–3.5)	76	328 (333.0)	1.4350	21.94 (21.78)	
8	2.72	*tert*-BuOH (9)	18	103–105 (2.5)	37.5	330 (333.0)	1.4355	22.00 (21.78)	
9	2.72	*tert*-BuOH (10) + EtOH (5)	40	123–125 (5.5)	80	294 (304.0)	1.4370	23.30 (23.80)	12.00 (11.72)
10	1.52[a]	*tert*-BuOH (10)	20	117 (6.0)	85	335 (333.0)	1.4350	22.50 (21.78)	

[a] $Bu_2Ge(OEt)$(*tert*-Bu)

TABLE 2

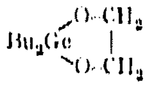
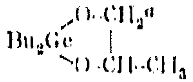
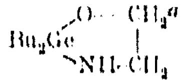
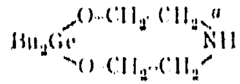
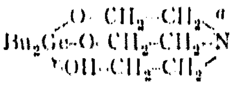
PREPARATION OF TRIBUTYLALKOXYGERMANES AND DIPHENYLDIALKOXYGERMANES FROM BIS(TRIBUTYLGERMANIUM)OXIDE AND DIPHENYLGERMANIUM OXIDE

No.	*Germoxane added*	*ROH (g)*	*Hours of refluxing*	*b.p. product [°C (mm)]*	*Yield (%)*	*Mol. wt. found (calcd.)*	*n_D^{20}*	*Analyses found (calcd.) (%)*	
								Ge	*OR*
	$(Bu_3Ge)_2O$								
1	2.0	EtOH (11)	4	127–128 (8.0)	82	291 (289.0)	1.4444	25.46 (25.12)	16.21 (15.59)
2	1.97	iso-PrOH (10)	12	113–114 (3.8)	85	301 (302.9)	1.4400	23.70[a] (23.96)	19.83 (19.50)
3	1.91	*tert*-BuOH (15)	20	116 (4)	30	314 (317.0)	1.4420	22.68[a] (22.90)	
	Ph_2GeO								
4	3.1	EtOH (13)	4	156–158 (3.0)	75	301 (316.9)	1.5400	22.99[a] (22.90)	28.77 (28.43)
5	2.0	iso-PrOH (10)	15	122–125 (0.6)	80	339 (345.0)	1.5230	21.00[a] (21.04)	34.46 (34.20)
6	1.36	*tert*-BuOH (20)	40	125 (0.4)	40	369 (373.0)	1.5240	19.20[a] (19.45)	

[a] New compound.

TABLE 3

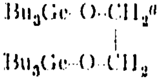
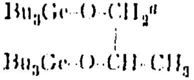
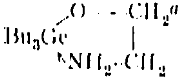
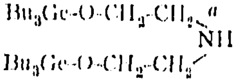
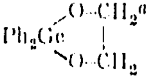
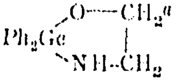
REACTIONS OF DIBUTYLGERMANIUM OXIDE WITH GLYCOLS AND ETHANOLAMINES

No.	*Bu_2GeO (g)*	*Ligand added (g)*	*Hours of refluxing*	*Product formed*	*b.p. product [°C(mm)]*	*Yield (%)*	*Mol. wt. found (calcd.)*	*n_D^{20}*	*Analyses found (calcd.) (%)*			
									C	*H*	*N*	*Glycol*
1	3·43	$HOCH_2CH_2OH$ (1.05)	16		98–103 (2.5–3.0)	60	330 (246.8)	1.4653	47·70 (48.68)	9.04 (8.98)		24.10 (24.32)
2	1.53	$HOCH_2CHMeOH$ (0.57)	25	 [a]	106–109 (3.5)	60	284 (260.8)	1.4540	49.85 (50.63)	9.62 (9·27)		28.23 (28.37)
3	1.33	$HOCH_2CH_2NH_2$ (0.80)	30	 [a]	121–122 (2)	50	343 (245.9)	1.4050	46.63 (48.85)	9.76 (9·47)	5.52 (5.69)	
4	1.47	$(HOCH_2CH_2)_2NH$ (0.75)	20	 [a]	127–130 (0.5–0.7)	75	292 (289.9)	1.4750	48.00 (49·71)	10.20 (9.38)	4·70 (4.82)	
5	1.33	$(HOCH_2CH_2)_3N$ (0.98)	20	 [a]	136 (0.1)	82	338 (333·9)	1.4810	49.67 (50.03)	9.70 (9.35)	3.88 (4.18)	

[a] New compound.

TABLE 4

REACTIONS OF BIS(TRIBUTYLGERMANIUM) OXIDE AND DIPHENYLGERMANIUM OXIDE WITH ACETYLACETONE, GLYCOLS AND ETHANOLAMINES

No.	Germoxane added (g)	Ligand added (g)	Hours of refluxing	Product formed	b.p. product [°C(mm)]	Yield (%)	Mol. wt. found (calcd.)	n_D^{20}	Analyses found (calcd.) (%) C	H	N	glycol
	$(Bu_3Ge)_2O$											
1	1.17	$CH_3COCH_2COCH_3$ (2)	20	$Bu_3Ge(acac)^a$	166–168 (1.75)	73	361 (343.0)	1.4670	57.13 (59.50)	10.90 (9.99)		
2	1.38	$HOCH_2CH_2OH$ (0.17)	20	 $\begin{array}{l}Bu_3Ge\text{-}O\text{-}CH_2{}^a\\ \qquad\qquad\;\; \vert \\ Bu_3Ge\text{-}O\text{-}CH_2\end{array}$	180 (0.4)	85	549 (547.8)	1.4565	56.37 (57.00)	10.83 (10.66)		10.50 (10.95)
3	1.60	$HOCH_2CHMeOH$ (0.24)	25	 $\begin{array}{l}Bu_3Ge\text{-}O\text{-}CH_2{}^a\\ \qquad\qquad\;\; \vert \\ Bu_3Ge\text{-}O\text{-}CH\text{-}CH_3\end{array}$	167–169 (0.2)	88	545 (561.8)	1.4580	57.95 (57.71)	11.30 (10.76)		12.90 (13.18)
4	1.65	$HOCH_2CH_2NH_2$ (0.40)	20		130 (2)	80	444 (303.9)	1.4585	57.71 (55.21)	11.76 (10.94)	4.80 (4.60)	
5	1.42	$(HOCH_2CH_2)_2NH$ (0.29)	30	 $\begin{array}{l}Bu_3Ge\text{-}O\text{-}CH_2\text{-}CH_2{}^a\\ \qquad\qquad\qquad\qquad\;\; NH\\ Bu_3Ge\text{-}O\text{-}CH_2\text{-}CH_2\end{array}$	152–155 (0.6)	77	590 (590.9)	1.4600	57.75 (56.90)	11.44 (11.74)	2.30 (2.36)	
	Ph_2GeO											
6	1.06	$CH_3COCH_2COCH_3$ (0.87)	20	$Ph_2Ge(acac)_2{}^a$	201 (0.6)	40	444 (425)		60.42 (62.16)	5.84 (5.67)		
7	1.1	$HOCH_2CH_2OH$ (0.29)	25		140–142 (0.1)	50	287 (286.8)		58.37 (58.60)	5.33 (4.92)		20.80 (20.92)
8	1.59	$HOCH_2CH_2NH_2$ (0.40)	35								4.00 (4.89)	

[a] New compound.

EXPERIMENTAL

All-glass apparatus with standard interchangeable joints was used throughout and special precautions were taken to exclude moisture. The reagents were dried as described earlier[5] and acetylacetone, glycols, ethanolamines were distilled before use.

Molecular weights were determined in boiling benzene in a semi-micro Gallenkamp ebulliometer.

Germanium was estimated as alkylgermanium oxides by hydrolysing the compounds with a little aqueous parent alcohol and evaporating slowly, first at 100° and then to 120–130° for about two h wherever possible. The alkoxy contents were estimated by an oxidimetric method[8]. Nitrogen was estimated by Kjeldhal's method and 1,2-glycols by the sodium periodate method. Carbon and hydrogen analysis were carried out at the Central Drug Research Institute, Lucknow.

Reaction between diphenylgermanium oxide and ethanol in the presence of benzene

Diphenylgermanium oxide (3.1 g) and ethanol (13 g) were taken in benzene (45 g) and the reaction mixture was refluxed at 100–120° for 4 h. The ternary azeotrope (ethanol/water/benzene) was then slowly fractionated at 66°; the temperature being taken finally to 80°. The excess solvent was removed under reduced pressure and then a colourless viscous liquid was obtained (75 %) on distillation at 156–157°/3 mm. (Found: Ge, 22.99; OEt, 28.77. $C_{16}H_{20}GeO_2$ calcd.: Ge, 22.90; OEt, 28.43 %.)

For brevity, other reactions have been tabulated in Tables 1 to 4.

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SUMMARY

A number of alkoxides, glycollates, acetylacetonates and substituted amino derivatives of alkylgermanes have been prepared directly from their germoxanes for the first time. Molecular weights and refractive indices of these compounds have been determined.

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