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ORGANIC DERIVATIVES OF GERMANIUM
VII. SYNTHESIS OF BUTYL TRIALKOXYGERMANES

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We have previously described the syntheses of dibutyldialkoxy-, tributylalkoxy- and diphenyldialkoxygermanes by the ammonia[1-2], alcohol interchange[3] and the oxide[4] methods. A survey of the literature reveals that the only alkyltrialkoxygermane compound reported is methyltrimethoxygermane, which was prepared by the sodium[5] method. It was thus considered of interest to explore the applicability of other possible methods for the preparation of alkyltrialkoxygermanes, and the reactions shown below have been used to synthesise a number of butyltrialkoxygermanes:

$$\mathrm{BuGeCl_3 + 3\ R'OH + 3\ NH_3 \rightarrow BuGe(OR')_3 + 3\ NH_4Cl}$$
$$\text{(where R}' = \text{Me, Et, iso-Pr)}$$
$$\mathrm{(BuGeO)_2O + 6\ BuOH \rightarrow 2\ BuGe(OBu)_3 + 3\ H_2O}$$
$$\mathrm{BuGe(OEt)_3 + 3\ R'OH \rightarrow BuGe(OR')_3 + 3\ EtOH}$$
$$\text{(where R}' = \text{Pr, Bu, sec-Bu, tert-Bu)}$$

All the butyltrialkoxygermanes are colourless, mobile liquids, which can be distilled under reduced pressure. Their molecular weights, determined ebullioscopically in benzene show their monomeric character.

EXPERIMENTAL

All glass apparatus was used throughout, and rigorous precautions were taken to exclude moisture. Alcohols and solvents were dried as described earlier[1]. Butyltrichloro germane was distilled before use. The alkoxy contents were estimated by the oxidimetric[6] method and germanium was estimated as butylgermanium oxide $\mathrm{(BuGeO)_2O}$ by hydrolysing the alkoxide in aqueous parent alcohol and drying at 120–130°C in an electric oven for 2 hours.

Methods of synthesis

1. *Ammonia method: preparation of butyltriethoxygermane.* Dry ammonia gas (passed through a battery of aluminium isopropoxide towers) was slowly bubbled into a solution of butyltrichlorogermane (6.55 g), ethanol (15 g) and benzene (60 g). There was immediate formation of ammonium chloride, first in the vapour phase then in solution, and an appreciable amount of heat was liberated. The supply of ammonia gas was discontinued when the reaction mixture cooled to room temperature. The reaction mixture was allowed to stand overnight, and the ammonium

TABLE 1

PREPARATION OF BUTYLTRIALKOXYGERMANES BY THE AMMONIA, ALCOHOLYSIS AND OXIDE METHOD

$BuGeX_3$ *(g)*	*Alcohol added (g)*	*B.p. (°C/mm)*	*Yield (%)*	*Product formed*	*Mol.wt.*		n_D^{20}	*Ge (%)*		*OR (%)*	
					Found	*Calcd.*		*Found*	*Calcd.*	*Found*	*Calcd.*
By the ammonia method from $BuGeCl_3$											
2.25	MeOH(15)	76–78/9	60	$BuGe(OMe)_3$	232	222.8	1.4245	32.36	32.58	41.45	41.78
6.55	EtOH(15)	90–93/8	90	$BuGe(OEt)_3$	270	264.9	1.4330	27.86	27.40	50.85	51.02
5.49	iso-PrOH(13)	94–95/7.5	85	$BuGe(O\text{-iso-}Pr)_3$	324	307	1.4151	24.28	23.65	57.11	57.71
By the alcoholysis method from $BuGe(OEt)_3$											
1.13	PrOH(6)	95–97/2.5	80	$BuGe(OPr)_3$	335	307	1.4250	24.32	23.65		
1.24	BuOH(6)	109–111/0.3	81	$BuGe(OBu)_3$	347	349	1.4310	21.30	20.83		
1.20	sec-BuOH(5)	96–98/1	98	$BuGe(O\text{-sec-}Bu)_3$	338	349	1.4260	21.30	20.83		
1.20	tert-BuOH(10)	99–100/4.5	66	$BuGe(\text{-tert-}Bu)_3$	350	349	1.4280	20.64	20.83		
By the oxide method from $(BuGeO)_2O$											
1.27	BuOH(12)	111–114/0.5	70	$BuGe(OBu)_3$	334	349	1.4310	21.33	20.83		

chloride was filtered off. Alcohol and benzene were distilled from the filtrate, and the residual butyltriethoxygermane was distilled at 90–92°/8 mm. Yield 90%. n_D^{20} 1.4330. (Found: Ge, 27.86; OEt, 50.83; mol.wt., 270. $C_{10}H_{24}GeO_3$ calcd.: Ge, 27.40; OEt, 51.02%; mol.wt., 264.9.)

2. *The oxide method: preparation of butyltri-n-butoxygermane.* Butanegermanonic oxide (1.27 g) was allowed to react with n-butanol (12 g) and benzene (40 g) and refluxed under a column for 6 h, while water formed in the reaction was removed azeotropically. The compound was dried under reduced pressure and distilled at 111–114°/0.5 mm. Yield 70%. n_D^{20} 1.4310. (Found: Ge, 21.33; mol.wt., 334. $C_{16}H_{36}GeO_3$ calcd.: Ge, 20.83%; mol.wt., 349.)

3. *The alcohol interchange method: preparation of butyltri-sec-butoxygermane.* Butyltriethoxygermane (1.20 g), sec-butanol (5 g) and benzene (45 g) were refluxed under column for 8–9 h in the presence of catalyst *p*-toluenesulfonic acid. The excess of benzene was fractionated and the catalyst was destroyed by a few drops of triethylamine. The compound was dried under reduced pressure and distilled at 96–98°/1 mm. Yield 98% n_D^{20} 1.4280. (Found: Ge, 20.64; mol.wt., 350. $C_{16}H_{36}GeO_3$ calcd.: Ge, 20.83%; Mol.wt., 349.

4. *Other preparations.* Details of the other preparations are given in Table 1.

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SUMMARY

A number of butyltrialkoxygermanes have been prepared for the first time by the ammonia, oxide or alcohol interchange methods.

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