

## ORGANIC DERIVATIVES OF GERMANIUM VI. REACTIONS OF ORGANOGERMANIUM ALKOXIDES WITH CARBOXYLIC ACIDS

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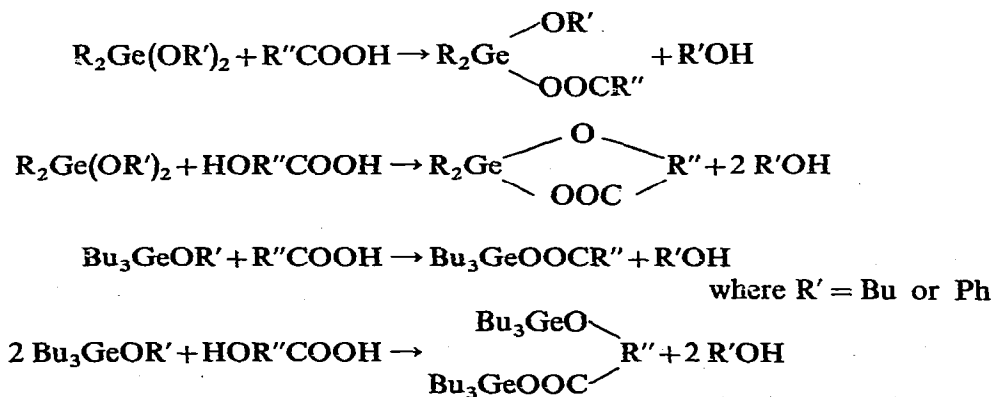
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The synthesis of a few organogermanium carboxylates has been described by Anderson<sup>1-5</sup> employing the reactions of the organogermanium oxide or halide with the corresponding acid or its silver salt respectively. Brook and Gilman<sup>6</sup> prepared triphenylgermanium carboxylates by the cleavage of hexaphenyldigermene with sodium-potassium alloy followed by carbonation. Lesbre and Satge<sup>7</sup> synthesised tributylgermanium acetate in quantitative yield by reacting tributylgermane with acetic acid in the presence of copper as a catalyst. Lutsenko and coworkers<sup>8-9</sup> prepared several such derivatives by the reactions of trialkyl and dialkylgermanes or their iodides with esters of mercuri-bisacetic acid. Recently Rijkens and Van der Kerk<sup>10</sup> have also reported the preparation of dibutylgermanium diacetate by refluxing a mixture of the appropriate oxide and excess acetic anhydride.

Reactions of carboxylic acids with alkoxydes of a number of elements (Zr<sup>11</sup>, Ge<sup>12</sup>, Ti<sup>13</sup>, Nd<sup>14</sup>, Pr<sup>14</sup>, Fe<sup>15</sup>, Si<sup>16</sup>, Al<sup>17</sup> and V<sup>18</sup>) have been studied in these laboratories. In view of interesting results<sup>12</sup> obtained in these reactions with tetraalkoxygermanes, it was considered worthwhile to study similar reactions with organogermanium alkoxydes also.

It has been found that the reactions with simple carboxylic acids (like acetic and benzoic) were straightforward, while with hydroxycarboxylic acids (such as salicylic and mandelic acids) the hydroxyl group took part in the reaction along with the carboxyl group. The reactions in general may be represented by the following equations:



Dibutylethoxygermanium acetate, tributylgermanium acetate and dibutylgermanium diacetate are distillable, colourless, mobile liquids, whereas diphenylethoxygermanium acetate distills as a colourless highly viscous liquid, which later on solidifies as white solid. Diphenylgermanium diacetate is a low melting solid. The derivatives of benzoic acid with all organogermanium alkoxides have been found to be highly viscous liquids and can be distilled under reduced pressure except in the case of diphenylgermanium dibenzoate, which appears to be very high boiling and could not be distilled. The reactions of dibutyl- and diphenyl-alkoxygermanes with salicylic and mandelic acids were completed in 1:1 molar ratios as represented above yielding distillable products. The mandelate is insoluble in benzene, whereas the salicylate is soluble and shows monomeric behaviour in the solvent.

The reactions of tributylgermanium alkoxide with salicylic and mandelic acids appear to be completed with a 2:1 ratio of alkoxide to acid; the products are

TABLE I

REACTIONS OF ALKYL ALKOXY GERMANES WITH CARBOXYLIC ACIDS (ACETIC AND BENZOIC ACID)

$R_2Ge(OR)_2$ or $Bu_3GeOR$ (g)	Acid added (g)	Product formed	Yield (%)	B.p. (°C/mm)
$Bu_2Ge(OEt)_2$ 1.10	$CH_3COOH$ 0.24	$Bu_2Ge \begin{array}{l} \diagup OEt \\ \diagdown OOCCH_3 \end{array}$	70	110/4
$Bu_2Ge(OEt)_2$ 1.30	0.57	$Bu_2Ge(OOCCH_3)_2$	60	127/5
$Ph_2Ge(OEt)_2$ 1.02	0.20	$Ph_2Ge \begin{array}{l} \diagup OEt \\ \diagdown OOCCH_3 \end{array}$	70	140/0.4
$Ph_2Ge(OEt)_2$ 1.26	0.48	$Ph_2Ge(OOCCH_3)_2$	60	150/0.2
$Bu_3GeOEt$ 1.30	0.28	$Bu_3GeOOCCH_3$	95	80/0.2
$Bu_2Ge(OEt)_2$ 1.22	$C_6H_5COOH$ 0.54	$Bu_2Ge \begin{array}{l} \diagup OEt \\ \diagdown OOC C_6H_5 \end{array}$	60	140/0.2
$Bu_2Ge(OEt)_2$ 1.33	1.18	$Bu_2Ge(OOC C_6H_5)_2$	80	198/0.4
$Bu_3GeOEt$ 1.23	0.52	$Bu_3GeOOC C_6H_5$	87	168/1.5
$Ph_2Ge(OEt)_2$ 1.16	0.45	$Ph_2Ge \begin{array}{l} \diagup OEt \\ \diagdown OOC C_6H_5 \end{array}$	40	180/0.2
$Ph_2Ge(OEt)_2$ 1.27	0.92	$Ph_2Ge(OOC C_6H_5)_2$		

colourless distillable viscous liquids, which are miscible with benzene and are monomeric in this solvent.

## EXPERIMENTAL

All glass apparatus with standard interchangeable joints was used throughout and extreme precautions were taken to exclude moisture. The reagents were dried as described earlier<sup>19</sup>. Alkyl germanium alkoxides were prepared either by the ammonia<sup>19</sup> or the oxide method<sup>20</sup>. Acetic acid was distilled before use. Benzoic, salicylic and mandelic acids were dried at 40–45°/1 mm for 2 h. Molecular weights were determined in a semimicro Gallenkamp ebulliometer and refractive indices determined by Abbe's refractometer.

Germanium was estimated in a few cases as alkyl germanium oxide by hydrolysing the compound with a little aqueous parent alcohol and evaporating slowly

$n_D^{20}$	Mol. wt. found (calcd.)	C (%) found (calcd.)	H (%) found (calcd.)	Ge (%) found (calcd.)	OR (%) found (calcd.)	Acid (%) found (calcd.)	Alcohol (%) found (calcd.)
1.4400	290 (290.9)			25.67 (24.96)	15.42 (15.49)	20.90 (20.31)	0.16 (0.18)
1.4475	321 (304.5)			24.32 (23.81)		38.35 (38.74)	0.40 (0.43)
1.5557	400 (330.9)			22.56 (21.94)		17.73 (17.84)	0.12 (0.14)
				21.37 (21.05)		33.11 (34.26)	0.32 (0.36)
1.4635	294 (302.9)			23.08 (23.96)		19.72 (19.47)	0.17 (0.20)
1.4955	355 (353)				12.82 (12.76)		0.17 (0.20)
	452 (429)	61.57 (61.58)	7.10 (6.58)			56.15 (56.45)	0.40 (0.44)
1.4930	371 (365)	62.64 (62.52)	9.08 (8.83)			33.50 (33.15)	0.20 (0.20)
1.5600		60.80 (58.08)	5.64 (5.13)				0.13 (0.16)
		63.78 (66.73)	4.72 (4.29)			52.1 (51.64)	0.34 (0.37)

TABLE 2  
REACTIONS OF ALKYL ALKOXY GERMANES WITH CARBOXYLIC ACIDS (SALICYLIC AND MANDELIC ACIDS)

$R_2\text{Ge}(\text{OR})_2$ or $R_3\text{GeOR}$ (g)	Acid added (g)	Product formed	B.p. (°C/mm)	Yield (%)	Mol. wt. found (calcd.)	$n_D^{20}$	C (%) found (calcd.)	H (%) found (calcd.)	Alcohol (g) found (calcd.)
$\text{Bu}_2\text{Ge}(\text{OEt})_2$ 1.14	$\alpha\text{-HOC}_6\text{H}_4\text{COOH}$ 0.57		158/0.5	85	330 (322.9)	1.5395	55.77 (56.37)	6.86 (6.96)	0.32 (0.38)
$\text{Bu}_3\text{GeOEt}$ 1.22	0.58		160/0.5	87	367 (381)	1.5065	58.92 (59.89)	8.45 (8.46)	0.14 (0.19)
$\text{Ph}_2\text{Ge}(\text{OEt})_2$ 1.60	0.70			95	406 (362.9)		63.66 (62.88)	4.85 (4.85)	0.40 (0.46)
$\text{Bu}_2\text{Ge}(\text{OEt})_2$ 1.26	$\text{C}_6\text{H}_5\text{CHOHCOOH}$ 0.69		Sublimes 150-160/0.4	90	Insoluble in benzene		56.89 (57.02)	7.52 (7.18)	0.38 (0.42)
$\text{Bu}_3\text{GeOEt}$ 1.44	0.38		203/0.4	70	576 (637.8)	1.4875	59.38 (60.26)	9.48 (9.44)	0.18 (0.23)

at 120–130°. Alkoxy contents were estimated by oxidimetric method<sup>21</sup>. Acetate and benzoate were estimated by titrating the compound against standard sodium hydroxide solution. Carbon and hydrogen analysis were carried out at the Central Drug Research Institute, Lucknow (India).

*Reaction between tributylgermanium ethoxide and benzoic acid in molar ratio 1 : 1 :*

Tributylgermanium ethoxide (1.23 g) was allowed to react with (0.52 g) of benzoic acid and benzene (50 g). Contents were refluxed under a column for 4 h and then binary azeotrope of ethanol and benzene was slowly fractionated. Alcohol found in the azeotrope was (0.20 g). The solvent was removed under reduced pressure and the compound was distilled at 160°/0.5 mm (1.35 g). Yield 87%. (Found: C, 62.64; H, 9.08; Benzoate, 33.50. C<sub>19</sub>H<sub>32</sub>GeO<sub>2</sub> calcd.: C, 62.52; H, 8.83; Benzoate, 33.15%.) For sake of brevity, all other reactions are summarised in Tables 1 and 2.

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#### SUMMARY

A number of carboxylates of alkyl germanes have been prepared for the first time from alkyl alkoxy germanes. Their molecular weights and refractive indices have been determined.

#### REFERENCES

- 1 H. H. ANDERSON, *J. Am. Chem. Soc.*, 72 (1950) 2089.
- 2 H. H. ANDERSON, *J. Am. Chem. Soc.*, 73 (1951) 5798.
- 3 H. H. ANDERSON, *J. Am. Chem. Soc.*, 73 (1951) 5800.
- 4 H. H. ANDERSON, *J. Am. Chem. Soc.*, 74 (1952) 2370.
- 5 H. H. ANDERSON, *J. Am. Chem. Soc.*, 78 (1956) 1692.
- 6 A. G. BROOK AND H. GILMAN, *J. Am. Chem. Soc.*, 76 (1954) 77.
- 7 M. LESBRE AND J. SATGE, *Compt. Rend.*, 254 (1962) 4051.
- 8 I. F. LUTSENKO, YU. I. BAUKOV AND B. N. KHASAPOV, *Zh. Obshch. Khim.*, 33 (1963) 2724.
- 9 YU. I. BAUKOV AND I. F. LUTSENKO, *Zh. Obshch. Khim.*, 34 (1964) 3453.
- 10 F. RIJKENS AND G. J. M. VAN DER KERK, *Investigations in the field of Organogermanium Chemistry*, 1964, 141.
- 11 R. N. KAPOOR AND R. C. MEHROTRA, *J. Am. Chem. Soc.*, 80 (1958) 3569.
- 12 G. CHANDRA AND R. C. MEHROTRA, *J. Indian. Chem. Soc.*, in press.
- 13 I. D. VARMA AND R. C. MEHROTRA, *J. Prakt. Chem.*, 10 (1960) 247.
- 14 R. C. MEHROTRA, T. N. MISRA AND S. N. MISRA, *J. Indian. Chem. Soc.*, 43 (1966) 61.
- 15 P. P. SHARMA AND R. C. MEHROTRA, private communication.
- 16 B. C. PANT, Ph. D. Thesis, University of Rajasthan, Jaipur (India), 1963.
- 17 A. K. RAI, R. K. MEHROTRA AND R. C. MEHROTRA, *J. Prakt. Chem.*, 4 (1963) 105.
- 18 R. K. MITTAL, Ph. D. Thesis, University of Rajasthan, Jaipur (India), 1963.
- 19 S. MATHUR, G. CHANDRA, A. K. RAI AND R. C. MEHROTRA, *J. Organometal. Chem.*, 4 (1965) 294.
- 20 R. C. MEHROTRA AND S. MATHUR, *J. Organometal. Chem.*, 6 (1966) 11.
- 21 D. C. BRADLEY, F. M. A. HALIM AND W. WARDLAW, *J. Chem. Soc.*, (1950) 3450.