774. *Peroxides of Elements other than Carbon. Part VI.*[1] *Peroxides of Germanium.*

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A number of peroxides of germanium have been prepared by treating alkylgermanium halides or germanium tetrachloride with alkyl hydroperoxides or hydrogen peroxide in the presence of a base under anhydrous conditions.

No peroxides of germanium appear to have been described. An obvious likely route to these compounds, by analogy with the preparation of the peroxysilanes,[2] would be the nucleophilic substitution by an alkyl hydroperoxide or hydrogen peroxide at a germanium atom, *e.g.*:

$$n\mathrm{RO{\cdot}OH} + \mathrm{R'_{4-n}GeCl_n} \longrightarrow \mathrm{R'_{4-n}Ge(O{\cdot}OR)_n} + n\mathrm{HCl} \quad (n = 1\text{—}4)$$

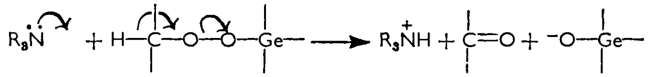
Reactions of this type have now been investigated.

Alkyl hydroperoxides and germanium chlorides react together readily in pentane, cyclohexane, or ether, in the presence of ammonia or triethylamine. The amine hydrochloride can be filtered off under anhydrous conditions, and the product isolated by distillation or crystallisation. By this method a number of organoperoxygermanium compounds have been prepared and characterised; typical examples are tripropyl-(t-butylperoxy)germanium, bis(decahydro-9-naphthylperoxy)dipropylgermanium, cyclopentamethylenedi-(t-butylperoxy)germanium, and tetrakis(decahydro-9-naphthylperoxy)-germanium. The analogous reaction of anhydrous hydrogen peroxide with tripropylgermanium chloride gave bis(tripropylgermanium)peroxide, $\mathrm{Pr_3Ge{\cdot}O{\cdot}O{\cdot}GePr_3}$.

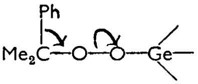
Our preliminary note [3] prompted Rieche and Dahlmann to report their results which have been obtained concurrently and independently.[4] They have prepared germanium peroxides $\mathrm{Ph_3Ge{\cdot}O{\cdot}OR}$ ($\mathrm{R = CMe_3}$, $\mathrm{CMe_2Ph}$, and $\mathrm{CPh_3}$), and bis(triphenylgermanium) peroxide, $\mathrm{Ph_3Ge{\cdot}O{\cdot}O{\cdot}GePh_3}$, by treating triphenylgermanium bromide successively with ammonia and the appropriate hydroperoxide or hydrogen peroxide, or with the anhydrous sodium salt of the hydroperoxide.

The germanium peroxides which we have prepared are stable up to about 70° for short periods, but some decomposition apparently occurs during distillation above this temperature. They catalyse the polymerisation of vinyl monomers, indicating that O–O homolysis can take place. All the peroxides are readily hydrolysed, and the hydroperoxide can be recovered; for example, tetrakis(decahydro-9-naphthylperoxy)germanium gives germanium dioxide and decahydro-9-naphthyl hydroperoxide.

1,2,3,4-Tetrahydro-1-naphthyl hydroperoxide and germanium tetrachloride in the presence of pyridine gave 1,2,3,4-tetrahydro-1-oxonaphthalene. As the hydroperoxide alone is stable towards pyridine, it appears that a base-catalysed decomposition is occurring in the s-alkylperoxygermanium structure:



A similar decomposition takes place when trimethyl-(1,2,3,4-tetrahydro-1-naphthylperoxy)-silane is treated with triethylamine.[2]



(A)

The product of the reaction between 1-methyl-1-phenylethyl hydroperoxide and germanium tetrachloride became non-peroxidic in the course of a few days, liberating phenol. This reaction probably occurs by a nucleophilic migration of a phenyl group from carbon to oxygen in the structure (A), as is recognised in other derivatives of the hydroperoxide.[5]

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[1] Part V, Davies and Packer, *J.*, 1959, 3164.

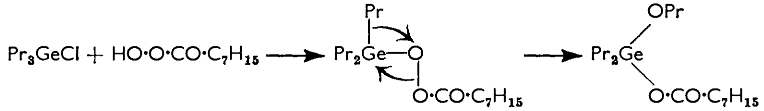
[2] Part I, Buncel and Davies, *J.*, 1958, 1550.

[3] Davies and Hall, *Chem. and Ind.*, 1958, 1695.

[4] Rieche and Dahlmann, *Angew. Chem.*, 1959, **71**, 169.

[5] Part II, Davies and Moodie, *J.*, 1958, 2372.

Buncel and Davies [2] showed that alkylchlorosilanes with peroxyacids gave non-peroxidic compounds which could be accounted for by assuming the nucleophilic rearrangement of an alkyl group from silicon to oxygen. A similar rearrangement apparently occurs when alkylgermanium chlorides are treated with peroxyacids, *e.g.*:



These peroxides of germanium are therefore on the whole very similar to the analogous peroxides of silicon. An apparent difference, however, arose in attempts to prepare propyltri-(t-butylperoxy)germanium and tetra-(t-butylperoxy)germanium; products with a low peroxide content were isolated, although tetrakis(decahydro-9-naphthylperoxy)germanium and tri- and tetra-(t-butylperoxy)silicon compounds can be isolated. This apparent decomposition may result from partial hydrolysis, despite our precautions, but we believe it may indicate a more fundamental instability. Discussion of this will be deferred until present work on the peroxides of other metals is completed.

EXPERIMENTAL

Analysis.—Peroxidic oxygen was determined iodometrically.

Compounds which gave germanium dioxide on hydrolysis were analysed for germanium gravimetrically, after ignition, as GeO_2, or volumetrically by titration with sodium hydroxide in the presence of glycerol, phenolphthalein being used as indicator. No method could be found which gave consistent results for compounds containing Ge–C bonds.

Microanalyses for carbon often gave low results, probably because some carbide was formed during combustion.

Preparation of Germanium Peroxides.—In these preparations the precautions against explosion described in Part I were observed;[2] in fact, no trouble was encountered. No quantitative investigation of the sensitivity of the germanium peroxides was carried out, but they gave the impression of being less liable to detonate than the silicon peroxides.

Peroxides of germanium

			Found (%)			Reqd. (%)		
Compound	B. p.	Press. (mm.)	C	H	Perox. O	C	H	Perox. O
1 $Ge(O{\cdot}OC_{10}H_{17})_4$ [a]	—	—	62·6	9·5	16·5	64·1	9·1	17·1
2 $Pr_2Ge(O{\cdot}OC_{10}H_{17})_2$	>95° (bath)	0·01	—	—	11·8	—	—	12·9
3 $[CH_2]_5{>}Ge(O{\cdot}OBu^t)_2$ ...	60°	0·001	45·7	8·4	19·1	48·8	8·7	19·9
4 $Me_3Ge{\cdot}O{\cdot}OC_{10}H_{17}$	65° (bath)	0·5	—	—	10·6	—	—	11·1
5 $Pr_3Ge{\cdot}O{\cdot}OBu^t$	35°	0·001	52·5	10·4	10·2	53·7	10·3	11·0
6 $Pr_3Ge{\cdot}O{\cdot}OC_{10}H_{17}$	65—70° (bath)	0·01	60·0	10·2	7·5	61·5	10·2	8·6
7 $Pr_3Ge{\cdot}O{\cdot}O{\cdot}GePr_3$ [b]	60—70° (bath)	0·05	47·2	9·4	6·3	49·7	9·7	7·4

[a] $C_{10}H_{17}$ = decahydro-9-naphthyl. [b] Prepared by using 100% H_2O_2 in ether. M. p.s: (1) 84—85°; (3) −35°; (6) *ca.* 20°. n_D^{26} (3) 1·4553; (5) 1·4383; (6) 1·4779; (7) 1·4608.

The germanium peroxides are readily hydrolysed and were exposed only to the atmosphere of a dry (P_2O_5) glove-box. All solvents and reactants were thoroughly dried; ammonia was obtained from the liquid dried with sodium. Some of the peroxides were distilled in the molecular still illustrated in Part II.[5]

The preparation of one germanium peroxide is described in detail; the others were prepared by similar methods. Ammonia was an alternative catalyst, and frequently the reaction was conducted completely at room temperature.

Tetrakis(decahydro-9-naphthylperoxy)germanium.—Germanium tetrachloride (0·3 g.) in pentane (5 c.c.) was added dropwise at room temperature to a stirred solution of the hydroperoxide (1·0 g.) and triethylamine (0·5 g.) in pentane (20 c.c.) and ether (5 c.c.); the amine hydrochloride was immediately precipitated. The mixture was heated under reflux for 0·5 hr., and the triethylammonium chloride, m. p. 251—253° (decomp.) (0·70 g.; calc., 0·70 g.), was filtered off in the glove-box. The solvent was removed from the filtrate under reduced pressure, leaving a white crystalline solid (0·8 g.) which was recrystallised from pentane at −70°, giving *tetrakis(decahydro-9-naphthylperoxy)germanium*, m. p. 84—85° [Found: C, 62·6; H, 9·5; Ge (gravimetrically), 9·2, (volumetrically), 10·1; peroxidic O, 16·5. $Ge(O_2C_{10}H_{17})_4$ requires C, 64·1; H, 9·1; Ge, 9·7; peroxidic O, 17·1%].

Infrared Spectra.—The infrared spectra of tripropyl-(t-butylperoxy)germanium, (decahydro-9-naphthylperoxy)tripropylgermanium, bistripropylgermanium peroxide, and cyclopentamethylenedi-(t-butylperoxy)germanium were determined. All gave bands between 11·70 and 11·95 μ and between 9·90 and 10·08 μ, and a series from 7·0 to 8·5 μ; these appear to be characteristic of the Ge–C bond.[6] Bands at 9·70 μ (weak) and 14·50—14·80 μ (strong) were also common to all four compounds; these bands are also present in the spectra of germanium tetra-alkoxides.[7] The characteristic absorption of the peroxide group at about 11·65 μ appeared only as a shoulder on the peak ascribed to the Ge–C bond.

Reaction between 1-Methyl-1-phenylethyl Hydroperoxide and Germanium Tetrachloride.—Treatment of germanium tetrachloride with the hydroperoxide in the presence of triethylamine gave a pale yellow liquid [Found: peroxidic O, 15·8. Calc. for $Ge(O_2C_9H_{11})_4$: peroxidic O, 18·9%]. After 2 days it had a dark red-brown colour and smelled strongly of phenol (Found: peroxidic O, 5%). When an attempt was made to distil the peroxide at 75° (bath)/0·01 mm., rapid decomposition occurred.

Reaction between 1,2,3,4-Tetrahydro-1-naphthyl Hydroperoxide and Germanium Tetrachloride.—A solution of the hydroperoxide and pyridine in pentane–ether was treated with germanium tetrachloride, yielding a white precipitate. The mixture was stirred for 1 hr., and the pyridine hydrochloride filtered off. Analysis of a portion of the filtrate showed that only 20% of the original peroxide remained. The solvent was removed at 15 mm., leaving 1,2,3,4-tetrahydro-1-oxonaphthalene (2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 255—257°).

Reaction between t-Butyl Hydroperoxide and Germanium Tetrachloride.—A solution of germanium tetrachloride (0·5 g.) in pentane (5 c.c.) was added dropwise at room temperature to a stirred solution of t-butyl hydroperoxide (0·95 g.) and triethylamine (0·94 g.) in pentane (20 c.c.). After 20 min., triethylammonium chloride, m. p. 249—251° (decomp.) (1·3 g.; calc., 1·3 g.), was filtered off. Analysis of a portion of the filtrate showed that 76% of the original peroxide remained. Removal of the solvent at 40° (bath)/15 mm. left a colourless liquid (0·5 g.) [Found: Ge, 15·4; peroxidic O, 22·2. Calc. for $Ge(O_2C_4H_9)_4$: Ge, 16·9; peroxidic O, 29·8; for $Ge(OC_4H_9)(O_2C_4H_9)_3$: Ge, 17·3; peroxidic O, 23·3%]. Similarly, on use of ammonia as the catalyst, ammonium chloride was precipitated quantitatively. A viscous liquid was recovered which could not be distilled in the molecular still (Found: peroxidic O, 21·1%); in air it rapidly gave a white solid.

Reaction between t-Butyl Hydroperoxide and Propylgermanium Trichloride.—n-Propylgermanium trichloride (2·0 g.) in pentane (5 c.c.) was added dropwise at 20° to a solution of the hydroperoxide (2·8 g.) and triethylamine (2·8 g.) in pentane (35 c.c.). The mixture was heated under reflux for 0·5 hr., and filtered free from the amine hydrochloride (3·4 g., calc., 3·7 g.), and the pentane removed at 14 mm., leaving a colourless liquid (2·9 g.; calc., 3·9 g.) [Found: peroxidic O, 21·9. Calc. for $PrGe(O_2Bu)_3$: peroxidic O, 25·1%]. Distillation in the molecular still gave what was apparently *-n-propyldi-(t-butylperoxy)germanium oxide*, b. p. 60° (bath)/0·001 mm. [Found: C, 44·6; H, 8·6; peroxidic O, 21·0. $[(BuO_2)_2PrGe]_2O$ requires C, 43·8; H, 8·3; peroxidic O, 21·1%]. The infrared spectrum showed no evidence of an OH group,[7] rendering it unlikely that the product was the hydroxide corresponding to the above compound, which has a somewhat similar analysis.

Reaction between Tripropylgermanium Chloride and Peroxyoctanoic Acid.—Triethylamine (0·43 g.) was added at 20° to a stirred solution of tripropylgermanium chloride (1·0 g.) and peroxyoctanoic acid (0·7 g.) in pentane (25 c.c.). The amine hydrochloride was immediately precipitated and was filtered off after 15 min. (0·45 g.; calc., 0·55 g.). The solvent was removed from the filtrate at 15 mm., leaving a liquid (1·2 g.) (Found: peroxidic O, 0·3%), b. p. 100° (bath)/0·02 mm. (0·9 g.), n_D^{25} 1·4514 [Found: C, 57·7; H, 10·5%; *M* (by titration with NaOH), 364. Calc. for $Pr_2Ge(OPr)(O_2C_8H_{15})$: C, 56·6; H, 10·0%; *M*, 361]. Part was neutralised

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[6] Rochow, Hurd, and Lewis, "The Chemistry of Organometallic Compounds," Wiley, New York, 1957, p. 169; Rochow, Didtschenko, and West, *J. Amer. Chem. Soc.*, 1951, **73**, 5486; West, *ibid.*, 1953, **75**, 6080.

[7] Johnson and Fritz, *ibid.*, 1953, **75**, 718.

with aqueous sodium hydroxide, giving octanoic acid which was isolated as its S-*benzylisothiuronium salt,* m. p. and mixed m. p. 154° (Found: C, 61·8; H, 8·7; S, 10·2. $C_{16}H_{16}O_2N_2S$ requires C, 61·9; H, 8·4; S, 10·3%). The remainder of the liquid was hydrolysed with dilute sulphuric acid; an ethereal extract showed the presence of a trace of propyl alcohol on the vapour-phase chromatogram.

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