308. *Peroxides of Elements Other than Carbon. Part I. The Preparation and Reactions of Peroxysilanes.*

By E. Buncel and Alwyn G. Davies.

From the nucleophilic reaction of alkyl hydroperoxides with chlorosilanes a number of organoperoxysilanes, $R_{4-n}Si(O{\cdot}OR')_n$, have been isolated. Hydrogen peroxide similarly gives disilyl peroxides, but perbenzoic acid gives alkoxysilyl benzoates rather than alkylsilyl perbenzoates; the mechanism of this rearrangement is discussed.

Two main types of reaction, illustrated in equations (1) and (2), have been used for the preparation of organic peroxides. The first is a nucleophilic substitution,[1] the second is generally homolytic, and is frequently a chain reaction.[2]

$$\mathrm{RO{\cdot}OH + R'X \longrightarrow RO{\cdot}OR' + HX} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

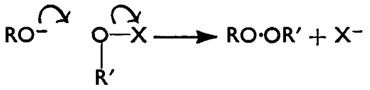
$$(\mathrm{R} = \mathrm{H\ or\ alkyl};\ \mathrm{R}' = \mathrm{alkyl\ or\ acyl};\ \mathrm{X} = \mathrm{an\ electronegative\ group})$$

$$\mathrm{O_2 + RR' \longrightarrow RO{\cdot}OR'} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

$$(\mathrm{R} = \mathrm{alkyl};\ \mathrm{R}' = \mathrm{H\ or\ alkyl})$$

Only diaryl peroxides have been prepared by the pairing of two oxygen radicals (eqn. 3),[3] and there seems to be no unequivocal example of the formation of a peroxide bond by the attack of nucleophilic oxygen on electrophilic oxygen (eqn. 4):[4]

$$\mathrm{2ArO{\cdot} \rightleftharpoons ArO{\cdot}OAr} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$



$$\mathrm{RO^-}\quad \underset{\mathrm{R'}}{\mathrm{O}}\!-\!\mathrm{X} \longrightarrow \mathrm{RO{\cdot}OR' + X^-} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

This series of papers will describe attempts to extend reactions of these types to the preparation of peroxides of elements other than carbon.

The Preparation of Peroxysilanes.—The similarity of the chemistry of carbon and of silicon compounds and the ready availability of many organosilanes led us to investigate the reaction between chlorosilanes and alkyl hydroperoxides (eqn. 5).[5] The reaction takes place readily in ether or pentane in presence of pyridine, triethylamine, or ammonia.

$$\mathrm{R_{4-\mathit{n}}SiCl_{\mathit{n}} + \mathit{n}R'O{\cdot}OH \longrightarrow R_{4-\mathit{n}}Si(O{\cdot}OR')_{\mathit{n}} + \mathit{n}HCl} \quad . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$(n = 1\text{—}4)$$

The hydrochloride of the base is precipitated and from the filtrate the peroxysilane can be isolated in good yield. The use of ammonia is preferable to that of pyridine since pyridinium chloride is incompletely precipitated and tends to distil with the peroxysilane. The salt was sometimes removed by water but care must be taken not to hydrolyse the peroxysilane. By this method, eleven alkylperoxysilanes have been prepared and characterised; typical examples are trimethyl-($\alpha\alpha$-dimethylbenzylperoxy)silane, triphenyl-(*tert.*-butylperoxy)silane, trimethyl-(1 : 2 : 3 : 4-tetrahydro-1-naphthylperoxy)silane, methyltri-(*tert.*-butylperoxy)silane, and tetra-(*tert.*-butylperoxy)silane. Trimethyl-(*tert.*-butylperoxy)silane was also obtained from the hydroperoxide and hexamethyldisilazine, but trimethylmethoxysilane was unreactive.

The peroxide structure of these compounds is well established. They are stable for some months at room temperature, but catalyse the polymerisation of styrene and of methyl methacrylate, and may detonate on local heating. They oxidise iodide to iodine quantitatively,

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[1] Davies, *Adv. Catalysis*, 1957, **9**, 359.

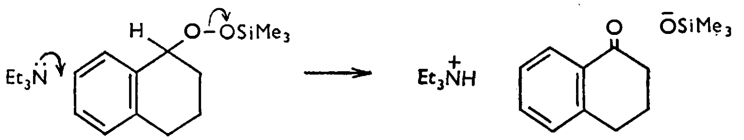
[2] Frank, *Chem. Reviews*, 1950, **46**, 155; Hock and Kropf, *Angew. Chem.*, 1957, **69**, 313.

[3] References are given by Dimroth and Neubauer, *ibid.*, p. 95.

[4] But see Bladon, *J.*, 1955, 2176; Levitt, *Canad. J. Chem.*, 1953, **31**, 915; Levitt and Malinowski, *J. Amer. Chem. Soc.*, 1955, **77**, 4517.

[5] Buncel and Davies, *Chem. and Ind.*, 1956, 1052.

and are readily hydrolysed to the corresponding silanol and hydroperoxide. The infrared absorption spectra of trimethyl-(*tert.*-butylperoxy)silane and tetra-(*tert.*-butylperoxy)silane show strong absorption at 11·56 μ and 11·65 μ respectively, ascribed to the oxygen–oxygen stretching frequency. Trimethyl-(1 : 2 : 3 : 4-tetrahydro-1-naphthylperoxy)silane, in common with other primary and secondary alkyl peroxides,[6] undergoes base-catalysed decomposition forming the corresponding ketone:



. . (6)

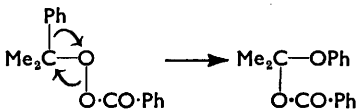
Disilyl peroxides are similarly prepared from chlorosilanes and hydrogen peroxide. Triphenylchlorosilane gave triphenylsilyl peroxide, but unlike triphenylmethyl peroxide or any of the alkylperoxysilanes it is unstable and the peroxide content drops to zero in a few days. In an attempt to prepare trimethylsilyl peroxide similarly the product detonated on distillation and this discouraged attempts to prepare similar compounds.

Meanwhile, three reports appeared of the preparation of silicon peroxides. Hahn and Metzinger [7] described the preparation of trimethyl-(*tert.*-butylperoxy)silane, trimethylsilyl hydroperoxide, and trimethylsilyl peroxide from chlorosilanes and *tert.*-butyl hydroperoxide or hydrogen peroxide in the presence of pyridine. They find that trimethylsilyl peroxide is stable to 135°, but that the hydroperoxide disproportionates readily into the disilyl peroxide and hydrogen peroxide, and decomposes with rapid evolution of oxygen above 35° under vacuum. This hydroperoxide may have been the cause of the detonation during our preparation of the disilyl peroxide.

Jenker [8] found that diethyldifluorosilane was oxidised by 100% hydrogen peroxide in presence of ammonia giving the ethoxysilane. The corresponding dichlorosilane gave a polymeric silyl peroxide containing some ethoxide and siloxane groups; these reactions are discussed later.

A patent [9] reports the formation of silicon peroxides by chlorosilanes and silanols with hydrogen peroxide. The formation of triphenyl- and triethyl-silyl peroxide by reaction of chlorine with the appropriate sodium siloxane is also described. This reaction, which has no analogy in the formation of dialkyl peroxides, presumably proceeds by the mechanism outlined in equation (3) or (4).

Oxygen–Oxygen Heterolysis in Peroxysilanes.—Tertiary alkyl peroxides undergo acid-catalysed oxygen–oxygen heterolysis by a nucleophilic 1 : 2-rearrangement; [10] *e.g.* equation (7) for αα-dimethylbenzyl perbenzoate.[11] In these rearrangements the bond-fission and bond-formation processes are all synchronous.[10a, 12]



$$\underset{\text{O·CO·Ph}}{\overset{\text{Ph}}{\text{Me}_2\text{C—O}}} \longrightarrow \underset{\text{O·CO·Ph}}{\text{Me}_2\text{C—OPh}} \qquad . \ . \ . \ . \ . \ . \ . \ . \ (7)$$

A number of nucleophilic 1 : 2-rearrangements from carbon to silicon are also recorded: Whitmore and his co-workers [13] showed electrophilic catalysis at the migration terminus

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[6] Kornblum and de la Mare, *J. Amer. Chem. Soc.*, 1951, **73**, 880.

[7] Hahn and Metzinger, *Makromol. Chem.*, 1956, **21**, 113.

[8] Jenker, *Z. Naturforsch.*, 1956, **11b**, 757.

[9] U.S.P. 2,692,887; *Chem. Abs.*, 1955, **49**, 13,290.

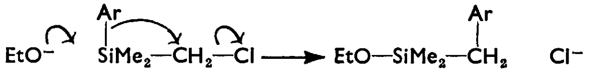
[10] (*a*) Criegee, *Annalen*, 1948, **560**, 127; (*b*) Robertson and Waters, *J.*, 1948, 1574; (*c*) Reviewed by Leffler, *Chem. Reviews*, 1949, **45**, 385; "The Reactive Intermediates of Organic Chemistry," Interscience Publishers, New York, 1956, p. 166.

[11] Hock and Kropf, *Ber.*, 1955, **88**, 1544.

[12] Denney, *J. Amer. Chem. Soc.*, 1955, **77**, 1706; 1956, **78**, 590; Bassey, Bunton, Davies, Lewis, and Llewellyn, *J.*, 1955, 2471.

[13] Whitmore, Sommer, and Gould, *J. Amer. Chem. Soc.*, 1947, **69**, 1976; Sommer, Bailey, Gould, and Whitmore, *ibid.*, 1954, **76**, 801; Sommer and Evans, *ibid.*, p. 1186.

and Eaborn and Jeffrey[14] established an example of rearrangement initiated by nucleophilic attack at the migration origin (eqn. 8).



$$EtO^- \; \overset{Ar}{SiMe_2}—CH_2—Cl \longrightarrow EtO—SiMe_2—\overset{Ar}{CH_2} \quad Cl^- \quad \ldots . \; (8)$$

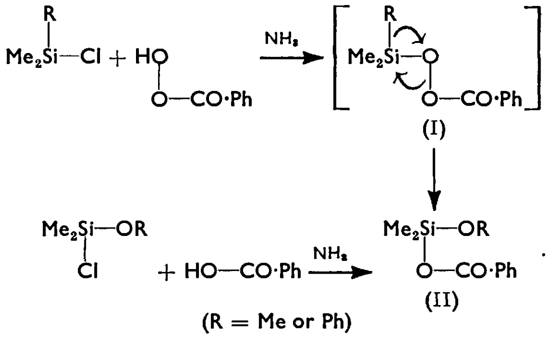
We observed nucleophilic migration of alkyl groups from silicon to oxygen in the attempted preparation of trimethylsilyl perbenzoate (I; R = Me) from trimethylchlorosilane and perbenzoic acid (eqn. 9).[15]

The product was isomeric with compound (I; R = Me) but was not a peroxide and was hydrolysed readily to benzoic acid. It was identified as the ester (II; R = Me) which was synthesised unambiguously from dimethylmethoxychlorosilane and benzoic acid (eqn. 10).

In support of the suggested mechanism, dimethylphenylchlorosilane with peroxybenzoic acid gave dimethylphenoxysilyl benzoate (II; R = Ph), the phenyl group migrating instead of the methyl group. This relative migration order is the same as that observed previously in carbon to carbon,[16] silicon to carbon,[14] and carbon to oxygen [10c,17] nucleophilic rearrangements, and differs from that found in homolysis of alkoxy-radicals.[18]

The stability of silylperoxy- and the corresponding alkylperoxy-esters can be compared. *tert.*-Butyl perbenzoate is stable below about 100°,[19] but during 15 minutes in boiling chloroform containing a trace of perchloric acid it decomposes giving acetone (82%) and benzoic acid (95%).[20] αα-Dimethylbenzyl per-esters are much less stable and have only recently been prepared;[11,20] on warming,[11] or with a trace of acid,[20] rearrangement readily takes place according to eqn. 7. The replacement of the carbon atom by a silicon atom therefore makes the ester more susceptible to rearrangement.

An attempt was made to prepare trimethoxysilyl perbenzoate by a reaction of the type shown in equation (9); rearrangement of this compound would involve the unfamiliar nucleophilic attack of oxygen on oxygen (eqn. 4), and the product would still be a peroxide. However, although trimethoxy-(*tert.*-butylperoxy)silane was readily prepared by the usual method, we were not able to isolate the corresponding perbenzoate.



$$\overset{R}{Me_2Si}—Cl + HO—O—CO{\cdot}Ph \xrightarrow{NH_3} \left[\overset{R}{Me_2Si}—O—O—CO{\cdot}Ph \right] \; \ldots\ldots \; (9)$$

(I)

$$Me_2Si(OR)—Cl + HO—CO{\cdot}Ph \xrightarrow{NH_3} Me_2Si(OR)—O—CO{\cdot}Ph \; \ldots\ldots \; (10)$$

(II)

(R = Me or Ph)

The action of acidic hydrogen peroxide on dimethylphenylchlorosilane gave phenol, presumably by rearrangement of the intermediate hydroperoxide, but a similar acid-catalysed rearrangement of triphenyl-(*tert.*-butylperoxy)silane, or a base-catalysed rearrangement of dimethylphenyl-(*tert.*-butylperoxy)silane was not observed. The rearrangement [8] of the ethylsilylperoxy-structure to the ethoxysiloxy-structure may proceed by the mechanism described.

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[14] Eaborn and Jeffrey, *J.*, 1957, 137.

[15] Buncel and Davies, *Chem. and Ind.*, 1957, 492.

[16] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 473; *J.*, 1953, 2845.

[17] Kharasch, Fono, and Nudenberg, *J. Org. Chem.*, 1950, **15**, 775.

[18] *Idem, ibid.*, p. 763.

[19] Milas and Surgenor, *J. Amer. Chem. Soc.*, 1946, **68**, 642.

[20] Davies and Nery, unpublished work; Davies and Moodie, *Chem. and Ind.*, 1957, 1622.

It is apparent that these nucleophilic rearrangements will be widespread in the chemistry of the peroxides of elements other than carbon, and may prevent the isolation of some of these compounds. For example, peroxides oxidatively dealkylate[21] organoboron compounds by a rearrangement of this kind, and a similar mechanism probably applies in the reduction of peroxides with Grignard reagents.[22] If such reduction can be avoided, the autoxidation of an organometallic or organometalloid compound will yield a peroxide[23] (cf. eqn. 2). Preparations of this type will be described later.

EXPERIMENTAL

General.—Certain operations involving peroxides, such as the mixing of reaction components and the distillation of products, were performed behind a " Perspex " safety screen, and whenever possible the products were not heated above 100°. Samples of diethyldi-(*tert.*-butylperoxy)silane and of tetra-(*tert.*-butylperoxy)silane exploded while being sealed for analysis.

Analytical.—*Silicon.* The compound (0·1—0·2 g.) in a silica beaker (8 cm. high, 2·5 cm. diam.) was covered with chlorobenzene (0·3 c.c.) to moderate the subsequent reaction. Concentrated sulphuric acid (1·5 c.c.) and nitric acid (0·5 c.c.) were added and the mixture gently heated until it solidified. The silica was then ignited to constant weight at 800°.

Volatile liquids were weighed into a gelatin capsule which was placed in a small test-tube, and the whole transferred to a Carius tube containing the mixed acids. The tube was sealed, the contents mixed, and the whole heated in a furnace at 240° for 6 hr. The contents were washed quantitatively into a weighed platinum beaker and ignited to silica as above.

Peroxidic oxygen. The sample (0·1—0·2 g.), glacial acetic acid (5 c.c.), and saturated sodium iodide (5 c.c.) were added successively to *iso*propyl alcohol (50 c.c.). The mixture was kept overnight in the dark. Next day the liberated iodine was titrated with 0·1N-sodium thiosulphate. A blank estimation was run concurrently.

Carbon and hydrogen. Samples of peroxysilanes usually exploded in the combustion train, although they were carefully heated in a stream of air at reduced pressure rather than in oxygen. It was difficult to obtain reproducible analytical results on the same specimen, particularly for carbon.

Preparation of Organoperoxysilanes.—(i) *Trimethyl-*(tert.*-butylperoxy*)*silane.* (*a*) A solution of *tert.*-butyl hydroperoxide (2·70 g.) and pyridine (2·37 g.) in pentane (20 c.c.) was added at 0° to a solution of trimethylchlorosilane (3·34 g.) in pentane (20 c.c.). Pyridinium chloride (3·54 g.) was immediately precipitated. Distillation of the filtrate yielded trimethyl-(*tert.*-butylperoxy)silane (4·33 g.), b. p. 79°/215 mm., n_D^{25} 1·3935, d_D^{25} 0·8219 (Found: C, 52·6; H, 11·3; Si, 16·6; peroxidic O, 9·45%; *M*, 159. Calc. for $C_7H_{18}O_2Si$: C, 51·8; H, 11·2; Si, 17·3; peroxidic O, 9·85%; *M*, 162). Hahn and Metzinger report b. p. 41°/41 mm., d^{20} 0·798, n^{20} 1·3933.

The same product was obtained in 60% yield in the absence of pyridine.

(*b*) A mixture of hexamethyldisilazine (1·61 g.) and *tert.*-butyl hydroperoxide (1·80 g.) in ether (35 c.c.) was heated under reflux for 9 hr., and was then distilled, giving three fractions all of b. p. 39°/40 mm., but with n_D^{25} 1·3891, 1·3906, and 1·3914 (Found for the final fraction: C, 51·6; H, 11·0; peroxidic O, 9·67%).

An attempt to carry out a similar reaction with methoxytrimethylsilane led to its recovery, b. p. 57°, n_D^{25} 1·3653.

(ii) *Trimethyl-*(tert.*-pentylperoxy*)*silane.* From *tert.*-pentyl hydroperoxide (4·42 g.), pyridine (3·56 g.), and trimethylchlorosilane (4·59 g.) in pentane (60 c.c.) at 0°, *trimethyl-*(tert.*-pentylperoxy*)*silane* (6·18 g.) was obtained, b. p. 78°/95 mm., n_D^{25} 1·4032, d_4^{25} 0·8419 (Found: C, 55·4; H, 11·4; Si, 15·6; peroxidic O, 9·1%; *M*, 174. $C_8H_{20}O_2Si$ requires C, 54·5; H, 11·4; Si, 15·9; peroxidic O, 9·1%; *M*, 176).

(iii) *Trimethyl-*(*αα-dimethylbenzylperoxy*)*silane.* A mixture of αα-dimethylbenzyl hydroperoxide (3·04 g.), pyridine (1·58 g.), and trimethylchlorosilane (2·16 g.) in pentane (40 c.c.) at 0° gave a precipitate of pyridinium chloride (2·25 g.). The filtrate was washed rapidly with ice-cold water, dried (Na_2SO_4), and distilled, yielding *trimethyl-*(*αα-dimethylbenzylperoxy*)*silane*

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[21] Kuivila, *J. Amer. Chem. Soc.*, 1954, **76**, 870; R. Moodie, unpublished work.

[22] Walling and Buckler, *ibid.*, 1955, **77**, 6032.

[23] Anderson, *ibid.*, 1952, **74**, 2371.

(2·20 g.), b. p. 43°/0·05 mm., n_D^{25} 1·4780, d_4^{25} 0·9501 (Found: C, 64·5; H, 9·1; Si, 11·9; peroxidic O, 7·4. $C_{12}H_{20}O_2Si$ requires C, 64·3; H, 9·0; Si, 12·5; peroxidic O, 7·1%).

(iv) *Trimethyl-*(1 : 2 : 3 : *4-tetrahydro-*1-*naphthylperoxy*)*silane.* Dry ammonia was passed for 30 min. through a solution of 1 : 2 : 3 : 4-tetrahydro-1-naphthyl hydroperoxide (3·28 g.) and trimethylchlorosilane (2·16 g.) in ether (30 c.c.) at 0°. Ammonium chloride (0·46 g.) was filtered off; the filtrate yielded *trimethyl-*(1 : 2 : 3 : *4-tetrahydro-*1-*naphthylperoxy*)*silane* (4·61 g.), b. p. 53°/0·01 mm., n_D^{25} 1·5102, d_4^{25} 1·015 (Found: C, 65·4; H, 8·4; Si, 11·0; peroxidic O, 7·0. $C_{13}H_{20}O_2Si$ requires C, 66·0; H, 8·5; Si, 11·9; peroxidic O, 6·8%).

(v) *Triphenyl-*(tert.*-butylperoxy*)*silane.* A solution of *tert.*-butyl hydroperoxide (0·90 g.) and triphenylchlorosilane (2·94 g.) in ether (30 c.c.) was treated as in (iv), yielding ammonium chloride (0·45 g.). The filtrate was evaporated to dryness, and the residue recrystallised from pentane yielding *triphenyl-*(tert.*-butylperoxy*)*silane* (2·71 g.), m. p. *ca.* 50° (Found: C, 76·2; H, 6·9; Si, 8·0; peroxidic O, 4·5. $C_{22}H_{24}O_2Si$ requires C, 75·8; H, 6·9; Si, 8·05; peroxidic O, 4·6%).

(vi) *Dimethylphenyl-*(tert.*-butylperoxy*)*silane.* A solution of *tert.*-butyl hydroperoxide (2·96 g.) and dimethylphenylchlorosilane (5·60 g.) in ether (80 c.c.), was treated as in (iv), yielding ammonium chloride (1·47 g.) and a liquid (6·55 g.) which was distilled in a molecular still from a bath at 45—55°. The following fractions were collected: (*a*) 3 c.c., b. p. 40°/0·05 mm., n_D^{25} 1·4762; (*b*) 2 c.c., b. p. 50°/0·05 mm., n_D^{25} 1·4748; (*c*) <0·5 c.c., b. p. 50°/0·001 mm., n_D^{25} 1·4885 [Found: peroxidic O, (*a*) 6·85, (*b*) 6·75, (*c*) 3·06%]. A non-volatile residue (*ca.* 0·5 c.c.) remained. The first fraction consisted of impure dimethylphenyl-(*tert.*-butylperoxy)silane (Found: C, 62·8; H, 8·9; peroxidic O, 6·8. $C_{12}H_{20}O_2Si$ requires C, 64·3; H, 9·0; peroxidic O, 7·1%).

(vii) *Trimethoxy-*(tert.*-butylperoxy*)*silane.* All manipulations of trimethoxysilyl compounds were conducted in the dry box. Dry ammonia was passed for 45 min. through a solution of *tert.*-butyl hydroperoxide (1·10 g.) and trimethoxychlorosilane (1·92 g.) in ether (40 c.c.) at 0°, yielding ammonium chloride (0·63 g.; calc. 0·65 g.) and a liquid residue (2·33 g.) which gave *trimethoxy-*(tert.*-butylperoxy*)*silane,* b. p. 49°/6 mm. (Found: C, 40·1; H, 8·9; Si, 13·5; peroxidic O, 7·25. $C_7H_{18}O_5Si$ requires C, 40·0; H, 8·6; Si, 13·4; peroxidic O, 7·6%).

Two attempts to prepare trimethoxysilyl perbenzoate by a similar method from perbenzoic acid did not give any clearly defined product. From both experiments a liquid was obtained in poor yield, b. p. 50° (bath)/0·001 mm., which had a very low peroxide content and an analysis corresponding roughly to that of trimethoxysilanol ($C_3H_{10}O_4Si$).

(viii) *Diethyldi-*(tert.*-butylperoxy*)*silane.* A solution of *tert.*-butyl hydroperoxide (5·40 g.), diethyldichlorosilane (4·71 g.), and pyridine (4·74 g.) in pentane (60 c.c.) yielded *diethyldi-*(tert.*-butylperoxy*)*silane* (4·82 g.), b. p. 40°/1 mm., n_D^{25} 1·4149, d_4^{25} 0·9415 (Found: C, 55·1; H, 10·7; Si, 11·1; peroxidic O, 11·8%; *M*, 257. $C_{12}H_{28}SiO_4$ requires C, 54·5; H, 10·7; Si, 10·6; peroxidic O, 12·1%; *M*, 264).

(ix) *Diphenyldi-*(tert.*-butylperoxy*)*silane.* *tert.*-Butyl hydroperoxide (3·77 g.), pyridine (3·31 g.), diphenyldichlorosilane (5·30 g.), and pentane (50 c.c.) were mixed at 0°. Next day the precipitate of pyridinium chloride was removed (4·50 g.); the filtrate yielded *diphenyldi-*(tert.*-butylperoxy*)*silane* as a viscous liquid, b. p. 110°/0·001 mm., n_D^{25} 1·5103, d_4^{25} 1·033 (Found: C, 66·7; H, 7·7; Si, 6·95; peroxidic O, 8·7. $C_{20}H_{28}SiO_4$ requires C, 66·6; H, 7·8; Si, 7·8; peroxidic O, 8·9%).

(x) *Methyltri-*(tert.*-butylperoxy*)*silane.* Similarly, a mixture of *tert.*-butyl hydroperoxide (8·10 g.), pyridine (7·11 g.), and methyltrichlorosilane (4·50 g.) in pentane (60 c.c.) at 0°, yielded *methyltri-*(tert.*-butylperoxy*)*silane* (4·56 g.), b. p. 50°/0·1 mm., n_D^{25} 1·4097 (Found: C, 51·2; H, 10·1; Si, 9·4%; *M*, 307. $C_{13}H_{30}SiO_6$ requires C, 50·3; H, 9·75; Si, 9·0%; *M*, 310).

(xi) *Tetra-*(tert.*-butylperoxy*)*silane.* *tert.*-Butyl hydroperoxide (7·18 g.) in ether (75 c.c.) was added (dry box) to silicon tetrachloride (3·27 g.) and dry ammonia was passed through the solution for 1 hr. at 0°. The precipitate of ammonium chloride (4·00 g.; calc. 3·98 g.) was filtered off, and the filtrate evaporated. Vacuum sublimation at 0·001 mm. of the residue (7·20 g.) from a bath at 50° gave fine white crystals of *tetra-*(tert.*-butylperoxy*)*silane,* m. p. (sealed tube) 35—40° (Found: C, 50·2; H, 9·8%; *M*, 379. $C_{16}H_{36}O_8Si$ requires C, 50·0; H, 9·4; Si, 73%; *M*, 384).

Similarly the hydroperoxide (7·20 g.), pyridine (6·32 g.), and silicon tetrachloride (3·38 g.) in pentane (60 c.c.) at 0° gave pyridinium chloride and the silyl peroxide (Found: C, 50·6; H, 9·7; Si, 7·7%; *M*, 377). Determination of the peroxidic oxygen gave erratic, but approximately correct, results.

Attempts to prepare the peroxide by treating tetramethoxysilane with *tert.*-butyl hydroperoxide were not successful. The presence of an acid ion-exchange resin as catalyst led to hydrolysis of the tetramethoxysilane; the use of hydrogen chloride caused alkyl–oxygen heterolysis of the hydroperoxide giving principally *tert.*-butyl chloride and *tert.*-butyl peroxide, identified by vapour-phase chromatography and infrared absorption spectra.

Experiments on Disilyl Peroxides.—(i) *Trimethylsilyl peroxide.* A solution of 87% hydrogen peroxide (1·56 g.) and trimethylchlorosilane (4·32 g.) in ether (20 c.c.) at 0° was kept for 16 hr. in a desiccator containing solid potassium hydroxide. The ether was removed and distillation continued at 260 mm. Liquid began to distil, b. p. 36°; this temperature gradually rose to 55° whereupon a violent explosion occurred.

(ii) *Triphenylsilyl peroxide.* From a similar experiment with triphenylchlorosilane it was recovered, m. p. and mixed m. p. 90—92°; similarly no peroxide could be isolated from the interaction of triphenylsilanol and hydrogen peroxide in acetic acid or acetic acid–sulphuric acid.

After 2 hr., pentane (20 c.c.) was added to a solution of 87% hydrogen peroxide (0·08 g.), pyridine (0·16 g.), and triphenylchlorosilane (0·59 g.) in ether (15 c.c.) at 0°. Pyridinium chloride (0·24 g.) was precipitated. The filtrate was washed rapidly with water and dried (Na_2SO_4) yielding a white crystalline solid (0·48 g.), m. p. *ca.* 85° (Found: peroxidic O, 4 hr. after start of reaction: 1·8%; after 91 hr., 0·2%).

The reaction was therefore repeated as rapidly as possible on twice the above scale (Found: peroxidic O, after 1·5 hr., 2·1%; after 21 hr., 0·9%; C, 78·1; H, 6·1%). After several weeks the m. p. of the solid was 130° (Found: C, 77·9; H, 6·0%). *Triphenylsilyl peroxide* ($C_{36}H_{30}Si_2O_2$) requires C, 78·5; H, 5·5; peroxidic O, 2·9%.

Reduction of Trimethyl-(tert.*-butylperoxy)silane.*—The peroxysilane (5·0 g.) was shaken for 5 hr. with aqueous sodium sulphite heptahydrate (8·5 g.; 2·5 mol.). A pentane extract yielded two main fractions: (i) b. p. 82—89°, n_D^{25} 1·3797; (ii) b. p. 89—95°, n_D^{25} 1·3848. It is known that trimethylsilanol (b. p. 99°, n_D^{20} 1·3880) with hexamethyldisiloxane (b. p. 100°, n_D^{25} 1·3748) forms a binary azeotrope (b. p. 89—91°, n_D^{20} 1·3800). Fractions (i) and (ii) combined were therefore heated under reflux with 6N-hydrochloric acid for 1 hr. A pentane extract yielded hexamethyldisiloxane, b. p. 98°, n_D^{25} 1·3752.

The aqueous solution from the reduction was distilled giving as a first fraction the *tert.*-butyl alcohol–water azeotrope, from which *tert.*-butyl alcohol was salted out with potassium chloride.

Silicon–Oxygen Heterolysis in Peroxysilanes.—(i) Trimethyl-(*tert.*-butylperoxy)silane (0·49 g.) and triphenylmethanol (0·78 g.) were dissolved in acetic acid (100 c.c.) containing sulphuric acid (0·1 c.c.). Next day the mixture was poured on ice, and the precipitate (0·83 g.) recrystallised from ethanol giving *tert.*-butyl triphenylmethyl peroxide (0·34 g.), m. p. and mixed m. p. 69—71°.

(ii) Trimethyl-(*tert.*-pentylperoxy)silane (0·35 g.) and xanthhydrol were dissolved in acetic acid (10 c.c.). Next day, *tert.*-pentyl 9-xanthenyl peroxide (recrystallised, 0·42 g.) was isolated, m. p. 39°.

(iii) Trimethyl-(αα-dimethylbenzylperoxy)silane (0·22 g.) and xanthhydrol (0·20 g.) in acetic acid yielded αα-dimethylbenzyl 9-xanthenyl peroxide (recrystallised, 0·20 g.), m. p. and mixed m. p. 96—97°.

Oxygen–Oxygen Heterolysis in Peroxysilanes.—(i) *The reaction of trimethylchlorosilane with perbenzoic acid.* Dry ammonia was passed through a solution of 80% perbenzoic acid (5·48 g.) and trimethylchlorosilane (6·48 g.) in ether (80 c.c.) for 30 min. at 0°. After 16 hr. the precipitate of ammonium chloride and ammonium benzoate (2·75 g.) was filtered off. Distillation of the filtrate gave two fractions: (*a*) b. p. 40—42°/0·1 mm., n_D^{25} 1·4817; and (*b*) b. p. 33—36°/0·01 mm., n_D^{25} 1·4810.

Fraction (*a*) was non-peroxidic. It was hydrolysed readily in the air and was identified as trimethylsilyl benzoate [Found: C, 61·5; H, 7·2; Si, 13·4%; *M* (by titration with NaOH), 200. Calc. for $C_{10}H_{14}O_2Si$: C, 61·8; H, 7·3; Si, 14·4%; *M*, 194]. Anderson [23] reports b. p. 221°/760 mm.

Fraction (*b*) was also non-peroxidic and was hydrolysed readily. Elementary analysis showed it to be *dimethylmethoxysilyl benzoate* (II; R = Me) (Found: C, 57·2; H, 6·8; Si, 13·0%; *M*, 207. $C_{10}H_{14}O_3Si$ requires C, 57·1; H, 6·7; Si, 13·4%; *M*, 210).

This was confirmed by an unambiguous preparation: The reaction between dimethylchlorosilane and methanol in pentane in the presence of ammonia gave dimethylmethoxychlorosilane. This (3·15 g.) and benzoic acid (3·05 g.) in ether (35 c.c.) were treated with ammonia for 30 min.

at 0° yielding ammonium chloride (1·0 g.) and dimethylmethoxysilyl benzoate, b. p. 33—35°/0·01 mm. (Found: C, 56·7; H, 6·89%; *M*, 212).

(ii) *The reaction of dimethylphenylchlorosilane with perbenzoic acid.* By the usual method, dimethylphenylchlorosilane (3·42 g.) and perbenzoic acid (3·46 g.) in ether was treated with ammonia, giving a liquid (3·50 g.). Distillation gave *dimethylphenoxysilyl benzoate* (II; R = Ph), b. p. 50°/0·001 mm., n_D^{25} 1·5261 (Found: C, 66·6; H, 6·9. $C_{15}H_{16}O_3Si$ requires C, 66·2; H, 5·9%). Hydrolysis gave phenol in 66% yield (toluene-*p*-sulphonate, m. p. 93°), and benzoic acid, m. p. 120°.

Identity was confirmed by independent synthesis: Dimethyldichlorosilane (25 g.) and phenol (15·6 g.) in pentane–ether when treated with pyridine (13·2 g.) gave only *dimethyldiphenoxysilane*, b. p. 135°/6 mm. (Found: C, 68·3; H, 6·5; Si, 11·6. $C_{14}H_{16}O_2Si$ requires C, 68·8; H, 6·6; Si, 11·5%). However, when ammonia was passed through a solution of the dichlorosilane (50 g.) and phenol (32 g.) in ether (150 c.c.) for 1 hr. at 0°, dimethylphenoxychlorosilane (9·7 g.) was obtained, b. p. 200°/760 mm. (Found: Cl, 16·9. Calc. for $C_8H_{11}OClSi$: Cl, 18·8%), together with a considerable residue of dimethyldiphenoxysilane, b. p. 130—132°/5 mm.

Dimethylphenoxychlorosilane (3·78 g.) and benzoic acid (2·45 g.), by the ammonia method, gave dimethylphenoxysilyl benzoate, b. p. 50°/0·001 mm., n_D^{25} 1·5259 (Found: C, 65·7; H, 6·6%). Hydrolysis gave phenol (toluene *p*-sulphonate, m. p. 93°).

(iii) *The action of acidic hydrogen peroxide on dimethylphenylchlorosilane.* A solution of 87% hydrogen peroxide (0·50 g.) and dimethylphenylchlorosilane (1·71 g.) in glacial acetic acid (20 c.c.) containing concentrated sulphuric acid (0·05 c.c.) was kept for 48 hr., bromine was then added, and, after a further 20 min., the mixture was poured into water. The precipitate, which was reprecipitated on acidification of its solution in 2N-sodium hydroxide, was recrystallised from light petroleum; it then had m. p. 65°. It was identified as *p*-bromophenol by formation of its toluene-*p*-sulphonate, m. p. 93°.

(iv) *Action of base on trimethyl-*(1 : 2 : 3 : 4*-tetrahydro-*1*-naphthylperoxy*)*silane.* A solution of the peroxysilane (0·59 g.) in triethylamine (1·28 g.) became pink during 65 hr. at 35°. It yielded 1 : 2 : 3 : 4-tetrahydro-1-oxonaphthalene 2 : 4-dinitrophenylhydrazone (0·5 g.), m. p. and mixed m. p. 257°.

(v) *The action of acid on triphenyl-*(tert.*-butylperoxy*)*silane.* (*a*) The peroxysilane was recovered after being treated in pentane with a cation-exchange resin (acid form).

(*b*) Hydrogen chloride was passed into an ethereal solution of the peroxysilane; the exothermic reaction caused the ether to boil, and after 4 hr. it was removed. The residue was largely triphenylchlorosilane; no phenol could be isolated after hydrolysis.

(*c*) The peroxysilane (2·50 g.) was suspended in acetic acid (100 c.c.) containing sulphuric acid (0·3 c.c.). Next day, excess of sodium hydroxide was added, and the solution then saturated with carbon dioxide. An ethereal extract gave a moist mixture (2·10 g.), m. p. *ca.* 135°, of triphenylsilanol, m. p. 150°, and *tert.*-butyl hydroperoxide. No phenol could be detected.

(*d*) The peroxysilane was treated with aluminium chloride (up to 1 mol.) in pentane or benzene at 65° for periods of up to 3 hr. From all these experiments the peroxysilane was recovered and no phenol could be detected.

(vi) *The action of base on dimethylphenyl-*(tert.*-butylperoxy*)*silane.* (*a*) A solution of the peroxysilane (0·59 g.) and triethylamine (1·36 g.) in benzene (20 c.c.) was kept at 50° for 24 hr. and at 80° for 4 hr. The peroxysilane (0·63 g.) was recovered (Found: peroxidic O, 5·75%).

(*b*) A solution of the peroxysilane (0·57 g.), triethylamine (1·98 g.), and *tert.*-butyl hydroperoxide (1·06 g.) in benzene (20 c.c.) was kept at 50° for 6 days. Evacuation at 0·1 mm. left an oil (1·05 g.) containing some solid (Found, on the mixture: peroxidic O, 2·28%). The residue was heated at 100° for 1 hr. with 6N-hydrochloric acid (20 c.c.), then decolorised with charcoal. No phenol could be detected by the bromate–bromide method.

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