THE CHEMISTRY OF ORGANOMETALLIC AND ORGANOMETALLOID PEROXIDES

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I. INTRODUCTION

A. HISTORICAL

The chemistry of organometallic and organometalloid peroxides has received increasing attention over the past decade because of its importance in autoxidation and polymerization processes. The study of the chemistry of organometallic and organometalloid peroxides probably commenced more than a century ago, when Frankland (76, 77) reported the autoxidation of dimethylzinc; but it was Demuth and Meyer (71) about 40 years later who clearly defined that an organozinc peroxide was an intermediate in this reaction. After that time, a number of communications appeared dealing with oxidative processes of organometals and organometalloids involving peroxide intermediates. However, it was not until the 1950's that Davies and his students in England, and later Rieche and his group in Germany, made an effort to investigate systematically the preparation and properties of various organometallic and organometalloid peroxides. Their studies provided the basis for many other investigations, and, at present, an extensive literature exists on this subject. In spite of the large volume of literature, the available review articles (35, 51, 79a, 87, 95, 106, 134, 175, 181–183, 193a, 194, 195) are incomplete and some are printed in journals which are not readily available. The present article is an attempt to present a comprehensive and critical review of the chemistry of organometallic and organometalloid peroxides.

B. SCOPE AND LIMITATIONS

This review describes the chemistry of organometallic and organometalloid peroxides, *i.e.*, of compounds

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which have at least one peroxy group linked directly to a metal or metalloid. Compounds which meet this requirement are divided into the following major classes: hydroperoxides of structure I, unsymmetric peroxides of structure II, symmetric peroxides of structure III, and alkali and alkali earth derivatives of organic hydroperoxides of structure IV. The review covers the literature published through March 1966. It deals exhaustively with the literature of peroxides of structures I, II, and III, where M = Zn, Cd, Hg, B, Al, Si, Ge, Sn, Pb, P, As, Sb, and S. No attempt was made to survey all compounds of structure IV

R_nMOOH	R_nMOOR' or $R_nM(X)OOR'$	R_nMOOMR_n or $R_nM(X)OO(X)MR_n$	$(ROO)_nM$
I	II	III	IV

R = alkyl, acyl, alkoxy, aryloxy, aralkyl, aryl
R′ = alkyl, aralkyl
M = metal or metalloid
X = O, OH, halogen, peroxyalkyl
n = 1–4

where M = Li, Na, K, Cs, Rb, Mg, Ca, Sr, and Ba. Thus, not all autoxidative reactions of Grignard compounds and not all preparations and reactions of salts of organic hydroperoxides and peracids are included. Nevertheless, it is believed that the most important preparations and theoretical aspects of these peroxides are covered. Excluded from the review are almost all alkali and alkali earth base-catalyzed autoxidative reactions which have been postulated to proceed through organometallic intermediates of organic hydroperoxides. A review article covering this particular topic is now in preparation (193).

C. NOMENCLATURE

The nomenclature of *Chemical Abstracts* is used wherever possible. However, in some instances, the original nomenclature used by different authors was retained to avoid confusion and to facilitate cross-checking.

II. PHYSICAL PROPERTIES

The information concerning the physical properties of organometallic and organometalloid peroxides is scanty. Davies and co-workers (65, 66) investigated by nuclear magnetic resonance the structure and reactions of peroxyborons. A limited amount of information is also available about the infrared spectra of peroxides of silicon (46, 187, 197), germanium (60, 197), tin (197), and lead (197).

The ionic or covalent character of the metal–oxygen bond in various organometallic and organometalloid peroxides can be estimated by the use of the electronegativity scale (142, 173). On the basis of this estimate it can be expected that organoperoxides of groups Ia and IIa of the periodic table will have mostly ionic character. As one proceeds through groups IIb and IIIa to IVa, Va, and VIa, the partial ionic character should decrease as the partial covalent character increases. With this change, the physical properties of these peroxides should also change from those of typically ionic saltlike compounds to those of typically organic compounds. This trend has indeed been observed. Thus, while peroxides of groups Ia and IIa are insoluble in most organic solvents, the peroxides of groups IIb, IIIa, IVa, Va, and VIa become increasingly soluble. Furthermore, most solid peroxides of metalloids have well-defined melting points, while the liquid peroxides can be distilled. Thus, peroxides of metalloids behave as covalent organic compounds. Most organometallic and organometalloid peroxides are nonexplosive and insensitive to friction and impact, but can decompose violently on rapid heating. Some peroxides, notably those of lead, are unstable at room temperature and can be stored for prolonged periods of time only under refrigeration. Many peroxides are sensitive to moisture so that their preparation should be carried out under anhydrous conditions.

TABLE I

HYDROPEROXIDES PRODUCED BY AUTOXIDATION OF ORGANOLITHIUM COMPOUNDS

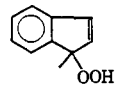
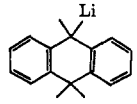
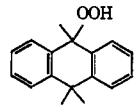
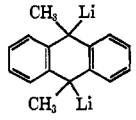
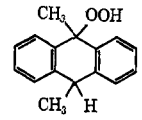
RLi	ROOH	Yield, %	Ref
BuLi	BuOOH	31	91
n-BuLi	n-BuOOH	36	201
		84	92
			93
			93

TABLE II

PRODUCTS OF THE AUTOXIDATION OF ALKYL AND ARALKYLLITHIUM COMPOUNDS

RLi	ROH	Yield, %	Ref
BuLi	BuOH	75	134
2-Picolyllithium	2-Pyridylmethanol		72
Tetrahydronaphthyl-		27	
lithium	Tetralol	47	134

III. CHEMICAL PROPERTIES

A. ORGANOPEROXIDES OF ELEMENTS OF GROUP Ia

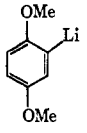
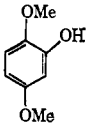
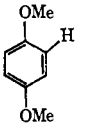
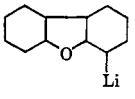
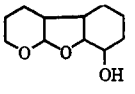
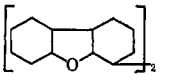
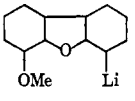
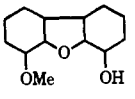
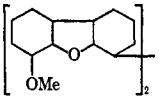
1. *Lithium*

a. Preparation of Organolithium Peroxides

Organolithium peroxides are prepared by the reaction of a hydroperoxide with either a concentrated

TABLE III

PRODUCTS OF THE AUTOXIDATION OF ARYLLITHIUM COMPOUNDS

RLi	ROH	Yield, %	RR	Yield, %	RH	Yield, %	Me | RCHOH	Yield, %	Ref
PhLi	PhOH	26	Ph_2	25					140, 156
	PhOH	30							38
	PhOH	18	Ph_2	64			Ph(Me)CHOH	6	134
Benzyllithium	Benzyl alcohol	28	Bibenzyl	14					134
p-Tolyllithium	*p*-Cresol	37	*p,p'*-Ditolyl	35	Toluene	8	*p*-Tolyl methyl carbinol	11	134
m-Tolyllithium	*m*-Cresol	54	*m,m'*-Ditolyl	17	Toluene	13	*m*-Tolyl methyl carbinol	22	134
o-Tolyllithium	*o*-Cresol	54	*o,o'*-Ditolyl	5	Toluene	10	*o*-Tolyl methyl carbinol	28	134
p-Anisyllithium	*p*-Anisyl alcohol	36	*p,p'*-Dianisyl	26					134
		40				54			134 38
p-Diphenyllithium			Terphenyl	86	Diphenyl	7			134
p-Diphenyllithium	*p*-Biphenyl alcohol	18							38
α-Naphthyllithium	*α*-Naphthol	28	*α,α'*-Dinaphthyl	5	Naphthalene	59			134
2-MeO-1-naphthyllithium	2-MeO-1-naphthol	7							38
		~45							80
		~20		3.3					80

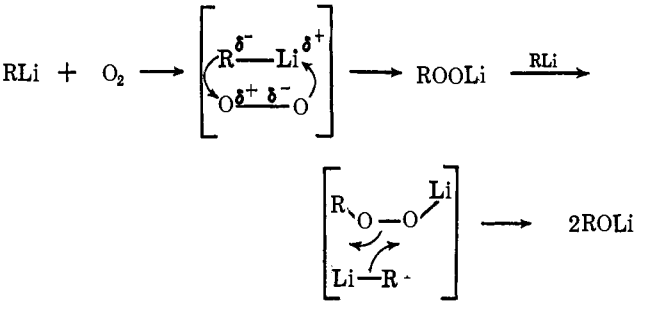
solution of lithium hydroxide (51) or with lithium hydride in tetrahydrofuran (50, 147). Lithium derivatives of organic peracids are similarly prepared (51, 147).

$$\text{ROOH} \xrightarrow[\text{LiH}]{\text{LiOH or}} \text{ROOLi}$$

R = alkyl or aralkyl

b. Organolithium Peroxides as Intermediates

Oxidations of alkyl-, aralkyl-, and aryllithium compounds by molecular oxygen have been postulated to proceed through organolithium peroxide intermediates (81, 91, 92, 95, 134). Although peroxides have been detected and even isolated (91, 92) (see Table I) from autoxidative experiments with organolithium compounds, the primary peroxy intermediates have not been isolated because of their reactivity. Thus, the oxidation of alkyl- and aralkyllithium compounds produces first a peroxy intermediate which interacts rapidly with the organolithium compound to give the corresponding lithium alcoholate. On hydrolysis, the alcoholate then produces the corresponding alcohol (72, 91, 92, 134) (see Table II). To account for this observation, Müller and Töpel proposed in 1939 the mechanism (134)



In accordance with this mechanism, it is found that the yield of the peroxy intermediate decreases as the ionic character of the organometallic compound increases (95).

The autoxidation of aryllithium compounds in solvents such as ether produces a complex mixture of products (see Table III).

$$\text{ArLi} + \text{O}_2 \xrightarrow{\text{RCH}_2\text{OR}'} \text{ArOH} + \text{ArAr} + \text{ArH} + \text{Ar}\underset{\underset{\text{R}}{|}}{\text{CH}}_2\text{OH}$$

To account for these products, the following mechanism is proposed (95)

$$\mathrm{ArLi} + \mathrm{O_2} \rightarrow \mathrm{ArOOLi} \xrightarrow{\mathrm{ArLi}} \mathrm{ArOLi}$$

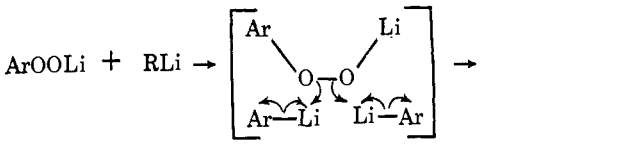
$$\mathrm{ArOOLi} \rightarrow \mathrm{Ar}\cdot + \cdot\mathrm{OOLi}$$

$$2\mathrm{Ar}\cdot \rightarrow \mathrm{Ar_2}$$

$$\mathrm{Ar}\cdot + \mathrm{RCH_2OR'} \rightarrow \mathrm{ArH} + \mathrm{\dot{C}HOR'}\ (\mathrm{R})$$

$$\mathrm{Ar}\cdot + \mathrm{\dot{C}HOR'}\ (\mathrm{R}) \rightarrow \mathrm{ArCHOH}\ (\mathrm{R}) + \mathrm{R'}\cdot \xrightarrow{\text{H donor}} \mathrm{R'H}$$

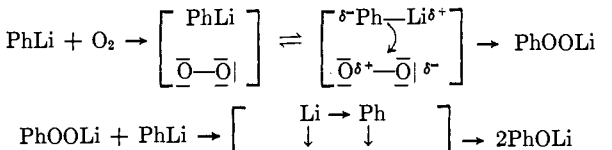
However, a concerted mechanism can also be invoked to explain the formation of biaryl and phenol (95)



$$\mathrm{ArOLi} + \mathrm{Ar_2} + \mathrm{Li_2O}$$

Similar mechanisms are advanced by Razuvayev and co-workers (156), who studied the autoxidation of phenyllithium in benzene labeled with ^{14}C. Two products were obtained, phenol and biphenyl. The phenol had no labeled atom but the biphenyl had an activity equal to 12.5% of the starting activity of benzene.

The formation of phenol is postulated to proceed *via* the metal hydroperoxide.



$$\mathrm{PhOOLi} + \mathrm{PhLi} \rightarrow \left[\begin{array}{c} \mathrm{Li} \rightarrow \mathrm{Ph} \\ \downarrow \quad\quad \downarrow \\ \mathrm{Ph{-}\underline{O}{-}\underline{O}} \leftarrow \mathrm{Li} \end{array}\right] \rightarrow 2\mathrm{PhOLi}$$

$$2\mathrm{PhOLi} + \mathrm{H_2O} \rightarrow 2\mathrm{PhOH} + \mathrm{Li_2O}$$

Two mechanisms for the formation of biphenyl are considered. The first mechanism is the reaction between two molecules of phenyllithium and a molecule of oxygen to yield inactive biphenyl

$$2\mathrm{PhLi} + \mathrm{O_2} \rightarrow \left[\begin{array}{l} \mathrm{Ph\ Li}\ldots\ldots\mathrm{O} \\ \vdots \quad\quad\quad\quad | \\ \mathrm{Ph\ Li}\ldots\ldots\mathrm{O} \end{array}\right] \rightarrow \mathrm{Ph_2} + \mathrm{Li_2O_2}$$

The second mechanism accounts for the formation of labeled biphenyl through the loss of hydrogen and lithium from the intermediate complex of phenyllithium and the solvent

$$\mathrm{PhLi} + {}^{14}\mathrm{C_6H_6} \rightarrow [\mathrm{C_6H_5Li}{}^{14}\mathrm{C_6H_6}] \xrightarrow{\mathrm{PhOOLi}} \mathrm{C_6H_5}{}^{14}\mathrm{C_6H_5} + \mathrm{PhOH} + \mathrm{Li_2O}$$

The first interpretation is favored because only 12.5% of the label is detected in the biphenyl product.

A peroxy intermediate and a free radical mechanism was suggested by Gilman and George (81) to account for the products of autoxidation of triphenylsilyllithium in tetrahydrofuran (THF).

$$\mathrm{Ph_3SiLi} + \mathrm{O_2} \rightarrow \mathrm{Ph_3SiOOLi} \rightarrow \mathrm{Ph_3SiO}\cdot + \mathrm{LiO}\cdot$$

$$\mathrm{Ph_3SiO}\cdot + \mathrm{Ph_3SiLi} \rightarrow \mathrm{Ph_3SiOLi} + \mathrm{Ph_3Si}\cdot$$

$$\mathrm{Ph_3Si}\cdot + \mathrm{THF} \rightarrow \mathrm{Ph_3SiH}$$

The observation that products of autoxidation of organolithium compounds (R = *n*-Bu) initiate polymerization of vinyl monomers supports the suggestion that free radical intermediates are formed in autoxidative processes of organolithium compounds (78).

Autoxidations of alkali derivatives of aromatic hydrocarbons with condensed ring systems (A), such as naphthalene and anthracene, frequently yield the original hydrocarbon and an inorganic peroxide. The reaction of a hydrocarbon (A) with one alkali metal (M) produces a paramagnetic adduct; whereas with two alkali metals, a diamagnetic adduct is obtained.

$$\mathrm{A} \underset{-\mathrm{M}}{\overset{+\mathrm{M}}{\rightleftharpoons}} \mathrm{A}\cdot^{-}\mathrm{M}^{+} \underset{-\mathrm{M}}{\overset{+\mathrm{M}}{\rightleftharpoons}} \mathrm{A}^{2-}$$

In spite of an odd electron, the 1:1 adducts do not dimerize or combine with oxygen readily. Instead, a transfer of electrons to oxygen occurs and the original hydrocarbon and an inorganic peroxide are obtained.

$$\mathrm{A}\cdot^{-}\mathrm{M}^{+} + \mathrm{O_2} \rightarrow \mathrm{A} + \mathrm{M}^{+}\mathrm{O_2}^{-}$$

Nevertheless, organic hydroperoxides have been observed, but they are derived from the corresponding hydroaromatic compound. This result is attributed to the interaction of the alkali adduct with solvent molecules with subsequent autoxidation of the hydroaromatic–alkali adduct to give the observed products (95).

$$\mathrm{A}^{2-} + (\mathrm{RCH_2CH_2OR'}) \rightarrow \mathrm{HA}^{-} \xrightarrow{\mathrm{M}^{+}} \mathrm{HA}^{-}\mathrm{M}^{+} + \mathrm{R'O}^{-} + \mathrm{CH_2{=}CHR}$$

$$\mathrm{HA}^{-}\mathrm{M}^{+} + \mathrm{O_2} \rightarrow \mathrm{HAOOM} \xrightarrow{\mathrm{H_2O}} \mathrm{HAOOH}$$

Thus, autoxidation of monolithium anthracene and dilithium 9,10-dimethylanthracene produces hydrogen peroxide and 9-hydroperoxy-9,10-dihydroanthracene and 9-hydroperoxy-9,10-dimethyldihydroanthracene, respectively (93).

2. *Sodium*

a. Preparation of Organosodium Peroxides

The saltlike organosodium peroxides are prepared by the reaction of an alkyl or aralkyl hydroperoxide with a concentrated solution of sodium hydroxide at room temperature (37, 51, 86, 94, 96, 97, 190). The sodium salt of a number of tertiary alkyl hydroperoxides, *e.g.*, triphenylmethyl hydroperoxide, cannot be prepared by this method. In such cases, the sodium salt can usually be obtained by shaking a solution of the hydroperoxide with solid sodium hydroxide for a prolonged period (40, 51). Sodium salts are also obtained from the reaction of hydroperoxides or peracids with sodium hydride in tetrahydrofuran (50, 147).

Other methods employ sodium alkoxides (70, 161, 165, 167, 168) or sodamide (163, 165, 166, 168) to prepare sodium salts of hydroperoxides. Sodium salts of peracids are also obtained by the reaction of the peracid with an alcoholic solution of sodium hydroxide (98).

$$\mathrm{ROOH + NaX \rightarrow \underset{V}{ROONa} + HX}$$

$$\mathrm{X = H, OH, alkoxy, NH_2}$$

Sodium *t*-butylate and an excess of *t*-butyl hydroperoxide react in *t*-butyl alcohol to give the sodium salt of *t*-butyl hydroperoxide containing *t*-butyl alcohol of crystallization (129).

$$t\text{-BuONa} + t\text{-BuOOH} \xrightarrow{t\text{-BuOH}} t\text{-BuOONa}\cdot t\text{-BuOH}$$

The reaction of cumyl hydroperoxide with a 25% solution of sodium hydroxide yields a hexahydrate which is converted to a trihydrate at 80° (22).

$$\mathrm{PhMe_2COONa\cdot 6H_2O \xrightarrow[\Delta]{80^\circ} PhMe_2COONa\cdot 3H_2O}$$

Addition of *n*-heptane to a concentrated solution of equimolar quantities of cumyl hydroperoxide and its sodium salt in toluene produces a crystalline addition compound, VI (23, 189).

$$\underset{VI}{\mathrm{PhMe_2COONa\cdot PhMe_2COOH}}$$

Sodium cumyl peroxide (V, R = CMe_2Ph) is a colorless crystalline substance which is unstable in air and which readily absorbs moisture. It is stable at room temperature, but on heating it decomposes without melting, by second-order kinetics with loss of peroxidic oxygen (189). Addition of cumyl hydroperoxide to a solution of sodium cumyl peroxide in toluene accelerates the rate of decomposition of both peroxides (23, 189). Crystals of V, R = CMe_2Ph, 99% pure, are obtained by keeping the compound V at 0° for 10–15 hr in petroleum ether (190). The reaction of sodium cumyl peroxide in aqueous carbon dioxide yields cumyl hydroperoxide (190).

Kato (108) reported the autoxidation of cumene in a 50% solution of sodium hydroxide in the presence manganese naphthalate. The reaction of the product in aqueous carbon dioxide yielded cumene, α-cumyl alcohol, a trace of acetophenone, and cumyl hydroperoxide.

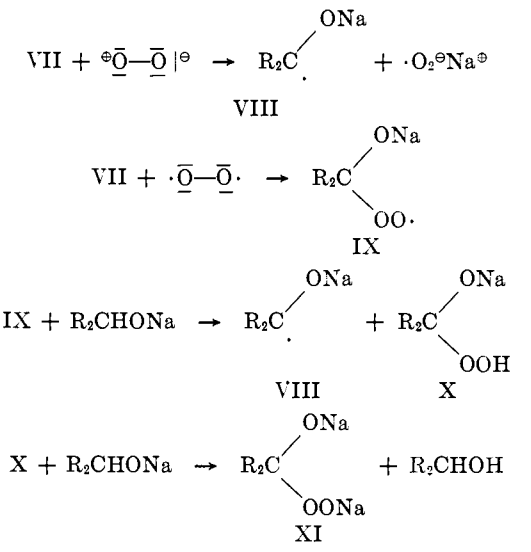
b. Organosodium Peroxides as Intermediates

Triphenylmethylsodium reacts with oxygen to form first the triphenylmethyl radical which is then converted by molecular oxygen to triphenylmethylperoxide (16, 178, 181).

$$\mathrm{2Ph_3CNa + O_2 \rightarrow 2Ph_3C\cdot + Na_2O_2}$$

$$\mathrm{2Ph_3C\cdot + O_2 \rightarrow Ph_3COOCPh_3}$$

SCHEME I



The sodium salt of triphenylmethyl hydroperoxide is a possible intermediate. In contrast to the oxidation of alkali triarylmethyls, oxidation of diphenylmethylsodium leads to the formation of a hydrocarbon (207).

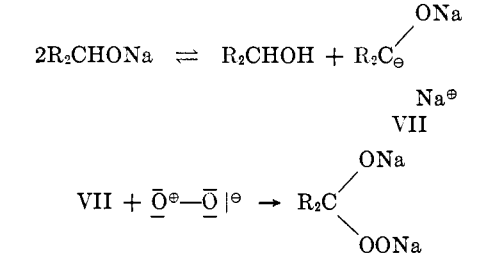
$$\mathrm{2Ph_2CHNa + O_2 \rightarrow Na_2O_2 + Ph_2CHCHPh_2}$$

Similarly, disodium stilbene is converted to stilbene by dry oxygen gas (177).

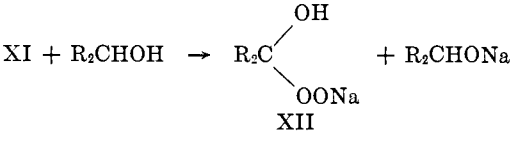
Autoxidation of secondary alcohols in benzene in the presence of sodium butyl alcoholate gives sodium hydroperoxide and the corresponding ketone. For example, benzhydrol is converted to benzophenone (119).

$$\mathrm{Ph_2CHOH} + t\text{-BuONa} \xrightarrow[O_2]{20^\circ} \mathrm{Ph_2C{=}O + NaOOH}$$

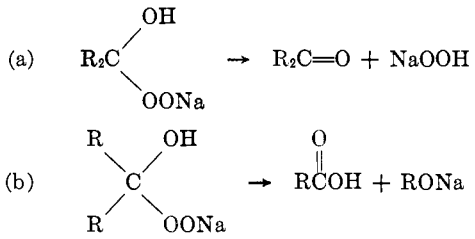
Autoxidation of sodium benzophenone in tetrahydrofuran yields a sodium peroxide (NaO_2) and benzophenone (119). Le Berre (117, 118, 119, 120) postulates a sodium peroxide intermediate in the autoxidation of secondary sodium alcoholates. The following mechanism is proposed



Le Berre also postulates a radical mechanism (Scheme I) to arrive at the same intermediate (XI). The intermediate, XI, then reacts with the alcohol

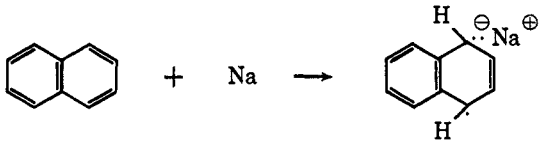


XII may decompose either by path a or b.



Le Berre has written a review on the autoxidation of alkali alcoholates (117).

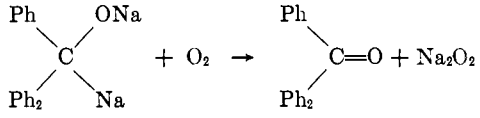
Like the reaction of lithium, the condensation of sodium with an aromatic ring system such as naphthalene produces a paramagnetic radical anion. In contrast to lithium, the sodium metal forms only a monoadduct.



Autoxidation of this adduct results in the recovery of naphthalene and the formation of sodium peroxide (93). As in the case of lithium, no organic peroxide is observed and the electrons are transferred from the hydrocarbon to the oxygen. Similarly, autoxidation of anthracenyl-, pyridyl-, tetraphenylethylene-, and azobenzenylsodium compounds produces a sodium peroxide (NaO_2) (120). Also, the reaction of benzophenonesodium with oxygen results in the recovery of benzophenone and the formation of a sodium peroxide (NaO_2) (119). The reaction may proceed as follows

$$Ph_2\dot{C}ONa + O_2 \rightarrow Ph_2\underset{\underset{O_2\cdot}{|}}{C}ONa \rightarrow Ph_2C{=}O + NaO_2$$

The reaction of disodium phenyl biphenyl ketone with molecular oxygen (177) probably proceeds by an analogous mechanism.



3. *Potassium*

a. Preparation of Organopotassium Peroxides

Organopotassium peroxides are prepared by the reaction of a hydroperoxide with a concentrated solution of potassium hydroxide at room temperature (37, 88). Solid potassium *t*-butyl peroxide was prepared by mixing *t*-butyl hydroperoxide with a 5–6 *M* solution of potassium hydroxide in methanol. Methanolic solutions of potassium *t*-butyl peroxide loose all peroxidic oxygen on boiling for 30 min (37).

A potassium salt of *t*-butyl hydroperoxide containing *t*-butyl alcohol of crystallization is obtained from the reaction of potassium *t*-butylate and excess *t*-butyl hydroperoxide in *t*-butyl alcohol (129).

$$t\text{-BuOK} + t\text{-BuOOH} \xrightarrow{t\text{-BuOH}} t\text{-BuOOK}\cdot t\text{-BuOH}$$

b. Organopotassium Peroxides as Intermediates

Autoxidation of a secondary alcohol in benzene solution in the presence of potassium *t*-butyl alcoholate yields the corresponding ketone and a potassium peroxide. For example, autoxidation of benzhydrol produces benzophenone (118, 120).

$$t\text{-BuOK} + Ph_2CHOH \xrightarrow[O_2]{20^\circ} Ph_2C{=}O + KOOH$$

$$2KOOH \rightarrow KO_2 + KOH + H_2O$$

Autoxidation of a potassium adduct of benzophenone results in the formation of a potassium peroxide and recovery of benzophenone. For mechanistic considerations of these reactions, see the sections on lithium and sodium.

B. ORGANOPEROXIDES OF ELEMENTS OF GROUP IIa

1. *Magnesium*

Organomagnesium Peroxides as Intermediates

Peroxides of magnesium have been postulated as intermediates in the oxidation of Grignard reagents by molecular oxygen (95, 175, 200, 201). However, in most cases, alcohols or phenols are isolated from the autoxidations of alkyl or aryl Grignard compounds, respectively (see Table IV). In 1903, Bouveault (34) obtained benzyl alcohol from benzylmagnesium chloride, and Bodroux (32) converted phenylmagnesium halide to phenol by autoxidation. Grignard (83), Sabatier (176), and Hesse (89) converted other Grignard reagents with molecular oxygen to the corresponding hydroxy derivatives. In 1909, Wuyts (209) proposed that these reactions proceed *via* peroxide intermediates which are reduced by the unreacted Grignard reagent to yield the hydroxy derivatives (95, 130, 135, 146).

$$R_3CMgX + O_2 \rightarrow R_3COOMgX \xrightarrow{R_3CMgX} 2R_3COMgX \xrightarrow{H_2O} 2R_3COH$$

However, autoxidation of α-methylindole magnesium halide produces an indoxyl ether instead of a hydroxy derivative (136).

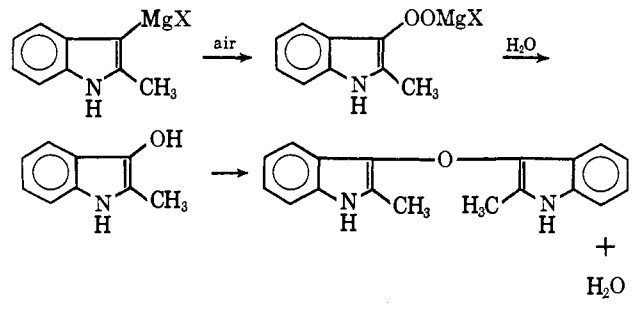


TABLE IV

PRODUCTS OF AUTOXIDATION OF GRIGNARD REAGENTS: ALCOHOLS AND PHENOLS

Grignard reagent	Product	Yield, %	Ref
EtMgBr	EtOH	78	208
Cyclohexyl MgCl	Cyclohexanol	80	208
PhMgBr	PhOH	27.8	208
	PhOH	24	175
	PhOH	37	93
	PhOH	26	82
	PhOH	30–36	20
	PhOH	10	32
PhMgI	PhOH	8.5	128
p-Tolyl MgBr	*p*-Cresol	15.3	82
$PhCH_2MgCl$	PhCHOH	80	34
$PhCH_2CH_2MgBr$	$PhCH_2CH_2OH$	60	83
PhOPhMgCl-*p*	PhOPhOH-*p*		127
Ph_3CMgBr	Ph_3COH	54	15
p-$CH(CH_3)_2C_6H_4CH_2MgCl$	*p*-$CH(CH_3)_2C_6H_4CH_2OH$	60	25
Bornyl MgCl	Borneol	65–85	89
	Isoborneol[a]	5–8	89
Camphene chlorohydrate Mg	Borneol	45	89
	Isoborneol[b]		

[a] +10–20% hydrodicamphene. [b] +21% hydrodicamphene and 34% camphene–camphane.

Oxidation of aryl Grignard reagents in ether results in a complex mixture of products.

$$\mathrm{ArMgX} \xrightarrow[\text{ether}]{O_2} \underset{\text{XIII}}{\mathrm{ArOH}} + \underset{\text{XIV}}{\mathrm{Ar_2}} + \underset{\text{XV}}{\mathrm{ArH}} + \underset{\text{XVI}}{\mathrm{Ar\underset{\underset{R}{|}}{CHOH}}}$$

$$R = CH_3;\ X = Cl, Br$$

In almost all autoxidative studies of Grignard reagents, either chloro or bromo derivatives were employed. With iodo derivatives different results were reported. Meisenheimer and Schlichenmaier (128) observed the formation of alkyl and aryl iodides. They proposed a complex mechanism to account for these products (95, 128).

The autoxidation products of phenylmagnesium halides in ether have been found to be: phenol (XIII, Ar = Ph) (20, 32, 82, 93, 95, 128, 146, 148, 175, 208); biphenyl (XIV, Ar = Ph) (34, 82, 93, 95, 128, 148, 175, 208, 209); benzene (XV, Ar = Ph) (82, 93, 128, 208, 209); methylphenyl carbinol (XVI, Ar = Ph, R = Me) (82, 93, 128, 208, 209); and benzoic acid (93).

Hock and Ernst proposed a radical mechanism to account for the mixture of products in the autoxidation of arylmagnesium halides in ether (95).

$$\mathrm{ArMgX} + O_2 \rightarrow \mathrm{ArOOMgX} \xrightarrow{\mathrm{ArMgX}} \underset{\text{XIII}}{2\mathrm{ArOH}}$$

$$2\mathrm{Ar}\cdot + \mathrm{EtOEt} \rightarrow \underset{\text{XV}}{\mathrm{ArH}} + CH_3\dot{C}HOEt$$

$$CH_3\dot{C}HOEt + \mathrm{ArMgX} \rightarrow \underset{\text{XVI}}{\mathrm{Ar\underset{\underset{CH_3}{|}}{CHOMgX}}} + \mathrm{Et}\cdot$$

$$2\mathrm{Ar}\cdot \rightarrow \underset{\text{XIV}}{\mathrm{Ar_2}}$$

With increasing dilution, the yield of biaryl decreases and the yield of carbinol increases (95). The yield of phenol in the autoxidation of phenylmagnesium bromide is increased by admixing aliphatic Grignard reagents to the aryl Grignard compounds (100, 109). The following mechanism was proposed to account for this observation

$$\mathrm{EtMgBr} + O_2 \rightarrow \mathrm{EtOOMgBr} \xrightarrow{\mathrm{EtMgBr}} \mathrm{EtOMgBr}$$

$$\mathrm{PhMgBr} + \mathrm{EtOOMgBr} \rightarrow \mathrm{EtOMgBr} + \mathrm{PhOMgBr}$$

However, the addition of a cobalt salt catalyst results in a diminished yield of phenols, and mainly biaryls are isolated (109).

Porter and Steel (146) found as autoxidation products of phenylmagnesium halide compounds XIII, XIV, XV, XVI (Ar = Ph), and, in addition, phenyl ether, XVII, XVIII, and a quinone. To account for some

$$\underset{\text{XVII}}{C_6H_5C_6H_4C_6H_5} \qquad \underset{\text{XVIII}}{HOC_6H_4C_6H_4OH}$$

of these products, Scheme II was proposed (175).

SCHEME II

$$\mathrm{PhMgBr} + O_2 \rightarrow \mathrm{PhOOMgBr} \xrightarrow{\mathrm{PhMgBr}} 2\mathrm{PhOMgBr}$$

$$\downarrow \mathrm{PhOMgBr} \qquad\qquad \downarrow H_2O$$

$$\underset{\text{XIX}}{[\mathrm{PhOOPh}]} + (\mathrm{MgBr})_2O \qquad \mathrm{PhOH} + \mathrm{MgBrOH}$$

$$\mathrm{XIX} \rightarrow \mathrm{PhOPh} + O_2$$

$$\mathrm{XIX} \rightarrow \underset{\text{XVIII}}{HOC_6H_4C_6H_4OH}$$

Phenyl peroxide (XIX) has not been isolated. However, triphenylmethyl peroxide was detected in an analogous autoxidation of triphenylmethylmagnesium chloride (15, 179, 180).

TABLE V

HYDROPEROXIDES PRODUCED BY AUTOXIDATION OF GRIGNARD REAGENTS

Grignard reagent	Hydroperoxide	Yield, %	Ref
EtMgCl	EtOOH	57	201
EtMgBr	EtOOH	28	201
n-BuMgCl	*n*-Butyl hydroperoxide	57	201
	n-Butyl hydroperoxide	80	91
t-BuMgCl	*t*-Butyl hydroperoxide	84	91
	t-Butyl hydroperoxide	86	201
t-AmMgCl	*t*-Amyl hydroperoxide	92	201
i-AmMgCl	Isoamyl hydroperoxide	74	91
i-AmMgBr	Isoamyl hydroperoxide	10	91
3-MeBu-2-MgBr	3-Methylbutyl 2-hydroperoxide		42
2-*n*-Octyl MgCl	2-*n*-Octyl hydroperoxide	91	201
$ClMg(CH_2)_6MgCl$	$HOO(CH_2)_6OOH$	44	92
Cyclohexyl MgCl	Cyclohexyl hydroperoxide	83	91
	Cyclohexyl hydroperoxide	66	201
	Cyclohexyl hydroperoxide	79	92
Cyclohexyl MgBr	Cyclohexyl hydroperoxide	30	201
Benzyl MgCl	Benzyl hydroperoxide	30	91, 201
Bornyl MgCl	Bornyl hydroperoxide	56	202
	Isobornyl hydroperoxide	44	202
Mesitylene MgBr	Mesitylene hydroperoxide	30	74

In support of Wuyts' original suggestion (209), Walling and Buckler (200, 201) and Hock and Ernst (92) showed that peroxides can be isolated from autoxidation of Grignard compounds (see Table V). The intermediate magnesium peroxide was not isolated but was detected by titration (92).

2. *Calcium, Strontium, and Barium*

Preparation of Organoperoxides of Calcium, Strontium, and Barium

The saltlike derivatives of *t*-butyl hydroperoxide are prepared in high yield from the corresponding metal salt oxide and *t*-butyl hydroperoxide (129).

$$2t\text{-BuOOH} + \text{MO} \rightarrow \text{M(OO-}t\text{-Bu)}_2 + \text{H}_2\text{O}$$

M = Sr, Ba

Calcium and barium salts of peracetic acid are prepared by the reaction of the acid with calcium or barium hydride (50).

$$2\underset{\underset{\text{O}}{\|}}{\text{CH}_3\text{COOH}} + \text{MH}_2 \rightarrow \underset{\underset{\text{O}}{\|}}{(\text{CH}_3\text{COO})_2\text{M}} + 2\text{H}_2$$

M = Ca, Ba

C. ORGANOPEROXIDES OF ELEMENTS OF GROUP IIb

1. *Zinc*

a. Preparation of Organozinc Peroxides

Zinc peroxides have been prepared by autoxidation. Frankland (76) found in 1853 that dimethylzinc inflames in air forming white fumes. In contact with pure oxygen, an explosion occurs. Later work on the oxidation of diethylzinc in ethereal solution led him to propose the formation of an alkoxide, XX (77). Butlerow (36) argued for the formation of a methyl–methoxy derivative in the oxidation of dimethylzinc in methyl iodide solution. Analysis of the crystalline product indicated methylmethoxyzinc, XXI, mixed with a

$$\underset{\text{XX}}{\text{Zn(OR)}_2}$$

R = Me, Et

$$\underset{\text{XXI}}{\text{ZnMe(OMe)}}$$

little XX (R = Me). Demuth and Meyer (71) found, in 1890, that the product formed in the autoxidation of diethylzinc liberates iodine from potassium iodide and decomposes explosively on heating. They proposed the formation of a monoperoxide, XXII.

$$\text{ZnEt}_2 + \text{O}_2 \rightarrow \underset{\text{XXII}}{\text{EtZnOOEt}}$$

An attempt to reconcile the various observations was made by Thompson and Kelland (196). Dimethylzinc under certain conditions undergoes a slow oxidation in which methylzinc methoxide is the final product, but the peroxidic compound, XXII (R = Me), may be an intermediate in this reaction (17, 181, 196). Similarly, Hock, Kropf, and Ernst proposed intermediate peroxides in the first step of autoxidation (95). The peroxide is then decomposed in the next step by some of the unreacted metal organic compound.

$$\text{R}_2\text{Zn} + \text{O}_2 \rightarrow \underset{\text{XXII}}{\text{ROOZnR}} \xrightarrow{\text{R}_2\text{Zn}} \underset{\text{XXI}}{2\text{ROZnR}}$$

In the case of lithium or magnesium, the first step proceeds rapidly at room temperature and no peroxide can be isolated. But, at −70°, such peroxides are stabilized and can be detected. In the case of zinc and cadmium alkyls, the first step is a slow process and the reaction produces even at 0° good yields of peroxides. Abraham (1, 2) showed that autoxidation of diethyl- and di-*n*-butylzinc with a rapid stream of oxygen yields peroxides XXIII, R = Et, *n*-Bu. However,

$$\underset{\text{XXIII}}{\text{Zn(OOR)}_2}$$

slow oxidation of diethyl-, di-*n*-butyl-, and di-*t*-butylzinc produces mainly the corresponding dialkoxy derivatives, XX, and only a small quantity of peroxide, XXIV. The initial product of the autoxidation

$$\underset{\text{XX}}{\text{Zn(OR)}_2} \qquad \underset{\text{XXIV}}{\text{Zn(R)OOR}}$$

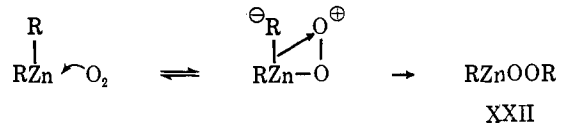
appears to be the peroxide, XXII, which can react further with oxygen to give the product XXIII. Com-

$$\text{R}_2\text{Zn} \xrightarrow{\text{O}_2} \underset{\text{XXII}}{\text{RZnOOR}} \xrightarrow{\text{O}_2} \underset{\text{XXIII}}{\text{Zn(OOR)}_2}$$

pounds XXII and XXIII also can be reduced by the dialkylzinc derivatives to give XXI and XX, respectively.

$$\underset{\text{XXI}}{RZnOR} \qquad \underset{\text{XX}}{Zn(OR)_2}$$

A mechanism for the autoxidation of dialkylzinc compounds was proposed by Abraham (2). It involves the coordination of oxygen to the zinc atom and a migration of an alkyl group from zinc to oxygen.



Recently the autoxidation of diphenylzinc in labeled benzene was studied by Razuvayev and co-workers (148). The products are phenol and biphenyl. It was shown that phenol contains no label while biphenyl is formed with the participation of the solvent molecules. The products seem to indicate a peroxy intermediate.

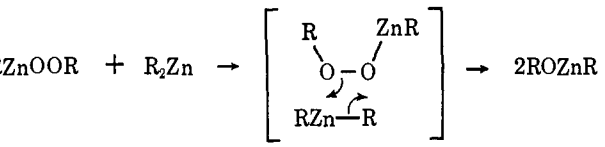
b. Reactions of Organozinc Peroxides

(*1*) *Reduction.*—Reduction of dialkylperoxyzinc (XXIII) by an excess of dialkylzinc gives either zinc dialkoxide (XX) or alkylperoxyzinc alkoxide (XXIV) (2).

$$\text{XXIII} + R_2Zn \rightarrow \underset{\text{XXIV}}{ROZnOOR} \xrightarrow{R_2Zn} \underset{\text{XX}}{Zn(OR)_2}$$

R = Et, *n*-Bu, *t*-Bu

The following mechanism is proposed (95)



(*2*) *Hydrolysis.*—Hydrolysis of XXIII yields organic hydroperoxides (91, 174, 201).

$$\underset{\text{XXIII}}{Zn(OOR)_2} + H_2O \rightarrow 2ROOH + ZnO$$

$R = C_4H_9$

(*3*) *Polymerization.*—The products of autoxidation of diethylzinc initiate the polymerization of vinyl acetate and methyl methacrylate (78).

2. Cadmium

a. Preparation of Organocadmium Peroxides

Alkylperoxycadmium compounds have been prepared by (1) nucleophilic substitution of alkylcadmium compounds with a hydroperoxide, and (2) autoxidation of cadmium alkyls.

(*1*) *Preparation by Nucleophilic Substitution.*—Unlike zinc or boron alkyls, cadmium alkyls undergo nucleophilic substitution with alkyl hydroperoxides to give peroxides of structure XXV and XXVI (69, 70)

$$CdR_2 \xrightarrow{R'OOH} RH + \underset{\text{XXV}}{RCdOOR'} \xrightarrow{R'OOH} RH + \underset{\text{XXVI}}{Cd(OOR')_2}$$

The following radical path for this reaction was suggested by Davies and Packer (70)

$$R'OOH + RCd\cdot \rightarrow R'OOCd\cdot + RH$$

The reaction of dimethylcadmium with one mole of cumyl hydroperoxide in cyclohexane produced, in 24 hr, one mole of methane and a white solid peroxide, XXV, R = CH_3, R′ = $PhMe_2C$ (70). Under similar conditions the reaction with 9-decalyl hydroperoxide produced the analogous 9-decalylperoxymethylcadmium, XXV, R′ = $C_{10}H_{17}$, plus methane (70). If diethyl- or dibutylcadmium is used, the reaction is more vigorous and both alkyl groups are eliminated (70). Thus, the reaction of two moles of 9-decalyl hydroperoxide with diethylcadmium produced ethane and di-9-decalylperoxycadmium, XXVI, R′ = $C_{10}H_{17}$, which was contaminated with reduced products (70).

An attempt to prepare cumylperoxycadmium compounds by the reaction of anhydrous sodium cumyl peroxide with either cadmium iodide or acetate was unsuccessful (70).

Reaction of two moles of dimethylcadmium with one mole of anhydrous hydrogen peroxide produces two moles of methane. The reaction mixture liberates further two moles of methane on acidification with acetic acid. A symmetric methylcadmium peroxide, XXVII, was apparently produced, but it was not isolated (70).

$$\underset{\text{XXVII}}{CH_3CdOOCdCH_3}$$

Autoxidation of diphenylcadmium in labeled benzene produces a mixture of unlabeled phenol and labeled biphenyl (141). The composition of the product mixture indicates a free radical mechanism and peroxide intermediates.

(*2*) *Preparation by Autoxidation.*—Cadmium alkyls undergo autoxidation in a manner similar to that of zinc alkyls (62, 69, 70).

$$R_2Cd \xrightarrow{O_2} \underset{\text{XXV}}{RCdOOR} \xrightarrow{O_2} \underset{\text{XXVI}}{Cd(OOR)_2}$$

Dimethylcadmium gives the peroxide, XXV, R = Me, upon autoxidation. Diethyl- and dibutylcadmium are more reactive and form the insoluble peroxides, XXVI, R = Et, Bu (69, 70). The structure XXVI, R = Et, was confirmed by the reaction of the peroxide with terephthaloyl chloride to give diethyl peroxyterephthalate (70). When diethylcadmium is allowed to absorb only one mole of oxygen, a stable peroxide, XXV, R = Et, can be isolated (70).

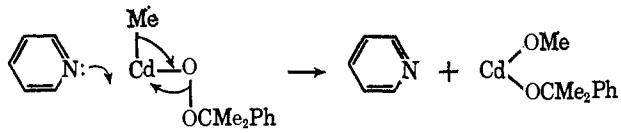
b. Reactions of Organocadmium Peroxides

(*1*) *Hydrolysis.*—Hydrolysis of cadmium peroxides yields organic hydroperoxides.

$$\underset{\text{XXVI}}{Cd(OOR)_2} + H_2O \rightarrow 2ROOH + CdO$$

Ethyl (174), butyl (70, 91, 174), *n*-octyl (91), benzyl (91), and 9-decalyl (70) hydroperoxides have been prepared by this method.

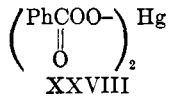
(*2*) *1,2 Rearrangement.*—When cumylperoxymethylcadmium, XXV (R = Me, R′ = CMe_2Ph), is kept at 50° for about 12 hr in the presence of pyridine, the peroxide content is reduced to about 25%. The reaction is interpreted to involve a nucleophilic migration of an alkyl group from cadmium to oxygen (70), similar to that postulated for boron (52, 64, 65, 68, 143), aluminum (61, 149, 151), silicon (55, 56, 144), germanium (56, 60), and tin (53, 186).



3. *Mercury*

a. Preparation of Organomercury Peroxides

A mercury salt of perbenzoic acid, XXVIII, was prepared from an aqueous solution of the sodium salt



XXVIII

of perbenzoic acid and mercuric chloride. This compound is a white solid, melting at 110° with explosive decomposition. It was used to convert 5-dihydroergosteryl acetate to 3-β-acetoxy-9α,11α-oxido-7,22-ergostadiene, melting at 203° (205).

b. Organomercury Peroxides as Intermediates

Razuvayev and co-workers studied the autoxidation of diisopropyl- (159) and dicyclohexylmercury in isopropyl alcohol, chloroform, and carbon tetrachloride (158). Complex mixtures of products were obtained in all cases. Peroxymercury compounds were assumed as intermediates.

D. ORGANOPEROXIDES OF ELEMENTS OF GROUP IIIa

1. *Boron*

a. Preparation of Organoboron Peroxides

There are two general methods of preparation of boron peroxides: (1) nucleophilic substitution, and (2) autoxidation.

(*1*) *Preparation by Nucleophilic Substitution* (See Table VI).—Boron trichloride reacts with alkyl hydroperoxides to give good yields of the corresponding tri(alkylperoxy)borons, XXIX (67, 68).

$$BCl_3 + 3ROOH \rightarrow \underset{\text{XXIX}}{B(OOR)_3} + 3HCl$$

R = *t*-Bu, *n*-Bu

Similarly, *t*-butyl hydroperoxide reacts with *o*-nitrophenyl dichloroboronite or di-*o*-nitrophenyl chloroboronite in methylene chloride to give di(*t*-butylperoxy)-*o*-nitrophenoxyboron and *t*-butylperoxydi-*o*-nitrophenoxyboron, respectively (67, 68).

TABLE VI

ORGANOBORON PEROXIDES PREPARED BY NUCLEOPHILIC SUBSTITUTION

Peroxide	Mp, °C	Bp, °C (mm)	Ref
$B(OO\text{-}n\text{-}Bu)_3$		50–60 (0.001)	67, 68
$B(OO\text{-}t\text{-}Bu)_3$	18	60–70 (0.001)	67, 68
$(t\text{-}BuOO)_2BOH$	38–42		67, 68
$(o\text{-}NO_2C_6H_4O)_2BOO\text{-}t\text{-}Bu$	~15		67, 68
$o\text{-}NO_2C_6H_4OB(OO\text{-}t\text{-}Bu)_2$			67, 68

$$Cl_2BOC_6H_4NO_2 + 2t\text{-}BuOOH \rightarrow (t\text{-}BuOO)_2BOC_6H_4NO_2$$

$$ClB(OC_6H_4NO_2)_2 + t\text{-}BuOOH \rightarrow t\text{-}BuOOB(OC_6H_4NO_2)_2$$

Tetraacetyl diborate reacts with *t*-butyl hydroperoxide to give di(*t*-butylperoxy)boron hydroxide (68).

$$(AcO)_2BOB(AcO)_2 + 4t\text{-}BuOOH \rightarrow 2(t\text{-}BuOO)_2BOH$$

An attempt to prepare a triacylperoxyboron compound by the reaction of boron trichloride with peroxyoctanoic acid resulted in the formation of a mixture of chlorine, boric oxide, and hexanoic acid. Similarly, the reaction of perbenzoic acid with trialkylborines did not produce an alkylperoxyborine. Instead, a trialkoxyborine was obtained, which, on hydrolysis yielded three moles of alcohol (102, 212).

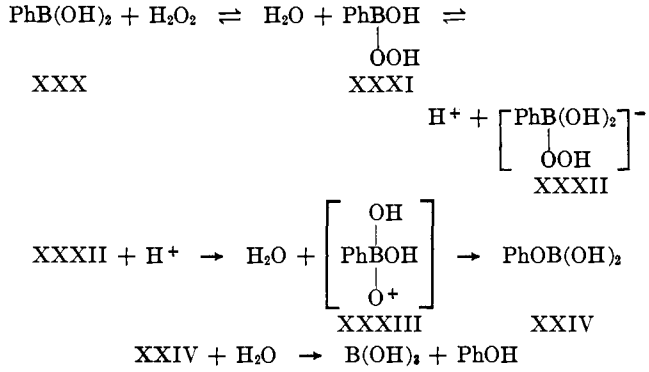
$$R_3B + 3PhC(=O)OOH \rightarrow B(OR)_3 + 3PhC(=O)OH$$

$$B(OR)_3 + 3H_2O \rightarrow 3ROH + H_3BO_3$$

An analogous reaction of phenylboronic acid with hydrogen peroxide results in the formation of a mixture of phenol and boric acid (113–116, 212).

$$PhB(OH)_2 + H_2O_2 \rightarrow PhOH + B(OH)_3$$

The following reaction mechanism is postulated



A similar mechanism involving a peroxide intermediate was proposed by Wechter for the oxidation of the alkyl–boron bond (203, 212).

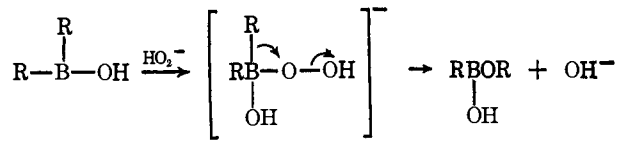


TABLE VII

ORGANOBORON PEROXIDES PREPARED BY AUTOXIDATION

(A) $RB(OOR)_2$

R	Yield, %	Ref
sec-Butyl		62
Isobutyl	56.6	65, 206
2-Ethylhexyl	59.5	206
Octyl	88	206
Decyl	90	206
Undecyl	84	206
2-Phenylpropyl	88	206
Cyclohexyl	95	206
Cyclooctyl	91.7	206
Cyclododecyl	95	206
Indyl	86	206
Styryl	62.4	206
Benzyl	54.5	206

(B) $R^1B(OOR^2)(OOR^3)$

R^1	R^2	R^3	Ref
t-Butyl	Isobutyl	*t*-Butyl	66

Davies and Moodie confirmed these mechanisms using phenyl (O^{18}) boronic acid and (O^{18}) water. Since the phenol produced had a normal isotopic composition, its oxygen must have had its origin in the hydrogen peroxide (68). Similarly, the reaction of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide with (O^{18}) boronic acid in (O^{18}) aqueous dioxane produced isotopically normal 1,2,3,4-tetrahydro-1-naphthol (68). Further confirmation was obtained by the reaction of optically active 1-phenylethyl hydroperoxide with phenylboronic acid, which yielded optically active 1-phenylethanol with retention of configuration (68).

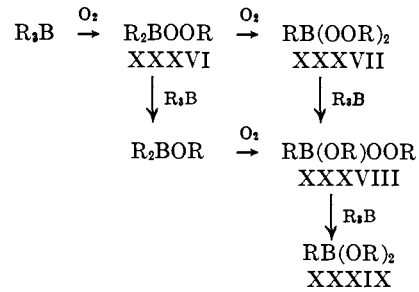
(*2*) *Preparation by Autoxidation* (See Table VII).—In 1862, Frankland obtained the diethyl ester of ethaneboronic acid by slow autoxidation of triethylboron (77). Krause and co-workers examined a number of trialkylborines and found that the autoxidation produced either esters of aliphatic boronic acids or the alkylboron oxides (111, 112). Johnson and Van Campen postulated in 1938 that the autoxidation proceeds *via* an intermediate complex, a "borine-peroxide," XXXV (102, 211). However, the existence of such a

$$\underset{\text{XXXV}}{[R_3B\cdots O{=}O]}$$

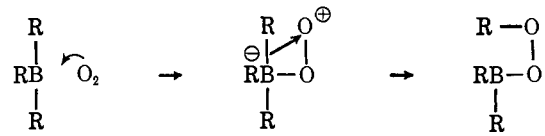
complex has been questioned (63). Generally, controlled autoxidation of trialkylboranes produces dialkyl alkylboronates (18, 52, 85, 91, 102, 124, 133) which on hydrolysis yield a mixture of the corresponding alkylboronic acids and alcohols

$$R_3B + O_2 \rightarrow \underset{\text{XXXIX}}{RB(OR)_2} \xrightarrow{H_2O} RB(OH)_2 + 2ROH$$

Davies and Abraham (52) were the first to show that the primary autoxidation product is a boron peroxide which then rearranges to the alkoxy derivative.



Autoxidation of triethylboron at 30° gives a mixture of peroxyboronates, XXXVII and XXXVIII, R = Et (124). Oxidation at lower temperatures yields the monoperoxyboronate, XXXVI, R = Et (124). The autoxidation of iso-, *sec*-, and *t*-butylboron gives the diperoxide of structure XXXVII, R = *i*-Bu, *s*-Bu, *t*-Bu (62, 64, 65, 68). Davies and co-workers suggested at first that the mechanism of autoxidation proceeds by a coordination of molecular oxygen to the boron atom accompanied by a polarization of oxygen and followed by a 1:3 shift of the alkyl group from boron to oxygen (52, 66).



R = *i*-Bu, *sec*-Bu, *t*-Bu

If the boron contains a *t*-butyl and an isobutyl group, the *t*-butyl group migrates in preference to the isobutyl group (66). However, in later work (63), Davies and co-workers could not confirm the formation of a molecular complex between oxygen and alkyl boranes. Recently, on the basis of kinetic and racemization studies and inhibitory effect of free radical scavengers, Davies and Roberts (70a) proposed a free radical mechanism for the autoxidation of optically active 1-phenylethaneboronic acid.

b. Reactions of Organoboron Peroxides

(*1*) *Hydrolysis*.—Autoxidations of trialkylborons usually result in the formation of dialkyl alkylboronates, $RB(OR)_2$ (XXXIX) (18, 52, 85, 91, 102, 124, 133), which on hydrolysis yield alcohols and alkylboronic acid.

$$\text{XXXIX} + 2H_2O \rightarrow RB(OH)_2 + 2ROH$$

R = Me, Et, *n*-Bu, *n*-hexyl

However, boron peroxides of structure XXXVII have been prepared which, on hydrolysis, give the corresponding alkyl hydroperoxide, alcohol, and boron hydroxide (66, 91, 206).

$$\underset{\text{XXXVII}}{RB(OOR)_2} + 3H_2O \rightarrow B(OH)_3 + 2ROH + ROOH$$

Dialkylperoxyboron alkoxides, $ROB(OOR)_2$ (XL), hydrolyze to yield two moles of the hydroperoxide and the alkoxy derivative of boronic acid (52, 206).

$$XL + 2H_2O \rightarrow ROB(OH)_2 + 2ROOH$$

(2) *Reaction of Organoboron Peroxides with Hydrogen Peroxide and Peracids.*—Peroxides of structure XXXVII react with hydrogen peroxide or peracids to give peroxides of structure XL (206). Wilke and

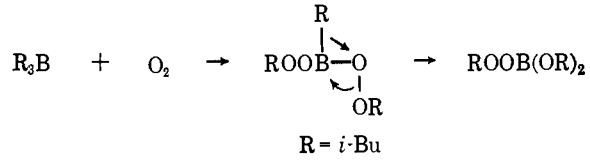
$$\underset{\text{XXXVII}}{RB(OOR)_2} + 2H_2O_2 \rightarrow \underset{\text{XL}}{ROB(OOR)_2}$$

$$\text{XXXVII} + R'\overset{O}{\overset{\|}{C}}OOH \rightarrow \text{XL}$$

Heimbach utilized this reaction to improve the yields of alkyl hydroperoxides synthesized from olefins *via* boron trialkyls by the following route (206): the boron trialkyls were obtained by condensation of N-triethylborozane with an appropriate olefin and then were autoxidized to peroxides of structure XXXVII. The peroxides, XXXVII, were then allowed to react with hydrogen peroxide or a peracid to give the products, XL, which on hydrolysis produced the corresponding alkyl hydroperoxides.

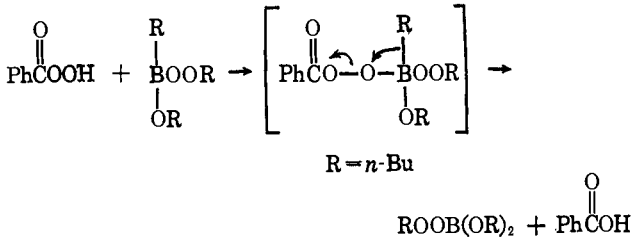
$$XL + 2H_2O \rightarrow ROB(OH)_2 + 2ROOH$$

(3) *1,2 Rearrangements.*—The products of autoxidation of trialkylborons lose peroxidic content upon storage. The peroxide loss probably occurs by a nucleophilic 1,2 rearrangement of an alkyl group from boron to oxygen (52, 64, 65). For example, autoxidation of triisobutylboron yields isobutyldi(isobutylperoxy)boron, which on storage rearranges to the monoperoxy compound (65).



Similarly, dimethyl(methylperoxy)boron rearranges to dimethoxymethylboron (143). Davies and co-workers produced evidence by nmr studies in support of the above mechanism (65, 66).

A similar mechanism was proposed for the reaction of the peroxide produced from trialkylborons with peroxybenzoic acid (52).



This type of rearrangement is believed to be responsible for the failure in preparing peroxy analogs of boronic acid, XXXVII, and boronous acids, XXXVI, by nucleophilic substitution (68).

(4) *Polymerization.*—Acrylonitrile, which is stable toward boron alkyls under nitrogen, is polymerized rapidly if oxygen is admitted (66). Hansen and Hamann showed that free radicals are not intermediates in the autoxidation of triethylboron (85). They suggest that the ethyl radical detected by iodine was produced in a reaction between triethylboron and the boron peroxide in which the peroxide was reduced. It is unlikely that the ethyl radical was the only one produced, but the structure of other radicals could not be determined. There was no evidence of radicals arising from homolytic decomposition of the peroxide (85). Bawn and co-workers (21) suggested that the organoboron peroxide and the monomer form a complex which undergoes oxygen–oxygen homolysis and induces polymerization, while the peroxide alone does not induce polymerization. The mechanism shown in Scheme III was suggested.

SCHEME III

$$R_3B + m \rightarrow \underset{\text{complex}}{R_3B,m}$$

$$R_3B,m + R_2BOOR \rightarrow \underset{\text{complex}}{R_3B,mRO\cdot} + R_2BO\cdot$$

$$R_3B,mRO\cdot + m \rightarrow m_1\cdot$$

$$R_2BO\cdot + m \rightarrow m_1\cdot$$

$$m_1\cdot + m \rightarrow m_2\cdot$$

$$m_1\cdot + m_2\cdot \rightarrow m_{1+2}$$

$$m = \text{monomer}$$

Homo- and copolymers of thiocarbonyl fluoride have been made by a free radical polymerization in which the radicals are generated by a trialkylborane–oxygen initiator at temperatures as low as −100° (185). The first step in this reaction is believed to be the formation of a peroxide from the trialkylborane and oxygen. The peroxide then reacts with more trialkylborane to produce alkyl radicals. These radicals in turn initiate the polymerization.

$$R_3B + O_2 \rightarrow \underset{\text{XXXVI}}{R_2BOOR}$$

$$\text{XXXVI} + 2R'_3B \rightarrow 2R'\cdot + R_2BOBR'_2 + R'_2BOR$$

$$R = \text{Et, } n\text{-Bu}$$

Kato, *et al.* (107), have also used trialkylboron–oxygen mixtures to initiate the polymerization of vinyl monomers.

2. *Aluminum*

a. Preparation of Organoaluminum Peroxides (See Table VIII)

Organoaluminum peroxides of the structure XLI

$$\underset{\text{XLI}}{Al(OR)_2OOR'}$$

have been synthesized by the following reactions of various organoaluminum compounds with hydroperoxides.

TABLE VIII

ORGANOALUMINUM PEROXIDES PREPARED BY NUCLEOPHILIC SUBSTITUTION

(A) $(RO)_2AlOOR'$

R	R′	Mp, °C	Ref
Et	CMe_3		105
Et	CMe_2Ph	113 dec	149, 151

(B) $ROAl(OOR')_2$

R	R′	Ref
Et	CMe_3	105

(i) Reaction of diethoxyethylaluminum with cumyl hydroperoxide (151)

$$EtAl(OEt)_2 + HOOCMe_2Ph \rightarrow XLI + C_2H_6$$
$$R = Et,\ R' = CMe_2Ph$$

This reaction occurs only above 15–20° with spontaneous evolution of heat and does not go to completion.

(ii) Reaction of aluminum triethoxide with cumyl hydroperoxide (149, 151)

$$Al(OEt)_3 + HOOCMe_2Ph \rightarrow XLI + EtOH$$
$$R = Et,\ R' = CMe_2Ph$$

This reaction does not go to completion.

(iii) Reaction of diethoxyaluminum chloride with cumyl hydroperoxide (149)

$$ClAl(OEt)_2 + HOOCMe_2Ph \xrightarrow{Na\text{–}EtOH} XLI + NaCl + EtOH$$
$$R = Et,\ R' = CMe_2Ph$$

(iv) Reaction of diethoxyaluminum chloride with sodium cumyl hydroperoxide (149, 151)

$$ClAl(OEt)_2 + NaOOCMe_2Ph \rightarrow XLI + NaCl$$
$$R = Et,\ R' = CMe_2Ph$$

In all cases, a reductive side reaction of the peroxy group occurred.

(v) Reaction of diethoxyaluminum chloride with *t*-butyl hydroperoxide (105). The preparation of a peroxide of structure XLI, R = Et, R′ = *t*-Bu, by reaction of diethoxyaluminum chloride and *t*-butyl hydroperoxide in anhydrous ammonia is reported.

$$ClAl(OEt_2) + HOOCMe_3 \rightarrow XLI + NH_4Cl$$

A peroxide of structure XLII was also prepared (105)

$$Cl_2AlOEt + 2HOOCMe_3 + 2NH_3 \rightarrow \underset{XLII}{Al(OR)(OOR')_2} + 2NH_4Cl$$
$$R = Et,\ R' = CMe_3$$

b. Organoaluminum Peroxides as Intermediates

It has been postulated that an aluminum peroxide is formed as an intermediate in the autoxidation of triphenylaluminum in ether. The products of this oxidation are: phenol, acetophenone, acetaldehyde, aluminum oxide, and tar (150, 155, 156, 157). The following mechanism (156) involves as a first step the formation of an organoaluminum peroxide

$$Ph_3Al \cdot + O_2 \rightarrow [Ph_3AlOO\cdot] \rightarrow \underset{XLIII}{Ph_2AlOOPh}$$

The peroxide is then reduced by triphenylaluminum

$$XLIII + Ph_3Al \rightarrow 2Ph_2AlOPh$$
$$Ph_2AlOPh \xrightarrow{H_2O} PhOH + Al(OH)_3 + C_6H_6$$

Benzene, however, was not found. In the presence of a solvent, such as ether, the solvent molecules also undergo a reaction. As a result, products such as acetophenone and acetaldehyde are formed. The oxidation process is very complex as indicated by the high yield of products of oxidation (52%) (156). An organoaluminum peroxide has been postulated as an intermediate in the free radical chain mechanism of the explosive combustion of trimethylaluminum (42a).

Alcohols are produced in high yields by the hydrolysis of products of the reaction of organoaluminum compounds with oxygen (39, 184, 188, 198, 210a). The reaction was developed into an industrial process (39). Sladkov, *et al.* (188), postulate that the process proceeds through intermediate peroxides which either rearrange or are reduced by trialkylaluminum to give the aluminum alcoholate.

$$(RCH_2CH_2)_3Al + O_2 \rightarrow \underset{XLIV}{(RCH_2CHO)_3Al}$$

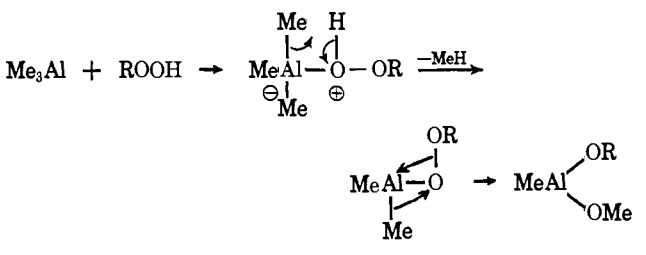
$$XLIV + H_2O \rightarrow 3RCH_2CH_2OH + Al(OH)_3$$

c. Reactions of Organoaluminum Peroxides

(*1*) *Thermal Decomposition.*—Heating of aluminum peroxides of structure XLI, R = Et, R′ = CMe_2Ph, to 90° results in a vigorous reaction. Hydrolysis of the decomposition mixture yields acetophenone, α-methylstyrene, cumyl alcohol, ethanol, and water. This product mixture indicates a homolytic cleavage of diethoxy(cumylperoxy)aluminum (151).

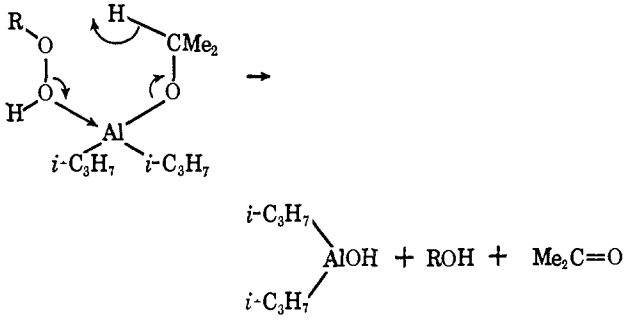
(*2*) *Hydrolysis.*—Hydrolysis of well-defined aluminum peroxides was little investigated. The organoaluminum peroxide of structure XLI, R = Et, R′ = CMe_2Ph, is completely hydrolyzed in acidic solutions (149). Hydrolysis of decahydro-9-naphthylperoxyaluminum produces decahydro-9-naphthyl hydroperoxide (61).

(*3*) *Rearrangements.*—Peroxyaluminum derivatives containing alkyl groups are unstable and readily undergo an intermolecular rearrangement to form the corresponding alkoxyaluminum derivatives (149, 151). The reaction of trimethyl- or triethylaluminum with hydroperoxides carried out in the presence of methyl methacrylate or styrene does not lead to polymeri-



zation. It was, therefore, concluded that this reaction proceeds by a heterolytic process (61) (see above).

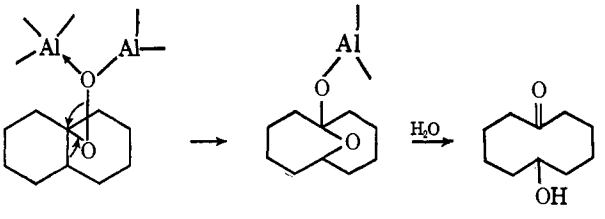
For the reaction of alkylhydroperoxides with aluminum isopropoxide, Davies and Hall (61) postulated the rearrangement of a cyclic transition state similar to that commonly written for the Meerwein–Ponndorf reduction of aldehydes and ketones



The reaction of decahydro-9-naphthyl hydroperoxide with aluminum *t*-butoxide in ethylbenzene produces *t*-butyl alcohol. In the absence of the solvent, the product contains only about one-third of the expected peroxide content. When this reaction is carried out in dioxane, two peroxy groups are found. However, elemental analysis indicates a composition corresponding to tris(decahydro-9-naphthylperoxy)aluminum (61). It appears that aluminum peroxides of the structure XLV can be prepared, but that extensive decomposition occurs during attempted isolation (61).

$$\underset{\text{XLV}}{Al(OOR)_3}$$

Hydrolysis of the product gave decahydro-9-naphthyl hydroperoxide and an unidentifiable oil, but no *t*-butyl alcohol. The following reaction scheme was suggested by Davies and Hall (61)



(*4*) *Polymerization.*—The aluminum peroxide of structure XLI, R = Et, R′ = CMe_2Ph, promotes the polymerization of vinyl monomers (149, 151).

Triisobutylaluminum, diisobutylisobutoxyaluminum, triethylaluminum, diethylethoxyaluminum, or diisobutylaluminum chloride in the presence of oxygen in xylene initiate free radical polymerization of vinyl monomers (79, 132). Similarly, a mixture of triethylaluminum and cumyl hydroperoxide in octane initiates the polymerization of vinyl monomers. In all cases, evidence exists for the presence of organoaluminum peroxide intermediates (132).

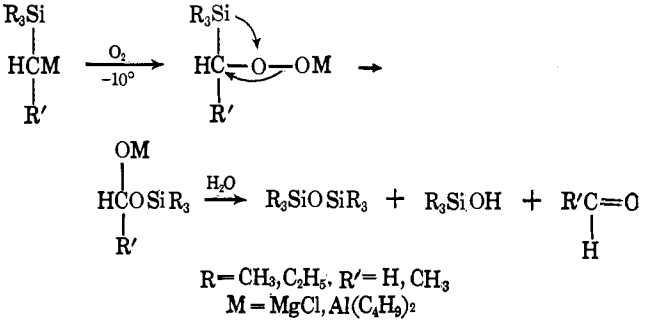
E. ORGANOPEROXIDES OF ELEMENTS OF GROUPS IVa

1. *Introduction to Group IVa*

In contrast to the organoperoxides of elements of groups Ia and IIa of the periodic table, which have ionic properties and can be considered as salts of organic hydroperoxides, the organoperoxides of group IVa, such as silicon, germanium, tin, and lead, can be considered as true metal or metalloid organic peroxides containing a metal–oxygen bond which is to a large extent covalent (165). This fact is supported by the solubility properties of these peroxides. For example, trialkyl- and triarylperoxysilanes, -germanes, -stannanes, and -plumbanes are readily soluble in typical organic solvents such as ether, pentane, benzene, chloroform, etc.

Trialkyl- or triarylperoxysilanes, -germanes, and -stannanes are fairly stable thermally and can be kept at room temperature in the absence of moisture for prolonged periods of time. However, they decompose readily on heating. Peroxyplumbanes are more sensitive and decompose readily at room temperature. All organoperoxides of group IV are insensitive to impact or friction (165).

It has been shown in the preceding sections that organometallic compounds of elements of groups I, II, and III of the periodic table readily interact with molecular oxygen at room temperature to give organometallic peroxides. In contrast, most alkyls of elements of group IV are less readily attacked by oxygen at room temperature, and elevated temperatures are required to achieve a reaction at which stage the intermediate peroxy derivatives are also decomposed. However, a facile oxidation of the carbon–silicon bond occurs with α-trialkylsilyl organometallic compounds (73). But, in this case, no silylperoxy compound is obtained. Instead, the carbon–metal bond is attacked to give an organometal peroxide which undergoes subsequent rearrangement with migration of the silyl group to oxygen.



2. *Silicon*

a. Preparation of Unsymmetric Organosilicon Peroxides (See Table IX)

A general method for the preparation of organosilicon peroxides of general structure XLVI is the nucleophilic

TABLE IX

UNSYMMETRIC ORGANOSILICON PEROXIDES $R_{4-n}Si(OOR')_n$

Starting materials[a] $SiR_{4-n}Cl_n + nR'OOH$, $n = 1-4$ R	R'	n	Product $R_{4-n}Si(OOR')_n$	Yield, %	Bp, °C (mm) or mp, °C	n_D (°C)	Ref
Me	CMe_3	1	$Me_3SiOOCMe_3$	54	41 (41)		84
			$Me_3SiOOCMe$	89	78 (215)	1.3935 (25)	54, 56, 57
Me	CMe_2Et	1	$Me_3SiOOCMe_2Et$	84	78 (95)	1.4032 (25)	54, 56, 57
Me	CMe_2Ph	1	$Me_3SiOOCMe_2Ph$	53	43 (0.05)	1.4780 (25)	54, 56, 57
Me	$CH_2(CH_2)_3CH_3$	1	$Me_3SiOOCH_2(CH_2)_3CH_3$		78 (95)	1.4032 (25)	57
Me	1,2,3,4-Tetrahydro-1-naphthyl	1	$Me_3SiOOC_{10}H_{11}$	98	53 (0.01)	1.5102 (25)	54, 56, 57
Et	CMe_3	1	$Et_3SiOOCMe_3$		38–40 (0.05)		104
Et (Br)	CMe_3	1	$Et_3SiOOCMe_3$		44–5.5 (1)	1.4198 (20)	13
$CH_2{=}CH(Me)$ (Et)	CMe_2Et	1	$CH_2{=}CH(Me)(Et)SiOOCMe_2Et$	59	38 (1–2)	1.4308 (20)	123
$CH_2{=}CH(Me)$ (Et)	CMe_2Ph	1	$CH_2{=}CH(Me)(Et)SiOOCMe_2Ph$	43	55 (0.1)	1.4910 (20)	123
Ph	CMe_3	1	$Ph_3SiOOCMe_3$		50		54, 56
MeO	CMe_3	1	$(MeO)_3SiOOCMe_3$		49 (6)		56
$CH_2{=}CH$ (Me)	CMe_3	2	$CH_2{=}CH(Me)Si(OOCMe_3)_2$	40	31 (0.1)	1.4182 (20)	123
$CH_2{=}CH$ (Me)	CMe_2Et	2	$CH_2{=}CH(Me)Si(OOMe_2Et)_2$	58	62 (0.5–1)	1.4312 (20)	123
Et	CMe_3	2	$Et_2Si(OOM_3)_2$		40 (1)	1.4149 (25)	54, 56, 57
$CH_2{=}CH$ (C_3H_7)	CMe_3	2	$CH_2{=}CH(C_3H_7)Si(OOCMe_3)_2$	45	76 (1–1.5)	1.4269 (20)	123
$CH_2{=}CH$ (C_3H_7)	CMe_2Et	2	$CH_2{=}CH(C_3H_7)Si(OOCMe_2Et)_2$	66	56 (0.05)	1.4359 (20)	123
Ph	CMe_3	2	$Ph_2Si(OOCMe_3)_2$		110 (0.001)	1.5103 (25)	54, 56, 57
Me	CMe_3	3	$MeSi(OOCMe_3)_3$		50 (0.1)	1.4097 (25)	54, 56, 57
	CMe_3	4	$Si(OOCMe_3)_4$		35–40		56
					78 (0.5)		54

[a] Condensing agent, pyridine, NH_3, $R_3''N$.

reaction of alkyl, aryl, or aralkyl hydroperoxides with a halosilane.

$$R_{4-n}SiX_n + nR'OOH \rightarrow \underset{\text{XLVI}}{R_{4-n}Si(OOR')_n} + nHX$$

R, R′ = alkyl, aralkyl, aryl

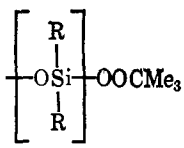
X = F, Cl, Br

The reaction is carried out in either ether or petroleum ether in the presence of a base such as pyridine (31, 47, 54, 56, 57, 84, 122, 123, 187), ammonia (13, 54, 56, 57, 103, 104), or a tertiary amine (56, 103, 104). Organosilicon peroxides containing a vinyl group (XLVII) have also been prepared by the same method (122, 123). The

$$\underset{\text{XLVII}}{CH_2{=}CHSi(OOCR'_3)_n \atop \quad | \atop \quad R_m}$$

$m + n = 3$; $n = 1, 2$

reaction of either dialkyl or diaryl dichlorosilane with *t*-butyl hydroperoxide produces a polymeric material, XLVIII (31). An analogous reaction of ethyltrifluoro-,



XLVIII

R = alkyl, aryl

diethyldifluoro-, triethoxyfluoro-, and tetrafluorosilane with *t*-butyl hydroperoxide in the presence of ammonia is claimed to produce monomeric peroxides (103).

Organosilicon peroxides were also prepared by methods less widely used. Pike and Shaffer (144) condensed trimethylsilyl alkylamine with *t*-butyl hydroperoxide to give a 20% yield of trimethylsilyl *t*-butyl peroxide, XLVI, R = Me, R′ = CMe_3, $n = 1$

$$Me_3SiNHR + Me_3COOH \rightarrow \underset{\text{XLVI}}{Me_3SiOOCMe_3} + RNH_2$$

and Plueddemann (145) condensed an alcohol containing a siloxane moiety, XLIX, with *t*-butyl hydroperoxide in the presence of 70% sulfuric acid to give the peroxide, L.

$$\underset{\text{XLIX}}{Me_3Si{-}O{-}SiMe_2CH_2CH_2CMe_2OH} + HOOCMe_3 \rightarrow \underset{\text{L}}{Me_3Si{-}O{-}SiMe_2CH_2CH_2CMe_2OOCMe} + H_2O$$

b. Preparation of Organosilicon Hydroperoxides (See Table X)

In 1954, Berry described in a patent (24) the formation of triethyl and triphenylsilyl hydroperoxides by the reaction of 90% hydrogen peroxide with the corresponding silanol. Two years later, Hahn and Metzinger (84) prepared the better defined trimethylsilyl hydroperoxide by the reaction of trimethylchlorosilane with hydrogen peroxide in the presence of pyridine. The peroxide was unstable; it disproportionated readily into disilyl peroxide and hydrogen peroxide and decomposed on heating above 35° with evolution of oxygen gas. Recently, Dannley and Jalics reinvestigated this type of peroxide using either a mixture of ammoniacal hydrogen peroxide and chloro-

TABLE X

ORGANOSILICON HYDROPEROXIDES, R_3SiOOH

Starting materials $R_3SiNH_2 + H_2O_2$ R_3	Condensing agent	Product R_3SiOOH	Yield, %	Mp, °C	n_D (°C)	Ref
$MePh_2$	NH_3	$MePh_2SiOOH$	54	40–41		46
$(PhCH_2)_3$	NH_3	$(PhCH_2)_3SiOOH$	63	60–61		46
(*n*-Hexyl)$_3$	NH_3	$(C_6H_{13})_3SiOOH$	83		1.4550 (20)	46
Ph_3	NH_3	Ph_3SiOOH	56	110–112		46

silane (46) or a mixture of hydrogen peroxide and a silylamine. They were able to prepare well-defined products (46).

$$R_3SiCl + H_2O_2 + NH_3 \rightarrow R_3SiOOH + NH_4Cl$$

$$R_3SiNH_2 + HOO^{\ominus} \rightarrow [HOOSiR_3NH_2^{\ominus}] \xrightarrow{H_2O_2} R_3SiOOH + NH_3 + HOO^{\ominus}$$

Triphenyl-, methyldiphenyl-, tribenzyl-, and tri-*n*-hexylsilyl hydroperoxides were prepared by these methods (46). These peroxides are quite stable when pure but decompose rapidly in the presence of alkali (46).

c. Preparation of Symmetric Organosilicon Peroxides (See Table XI)

Symmetric silyl organoperoxides, LI, are prepared by nucleophilic substitution reactions of hydrogen peroxide with chlorosilanes in the presence of a base (84, 187).

$$2R_3SiCl + H_2O_2 \xrightarrow{\text{pyridine}} \underset{\text{LI}}{R_3SiOOSiR_3} + 2HCl\cdot\text{pyridine}$$

R = alkyl, aryl

Instead of a mixture of hydrogen peroxide and pyridine, sodium peroxide can be used (144).

$$2R_3SiCl + Na_2O_2 \rightarrow \underset{\text{LI}}{R_3SiOOSiR_3} + 2NaCl$$

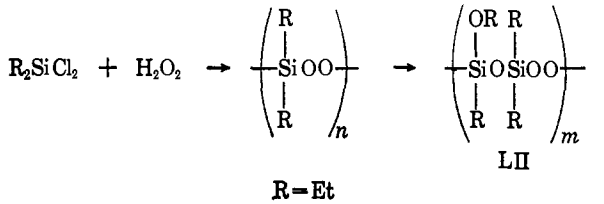
R = Me

In a modification of this procedure, silyl hydroperoxides are condensed with silylamines to give symmetric organosilyl peroxides, LI (46, 47, 144).

$$R_3SiOO^{\ominus} + R_3SiNH_2 \rightarrow [R_3SiOOSiRNH_2^{\ominus}] \xrightarrow{R_3SiOOH} \underset{\text{LI}}{(R_3SiO)_2} + NH_3 + R_3SiO_2^{\ominus}$$

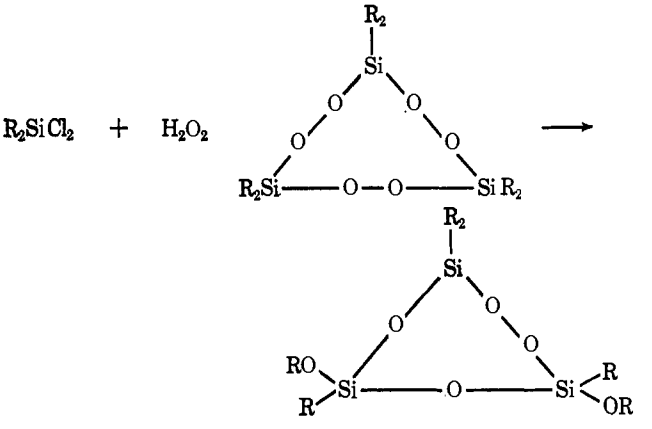
R = Me, Ph, $PhCH_2$

Condensation of diethyldifluorosilane with 100% hydrogen peroxide in the presence of ammonia results in the formation of ethoxysilane (101), whereas the analogous condensation with diethyldichlorosilane produces polymeric peroxides containing ethoxy and siloxane units (101). Jenker suggested that the initially formed straight chain or cyclic peroxides rearrange to products, LII, LIII, containing alkoxy and siloxane moieties (101).



LII

R=Et



LIII

Another method for the preparation of symmetric silyl peroxides was discovered by Pike and Shaffer (144). Trimethyl-*n*-butylsilane was allowed to react with hydrogen peroxide in the presence of sulfuric acid to give the symmetric peroxide, LI.

$$n\text{-}C_4H_9SiMe_3 \xrightarrow{H_2SO_4} [n\text{-}C_4H_9SiMe_2OSO_3H] + CH_4 \xrightarrow{H_2O_2} \underset{\text{LI}}{(n\text{-}C_4H_9SiMe_2O)_2} + H_2SO_4$$

d. Reactions of Organosilicon Peroxides

(*1*) *Reaction of Organosilicon Peroxides with Alcohols.*—Unsymmetric organosilicon peroxides, XLVI, react with tertiary alcohols in acidic ethereal solutions with elimination of the silicon moiety to form unsymmetric carbon peroxides of structure LIV (138, 139).

$$ROH + \underset{\text{XLVI}}{Me_3SiOOR'} \xrightarrow{H^+} \underset{\text{LIV}}{ROOR'} + Me_3SiOH$$

$$4ROH + \underset{\text{XLVI}}{Si(OOCMe_3)_4} \xrightarrow{H^+} 4Me_3COOR + Si(OH)_4$$

R = Ph, 1-phenylcyclohexyl; R′ = $PhMe_2C$, Ph_2CH

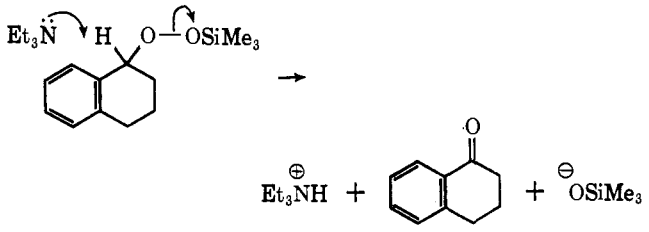
(*2*) *Base-Catalyzed Decomposition.*—Trimethyl(1,-2,3,4-tetrahydro-1-naphthylperoxy)silane, like primary

TABLE XI

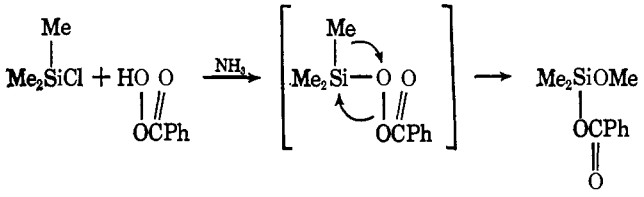
SYMMETRIC ORGANOSILICON PEROXIDES, $R_3SiOOSiR_3$

Starting materials R	Starting materials X	Condensing agent	Product $R_3SiOOSiR_3$	Yield, %	Bp, °C (mm) or Mp, °C	n_D (°C)	Ref
			(1) $R_3SiX + H_2O_2$				
Me	Cl	Pyridine	$Me_3SiOOSiMe_3$	43	38 (30)		84
					36 (30)	1.3970 (20)	187
Et	Cl		$Et_3SiOOSiEt_3$		62 (0.02)	1.4362 (20)	187
Ph	Cl	NH_3	$Ph_3SiOOSiPh_3$	53	140–141		46
Ph	NH_2		$Ph_3SiOOSiPh_3$	41	140–141		46
			(2) $R_3SiX + R_3SiOOH$				
Ph	Cl	$(CH_3)_3N$	$Ph_3SiOOSiPh_3$	36	140–141		46
Ph	NH_2		$Ph_3SiOOSiPh_3$	27	140–141		46
$PhCH_2$	NH_2		$(PhCH_2)_3SiOOSi(PhCH_2)_3$	37	110–111		46

and secondary alkyl peroxides of carbon, undergoes base-catalyzed decomposition to form the corresponding ketone (56, 139).



(3) *1,2 Rearrangements.*—A number of nucleophilic 1,2 rearrangements (55, 56, 144) from silicon to oxygen have been observed. While most peresters of carbon are well defined, stable compounds, the silicon analogs undergo rearrangements and cannot be isolated. Thus, attempted preparation of trimethylsilyl perbenzoate from trimethylchlorosilane and perbenzoic acid results in the formation of an acyloxy derivative involving a nucleophilic rearrangement of a silyl perbenzoate intermediate (56).



If this reaction is carried out with dimethylphenylchlorosilane, the phenyl group migrates in preference to the methyl group (56).

Similarly, the reaction of dimethylphenylchlorosilane with hydrogen peroxide in the presence of acid produces phenol, presumably by rearrangement of the intermediate dimethylphenylsilyl hydroperoxide (55, 56).

(4) *Reduction.*—Reduction of trimethyl(*t*-butylperoxy)silane with sodium sulfite yields *t*-butyl alcohol, *t*-butylsilanol, and trimethylsilyl oxide (54, 139).

$$\underset{\text{XLVI}}{Me_3SiOOCMe_3} \xrightarrow{Na_2SO_3} Me_3COH + Me_3SiOH + (Me_3Si)_2O$$

(5) *Hydrolysis.*—Hydrolysis of unsymmetric silicon peroxides yields the corresponding hydroperoxides and silanols (56).

$$\underset{\text{XLVI}}{R_3SiOOR'} \xrightarrow{H_2O} R'OOH + R_3SiOH$$

$$R = Ph,\ R' = t\text{-Bu}$$

(6) *Reaction with Hydrochloric Acid.*—The reaction of silicon peroxides with a 6 *N* hydrochloric acid solution gives the corresponding chlorosilanes and hydroperoxides (56, 139)

$$\underset{\text{XLVI}}{R_3SiOOR'} + HCl \rightarrow R'OOH + R_3SiCl$$

$$R = Ph,\ R' = t\text{-Bu}$$

(7) *Thermal Decomposition.*—Trimethyl(*t*-butylperoxy)silane decomposes at a higher temperature than its carbon analog (90). Unlike the carbon analog, which is relatively indifferent to its environment, the decomposition of the silyl peroxide is markedly affected by solvents. The decomposition occurs by a unimolecular process in a number of solvents (90). Free-radical-induced decomposition is not a complicating factor (90). Since the reaction is faster in more polar solvents, it might be inferred that decomposition proceeds mainly by a heterolytic process. Some homolytic decomposition cannot be ruled out, but the relative extent of heterolytic and homolytic decomposition remains still in doubt.

Dannley and Jalics (48) studied the decomposition of triphenylsilyl hydroperoxide in anisole. They postulate that the decomposition proceeds by a radical process because it is not catalyzed by acid or dependent on solvent and it is catalyzed by light. They postulate that the homolysis of the peroxide linkage is the first step of the decomposition.

$$Ph_3SiOOH \rightarrow Ph_3SiO\cdot + HO\cdot$$

The free radicals then undergo the following reactions: the triphenylsiloxy radical rearranges to a silyl radical which reacts with the hydroxy radical

TABLE XII

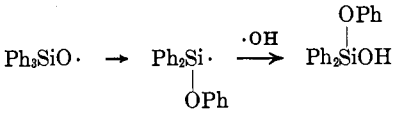
ORGANOGERMANIUM PEROXIDES

(A) $R_3GeOOGeR_3$

Starting materials $R_3GeX + H_2O_2$ R	X			Condensing agent	Product $R_3GeOOGeR_3$	Yield, %	Bp, °C (mm) or mp, °C	n_D (°C)	Ref
Et	OMe				$Et_3GeOOGeEt_3$	77	56–57 (0.05)	1.4603 (20)	165
Pr	Cl			NH_3 or tertiary amines	$Pr_3GeOOGePr_3$		65 (0.1–0.05)	1.4608 (26)	59, 60
Ph	Br				$Ph_3GeOOGePh_3$	83	126–128		165

(B) $R_{4-n}Ge(OOR')_n$

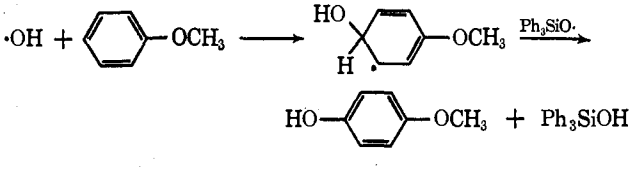
$R_{4-n}GeX_n + R'OOH$ R	R'	X	n		$R_{4-n}Ge(OOR')_n$				
Me	Decahydro-9-naphthyl	Cl	1	NH_3 or Et_3N	$Me_3GeOOC_{10}H_{17}$		65 (0.5)		60
Et	CMe_3	Cl	1		$Et_3GeOOCMe_3$	55	78–79 (14–15)	1.4368 (20)	165
		OMe	1		$Et_3GeOOCMe_3$	80			165
Pr	CMe_3	Cl	1	Tertiary amines	$Pr_3GeOOCMe_3$		35 (0.001)	1.4383 (26)	59, 60
Pr	Decahydro-9-naphthyl	Cl	1	Tertiary amines	$Pr_3GeOOC_{10}H_{17}$		70 (0.01)	1.4779 (26)	59, 60
Ph	CMe_3	Br	1	$NaNH_2$	$Ph_3GeOOCMe_3$	92	55–57		165
Ph	CMe_2Ph	Br	1		$Ph_3GeOOCMe_2Ph$	78	106–108		165
Ph	CPh_3	Br	1		$Ph_3GeOOCPh_3$	54	193–195		165
Ph	Isochromanyl	Br	1		$Ph_3GeOOC_9H_9O$	86	159–161		165
Ph	Tetralyl	Br	1		$Ph_3GeOOC_{10}H_{11}$	95	112–114		165
Pr	Decahydro-9-naphthyl	Cl	2	Tertiary amines	$Pr_2Ge(OOC_{10}H_{17})_2$		>95 (0.01)		59, 60
$(CH_2)_5$	CMe_3	Cl	2	NH_3 or Et_3N	$(CH_2)_5>Ge(OOCMe_3)_2$		60 (0.001), −35	1.4553 (26)	60
				Tertiary amines	$(CH_2)_5>Ge(OOCMe_3)_2$		65 (0.2), −35	1.4553 (26)	59
	Decahydro-9-naphthyl	Cl	4	Tertiary amines	$Ge(OOC_{10}H_{17})_4$		84–85		59, 60



the phenoxysilanol degrades to phenol and diphenyldisilanol

$$Ph_2Si(OPh)OH \rightarrow PhOH + Ph_2Si(OH)_2$$

and the hydroxy radical reacts with the solvent.



Gilman and George (81) proposed a lithium salt of triphenylsilyl hydroperoxide as an intermediate in the autoxidation of triphenylsilyllithium. In their mechanism, the first step of the decomposition also involves a homolysis of the oxygen–oxygen bond to give the triphenylsiloxy radical. However, the further fate of this species is different from that proposed by Dannley and Jalics.

$$Ph_3SiLi + O_2 \rightarrow Ph_3SiOOLi \rightarrow Ph_3SiO\cdot + LiO\cdot$$
$$Ph_3SiO\cdot + Ph_3SiLi \rightarrow Ph_3SiOLi + Ph_3Si\cdot$$
$$Ph_3Si\cdot + \text{solvent} \rightarrow Ph_3SiH$$
$$2Ph_3Si\cdot \rightarrow Ph_3SiSiPh_3$$

(*8*) *Polymerization.*—Organosilicon peroxides catalyze the polymerization of styrene, methyl methacrylate, and other vinyl monomers (24, 57, 84, 123, 139).

3. *Germanium*

a. Preparation of Unsymmetric Organogermanium Peroxides (See Table XII)

Unsymmetric organogermanium peroxides have been prepared by a variety of methods, all involving nucleophilic displacement reactions. Davies and Hall (59) were the first to prepare germanium peroxides of the general structure LV *via* nucleophilic substitution by the following reaction.

$$nR'OOH + R_{4-n}GeCl_n \rightarrow \underset{\text{LV}}{R_{4-n}Ge(OOR')_n} + nHCl$$
$$n = 1\text{–}4$$

The reactions are carried out either in ether, cyclohexane, or pentane (60, 165) in the presence of a base

such as pyridine (165), dimethylaniline (165), ammonia (60), or triethylamine (60).

Trialkyl- or triarylgermanium bromides react with the anhydrous sodium salt of an alkyl hydroperoxide to give the corresponding unsymmetric organogermanium peroxide (162, 165).

$$R_3GeBr + NaOOR' \rightarrow \underset{LV}{R_3GeOOR'} + NaBr$$

Rieche and Dahlmann prepared alkyl- or arylgermanium peroxides by the reaction of trialkyl- or triarylaminogermanes with alkyl hydroperoxides (162, 165).

$$R_3GeNH_2 + R'OOH \rightarrow \underset{LV}{R_3GeOOR'} + NH_3$$

The reaction proceeds rapidly; even at room temperature (165).

Organogermanium alkoxides react with organic hydroperoxides to yield germanium peroxides of structure LV (165).

$$R_3GeOR'' + R'OOH \rightarrow LV + R''OH$$
$$R = Et,\ R' = CMe_3,\ R'' = Me$$

In the case of alkylgermanium alkoxides, good yields are obtained. However, the triphenyl(alkylperoxy)-germanes cannot be prepared in the same way because an equilibrium is established between the starting materials and the products.

$$Ph_3GeO\text{-}t\text{-}Bu + t\text{-}BuOOH \rightleftharpoons LV + t\text{-}BuOH$$
$$R = Ph,\ R' = CMe_3$$

In this case, the preparation of germanium peroxides can be achieved only if an excess of alkyl hydroperoxide is used and the alcohol is continuously removed, thus shifting the equilibrium to the right side.

b. Preparation of Symmetric Organogermanium Peroxides (See Table XII)

Symmetric germanium peroxides were prepared by the following nucleophilic substitution reaction (165)

$$2R_3GeX + H_2O_2 \rightarrow \underset{LVI}{R_3GeOOGeR_3} + 2HX$$

where X can be bromine or an amino or alkoxy group.

Symmetric germanium peroxides are stable and can be prepared in an analytically pure form. Bis(triphenylgermanium)peroxide (LVI, R = Ph) is more stable than the corresponding silyl peroxide. It can be kept at room temperature for a few weeks (165).

c. Reactions of Organogermanium Peroxides

(*1*) *Hydrolysis.*—Unsymmetric and symmetric organogermanium peroxides are stable under anhydrous conditions, but hydrolyze readily. In the presence of water, they give germanium hydroxides and either alkyl hydroperoxides or hydrogen peroxide (60, 165).

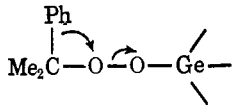
$$\underset{LV}{R_3GeOOR'} + H_2O \rightarrow R_3GeOH + R'OOH$$

$$\underset{LVI}{R_3GeOOGeR_3} + H_2O \rightarrow 2R_3GeOH + H_2O_2$$

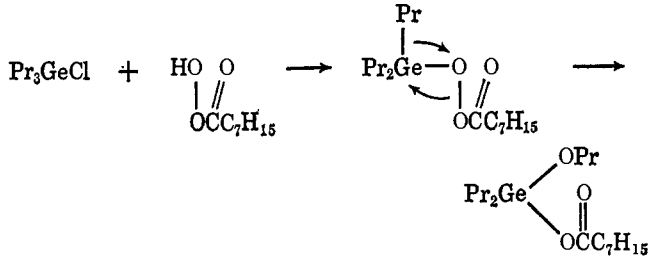
(*2*) *Reaction with Anhydrous Hydrogen Chloride.*—The reaction of germanium peroxides with anhydrous hydrogen chloride results in the formation of the corresponding trialkylgermanium chloride and the initial hydroperoxide (162, 165).

$$LV + HCl \rightarrow R_3GeCl + R'OOH$$

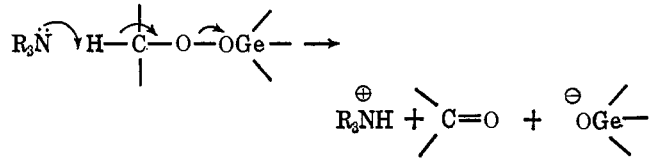
(*3*) *1,2 Rearrangements.*—As in the case of organoboron, -aluminum, and -silicon peroxides, evidence of 1,2 rearrangements of germanium peroxides has been found. Thus, the reaction between 1-methyl-1-phenylethyl hydroperoxide and germanium tetrachloride yields, in the course of a few days, nonperoxidic compounds (60). This reaction probably occurs by a nucleophilic migration of the phenyl group from carbon to oxygen.



Similarly, when alkylgermanium chlorides are treated with peroxy acids, nonperoxidic compounds are obtained. The reaction, as proposed by Davies and Hall, proceeds by a 1,2 rearrangement (60).



(*4*) *Base-Catalyzed Decomposition.*—The reaction of 1,2,3,4-tetrahydro-1-naphthyl hydroperoxide with germanium tetrachloride gives, in the presence of pyridine, 1,2,3,4-tetrahydro-1-oxonaphthalene. Since the hydroperoxide alone is stable toward pyridine, the following mechanism was suggested (60)



A similar decomposition takes place when trimethyl-(1,2,3,4-tetrahydro-1-naphthylperoxy)silane is treated with triethylamine (60).

(*5*) *Polymerization.*—Organogermanium peroxides are found to catalyze the polymerization of vinyl monomers (60, 165, 166). This result indicates a homolysis of the peroxides (60).

TABLE XIII

UNSYMMETRIC ORGANOTIN PEROXIDES

(A) $R_{4-n}Sn(OOR')_n$

Starting materials (1) $R_{4-n}SnX_n + nR'OOH$ R	R'	X	n	Condensing agent	Product $R_{4-n}Sn(OOR')_n$	Yield, %	Bp, °C (mm) or mp, °C	n_D (°C)	Ref
Me	Et	Cl	1	Na–MeOH	$Me_3SnOOEt$	89	95–97		165
Me	CMe_3	Cl	1	Na–MeOH	$Me_3SnOOCMe_3$	83	56 (12)	1.4529 (20)	161, 165
Et	CMe_3	OMe	1		$Et_3SnOOCMe_3$	90	55 (0.2)	1.4669 (20)	165
		Br	1	Na–MeOH	$Et_3SnOOCMe_3$		61–62 (0.9)		53
		Cl	1	Na–MeOH	$Et_3SnOOCMe_3$	92	56–57 (2)		161
		Cl	1	NH_3	$Et_3SnOOCMe_3$			1.4787 (25)	126
		OEt	1		$Et_3SnOOCMe_3$	98			161
Et	CMe_2Ph	OMe	1		$Et_3SnOOCMe_2Ph$	91	86–87 (0.04)	1.5188 (20)	165
		Cl	1	Na–MeOH	$Et_3SnOOCMe_2Ph$	16	105–10 (2)		161
Pr	Cyclohexenyl	OMe	1		$Pr_3SnOOC_6H_9$	79	71 (0.04)	1.5013 (20)	165
		OMe	1		$Pr_3SnOOC_6H_9$	97	109 (0.1–0.2) (partial dec)		161
Pr	Tetralyl	OMe	1		$Pr_3SnOOC_{10}H_{11}$	93			165
		OMe	1		$Pr_3SnOOC_{10}H_{11}$		100–10 dec		161
Bu	CMe_3	OMe	1		$Bu_3SnOOCMe_3$	91	80–81 (0.05)	1.4670 (20)	165
Bu	CMe_3	Cl	1	NaOMe	$Bu_3SnOOCMe_3$	84	71–72 (0.001)	1.4608 (25)	53
		Cl	1		$Bu_3SnOOCMe_3$	98	105–110 (1)		161
		Cl	1	NH_3	$Bu_3SnOOCMe_3$	85	87 (0.04)	1.417 (25)	126
		CN	1		$Bu_3SnOOCMe_3$		<100 (bath) (0.001)	1.4628 (26)	53
		H	1		$Bu_3SnOOCMe_3$	45	<100 (bath) (0.001)	1.4642 (25)	53
Bu	CMe_2Ph	Cl	1	NH_3	$Bu_3SnOOCMe_2Ph$			1.5033 (25)	126
Bu	1-Methyl-1-phenylethyl	OMe	1		$Bu_3SnOOC_9H_{11}$		110–120 (bath) (0.01)		53
Bu	Decahydro-9-naphthyl	OMe	1		$Bu_3SnOOC_{10}H_{17}$			1.4952 (19.5)	53
C_6H_{11}	CMe_3	Br	1	$NaNH_2$	$(C_6H_{11})_3SnOOCMe_3$	95	144–146		165
		Cl	1	Na–MeOH	$(C_6H_{11})_3SnOOCMe_3$	95	144–146		161
C_6H_{11}	CMe_2Ph	Br	1	$NaNH_2$	$(C_6H_{11})_3SnOOCMe_2Ph$	96			165
Ph	CMe_3	Cl	1		$Ph_3SnOOCMe_3$	83	63–65		165
Ph	CMe_2Ph	Cl	1		$Ph_3SnOOCMe_2Ph$	85	111–114		165
		Cl	1	$NaNH_2$	$Ph_3SnOOCMe_2Ph$	74	111–114		165
Ph	CPh_3	Cl	1		$Ph_3SnOOCPh_3$	79	123–125		165
Ph	Isochromanyl	Cl	1		$Ph_3SnOOC_9H_9O$	70	123–125		165
Ph	Isochromanyl	OMe	1		$Ph_3SnOOC_9H_9O$	77	123–125		165
Ph	Tetralyl	Cl	1		$Ph_3SnOOC_{10}H_{11}$	82	81.5–83		165
Ph	Decahydro-9-naphthyl	OMe	1		$Ph_3SnOOC_{10}H_{17}$		102–105		53
Me	CMe_3	Cl	2	NH_3	$Me_2Sn(OOCMe_3)_2$		160–161 dec		126
Bu	CMe_3	Cl	2	Na–MeOH	$Bu_2Sn(OOCMe_3)_2$		100 (<0.001)	1.4652 (25)	53
Me	CMe_3	Cl	3	Na–MeOH	$MeSn(OOCMe_3)_3$				53
(2) $R_3SnCl + R'OONa$ R	R'				R_3SnOOR'				
Me	CMe_3				$Me_3SnOOCMe_3$		56 (12)		160
Et	CMe_3				$Et_3SnOOCMe_3$		56–57 (12)		160
Et	CMe_2Ph				$Et_3SnOOCMe_2Ph$		105–110 dec (1–2)		160
Bu	CMe_3				$Bu_3SnOOCMe_3$		105–110 dec (1)		160
(3) $R_3SnOOSnR_3 + H_2O_2$ R					R_3SnOOR				
Et					$Et_3SnOOEt$		Room temp (0.2–0.5)		5

TABLE XIII (*Continued*)

(B) R_4Sn_2XYO

Starting materials		Condensing agent	Product	Yield, %	Bp, °C (mm) or mp, °C	n_D (°C)	Ref
(1) $(R_2SnO)_n$ + R′OOH			R_4Sn_2XYO				
R	R′		X = Y = CMe_3OO				
Et	CMe_3		$Et_4Sn_2(OOCMe_3)_2O$		135–143		58
Bu	CMe_3		$Bu_4Sn_2(OOCMe_3)_2O$		78–79		58
(2) $R_4Sn_2(OAc)_2O$ + R′OOH			R_4Sn_2XYO				
R	R′		X = Y = CMe_3OO				
Bu	CMe_3	Et_3N	$Bu_4Sn_2(OOCMe_3)_2O$		78–79		58
(3) $R_4Sn_2Cl_2O$ + R′OOH			R_4Sn_2XYO				
R	R′		X = CMe_3OO; Y = Cl				
Bu	CMe_3	Et_3N	$Bu_4Sn_2(OOCMe_3)(Cl)O$		57–62		58
(4) $R_4Sn_2Cl(OH)O$ + R′OOH			R_4Sn_2XYO				
R	R′		X = CMe_3OO; Y = Cl				
Et	CMe_3		$Et_4Sn_2(OOCMe_3)(Cl)O$		125–126		58
Bu	CMe_3		$Bu_4Sn(OOCMe_3)(Cl)O$		57–62		58

4. *Tin*

a. Preparation of Unsymmetric Organotin Peroxides (See Table XIII)

Triarylalkylperoxystannanes have been prepared by a nucleophilic substitution reaction between triaryltin chlorides and hydroperoxides in the presence of a base such as pyridine or ammonia (165).

$$R_3SnX + R'OOH \xrightarrow{B^\ominus} \underset{\text{LVII}}{R_3SnOOR'} + HB + X^\ominus$$

R = aryl, R′ = alkyl; X = Cl

However, attempts to prepare trialkylalkylperoxystannanes by this method failed because trialkyltin halides react with pyridine and ammonia to give complexes which do not react with the hydroperoxides to give the desired product (165). Trialkylalkylperoxystannanes (LVII, R, R′ = alkyl) can be prepared by the reaction of a trialkylalkoxystannane with an alkyl hydroperoxide (53, 161).

$$R_3SnOR'' + R'OOH \rightarrow \underset{\text{LVII}}{R_3SnOOR'} + R''OH$$

R, R′, R″ = alkyl

The reaction of the sodium salt of the hydroperoxide with trialkyltin halides in absolute methanol yields the corresponding trialkylalkylperoxystannanes (160, 161)

$$R_3SnX + R'OONa \rightarrow \underset{\text{LVII}}{R_3SnOOR'} + NaCl$$

R, R′ = alkyl

This method is particularly suited for the preparation of those peroxides which would ordinarily decompose in aqueous alkaline solutions (160). However, with more stable hydroperoxides, this reaction can be performed in aqueous solution (126).

The use of trialkyltin cyanides in the reaction with alkyl hydroperoxides has the advantage of producing a volatile by-product, but the cyanides are less reactive than the tin methoxides (53).

$$R_3SnCN + R'OOH \rightarrow \underset{\text{LVII}}{R_3SnOOR'} + HCN$$

R, R′ = alkyl

Tributyltin hydride reacts with an excess of *t*-butyl hydroperoxide to give tributyl(*t*-butylperoxy)-stannane. Compound LVIII is believed to be an intermediate in the reaction (165).

$$(n\text{-Bu})_3SnH + t\text{-BuOOH} \rightarrow \underset{\text{LVIII}}{[(n\text{-Bu})_3SnO\text{-}t\text{-Bu}]} + H_2O \xrightarrow{t\text{-BuOOH}} (n\text{-Bu})_3SnOO\text{-}t\text{-Bu} + t\text{-BuOH}$$

Attempts were made to extend these reactions to the preparation of di-, tri-, and tetraalkylperoxides of tin. It was found that as the number of alkylperoxy substituents is increased, the preparation of a peroxy derivative becomes progressively more difficult. The compounds are much less volatile and more thermally labile than the monoperoxides and usually cannot be distilled without decomposition. They are more readily hydrolyzed and are difficult to purify by crystallization (53). A reaction of tin tetrachloride with sodium *t*-butyl peroxide in methanol produced a crude tetra-*t*-butylperoxytin, but this compound decomposed violently at about 65° during an attempt to distil it (53). Dibutyl(di-*t*-butylperoxy)tin was prepared by treating dibutyltin dichloride in methanol with sodium methoxide and *t*-butyl hydroperoxide (53). *n*-Butyltin trihydride was found to react vigorously with an excess of *t*-butyl hydroperoxide, but no tin triperoxide could be isolated (53).

$$n\text{-BuSnH}_3 + 3t\text{-BuOOH} \rightarrow n\text{-BuSn(O-}t\text{-Bu)}_3 + 3H_2O$$

Aleksandrov (5) isolated ethyl triethyltin peroxide (LVII, R = Et, R′ = Et) from the reaction of triethyltin peroxide (LIX, R = Et) and anhydrous hydrogen

peroxide in absolute alcohol in the presence of sodium sulfate.

$$\underset{\text{LIX}}{(Et_3SnO)_2} + H_2O_2 \xrightarrow[Na_2SO_4]{C_2H_5OH} \underset{\text{LVII}}{Et_3SnOOEt}$$

Recently, Davies and Graham (58) prepared an interesting series of organotin peroxides of the general composition LX. The following reactions were used.

$$\underset{\text{LX}}{R_4Sn_2XYO}$$

X = OOR′, Y = OOR′ or halide

(i) Reaction of a dialkytin oxide with an alkyl hydroperoxide

$$(R_2SnO)_n + R'OOH \rightarrow \underset{\text{LX}}{R_2Sn(OOR')OR_2Sn(OOR')}$$

X = OOR′, Y = OOR′

(ii) Reaction of an oxyacetate with an alkyl hydroperoxide in the presence of triethylamine

$$R_4Sn(OAc)_2O + R'OOH \xrightarrow{Et_3N} LX$$

X = OOR′, Y = OOR′

(iii) Reaction of an oxychloride with an alkyl hydroperoxide in the presence of triethylamine

$$R_4Sn_2Cl_2O + R'OOH \xrightarrow{Et_3N} LX$$

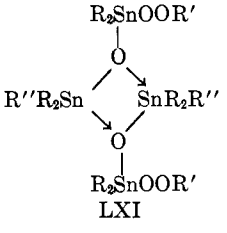
X = Cl, Y = OOR′

(iv) Reaction of an oxyhydroxide–chloride with an alkyl hydroperoxide

$$R_4Sn_2Cl(OH)O + R'OOH \rightarrow LX$$

X = Cl, Y = OOR′

Determination of the molecular weight of these compounds in benzene at 25° suggests that they may have the structure LXI.



LXI

R″ = Cl, OOR′

b. Preparation of Organotin Hydroperoxides (See Table XIV)

Trimethyltin and triphenyltin hydroperoxides have been prepared by the reaction of alkyl- and aryltin hydroxides with concentrated hydrogen peroxide. The products are stable at room temperature (43, 44). Triethyltin hydroperoxide was prepared using triethyltin oxide and anhydrous hydrogen peroxide in the presence of magnesium sulfate (5, 12).

$$(Et_3Sn)_2O + H_2O_2 \xrightarrow{MgSO_4} Et_3SnOH + \underset{\text{LXII}}{Et_3SnOOH}$$

$$Et_3SnOH + H_2O_2 \rightarrow LXII + H_2O$$

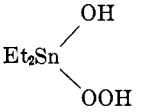
LXII separates as a white crystalline addition compound LXIII (12). Cryoscopic molecular weight

$$\underset{\text{LXIII}}{[Et_3SnOOH]_2 \cdot H_2O_2}$$

determinations in benzene showed that LXIII is completely dissociated into the triethyltin hydroperoxide and hydrogen peroxide

$$LXIII \rightarrow 2Et_3SnOOH + H_2O_2$$

LXIII decomposed even at room temperature, sometimes violently, to give a mixture of gases, liquids, and solids. Only one product, diethyltin hydroxyhydroperoxide (LXIV), has been identified (12).



LXIV

Peroxide LXII is also obtained from the reaction of triethyltin peroxide (LIX, R = Et) with hydrogen peroxide (12).

$$\underset{\text{LIX}}{(Et_3SnO)_2} + H_2O_2 \rightarrow \underset{\text{LXII}}{2Et_3SnOOH}$$

This reaction is the reverse of the analogous reaction of silicon derivatives, which yields the symmetric peroxide (84).

$$2Me_3SiOOH \rightarrow (Me_3SiO)_2 + H_2O_2$$

c. Preparation of Symmetric Organotin Peroxides (See Table XV)

The reaction of triphenyltin chloride with hydrogen peroxide in absolute ether in the presence of ammonia gives the expected symmetric tin peroxide, LIX (165).

$$2R_3SnCl + H_2O_2 \xrightarrow{NH_3} \underset{\text{LIX}}{R_3SnOOSnR_3} + 2HCl$$

R = Ph

The reaction of trialkyltin alkoxides with hydrogen peroxide produces bis(triarylstannyl) peroxides (165). Bis(triethylstannyl) peroxide (LIX, R = Et) was synthesized by allowing triethyltin oxide (LXV) to react with anhydrous hydrogen peroxide in ether (4, 11).

$$\underset{\text{LXV}}{(Et_3Sn)_2O} + H_2O_2 \rightarrow \underset{R = Et}{LIX} + H_2O$$

d. Reactions of Organotin Peroxides

(*1*) *Hydrolysis.*—Symmetric and unsymmetric organotin peroxides hydrolyze to give the corresponding organotin hydroxide and the original hydroperoxide (10, 11, 14, 160, 165, 186).

TABLE XIV

ORGANOTIN HYDROPEROXIDES, R_3SnOOH

Starting materials	Product	Yield, %	Mp, °C	Ref
(1) $R_3SnOH + H_2O_2$	R_3SnOOH			
R				
Me	Me_3SnOOH	90	97 dec	44
Ph	Ph_3SnOOH	45	75 expl	44
(2) $R_3SnOH + H_2O_2$	$[R_3SnOOH]_2 \cdot H_2O_2$			
R				
Et	$[Et_3SnOOH]_2 \cdot H_2O_2$		35–36	12
(3) $[R_3SnOOH]_2 \cdot H_2O_2 \xrightarrow{dec}$	$R_2Sn<^{OH}_{OOH}$			
Et	$Et_2Sn<^{OH}_{OOH}$		150–180 dec	12

TABLE XV

SYMMETRIC ORGANOTIN PEROXIDES, $R_3SnOOSnR_3$

Starting materials	Condensing agent	Product	Yield, %	Mp, °C	n_D (°C)	Ref
(1) $R_3SnX + H_2O_2$		$R_3SnOOSnR_3$				
R X						
Pr OMe		$Pr_3SnOOSnPr_3$	99		1.4910 (20)	165
Ph Cl		$Ph_3SnOOSnPh_3$				165
(2) $R_3SnOSnR_3 + H_2O_2$		$R_3SnOOSnR_3$				
R						
Et	Na_2SO_4	$Et_3SnOOSnEt_3$		60 expl		11

$$\underset{\text{LVII}}{R_3SnOOR'} + H_2O \rightarrow R_3SnOH + R'OOH$$

$$\underset{\text{LIX}}{R_3SnOOSnR_3} + 2H_2O \rightarrow 2R_3SnOH + H_2O_2$$

Tin peroxides are more sensitive to hydrolysis than germanium peroxides (165).

(*2*) *Reaction with Anhydrous Hydrogen Chloride.*—Unsymmetric organotin peroxides react with anhydrous hydrogen chloride to yield the halide of the corresponding tin compound and the original hydroperoxide (165).

$$\underset{\text{LVII}}{R_3SnOOR'} + HCl \rightarrow R_3SnCl + R'OOH$$

(*3*) *Reduction.*—Sodium sulfite reduces unsymmetric organotin peroxides to the corresponding trialkyltin hydroxides (160).

(*4*) *Decomposition.*—The symmetric organotin peroxide (LIX, R = Et) decomposes in *n*-nonane by first-order kinetics with the formation of LXVI and LXVII in equivalent amounts (9, 10, 11, 14). Aleksandrov

$$\underset{\text{LXVI}}{Et_3SnOEt} \qquad \underset{\text{LXVII}}{Et_2SnO}$$

and Shushunov (10) proposed the following free radical mechanism for this decomposition

$$\underset{\text{LIX}}{(Et_3SnO)_2} \rightarrow \underset{\text{LXVIII}}{2Et_3SnO\cdot}$$

$$\text{LXVIII} + (Et_3SnO)_2 \rightarrow Et_3SnOEt + \underset{\text{LXIX}}{Et_3SnOO\dot{S}nEt_2}$$

$$\text{LXIX} \rightarrow Et_3SnO\cdot + Et_2SnO$$

$$Et_3SnO\cdot + Et_3SnOO\dot{S}nEt_2 \rightarrow 2\text{LXVII} + \text{LXVI}$$

The decomposition of the peroxide LIX, R = Et, in the presence of hexaethylditin (LXX) is more rapid; triethyltin oxide (LXV) is produced as the main prod-

$$\underset{\text{LXX}}{(Et_3Sn)_2} \qquad \underset{\text{LXV}}{(Et_3Sn)_2O}$$

uct. Also, the autoxidation of hexaethylditin is accelerated by triethyltin peroxide (LIX) (10). The following radical-chain mechanism is proposed for the reaction of LIX with hexaethylditin (10)

$$\text{LIX} \rightarrow 2Et_3SnO\cdot$$

$$Et_3SnO\cdot + Et_3SnSnEt_3 \rightarrow Et_3SnOSnEt_3 + Et_3Sn\cdot$$

$$Et_3Sn\cdot + Et_3SnOOSnEt_3 \rightarrow Et_3SnOSnEt_3 + EtSnO\cdot$$

$$Et_3SnO\cdot + Et_3Sn\cdot \rightarrow Et_3SnOSnEt_3$$

$$2Et_3Sn\cdot \rightarrow Et_3SnSnEt_3$$

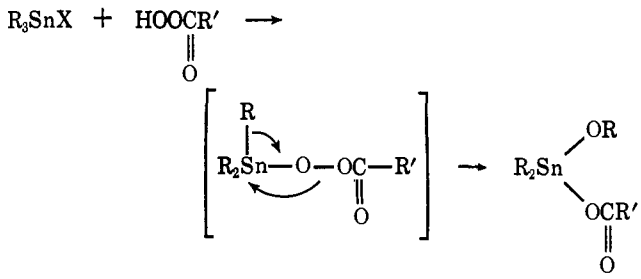
The decomposition of trimethyltin hydroperoxide in dioxane produces the following mixture of products.

$$Me_3SnOOH \rightarrow Me_2SnO + Me_3SnOH + MeOH + O_2$$

The reaction initially follows zero-order kinetics. At later stages of the reaction or at higher concentrations, first-order kinetics are observed. In acetonitrile, the hydroperoxide decomposes with first-order kinetics. The decomposition produces acetamide in addition to the above product mixture (43, 44).

(*5*) *1,2 Rearrangements.*—The reactions of trialkyl or triaryltin halides or alkoxides with peroxy acids or hydrogen peroxide (53, 186) produce nonperoxidic products. Davies and Alleston (53) proposed a mech-

anism involving peroxycarboxylate intermediates which undergo a 1,2 rearrangement.



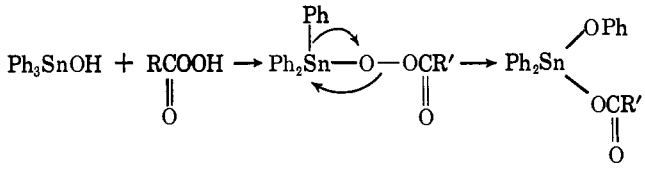
R = Bu, Ph; R′ = $CH_3(CH_2)_6$; X = Cl, OMe

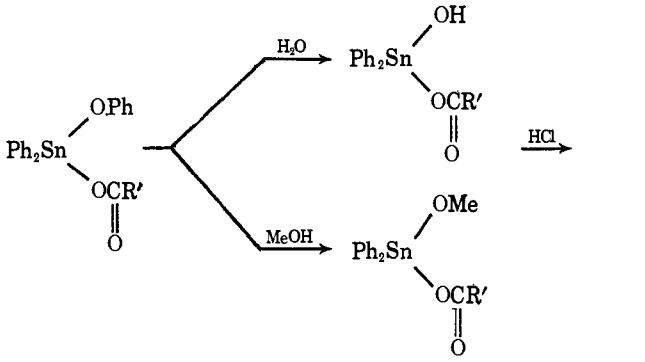
A similar rearrangement was recently proposed by Aleksandrov and co-workers (8, 186).

Condensation of triphenyltin hydroxide with peracetic or perpropionic acid in anhydrous methanol produces a white precipitate which on hydrolysis with aqueous hydrochloric acid yields phenol, compound

$Ph_2Sn(OH)Cl$
LXXI

LXXI, and acetic or propionic acid, respectively. The following reaction sequence was suggested.





$Ph_2Sn(OH)Cl$
LXXI

(6) *Polymerization.*—Vinyl monomers polymerize in the presence of organotin peroxides (10, 11, 14, 110, 165). The result indicates a homolytic cleavage of the organotin peroxides.

5. *Lead*

a. Preparation of Unsymmetric Organolead Peroxides (See Table XVI)

Trialkyl- or triaryllead bromides do not react with hydroperoxides even in the presence of ammonia or pyridine (165). Peroxides of the general formula LXXII can be prepared by condensing the sodium salt of a hydroperoxide with organolead bromides.

$$R_3PbBr + R'OONa \rightarrow \underset{\text{LXXII}}{R_3PbOOR'} + NaBr$$

Isolation of pure trialkylperoxyplumbanes is difficult since they are unstable and readily decompose at room temperature. Triarylperoxyplumbanes are more stable than the trialkyl derivatives (165).

Trialkyl- or triarylalkoxyplumbanes can also be used for the preparation of LXXII (165).

$$R_3PbOR'' + R'OOH \rightarrow \text{LXXII} + R''OH$$

Triethyllead oxide reacts with organic hydroperoxides to yield LXXII, R = Et (6, 8).

$$(Et_3Pb)_2O + R'OOH \rightarrow \underset{R = Et}{\text{LXXII}} + Et_3PbOH$$

The reaction of triethyllead oxide with the hydroperoxide, LXXIII, produces LXXIV (8).

$$(Et_3Pb)_2O + \underset{\text{LXXIII}}{p\text{-}(HOOCMe_2)_2C_6H_4} \rightarrow \underset{\text{LXXIV}}{p\text{-}(Et_3PbOOCMe_2)_2C_6H_4} + H_2O$$

b. Preparation of Symmetric Organolead Peroxides (See Table XVI)

Rieche and Dahlmann (165) reported the preparation of a symmetric lead peroxide by the reaction

$$Ph_3PbOMe + H_2O_2 \rightarrow Ph_3PbOOPbPh_3 + MeOH$$

c. Organolead Peroxides as Intermediates

The oxidation of hexaethyldilead by oxygen forms (7, 14) triethyllead peroxide as an intermediate which reacts rapidly with hexaethyldilead to form triethyllead oxide (7).

$$Et_6Pb_2 \xrightarrow{O_2} [Et_3PbOOPbEt_3] \xrightarrow{Et_6Pb_2} 2Et_2PbOPbEt_3$$

The reaction of an ethereal solution of triethyllead hydroxide with either peracetic or perbenzoic acid produced intermediate organolead peroxides which were not isolated (8, 186). The decomposition of these peroxidic intermediates proceeded slowly at low temperatures but the peroxidic content declined with time, and triethyllead acetate and triethyllead benzoate were isolated. Also formed was an unidentified water-soluble organolead derivative, which after prolonged standing in air yielded LXXV (186).

$Et_2Pb(OBz)_2$
LXXV

The reaction of triphenyllead hydroxide with peracetic acid in methanol produced diphenyllead oxide, LXXVI, after it was stored for 17 hr at room temperature in the dark and was then heated for 2.5 hr at 50° (78).

$Ph_2Pb{=}O$
LXXVI

TABLE XVI

ORGANOLEAD PEROXIDES

Starting materials			Condensing agent	Product	Yield, %	Mp, °C	Ref
			(A) $R_3PbOOPbR_3$				
$R_3PbX + H_2O_2$				$R_3PbOOPbR_3$			
R	X						
Ph	OMe			$Ph_3PbOOPbPh_3$	97	166–167	165
			(B) R_3PbOOR'				
(1) $R_3PbX + R'OOH$				R_3PbOOR'			
R	R'	X					
Me	CMe_3	Br	$NaNH_2$	$Me_3PbOOCMe_3$	97	81–83	165
		Br	Na–EtOH	$Me_3PbOOCMe_3$	74	81–83	165
Me	CMe_2Ph	Br	$NaNH_2$	$Me_3PbOOCMe_2Ph$	96	55–57	165
Et	CMe_3	Br	$NaNH_2$	$Et_3PbOOCMe_3$	84	34–36	165
Ph	CMe_3	Br	$NaNH_2$	$Ph_3PbOOCM_3$	89	99–101	165
		Br	$NaNH_2$	$Ph_3PbOOCMe_3$		97–99	166
Ph	CMe_2Ph	OMe		$Ph_3PbOOCMe_2Ph$	84	113–115	165
		Br	$NaNH_2$	$Ph_3PbOOCMe_2Ph$	92	113–115	165, 166
Ph	CPh_3	Br	$NaNH_2$	$Ph_3PbOOCPH_3$	86	110–112	165, 166
(2) $(R_3Pb)_2O + R'OOH$				R_3PbOOR'			
R	R'						
Et	CMe_3			$Et_3PbOOCMe_3$			6
Et	CMe_2Ph			$Et_3PbOOCMe_2Ph$			6

d. Reactions of Organolead Peroxides

(*1*) *Hydrolysis.*—Organolead peroxides hydrolyze more readily than germanium analogs (165, 166) to give the corresponding organolead hydroxides and organic hydroperoxides.

$$\underset{\text{LXXII}}{R_3PbOOR'} + H_2O \rightarrow R_3PbOH + R'OOH$$

R = alkyl, aryl; R′ = alkyl, aralkyl

(*2*) *Reaction with Anhydrous Hydrogen Chloride.*—Anhydrous hydrogen chloride reacts with LXXII to give the corresponding organolead chloride and the hydroperoxide (165, 166).

$$\text{LXXII} + HCl \rightarrow R_3PbCl + R'OOH$$

R = alkyl, aryl; R′ = alkyl, aralkyl

(*3*) *Polymerization.*—Organolead peroxides catalyze vinyl polymerizations (165, 166). This reaction suggests the occurrence of a homolytic cleavage of the organolead peroxide.

F. ORGANOPEROXIDES OF ELEMENTS OF GROUP IVb

Organoperoxides of Titanium and Zirconium

Attempts to prepare titanium or zirconium organoperoxides using simple halo derivatives failed (165). A peroxide intermediate is probably formed in the reaction of sandwich π complexes such as bis(cyclopentadienyl)titanium dichloride with *t*-butyl hydroperoxide in dioxane in the presence of pyridine or ammonia. In aqueous solution, hydrogen peroxide reacts with bis(cyclopentadienyl)titanium dichloride to give a yellow compound of probable structure LXXVII (165).

$$\underset{\text{LXXVII}}{(C_5H_5)_2TiOO\cdot 2H_2O}$$

G. ORGANOPEROXIDES OF ELEMENTS OF GROUP Va

1. *Phosphorus*

a. Preparation of Organophosphorus Peroxides (See Table XVII)

Peroxyesters of phosphoric acid of the general structure LXXVIII were first prepared by Rieche and co-workers (169). Thus, dimethyl or diethyl chlorophosphates react with *t*-butyl hydroperoxides in excess pyridine at −10 to −20° to give dimethyl or diethyl *t*-butylperoxyphosphate (169, 170, 171, 172).

$$\underset{\substack{\|\\ O}}{(RO)_2PCl} + Me_3COOH \rightarrow \underset{\substack{\|\\ O}}{(RO)_2POOR'} + HCl$$

LXXVIII

R = CH_3, C_2H_5; R′ = CMe_3

Mageli and Harrison prepared a series of various peresters, LXXVIII, by the reaction of chlorophosphates with hydroperoxides in the presence of aqueous solutions of hydroxides of the elements of group I (125). Recently, Dannley and Kabre reported the preparation of the symmetric bisdiphenylphosphinic peroxide (LXXX) by the reaction of diphenylphosphinic chloride with aqueous sodium peroxide (49).

$$\underset{\substack{\|\\ O}}{Ph_2PCl} + OOH^- \rightarrow \underset{\substack{\|\\ O}}{Ph_2POOH} \xrightarrow{OH^-} \underset{\substack{\|\\ O}}{Ph_2POO^-}$$

LXXIX

$$\text{LXXIX} + \underset{\substack{\|\\ O}}{Ph_2PCl} \rightarrow \underset{\substack{\|\\ O}}{Ph_2P}OO\underset{\substack{\|\\ O}}{P}Ph_2 + Cl^-$$

LXXX

TABLE XVII

ORGANOPHOSPHORUS PEROXIDES

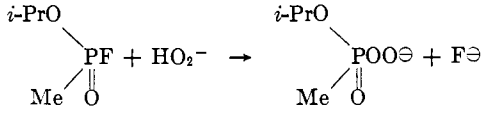
R	R′	Method of prepn	Yield, %	Bp, °C (mm) or mp, °C	n_D (°C)	Ref
			(A) $R_2P(O)OOR'$			
MeO	CMe_3	*a*	65	23–25		170
			65	70 (0.001)		170
			43	24–25		171–172
EtO	CMe_3	*a*	~65–85	60–65 (0.01–0.001)	1.419–1.421 (20)	170
				53–54 (0.003)	1.4208 (20)	169, 171, 172
				64–67 (0.1)	1.4148 (25)	192
EtO	CMe_3	*b*	76		1.4163 (25)	125
i-PrO	CMe_3	*a*				192
n-BuO	CMe_3	*b*	88.6		1.4248 (25)	125
n-BuO	Hexyl	*b*	89.3		1.4264 (25)	125
n-BuO	CMe_2Ph	*b*	90		1.4677 (25)	125
n-BuO	Pinanyl	*b*	98		1.4577 (25)	125
n-OctylO	CMe_3	*b*	78.7		1.4380 (25)	125
n-OctylO	CMe_2Ph	*b*	76			125
n-OctylO	Pinanyl	*b*	99		1.4593 (25)	125
PhO	CMe_3	*b*	80		1.4996 (25)	125
PhO	CMe_2Ph	*b*	78		1.5182 (25)	125
			(B) $R_2P(O)OOP(O)R_2$			
Ph		*c*	57	88–89		49
			(C) $(H_3C)_2C(CH_2)_2C(CH_3)_2$ with $R_2P(O)OO$ and $OOP(O)R_2$			
n-Bu		*b*			1.4320 (24)	125
Ph		*b*	81		1.5233 (28)	125

[a] $R_2P(O)Cl + R'OOH \xrightarrow[\text{pyridine}]{\text{anhydrous}} R_2P(O)OOR' + HCl$. [b] $R_2P(O)Cl + R'OOH \xrightarrow{MOH,\ H_2O} R_2P(O)OOR' + MCl$ (M = Li, Na, K, Cs). [c] $2R_2P(O)Cl + H_2O_2 \rightarrow R_2P(O)OOP(O)R_2 + 2HCl$.

The preparation of organophosphorus perhydrates by the reaction of phosphonates and phosphates with hydrogen peroxide is claimed in a Russian patent (30).

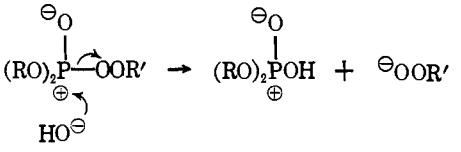
b. Organophosphorus Peracids as Intermediates

Although organophosphorus peracids have not been isolated, they have been proposed on various occasions as reaction intermediates. The interaction of isopropoxy methylphosphoryl fluoride (Sarin) with hydrogen peroxide has been extensively studied (3 and references therein).

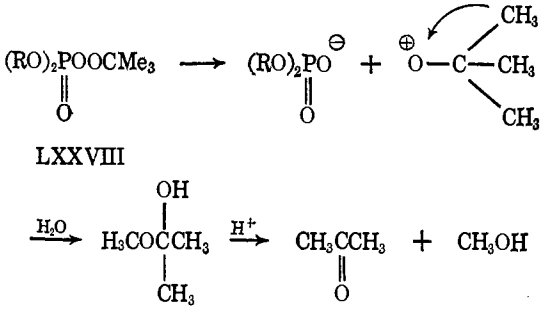


c. Reactions of Organophosphorus Peroxides

(*1*) *Hydrolysis.*—Dialkoxyperoxy phosphates, LXXVIII, can be cleaved in two different ways. In the presence of a strong base at a pH of above 14, the phosphorus–oxygen bond is preferentially attacked and *t*-butyl hydroperoxide and dialkylphosphoric acid are formed (170).



At a lower pH, heterolysis of the oxygen–oxygen bond occurs and dialkylphosphoric acid, methanol, and acetone are formed. This reaction is increasingly favored as the hydroxyl ion concentration is diminished, and in water this reaction occurs exclusively (170). The following mechanism is suggested for the hydrolytic cleavage (170).



This mechanism is similar to that proposed by Bartlett and Storey for the decomposition of *t*-butyl peroxyaryl sulfonates (19). It is of interest to compare the hydrolytic behavior of peroxyphosphates with that of carbon peroxides and of peroxides of metals and other metalloids. While in the carbon peroxides a cleavage of the carbon–oxygen bond is possible only if the peroxy group carrying carbon is activated by hydroxy or alkoxy substituents, in organometallic and organometalloid peroxides the cleavage always occurs at the metal–oxygen bond. Thus, peroxyphosphates seem to occupy a position between that of carbon peroxides and that of other metalloid and metal peroxides.

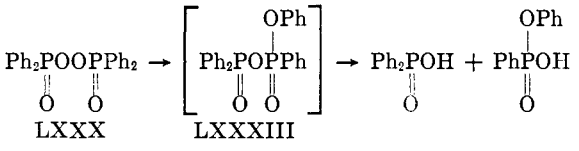
(*2*) *Decomposition.*—Rieche and co-workers noted that peroxyphosphates are thermally unstable and decompose rapidly on heating. However, they made no attempt to isolate products of this decomposition (170). Recently it was found (192) that anhydrous peroxyphosphates, LXXVIII (R = Et, *i*-Pr; R′ = CMe_3), undergo a facile decomposition under mild conditions to give the corresponding tetraalkyl pyrophosphates, LXXXI (R = Et, *i*-Pr), methanol, acetone, and *t*-butyl alcohol. However, decomposition of LXXVIII,

$$(RO)_2P(O)OP(O)(OR)_2$$
LXXXI

R = *n*-Bu, produces LXXXI, R = *n*-Bu, in very low yield, and di-*n*-butyl *t*-butylphosphate was suggested as the major product (192).

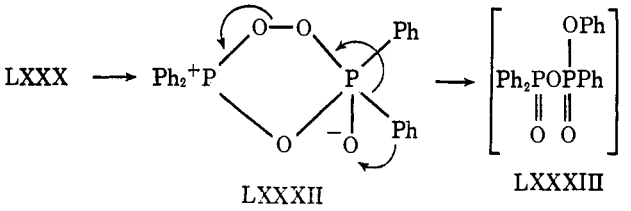
Dannley and Kabre (49) studied the (i) thermal, (ii) base-catalyzed, (iii) acid-catalyzed, and (iv) photochemical decompositions of bisdiphenylphosphinic peroxide, LXXX.

(*i*) *Thermal Decomposition of LXXX.*—Peroxide LXXX is stable at −80°, but undergoes a rearrangement on heating to give an unsymmetric anhydride, LXXXIII, which was not isolated. Instead, phenylhydrogen phenylphosphonate and diphenylphosphinic acid were obtained after hydrolysis of the reaction mixture (49).

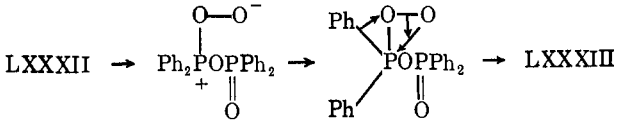


The same result was obtained by using either chloroform, tetrachloroethane, or dimethylformamide as solvents. However, the decomposition of LXXX in methylene chloride yielded bisphenyl phosphonic anhydride diphenyl ester, plus phenylhydrogen phenylphosphonate (49).

Two mechanisms are proposed to account for the formation of LXXXIII. One of the mechanisms involves migration of a carbonium ion.



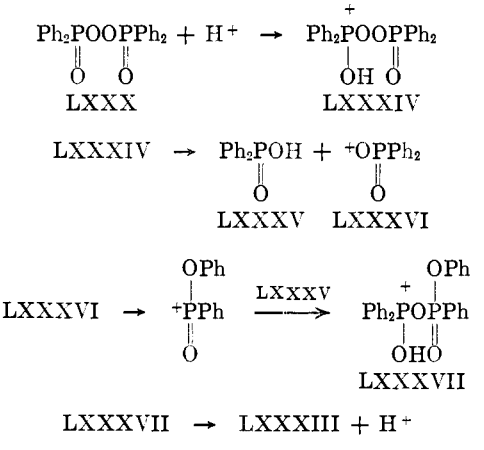
The other mechanism involves the migration of a carbanion (49).



(*ii*) *Base-Catalyzed Decomposition of LXXX.*—In the pyridine-catalyzed decomposition, the peroxide, LXXX, is reduced to diphenylphosphinic acid and the amine is recovered unchanged. However, the decomposition of LXXX in cyclohexene in the presence of an aqueous solution of sodium hydroxide produces *trans*-α-hydroxycyclohexyl diphenylphosphinate in a 16% yield (49).

(*iii*) *Acid-Catalyzed Decomposition of LXXX.*—Decomposition of LXXX in acetic acid at 25° produces a mixture of phenylhydrogen phenylphosphonate and diphenylphosphinic acid (49).

By analogy to the acid-catalyzed decomposition of carbon peroxides, the following mechanism was proposed.



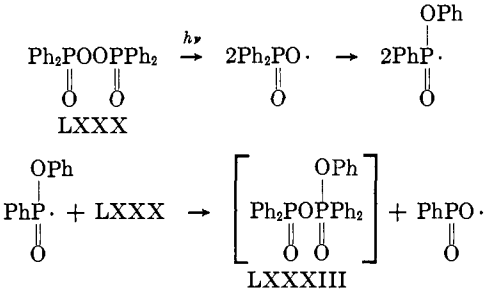
(*iv*) *Photochemically Induced Decomposition of LXXX.*—Dannley and Kabre showed that the decomposition of bisdiphenyl phosphinic peroxide (LXXX) by ultraviolet light produces the same products as those obtained by thermal decomposition (49). A homolytic reaction mechanism was proposed for the formation of the intermediate unsymmetric anhydride, LXXXIII, involving an unusual rearrangement of a phosphorus–oxygen radical to a phosphorus radical.

TABLE XVIII

ORGANOARSENIC PEROXIDES

R	R′	Method of prepn	Yield, %	Mp, °C or bp, °C (mm)	n_D (°C)	Ref
			(A) $R_3As(OOR')_2$			
Me	CMe_3	*a, c, d*	90	75–76		163, 167, 168
Me	CMe_2Ph	*c, d*	97	49–50		167, 168
Me	CPh_3	*a, c*	55	107–108		163, 168
Et	CMe_3	*d*	98	53–54 (0.02)	1.4478 (20)	167, 168
Et	CMe_2Ph	*b, d*	100	74–75 (0.1)	1.5282 (20)	168
Et	CPh_3	*c*	76	115		168
n-C_3H_7	CMe_3	*d*	37	82–83 (0.1)	1.4503 (20)	168
n-C_3H_7	CMe_2Ph	*d*	93	47–53 (0.05)	1.5185 (20)	168
n-C_4H_9	CMe_3	*d*	89		1.4522 (20)	168
Ph	CMe_3	*c, d, e, f*	97	121–122		167, 168
Ph	CMe_2Ph	*a, d*	56	81–83		167, 168
Ph	$C_{10}H_{11}$ (tetralyl)	*c*	60	126–127		167, 168
			(B) $(R_3AsOO)_n$			
Et		*b*	88	Solid; non-melting		167, 168
n-C_3H_7		*b*	89	117		168
Ph		*c*	68	95		168
			(C) $[Ph(Me)(Br)As-O-]_2$			
$[Ph(Me)(Br)As-O-]_2$		*g*		~110		210

[a] $R_3AsX_2 + R'OOH \xrightarrow{NaNH_2} R_3As(OOR')_2 + 2HX$. [b] $R_3As(OR'')_2 + R'OOH \rightarrow R_3As(OOR')_2 + 2R''OH$. [c] $R_3AsX_2 + R'OOH \xrightarrow{Na\text{-}MeOH} R_3As(OOR')_2 + 2HX$. [d] $R_3AsX_2 + R'OOH \rightarrow R_3As(OOR')_2 + 2HX$. [e] $R_3AsX_2 + NH_3 + R'OOH \rightarrow R_3As(OOR')_2 + 2NH_4X$. [f] $R_3As{=}NH_2Cl + R'OOH \rightarrow R_3As(OOR')_2 + NH_4Cl$. [g] $(R_3As)_2 + O_2 \rightarrow (R_3AsO)_2$.



(3) *Polymerization.*—It has been claimed that peroxyesters of phosphoric acid can be used to initiate polymerization of vinyl monomers (125, 172).

2. *Arsenic and Antimony*

a. Introduction to Arsenic and Antimony Organoperoxides

The organoarsenic and -antimony peroxides are true organometalloid peroxides; namely, the arsenic–oxygen and the antimony–oxygen bonds are to a large extent covalent. Thus, the monomeric arsenic and antimony peroxides are usually soluble in most organic solvents, such as ether, petroleum ether, benzene, and chloroform. Their thermal stability is similar to that of organoperoxides of elements of group IV. Antimony peroxides can be stored at room temperature for prolonged periods of time without noticeable decomposition. The organic peroxides of arsenic and antimony are usually nonexplosive and are insensitive to friction or impact. Also, the polymeric peroxides of arsenic and antimony have good thermal stability.

b. Preparation of Arsenic and Antimony Organoperoxides (See Tables XVIII and XIX)

Most organic peroxides of arsenic and antimony of the structure LXXXVIII can be prepared using the same methods. The following methods have been

$R_3M(OOR')_2$
LXXXVIII

M = As or Sb; R, R′ = alkyl, aralkyl, aryl

developed by Rieche and co-workers (167, 168): (i) Condensation of an organometallic halide with an organic hydroperoxide in the presence of sodamide to produce compounds LXXXVIII (163, 167, 168)

TABLE XIX

ORGANOANTIMONY PEROXIDES

R	R′	R	Method of prepn	Yield, %	Mp, °C	Ref
			(A) $R_3Sb(OOR')_2$			
Me	CMe_3		*a, c, g, h*	94	82–84	163, 164, 167, 168
Me	CMe_2Ph		*a, e*	70	47–49	163, 168
Me	C_9H_9O (isochromanyl)		*a, e*	84	82–84	163, 167, 168
C_6H_{11}	CMe_3		*a, e*	87	128–130	163, 167, 168
$PhCH_2$	CMe_3		*a, e*	91		163, 168
$PhCH_2$	CPh_3		*a*	97	166–168	163, 167, 168
$PhCH_2$	$C_{10}H_{11}$ (tetralyl)		*a, e*	88		163, 168
Ph	H		*a*	97.9	125 dec	163, 167
Ph	CMe_3		*a, c, e, g, h*	87	101–103	163, 164, 168
Ph	CMe_2Ph		*a, e, h*	85	87–88	163, 164, 167, 168
Ph	C_6H_9 (cyclohexene-1-yl)		*a, e*	81	84–85.5	163, 167, 168
Ph	$C_{10}H_{11}$		*a, b, e*	100	186–188	168
Ph	C_9H_9O		*a, b, e*	99	178–180	163, 168
			(B) $R_3Sb(X)OOR'$			
Ph	CMe_3	Et	*a*	97		163, 168
Ph	CMe_3	Br	*b*	90	117–118	168
Ph	CMe_3	OEt	*b*	80		168
Ph	CMe_3	OC_4H_9	*b*	85		168
Ph	CMe_3	OH	*a*		148–150	163
			(C) $(R_3Sb(OO)_n)$			
Me			*b*	92	222–223	168
Ph			*d, f*	98	205–210	168
Ph			*d, f*		150 dec	167
			(D) $R_3SbOOSbR_3$			
Ph			*f*	94.7	150–151	163
			(E) Organoperoxyantimony Oxides			
$(Me_3COOSbPh_3)_2O$			*a*	93	149–151	168
$[(Me_3COO)_2Sb]_2O$			*a*		100	163

[a] $R_3SbX_2 + R'OOH \xrightarrow{NaNH_2} R_3Sb(OOR')_2 + 2HX$. [b] $R_3Sb(OR'')_2 + R'OOH \rightarrow R_3Sb(OOR')_2 + 2R''OH$. [c] $R_3SbX_2 + R'OOH \xrightarrow{Na\text{-}MeOH} R_3Sb(OOR')_2 + 2HX$. [d] $R_3SbX_2 + H_2O_2 \xrightarrow{EtOH\text{-}NH_3} (R_3SbO)_2 + 2HX$. [e] $R_3SbX_2 + R'OOH \rightarrow R_3Sb(OOR')_2$. [f] $R_3SbX_2 + H_2O_2 \rightarrow (R_3SbO)_2 + 2HX$. [g] $R_3SbX_2 + NH_3 + R'OOH \rightarrow R_3Sb(OOR')_2 + 2NH_4X$. [h] $R_3SbO + R'OOH \rightarrow R_3Sb(OOR')_2 + H_2O$.

$$R'OOH + NaNH_2 \rightarrow R'OONa + NH_3$$

$$R_3MX_2 + 2R'OONa \rightarrow \text{LXXXVIII} + 2NaX$$

This reaction is carried out in anhydrous benzene at room temperature. (ii) Reactions of alkoxides of arsenic and antimony with organic hydroperoxides (167, 168) to give product LXXXVIII

$$R_3M(OR'')_2 + 2R'OOH \rightarrow \text{LXXXVIII} + 2R''OH$$

The same reaction may be carried out without the isolation of the intermediate dialkoxide by first condensing a dihalide with an alcohol in the presence of ammonia

$$R_3MX_2 + 2R''OH + 2NH_3 \rightarrow R_3M(OR'')_2 + 2NH_4X$$

and then adding the hydroperoxide to the reaction mixture. (iii) Condensation of dihalides of arsenic and antimony with organic hydroperoxides in the presence of either ammonia or amines (167, 168).

$$R_3MX_2 + 2R'OOH + 2NH_3 \rightarrow \text{LXXXVIII} + 2NH_4X$$

(iv) Peroxides of arsenic and antimony can be obtained by condensation of organic hydroperoxides with imino halides which are prepared *in situ* (167, 168).

$$R_3MX_2 + 2NH_3 \rightarrow \underset{\text{LXXXIX}}{[R_3M{=}NH_2]^+X^-} + NH_4X$$

$$\text{LXXXIX} + 2R'OOH \rightarrow \underset{\text{LXXXVIII}}{R_3M(OOR')_2} + NH_4X$$

c. Preparation of Organoantimony Peroxides (See Table XIX)

Organoantimony oxides or dihydroxides react with organic hydroperoxides to give compounds of structure LXXXVIII (164, 167, 168).

$$R_3Sb{=}O + 2R'OOH \rightarrow \text{LXXXVIII } (M = Sb) + H_2O$$

$$R_3Sb(OH)_2 + 2R'OOH \rightarrow \text{LXXXVIII } (M = Sb) + 2H_2O$$

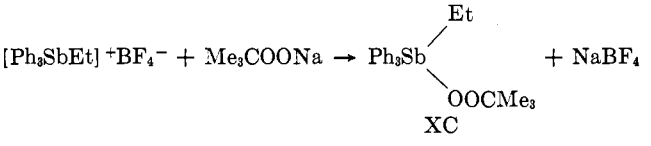
This method is only suitable for the preparation of antimony peroxides, which, as compared to arsenic compounds, are relatively resistant to hydrolysis.

Antimony peroxides of the general structure XC were prepared by the following methods (168). (i)

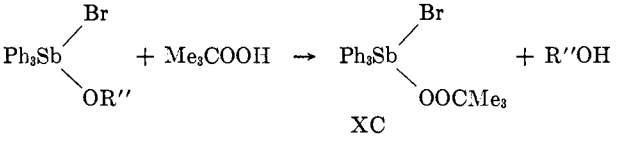
$$\underset{\text{XC}}{R_3Sb(X)OOR'}$$

X = Et, Br, OH, OR″; R = alkyl, aryl; R′ = CMe_3

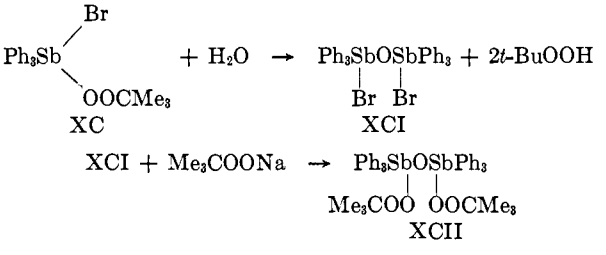
Preparation of XC (X = Et): triphenylethylantimony tetrafluoroboride reacts with the sodium salt of *t*-butyl hydroperoxide to give XC (X = Et).



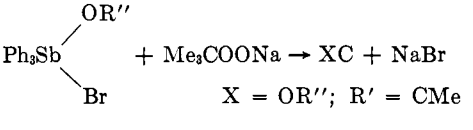
(ii) Preparation of XC (X = Br): triphenylalkoxyantimony bromide reacts with *t*-butyl hydroperoxide to give triphenyl-*t*-butylperoxyantimony bromide



The hydrolysis of XC (X = Br, R′ = CMe_3) produces XCI, which reacts with the sodium salt of *t*-butyl hydroperoxide to give a diperoxide, XCII.



(iii) Preparation of XC (X = OR″): triphenylalkoxyantimony bromide reacts with the sodium salt of the hydroperoxide to give triphenyl-*t*-butylperoxy antimony alkoxide, XC.

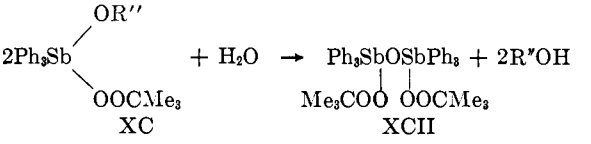


The same peroxide is also obtained from the reaction of triphenylantimony dialkoxide and *t*-butyl hydroperoxide.

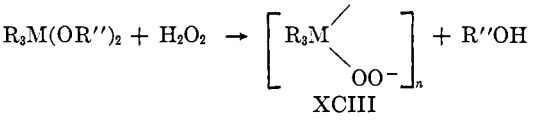
$$Ph_3Sb(OR'')_2 + Me_3COOH \rightarrow XC + R''OH$$

X = OR″; R = CMe_3

Hydrolysis of compound XC (X = OR″; R′ = CMe_3) yields a diperoxide XCII (168).

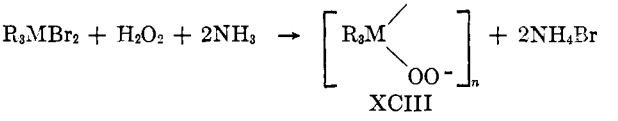


Polymeric arsenic and antimony peroxides have been prepared by the following methods (167, 168): (i) Condensation of organic metal dialkoxides with hydrogen peroxide



R″ = alkyl; M = As, Sb; R = alkyl, aryl

(ii) Condensation of organic metal dihalides with hydrogen peroxide in the presence of ammonia



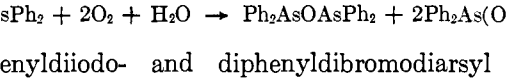
M = As, Sb; R = alkyl, aryl; R″ = alkyl

d. Arsenic and Antimony Organoperoxides as Intermediates

As early as 1929, Blicke and Smith found that tetraaryl diarsyls reacted rapidly with oxygen to give peroxides which, however, could not be identified (27, 29). In the presence of water, tetraphenyldiarsyl reacted with oxygen to yield a mixture of tetraphenylarsyl oxide and diphenylarsenic acid (28).

$$2Ph_2AsAsPh_2 + 2O_2 + H_2O \rightarrow Ph_2AsOAsPh_2 + 2Ph_2As(O)OH$$

Diphenyldiiodo- and diphenyldibromodiarsyl absorb only 0.5 mole of oxygen to give phenylarsenic oxide and phenylarsenic dihalide (28).



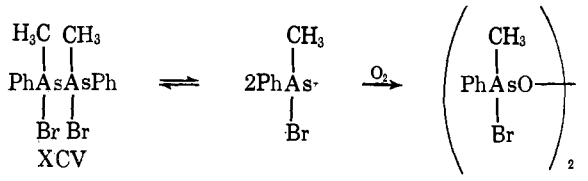
X = Br, I

Intermediate peroxides were assumed in these reactions (28).

Similarly, tetraphenyldistibyl readily reacts with oxygen. The amount of oxygen absorbed corresponds to a compound with structure XCIV; however, the product was not characterized (26). The autoxidation

$$\underset{\text{XCIV}}{Ph_2SbOOSbPh_2}$$

of dimethyldiphenyldibromodiarsyl (XCV) was proposed to proceed as follows (210)



The product is a white powder which decomposes at around 110°.

e. Reactions of Arsenic and Antimony Organoperoxides

(*1*) *Hydrolysis.*—The sensitivity of various arsenic and antimony peroxides varies appreciably; while the dialkylperoxy arsenic compounds are sensitive to hydrolysis, the corresponding antimony derivatives are comparatively stable. This stability toward hydrolysis increases with molecular weight. Thus, the triaryl derivatives are more stable than the corresponding trialkyl derivatives. The hydrolytic cleavage occurs at the arsenic–oxygen and antimony–oxygen bonds, respectively. Thus, the hydrolysis of peroxides LXXXVIII (M = As) gives organoarsenic oxides and the original hydroperoxide (168).

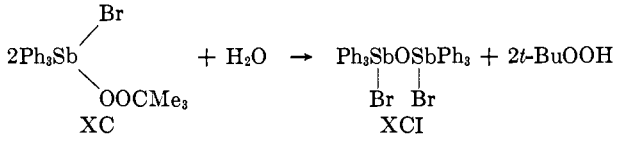
$$\underset{\text{LXXXVIII}}{R_3M(OOR')_2} + H_2O \rightarrow R_3As{=}O + 2R'OOH$$

M = As

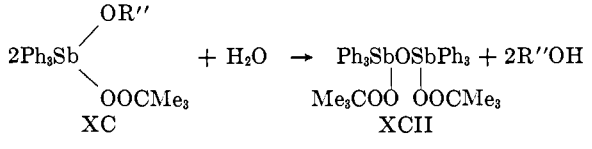
In contrast to compounds containing two alkylperoxy groups, the organoantimony peroxides containing one alkylperoxy group are sensitive to hydrolysis. Antimony peroxides of the general formula XC yield two

$$\underset{\text{XC}}{R_3Sb(X)OOR'}$$

different products depending on the nature of X. If X is a bromine atom, the hydrolysis produces a mixture of compound XCI and hydroperoxide (168).



If X is an alkoxy group, a diperoxide, XCII, is formed in addition to alcohol (168)



(*2*) *Reaction with Anhydrous Hydrogen Chloride.*—Reaction of peroxides of structure LXXXVIII (M = As or Sb) with anhydrous hydrogen chloride gives organometallo dihalides and the original hydroperoxide (168).

$$\underset{\text{LXXXVIII}}{R_3M(OOR')_2} + 2HCl \rightarrow R_3MCl_2 + 2R'OOH$$

(*3*) *Oxygen–Oxygen Cleavage and Rearrangement.*—Cleavage of the oxygen–oxygen bond with concomitant rearrangement, as found in peroxyphosphorus compounds, has not been observed with arsenic and antimony peroxides (167, 168).

(*4*) *Polymerization.*—Peroxides of arsenic and antimony initiate the polymerization of vinyl monomers (163, 164).

H. ORGANOPEROXIDES OF ELEMENTS OF GROUP VIa[3]

Sulfur

a. Preparation of Unsymmetric Organosulfur Peroxides (See Table XX)

Bartlett and Storey (19) prepared a series of unsymmetric *t*-butyl arylpersulfonates, XCVI, from sulfonyl chlorides and *t*-butyl hydroperoxide in the presence of pyridine.

$$p\text{-}XPhSO_2Cl + Me_3COOH \rightarrow \underset{\text{XCVI}}{p\text{-}XPhSO_2OOCMe_3}$$

X = H, Me, MeO, Cl, Br

An attempt to prepare a nitro derivative of XCVI (X = NO_2) was unsuccessful (19). The failure was attributed to a probable rearrangement of the peroxester (19).

b. Preparation of Symmetric Organosulfur Peroxides (See Table XX)

The first well-defined symmetric organosulfur peroxide, XCVII, was prepared by Weinland and Lewkowitz in 1903 (204). The reaction of phenylsulfonyl chloride with sodium peroxide in ice water yielded 10% of benzenesulfonyl peroxide, XCVII (75, 204). Jones and Friedrich (102a) report the preparation of peroxide XCVII (R = Me), mp 77°, by the electrolysis of methylsulfonic acid.

$$\underset{\text{XCVII}}{(RSO_2O)_2}$$

R = Ph

$$2RSO_2Cl + Na_2O_2 \rightarrow \underset{\text{XCVII}}{RSO_2OOSO_2R} + 2NaCl$$

R = Ph

Bolte, *et al.* (33), prepared XCVII and other arylsulfonyl peroxides of the structure XCVIII by the reaction of benzenesulfonyl chlorides, XCIX, with 30% hydrogen peroxide in the presence of sodium hydroxide.

$$\underset{\text{XCIX}}{XPhSO_2Cl} + H_2O_2 \xrightarrow{NaOH} \underset{\text{XCVIII}}{(XPhSO_2O)_2} + 2NaCl$$

X = H, Me, Cl, Br

Razuvayev, *et al.*, prepared a series of benzoyl alkanesulfonyl peroxides, C, by the reaction of the cor-

(3) Selenyl peresters, RSe(O)OO-*t*-Bu, have been proposed as reaction intermediates in the radical decomposition of *t*-butyl hydroperoxide by dialkyl diselenides and by alkane- and areneseleninic anhydrides and acids in benzene (206a).

TABLE XX

ORGANOSULFUR PEROXIDES

Starting materials	Condensing agent	Product	Yield, %	Mp, °C	n_D (°C)	Ref
		(A) RSO_2OOR'				
(1) p-$XPhSO_2Cl$ + t-BuOOH	Pyridine	p-$XPhSO_2OOCMe_3$				
X						
CH_3		p-$CH_3PhSO_2OOCMe_3$	65–75	36.5–37 dec		19
OCH_3		p-$OCH_3PhSO_2OOCMe_3$	80	47 expl		19
Br		p-$BrPhSO_2OOCMe_3$	2–5	40–41 expl		19
Cl		p-$ClPhSO_2OOCMe_3$	2–6	30–30.5 expl		19
H		$PhSO_2OOCMe_3$	34		1.4629 (25)	19
(2) RSO_2Cl + BaOOBz		RSO_2OOBz				
R						
Me		$MeSO_2OOBz$	43	54–55		121
Et		$EtSO_2OOBz$	60	46.5–47.5		121
n-Pr		n-$PrSO_2OOBz$	32.7	24–25		121
i-Pr		i-$PrSO_2OOBz$	35.0	49–50		121
$PhCH_2$		$PhCH_2SO_2OOBz$	28.5			121
(3) RH + SO_2 + O_2 + Ac_2O (or AcOH)		RSO_2OOAc				
R						
Cyclohexyl		$C_6H_{11}SO_2OOC(O)CH_3$	35			191
		(B) RSO_2OOSO_2R				
(1) $2RSO_2Cl$ + Na_2O_2		$(RSO_2O)_2$				
R						
Ph		$(PhSO_2O)_2$	10	53–54 dec		41
(2) $2RSO_2Cl$ + H_2O_2		$(RSO_2O)_2$				
R						
Ph	NaOH (aq)	$(PhSO_2O)_2$	20			33
p-MePh	NaOH (aq)	$(p$-$MePhSO_2O)_2$	80	50 dec		33
p-ClPh	NaOH (aq)	$(p$-$ClPhSO_2O)_2$	80	75 dec		33
p-BrPh	K_2CO_3	$(p$-$BrPhSO_2O)_2$		76 dec		45
o-NO_2Ph	K_2CO_3	$(o$-$NO_2PhSO_2O)_2$	22	97 dec		45
m-NO_2Ph	K_2CO_3	$(m$-$NO_2PhSO_2O)_2$	30	112 dec		45
p-NO_2Ph	K_2CO_3	$(p$-$NO_2PhSO_2O)_2$	45	128 dec		45

responding alkylsulfonyl chloride and the barium salt of perbenzoic acid in the presence of water (121, 152, 154).

$$RSO_2Cl + \underset{\underset{O}{\|}}{BaOOCPh} \xrightarrow{H_2O} \underset{C}{RSO_2OOBz}$$

R = Me, Et, n-Pr, i-Pr, $PhCH_2$

Dannley and Corbett (45) prepared nitro derivatives of benzenesulfonyl peroxides, XCVIII, by the reaction of nitrobenzenesulfonyl chlorides with hydrogen peroxide in ethanol at −20° in the presence of potassium carbonate.

$$x\text{-}NO_2PhSO_2Cl + H_2O_2 \xrightarrow{K_2CO_3} \underset{\text{XCVIII}}{(x\text{-}NO_2PhSO_2O)_2}$$

$x = o, m, p$

The stability of nitro derivatives of arylsulfonyl peroxides is postulated to arise from the electron-withdrawing inductive effect of the nitro group.

c. Organosulfur Peroxides as Intermediates: Sulfoxidation

The light or γ-ray induced reaction of alkanes and cycloalkanes with a mixture of sulfur dioxide and oxygen proceeds through a peroxysulfonic acid intermediate to give the corresponding sulfonic acids, CI.

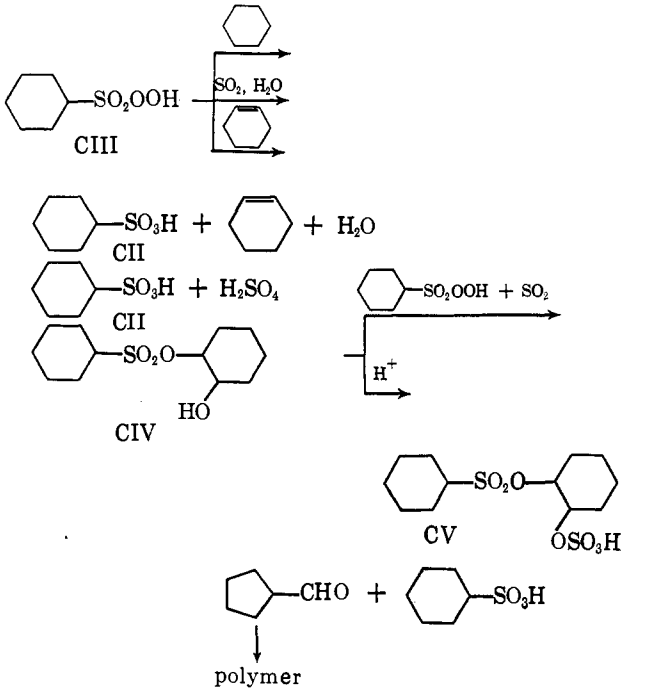
$$RH + SO_2 + O_2 \xrightarrow{h\nu} [RSO_2OOH] \rightarrow \underset{\text{CI}}{RSO_2OH}$$

A free-radical chain mechanism has been proposed for the formation of the peroxysulfonic acid intermediate (99, 199).

$$R\cdot + SO_2 \rightarrow RSO_2\cdot$$
$$RSO_2\cdot + O_2 \rightarrow RSO_2OO\cdot$$
$$RSO_2OO\cdot + RH \rightarrow RSO_2OOH + R\cdot$$

The γ-ray induced sulfoxidation of cyclohexane produced a high yield of cyclohexanesulfonic acid (CII). In addition, the following products were formed and identified: cyclohexaneperoxysulfonic acid (CIII),

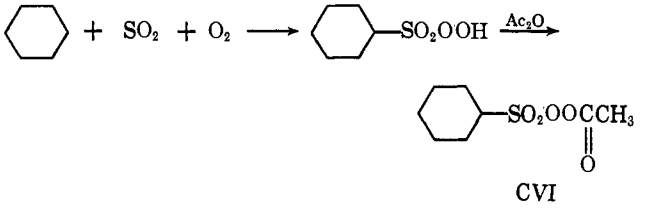
cyclohexanedisulfonic acid, the monoester of cyclohexanediol-1,2 (CIV), the mixed ester of cyclohexanediol-1,2 (CV), and trace quantities of cyclopentylformaldehyde and cyclohexene. To account for these products the following reaction scheme was proposed (99).



The photochemical sulfoxidation of *n*-hexane in acetic anhydride at 28° produced a 26% yield of hexanesulfonic acid (137). This reaction is sensitized by acetophenone and *p*-chloroacetophenone (137) and is inhibited by 2,3-dimethylbutane and 1-hexene. The reaction proceeds through an intermediate acetylhexanesulfonyl peroxide in accordance with the following scheme (137)

$$RSO_2OOH + Ac_2O \rightarrow RSO_2OOAc + AcOH$$
$$RSO_2OOAc \rightarrow RSO_2O\cdot + OAc$$
$$RSO_2O\cdot + RH \rightarrow \underset{CI}{RSO_2OH} + R\cdot$$
$$AcO\cdot + RH \rightarrow AcOH + R\cdot$$
$$R = C_6H_{13}$$

The photochemically induced sulfoxidation of cyclohexane in either acetic acid (191) or acetic anhydride (199) produces acetylsulfonyl peroxide (CVI) (191, 199).



A collection of pertinent references to the sulfoxidation reaction can be found in the literature (99, 137, 191, 199).

d. Reactions of Organosulfur Peroxides

(*1*) *Hydrolysis.*—The decomposition of benzenesulfonyl peroxide (XCVII) in water yielded phenol and sulfuric acid (75).

(*2*) *Decomposition.* (*a*) *Decomposition of Unsymmetric Organosulfur Peroxides.*—Bartlett and Storey studied the decomposition of peresters, XCVI, in methanol at room temperature. Only two products were isolated in quantitative yields: acetone and the corresponding arylsulfonic acid (19). Two mechanisms were proposed (19). The first involves rearrangement of XCVI to a hemiketal sulfonate, CVII, which then undergoes methanolysis to give the ketal, CVIII, which in turn is hydrolyzed to give the products.

$$\underset{XCVI}{p\text{-}XPhSO_2OOCMe_3} \rightarrow [(CH_3)_3CO^+OTs^-] \rightarrow \underset{CVII}{(CH_3)_2C(OCH_3)(OTs)}$$

$$CVII \xrightarrow{CH_3OH} \underset{CVIII}{(CH_3)_2C(OCH_3)_2} + HOTs$$

The second mechanism involves an attack on the cation, CIX, by the solvent molecule to give the ketal, CVIII.

$$\underset{XCVI}{p\text{-}XPhSO_2OOCMe_3} \rightarrow [(CH_3)_3CO^+OTs^-] \xrightarrow{CH_3OH} \underset{CIX}{[(CH_3)_2C^+OCH_3]} + OTs^-$$

$$CIX + TsO^- \xrightarrow{CH_3OH} \underset{CVIII}{(CH_3)_2C(OCH_3)_2} + HOTs$$

The isomerization of the benzoyl alkylpersulfonates, C, at 20–50° yields mixed anhydrides of the corresponding alkanesulfonic acids and phenoxyformic acid, CX (152, 154).

$$\underset{C}{RSO_2OOC(=O)Ph} \rightarrow \underset{CX}{RSO_2OC(=O)Ph}$$

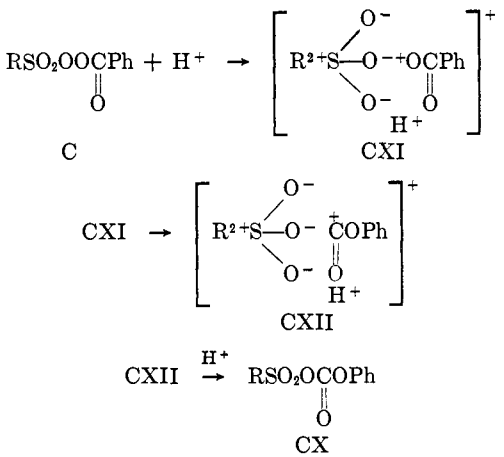
$$R = Me, Et, n\text{-}Pr, i\text{-}Pr, PhCH_2$$

The isomerization is catalyzed by the corresponding alkanesulfonic acid, which is initially formed by a homolytic decomposition of the peroxide. A mechanism is suggested in which a proton addition to C results in the formation of the sulfonic acid anion and the benzoyloxy cation, CXI. The rearrangement is facilitated by the electron-donating phenyl group. The formation of CX then occurs by proton loss.

TABLE XXI

PRODUCTS OF REACTION OF ARYLSULFONYL PEROXIDES WITH OLEFINS

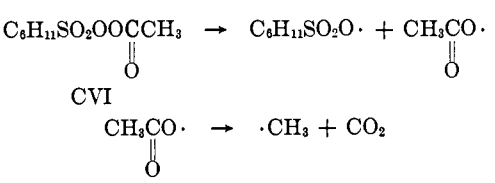
Peroxide	Olefin	Product	Mp, °C	Ref
$(PhSO_2O)_2$	*trans*-Stilbene	$PhCH(OSO_2Ph)CH(OSO_2Ph)Ph$	124	33
$(p\text{-}MePhSO_2O)_2$	*trans*-Stilbene	$PhCH(OSO_2PhMe\text{-}p)CH(OSO_2PhMe\text{-}p)Ph$	140–150 dec	33
$(p\text{-}MePhSO_2O)_2$	*cis*-Stilbene	$PhCH(OSO_2PhMe\text{-}p)CH(OSO_2PhMe\text{-}p\text{-})Ph$	140–150 dec	33
$(p\text{-}MePhSO_2O)_2$	Styrene	$PhCH(OSO_2PhMe\text{-}p)CH_2SO_2OPhMe\text{-}p$	116	33
$(p\text{-}ClPhSO_2O)_2$	*trans*-Stilbene	$PhCH(OSO_2PhCl\text{-}p)CH(OSO_2PhCl\text{-}p)Ph$	126	33
$(p\text{-}BrPhSO_2O)_2$	*trans*-Stilbene	$PhCH(OSO_2PhBr\text{-}p)CH(OSO_2PhBr\text{-}p)Ph$	135	33



Thermal decomposition of C in benzene, isopropyl alcohol, and CCl_4 yields 83, 80, and 45% of CX, respectively (152).

The peroxide C was decomposed in isopropyl alcohol in the presence of finely divided potash. In the solvent distillate, a 75% yield of acetone was found as compared to a 17% yield in the absence of potash. When sulfonic acid was introduced into a carbon tetrachloride solution of the peroxide, a 65% yield of the mixed anhydride was found as compared to a 45% yield in the absence of the sulfonic acid. Aprotic acids, such as aluminum trichloride, tin tetrachloride, and antimony pentachloride, favor heterolytic isomerization of the peroxides, C, and CX is produced in a 85% yield (152).

Thermal decomposition of acetylcyclohexanesulfonyl peroxide (CVI) in isopropyl alcohol, cyclohexane, benzene, and carbon tetrachloride was studied by Razuvayev, *et al.* (153). On the basis of the product mixture, they concluded that two reactions occur simultaneously (153): a free radical chain reaction



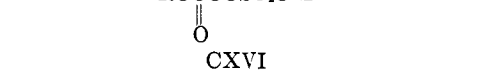
$$\cdot CH_3 + RH \rightarrow CH_4 + R\cdot$$

or

$$\cdot CH_3 + CCl_4 \rightarrow CH_3Cl + \cdot CCl_3$$
$$2\cdot CCl_3 \rightarrow C_2Cl_6$$
$$C_6H_{11}SO_2O\cdot + RH \rightarrow C_6H_{11}SO_2OH + R\cdot$$

CCl_4, RH = solvents

and a molecular reaction



(*b*) *Decomposition of Symmetric Organosulfur Peroxides.*—The decomposition of benzenesulfonyl peroxide (XCVII) in benzene at room temperature yields 48–52% of phenylbenzenesulfonate plus benzenesulfonic acid (41).

$$\underset{\text{XCVII}}{(PhSO_2O)_2} + C_6H_6 \rightarrow PhSO_2OPh + PhSO_2OH$$

The decomposition of nitro derivatives of benzenesulfonyl peroxide (XCVIII) in aromatic solvents yields the corresponding nitrosulfonic acids, CXIII, and a mixture of the *ortho* and *para* derivatives of the sulfonic esters, CXIV, exclusively (45).

$$\underset{\text{XCVIII}}{(x\text{-}O_2NPhSO_2O)_2} + PhX \rightarrow \underset{\text{CXIII}}{x\text{-}O_2NPhSO_2OH} + \underset{\text{CXIV}}{x\text{-}O_2NPhSO_2OPhX}$$

$x = o, m, p;$ X = H, F, Cl

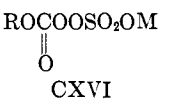
The ratio of the *ortho* and *para* derivatives of CXIV indicates an electrophilic reaction mechanism.

p-Toluenesulfonyl peroxide (XCVIII, X = *p*-Me) reacts with either *cis*- or *trans*-stilbene in benzene or chloroform to yield hydrobenzoin ditoluenesulfonate (CXV).

$$\underset{\text{XCVIII}}{(XPhSO_2O)_2} + PhCH{=}CHPh \rightarrow \underset{\text{CXV}}{PhCH(OSO_2PhMe\text{-}p)CH(OSO_2PhMe\text{-}p)Ph}$$

Similarly, *p*-toluenesulfonyl peroxide reacts with styrene to give a 1:1 adduct (33). Other arylsulfonyl peroxides, XCVIII (X = H, *p*-Cl, and *p*-Br), form analogous addition compounds with *trans*-stilbene (33) (see Table XXI).

(*3*) *Polymerization.*—It is claimed (73a) that organosulfur peroxides of structure CXVI are free radical catalysts for emulsion, dispersion, or suspension



R = cyclohexyl; M = alkali or alkali earth metal ion or NH_4^+

polymerization.

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