Chemistry of Organophosphorus Compounds Containing the Peroxide Bond

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Contents

I. Introduction

Peroxides of organic phosphorus derivatives have been postulated[1] for some time as possible intermediates in certain biological transformations, although they have never been isolated in such systems. Thus, in 1956, the reaction of isopropyl methylphosphonofluoridate with the hydroperoxide ion was thought to produce perhydroxylated intermediates.[2]

Likewise, the hydrolysis of paraoxon (1), a common

$$(C_2H_5O)_2P(O)\text{—}O\text{—}\bigcirc\text{—}NO_2 \xrightarrow{HO_2^-} (C_2H_5O)_2P(O)OO^-$$

1   2
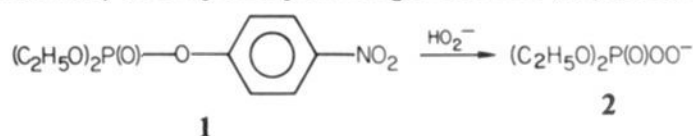
insecticide, was found to be accelerated by hydrogen peroxide, and hence the reaction was postulated to occur via the hydroperoxide intermediate 2.[3] However, it was not until 1959 that the first peroxy ester of phosphorus of the type 3 was synthesized, isolated, and

$$(RO)_2P(O)OOR'$$

3, R = CH$_3$, C$_2$H$_5$; R' = (CH$_3$)$_3$C

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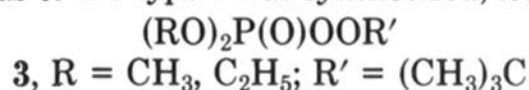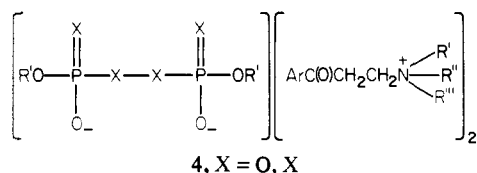
characterized by Rieche, Hilgetag, and Schramm.[4-6] Since that first report, considerable effort has been made in expanding the chemistry of organophosphorus compounds containing a peroxide bond. The area has been the subject of a number of short review articles.[7-12]

However, the coverage of the topic has been somewhat incomplete, and much of the literature published concerning peroxy esters of phosphorus has appeared in journals which are generally not readily accessible. The purpose of this work is to consolidate that information into a comprehensive and critical review, providing the incentive for further pursuit of some of the aspects of this topic.

II. Scope

Only peroxy compounds of phosphorus which are well-defined and relatively stable will be discussed in the present review. Compounds containing the peroxy moiety not directly linked to phosphorus are included, since the chemistry of these compounds involves the transformation of the phosphorus moiety. In most cases, the chemistry of these compounds, as of that of certain peroxy esters other than peroxy phosphates 3, is confined to only one or two reactions which were not extensively investigated and which are intertwined with the preparation of these compounds. Therefore, for purpose of simplicity, the chemistry of such compounds will not be covered in a separate section under reactions, but immediately following the discussion of their preparation.

Compounds of the type 4, reported with no experi-

$$\left[R'O{-}\underset{\underset{O_-}{\overset{X}{\|}}}{P}{-}X{-}X{-}\underset{\underset{O_-}{\overset{X}{\|}}}{P}{-}OR' \right]\left[ArC(O)CH_2CH_2\overset{+}{N}\underset{\underset{R'''}{\diagdown}}{\overset{\diagup R'}{-}}R'' \right]_2$$

4, X = O, X

mental details and proposed as antifungal agents against wheat rust,[13] will not be further considered. Likewise, phosphorus ozonides such as 5, products of

$$(RO)_3P + O_3 \xrightarrow{CH_2Cl_2} (RO)_3P\underset{O}{\overset{O}{\diagup\diagdown}}O$$

5
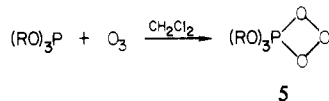
the reaction of trivalent phosphorus compound with ozone and a source of singlet oxygen,[14-16] will not be covered, since at no time was there any evidence found that these compounds react through a peroxy phosphorus intermediate.

The inorganic peroxy derivatives of phosphorus have been known for a number of years.[17,18] However, the discussion of their utilization in the hydroxylation reaction of phenols,[19] in the oxidation reaction of aromatic amines to the corresponding N-oxides,[20] in the thermal and photochemical oxidation of 2-propanol,[21] and in the oxidation of ketones to the carboxylic acid,[22] among others, is beyond the scope of this review article.

Several other aspects of peroxy phosphorus compounds will not be covered. The reaction of trialkyl phosphites with hydroperoxides was proposed to give the intermediate 6.[23,24] However, the evidence for the

$$(RO)_3P + R'OOH \longrightarrow (RO)_3P\text{--}\underset{\overset{|}{H}}{O}\text{--}O\text{--}R'$$

6
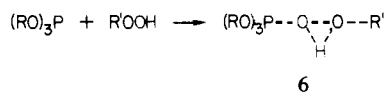
formation of 6 is not convincing.

The reaction of a dialkyl peroxide with a trialkyl phosphite in the presence of oxygen is thought to proceed via the short-lived (ca. a few minutes) tetraalk-

oxyphosphoranylperoxyl radical 7.[25,26] The phospho-

$$(RO)_3P + R'OOR' \xrightarrow{O_2} R'O(RO)_3POO\cdot$$

7
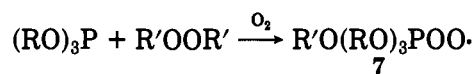
ranylperoxy radicals have also been postulated as intermediates in the autoxidation of alkanes in the presence of phosphorus trichloride,[27] in the deoxygenation of pyridine N-oxide by trialkyl phosphites,[28] and in the photoinduced oxidation of benzenoid compounds by trialkyl phosphites.[29] The chlorophosphoranylperoxyl radical 8 presumably is the intermediate in the

$$PCl_3 \xrightarrow{Cl\cdot} PCl_4 \xrightarrow{O_2} Cl_4POO\cdot \xrightarrow{PCl_3} POCl_3 + Cl\cdot$$

8
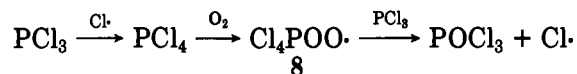
oxidation of phosphorus trichloride.[30,31] These reactions illustrate the formation of only a few of the intermediates in such oxidations. No attempt is made here at completeness in citing these intermediates, since no well-defined peroxyphosphorus derivatives derived from them are isolated.
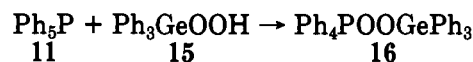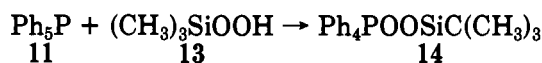
The reaction of singlet oxygen with phosphorin 9

9   10
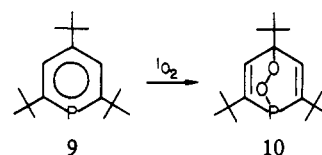
results in the unstable endoperoxide 10, which further rearranges to nonperoxy derivatives.[32] The reaction of pentaphenylphosphine (11) with tert-butyl hydroper-

$$Ph_5P + CMe_3OOH \rightarrow Ph_4POOCMe_3$$
$$11 \qquad\qquad\qquad 12$$
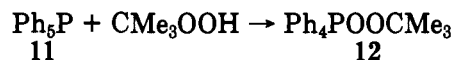
oxide gives the peroxy derivative 12 which likewise cannot be isolated.[33] Similarly, the reaction of pentaphenylphosphine (11) with hydroperoxides of silicon (13) and germanium (15) affords the phosphorus per-

$$Ph_5P + (CH_3)_3SiOOH \rightarrow Ph_4POOSiC(CH_3)_3$$
$$11 \qquad\quad 13 \qquad\qquad\qquad 14$$

$$Ph_5P + Ph_3GeOOH \rightarrow Ph_4POOGePh_3$$
$$11 \qquad\quad 15 \qquad\qquad\quad 16$$

oxides 14 and 16, respectively, which decompose readily to nonperoxidic derivatives.[34] Also apparently formed in the reaction of alkylidenephosphoranes 17 and the sodium salt of tert-butylhydroperoxide is compound 18,

$$Ph_3P{=}CRR' + NaOOCMe_3 \longrightarrow Ph_3P\text{--}\underset{\overset{|}{O}OCMe_3}{C}HRR'$$

17   18
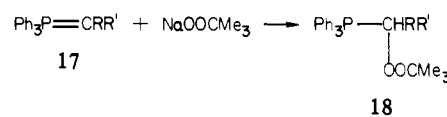
which could not be isolated[35] and characterized. The area of such transient, ill-defined species likewise will not be covered.

III. Peroxides Other Than Peroxy Esters

A. Preparation

1. Symmetric Bisphosphorus Peroxides

The inorganic salts of peroxydiphosphoric acid have been known for a number of years[17] and have been shown to be effective oxidizing agents.[18-22] However, it was only in 1965 that the first organic compounds containing the bisphosphorus peroxide linkage were

TABLE I. Symmetric Bisphosphorus Peroxides

compound	yield, %	mp or bp, °C (mm)	n^{20}D	ref
$(C_6H_5)_2P(O)OOP(O)(C_6H_5)_2$ (20)	57	88–89	a	36
$(RO)_2P(O)OOP(O)(OR)_2$ (22)				
R = C_2H_5	72	a	1.4220	37
R = C_3H_7	68	a	1.4270	37
R = C_4H_9	69	106 (1.5 × 10⁻³)	1.4320	37
R = i-C_4H_9	70	a	1.4279	37
$(C_5H_{11}O)(CH_3)P(O)OOP(O)(OC_5H_{11})(CH_3)$ (24)	64	a	1.4440	37

^{a} Not reported.

TABLE II. Phosphates Containing the Peroxy Moiety Not Directly Linked to Phosphorus[39,40]

|	$(RO)_2P(O)OCH_2OOR'^a$ (29)		
R	R'	n^{20}D	d^{20}
C_2H_5	$C(CH_3)_3$	1.4190	1.0672
n-C_3H_7	$C(CH_3)_3$	1.4238	1.0428
i-C_3H_7	$C(CH_3)_3$	1.4185	1.0348
C_4H_9	$C(CH_3)_3$	1.4274	1.0241
C_2H_5	$C(CH_3)_2C_2H_5$	1.4250	1.0777
C_4H_9	$C(CH_3)_2C_2H_5$	1.4314	1.0181

^{a} Yield not reported.

reported.[36] Bis(diphenylphosphinic) peroxide (20) is obtained in 57% yield by the reaction of diphenylphosphinic chloride (19) with sodium peroxide in a water/toluene solvent mixture. Attempts to prepare

$$2(C_6H_5)_2P(O)Cl + Na_2O_2 \xrightarrow[\text{tolene}]{H_2O}$$
$$\mathbf{19}$$

$$(C_6H_5)_2P(O)OOP(O)(C_6H_5)_2$$
$$\mathbf{20}$$
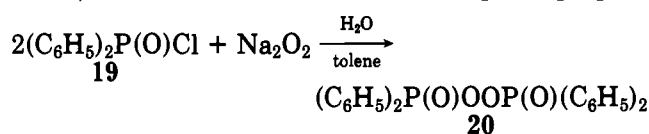
the p-nitrophenyl, p-chlorophenyl, and p-tolylphenyl analogues of 19 were unsuccessful, and only the corresponding phosphinic acids were isolated.

The phosphorus peroxides 22 (R = C_2H_5, C_3H_7, C_4H_9, i-C_4H_9) are obtained in 68–72% yield by the reaction of the corresponding dialkylphosphorochloridate 21

$$(RO)_2P(O)Cl + Na_2O_2 \xrightarrow{H_2O}$$
$$\mathbf{21}$$

$$(RO)_2P(O)OOP(O)(OR)_2$$
$$\mathbf{22}$$

$$R = C_2H_5, C_3H_7, C_4H_9, i\text{-}C_4H_9$$
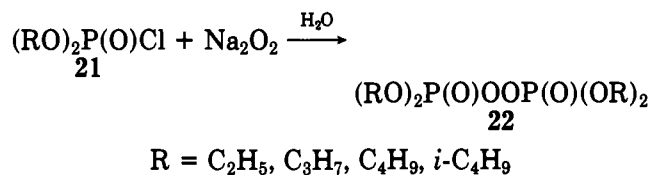
with aqueous sodium peroxide.[37] The bisphosphonate peroxide 24 is obtained in 64% yield by use of an analagous reaction with pentyl methylphosphonochloridate (23, R = C_5H_{11}, R' = CH_3).[37] Only peroxide


23   **24**
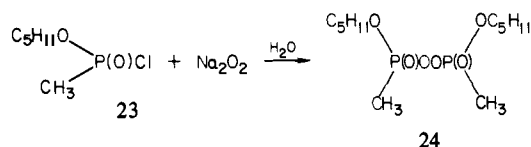
21, R = C_4H_9, can be distilled at 10⁻² torr. Attempts at the distillation of other peroxide 22 and 24 under similar conditions led to partial decomposition. Hence most products were purified by aqueous rinses. Determinations of active oxygen gave inconsistent results, presumably because of product instability. The available details concerning the bisperoxides 22 and 24 are shown in Table I.

2. Peroxides with Peroxy Group Not Linked to Phosphorus

a. Symmetric Bisperoxides

The autoxidation of 2,4,6-triphenyl-λ^3-phosphorin (25) in benzene gives 4,4'-dioxybis(1-hydroxy-1-oxo-

25

26
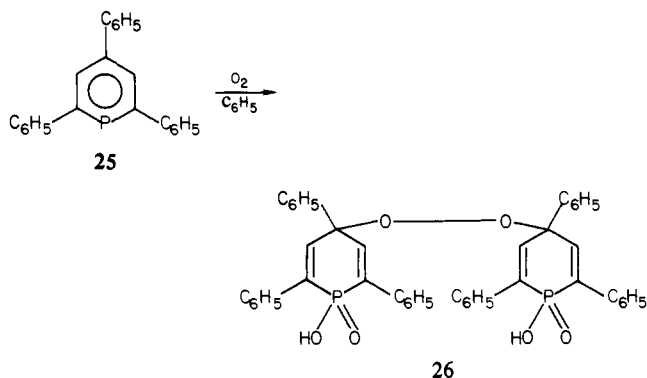
2,4,6-triphenyl-λ^5-1-phospha-2,5-cyclohexadiene (26)[38] in 58% yield. Compound 26 is exceptionally stable, and survives esterification with triethyloxonium tetrafluoroborate in the presence of ethyldiisopropylamine in dichloromethane to give a mixture of the E,E, E,Z, and Z,Z geometric isomers of compound 27. The E,E

$$26 \xrightarrow[\text{base}]{(C_2H_5)_3OBF_4}$$

27, E,E, E,Z, Z,Z
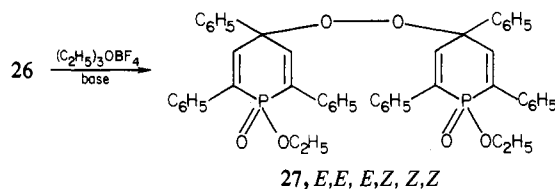
isomer is isolated by fractional crystallization in 25% yield, the remainder of the mixture consisted of a combination of the E,Z and Z,Z isomers. The stereochemical assignments of 27 are based on the ¹H NMR spectral data of the various isomers.[38]
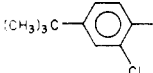
b. Asymmetric Monoperoxides

In 1966, a method for the preparation of monoperoxy compounds 29 whose phosphorus atom is not directly

$$(RO)_2P(O)Cl + HOCH_2OOR' \xrightarrow{\text{base}}$$
$$\mathbf{21} \qquad\qquad \mathbf{28}$$

$$(RO)_2P(O)OCH_2OOR'$$
$$\mathbf{29}$$
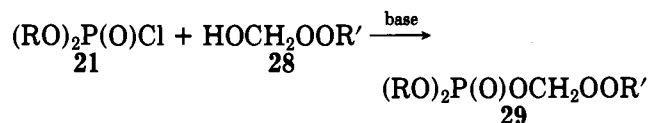
linked to the peroxide group was reported.[39] Compounds of the type 29 are prepared by use of the reaction of dialkylphosphonic acid chlorides 21 with the corresponding peroxyalkanols 28 in the presence of a base at –20 to +50 °C. However, few experimental details were disclosed at that time. Subsequently, the synthesis of compounds 29, R = alkyl, R' = $C(CH_3)_3$, $C(CH_3)_2CH_2CH_3$, was described.[40] The peroxides are obtained in high yield by use of pyridine as the condensing agent (Table II). Compounds 29 are remarkably stable, i.e., they are resistant to mineral acids and liberate iodine from acidic potassium iodide solution

TABLE III. Phosphonates Containing the Peroxy Moiety Not Directly Linked to Phosphorus

$$\text{RO}\diagdown \hspace{-0.5em}\text{P(O)R''} \quad \text{R'O}\diagup$$

| R	R'	R"	yield, %	ref
CH₃	CH₃	C(CH₃)₂OOC(CH₃)₃	25	41, 42
CH₃	CH₃	C(CH₃)₂OCH₂OOC(CH₃)₃	30	41, 42
CH₃	CH₃	CH₂OOC(CH₃)₃	47	41
C₂H₅	C₂H₅	CH₂OOC(CH₃)₃	15	41
			80	42
C₂H₅	C₂H₅	CH₂OCH₂OOC(CH₃)₃	28	41, 42
C₃H₇	C₃H₇	CH=CHOOC(CH₃)₃	65	41
C₄H₉	C₄H₉	CH=CHOOC(CH₃)₃	73	41
C₃H₇	C₃H₇	C(CH₃)=CHOOC(CH₃)₃	82	41
C₄H₉	C₄H₉	C(CH₃)=CHOOC(CH₃)₃	78	41
C₃H₇	C₃H₇	C(C₂H₅)=CHOOC(CH₃)₃	75	41
C₄H₉	C₄H₉	C(C₂H₅)=CHOOC(CH₃)₃	71	41
C₃H₇	C₃H₇	CH=C(CH₃)OOC(CH₃)₃	73	41
C₄H₉	C₄H₉	CH=C(CH₃)OOC(CH₃)₃	65	41
C₂H₅	CH₂OOC(CH₃)₃	CH₂Cl	48	42, 44
C₂H₅	CH₂CH₂OOC(CH₃)₃	CH₂Cl	70	42, 44
i-C₃H₇	CH₂CH₂OOC(CH₃)₃	CH₃ a	c	42, 44
(CH₃)₃C—⟨C₆H₃Cl⟩—	CH₂CH₂OOC(CH₃)₃	CH₃ b	c	42, 44

ᵃ n²⁰D 1.4283.⁴¹   ᵇ n²⁰D 1.4899;⁴¹ bp 65–75 °C (3 torr).   ᶜ Not reported.

only at or above 60 °C. As in the case of numerous other peroxy compounds, compounds 29 catalyze the polymerization of styrene very effectively at 10–110 °C.⁴⁰ No attempts were made to distill the compounds. Analytically pure 29 is obtained by concentrating the reaction mixture under vacuum at 70 °C.

Attempts were made to synthesize the dialkyl peroxymethylphosphonates 32, R = R' = CH₃, C₂H₅, R" = CH₂OOC(CH₃)₃, by the reaction of the sodium phosphite 30 with the chloro derivative 31 at 20–25 °C

$$(RO)_2PONa + ClCH_2OOC(CH_3)_3 \xrightarrow{-NaCl}$$
$$\mathbf{30} \qquad\qquad \mathbf{31}$$
$$(RO)_2P(O)CH_2OOC(CH_3)_3$$
$$\mathbf{32}$$
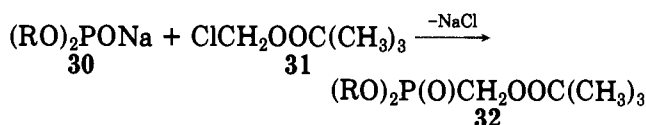
or by the reaction of phosphite 33 with the diethylamino derivative 34.⁴¹ However, yields were low. Best

$$(RO)_2POH + (CH_3)_3COOCH_2N(C_2H_5)_2 \rightarrow$$
$$\mathbf{33} \qquad\qquad \mathbf{34}$$
$$\mathbf{32} + (C_2H_5)_2NH$$
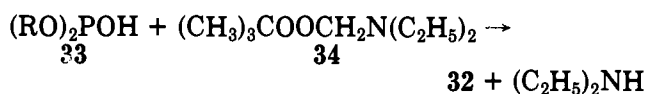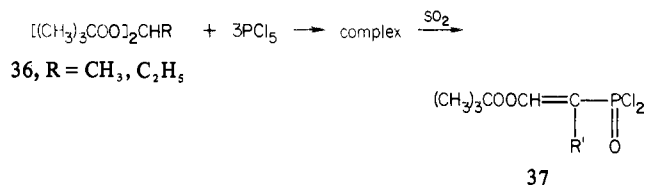
results are obtained by use of the reaction of dialkyl hydroxymethylphosphonates or substituted hydroxymethylphosphonates (35; R = R' = CH₃, C₂H₅; Y =

$$(RO)(R'O)P(O)Y + C(CH_3)_3OOH \xrightarrow[C_6H_6]{AlCl_3}$$
$$\mathbf{35}$$
$$(RO)(R'O)P(O)R''$$
$$\mathbf{32}$$
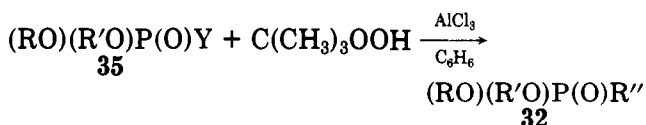
Y = CH₂OH, CH₂OCH₂OH, C(CH₃)₂OH;
　R" = CH₂OOC(CH₃)₃, CH₂OCH₂OOC(CH₃)₃,
　　　　　　　　　　　　　　　C(CH₃)₂OOC(CH₃)₃

CH₂OH, CH₂OCH₂OH, C(CH₃)₂OH) with tert-butyl hydroperoxide in benzene in the presence of an equimolar amount of aluminum chloride at room temperature to give the phosphonate 32 in yields of 15–18% (Table III).⁴¹,⁴² An alternative method to symmetric dialkyl phosphonates 32 was reported by Shreibert et al.⁴³ The reaction of 1,1-bis(tert-butylperoxy)ethane

(36, R = CH₃) and -propane (36, R = C₂H₅) with phosphorus pentachloride in benzene results in the

$$[(CH_3)_3COO]_2CHR + 3PCl_5 \longrightarrow complex \xrightarrow{SO_2}$$
$$\mathbf{36}, R = CH_3, C_2H_5$$

$$(CH_3)_3COOCH{=}C{-}PCl_2$$
$$\underset{R'}{|} \quad \underset{O}{\parallel}$$
$$\mathbf{37}$$

formation of a complex which is decomposed by sulfur dioxide to give [2-(tert-butylperoxy)vinyl]- (37, R = H) and [2-(tert-butylperoxy)-1-methylvinyl]phosphonic dichlorides (37, R = CH₃) in 75–82% yield. Compounds 37 are also prepared in 60–70% yield by use of the reaction of either phosphorus pentachloride with the acetic esters 38 or the ethers 39 of 1-hydroxyethyl and 1-hydroxypropyl tert-butyl peroxide. Compounds 37

$$(CH_3)_3COO\diagdown \hspace{-0.5em}CH{-}R' + 3PCl_5 \longrightarrow complex \longrightarrow 37$$
$$RO\diagup$$

38, R = CH₃CO; R' = CH₃, C₂H₅
39, R = n-C₄H₉; R' = CH₃, C₂H₅
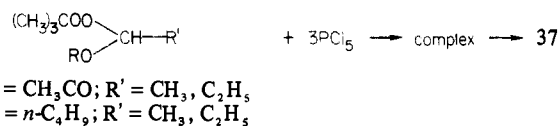
could not be analyzed quantitatively for their "active" oxygen content and thus were characterized through their derivatives, i.e., their dibutyl phosphonate ester 40 and the bromomethoxy derivative 41. Subse-

$$(n\text{-}C_4H_9O)_2P(O)CH{=}CHOOC(CH_3)_3 \qquad (n\text{-}C_4H_9O)_2P(O)CH{-}CHOOC(CH_3)_3$$
$$\mathbf{40} \qquad\qquad\qquad \underset{Br}{|}\quad\underset{OCH_3}{|}$$
$$\mathbf{41}$$
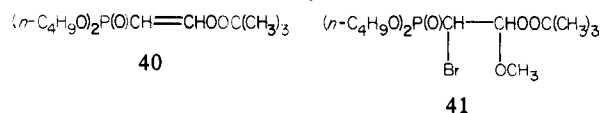
quently,⁴¹ the class of compounds 32 was expanded to include the unsaturated phosphonates containing the peroxy moiety shown in Table III.

The asymmetric phosphonates of the type 43 are obtained by the reaction of the corresponding alkyl or aryl alkylphosphonodichloridate 23 (R = C₂H₅, i-C₃H₇, 2-Cl-4-C(CH₃)₃C₆H₃; R' = ClCH₂, CH₃) with the tert-butylperoxy alcohol 42, n = 1, 2, in the presence of pyridine (Table III).⁴²,⁴⁴ Because of the high stability of compounds of this type, the iodometric determination of active oxygen is difficult.⁴⁴

$$RO \diagdown_{R'} P(O)Cl + HO(CH_2)_nOOC(CH_3)_3 \xrightarrow[\text{pyridine}]{Et_2O}$$

23   42, $n = 1, 2$

$$RO \diagdown_{R'} P(O)O(CH_2)_nOOC(CH_3)_3$$

43, $n = 1, 2$
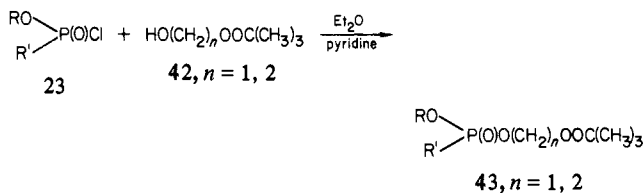
The phosphonates with the peroxy bond not directly linked to phosphorus of the type 45, containing the

$$(RO)_2P(O)(CH_2)_mC(O)Cl$$
44, $m = 1, 2$

$$+HO(CH_2)_nOOC(CH_3)_3 \xrightarrow[\text{-5 to $+20$ °C}]{R_3N}$$
42, $n = 1, 2$

$$(RO)_2P(O)(CH_2)_mC(O)O(CH_2)_nOOC(CH_3)_3$$
45, $m, n = 1, 2$
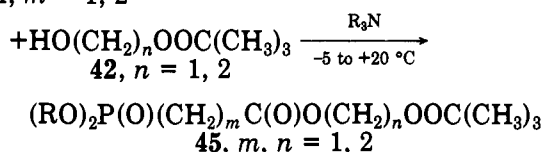
carbonyl moiety, are prepared[45] by treating the *tert*-butylperoxy alcohol 42 with the corresponding acid chloride 44 in the presence of a tertiary amine in an inert organic solvent at –5 to +20 °C. Compounds 45 are recommended as initiators for radical polymerization.[45]

c. Asymmetric Diperoxides

The phosphonates 47, containing two *tert*-butylperoxy moieties not directly linked to phosphorus, are prepared by using the condensation of the corresponding substituted phosphonic dichloride 46 with the

$$RP(O)Cl_2 + HO(CH_2)_nOOC(CH_3)_3 \xrightarrow{\text{base}}$$
46, R = CH$_3$,   42, $n = 1, 2$
ClCH$_2$

$$RP(O)[O(CH_2)_nOOC(CH_3)_3]_2$$
47

appropriate *tert*-butylperoxy alcohol 42[39–42,44–46] (Table IV). Compounds 47 are thermally rather stable. They can be utilized for the initiation of the polymerization of styrene.[40]

3. Peroxy Compounds Also Containing Other Heteroatoms

a. Asymmetric Monoperoxy Compounds

In 1970, Yurzhenko and Babyak reported the preparation of N-[(*tert*-butylperoxy)diphenyl-phosphoranylidene]arenesulfonamides (49).[47] Compounds 49, thick colorless or yellow oils, are prepared in 50–52% yield by the reaction of the corresponding N-(chlorodiphenylphosphoranylidene)arenesulfon-amides (48) with sodium *tert*-butyl peroxide under

48, R = H, Cl, CH$_3$, NO$_2$

49

anhydrous conditions. The peroxides cannot be distilled without decomposition even at 10^{-3} torr (Table V). Although insoluble in water, peroxides 49 are

TABLE IV. Asymmetric Diperoxides with the Peroxy Moiety Not Directly Linked to Phosphorus

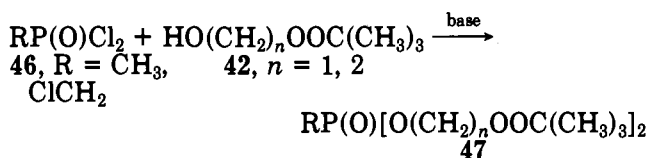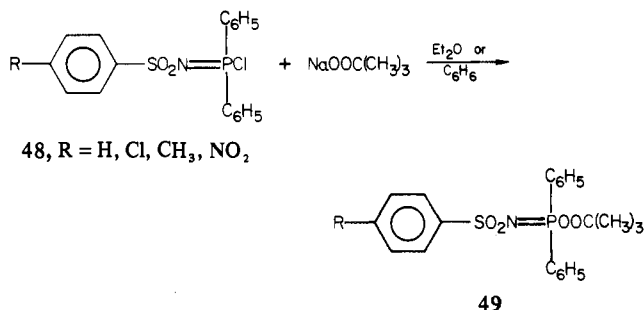|	RP(O)[O(CH$_2$)$_n$OOC(CH$_3$)$_3$]$_2$ (47)			
R	n	yield, %	n^{20}D	ref
CH$_3$	1	93	1.4302	39, 40
CH$_3$	2	a	1.4380	44, 45
ClCH$_2$	1	45	a	42
ClCH$_2$	2	85	a	42

a Not reported.

TABLE V. N-[(*tert*-Butylperoxy)diphenylphosphoranylidine]-arenesulfonamides (49)[47]

49

	% "active" oxygen	
R	calcd	found
H	3.72	3.59
Cl	3.47	3.32
CH$_3$	3.61	3.64
NO$_2$	3.38	3.32

TABLE VI. Phenyl Di-*tert*-butylperoxyphosphazo-sulfenylaryls (52)[49,50]

52

	% "active" oxygen	
R	calcd	found
H	7.24	7.16
Cl	6.73	6.15
CH$_3$	7.02	6.99
NO$_2$	6.52	6.80

gradually decomposed by water, resulting in the formation of N-(arylsulfonyl)diphenylphosphinic amides (50) with liberation of *tert*-butyl hydroperoxide. Thus,

R = H, Cl, CH$_3$, NO$_2$

50

C(CH$_3$)$_3$OOH
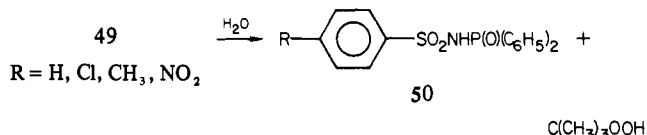
in the case of compounds of the type 49, it is the P=N bond which is susceptible to decomposition, and not the peroxy linkage.[48]

b. Asymmetric Diperoxy Compounds

By analogy to the preparation of N-[(*tert*-butylper-oxy)diphenylphosphoranylidene]arenesulfonamides (49, R = H, Cl, CH$_3$, NO$_2$),[47] the phenyl bis(*tert*-butylper-oxy)phosphazosulfenylaryls 52 are prepared in 50–60% yield from the corresponding dichloridates 51 and the sodium salt of *tert*-butyl hydroperoxide under anhydrous conditions.[49,50] No attempts were made to distill the peroxy derivatives 52 (Table VI). In the case that the reaction for the preparation of compounds 52 is performed in the presence of water, the dichloridate 51 presumably hydrolyzes to give the N-(chlorophenyl-phosphinyl)arenesulfonamide 53. Subsequent reaction

R—⟨C₆H₄⟩—SO₂N=PCl₂   + 48 $\xrightarrow{\text{Et}_2\text{O}}{\text{Na}_2\text{SO}_4}$
|
C₆H₅

51, R = H, Cl, CH₃, NO₂

R—⟨C₆H₄⟩—SO₂N=P(C₆H₅)—OOC(CH₃)₃
|
OOC(CH₃)₃

52

51
R = H, Cl, CH₃, NO₂ $\xrightarrow{\text{H}_2\text{O}}$ R—⟨C₆H₄⟩—SO₂NHP(O)Cl $\xrightarrow{(\text{CH}_3)_3\text{COONa}}$
|
C₆H₅

53

R—⟨C₆H₄⟩—SO₂NHP(O)C₆H₅
|
OOC(CH₃)₃

54
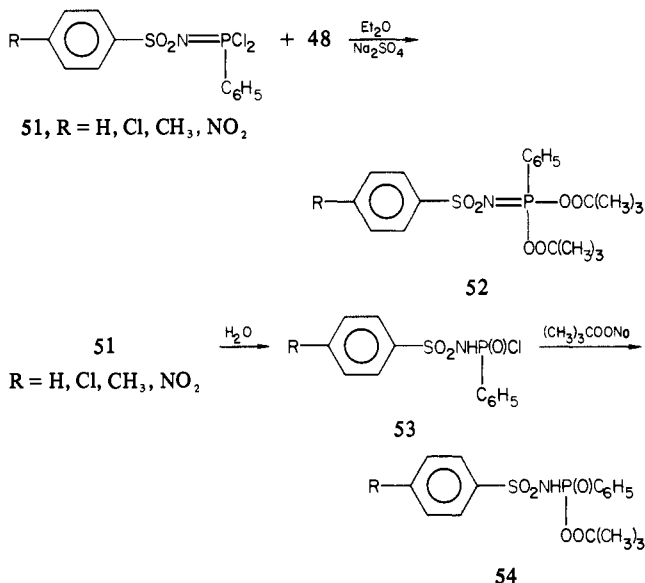
of **53** with sodium *tert*-butyl peroxide proceeds to give the *N*-[(*tert*-butylperoxy)phenylphosphinyl]arenesulfonamides **54** in 60–65% yield (Table VII). Although it is proposed that the formation of **54** results from the in situ hydrolysis of dichloridate **51** to monochloridate **53**, under the conditions of the experiment it is impossible to distinguish such in situ hydrolysis from the hydrolysis of diperoxide **52** to the monoperoxide **54**. Except in the case of **54**, R = NO₂, which is a yellow-colored peroxide, all of the compounds **54** are viscous, colorless oils.

The hydrolysis, acidolysis, and ammonolysis reactions of diperoxides **52** were studied.[47] Thus, depending on the amount of water present, compound **52** hydrolyzes to a variety of derivatives. With an equimolar amount of water, diperoxide **52** is converted to *N*-(*tert*-butylperoxy)phenylphosphinyl]arenesulfonamide (**54**). Ac-

R—⟨C₆H₄⟩—SO₂N=P(C₆H₅)—OOC(CH₃)₃ $\xrightarrow[-(\text{CH}_3)_3\text{COOH}]{\text{H}_2\text{O}}$
|
OOC(CH₃)₃

52, R = H, Cl, CH₃, NO₂

R—⟨C₆H₄⟩—SO₂NHP(O)OOC(CH₃)₃ $\xrightarrow[\text{H}_2\text{O}]{-(\text{CH}_3)_3\text{COOH}}$
|
C₆H₅

54

R—⟨C₆H₄⟩—SO₂NHP(O)OH $\xrightarrow{\text{H}_2\text{O}}$ R—⟨C₆H₄⟩—SO₂NH₂   +
|
C₆H₅

55   **56**

⟨C₆H₅⟩—P(O)(OH)₂

57
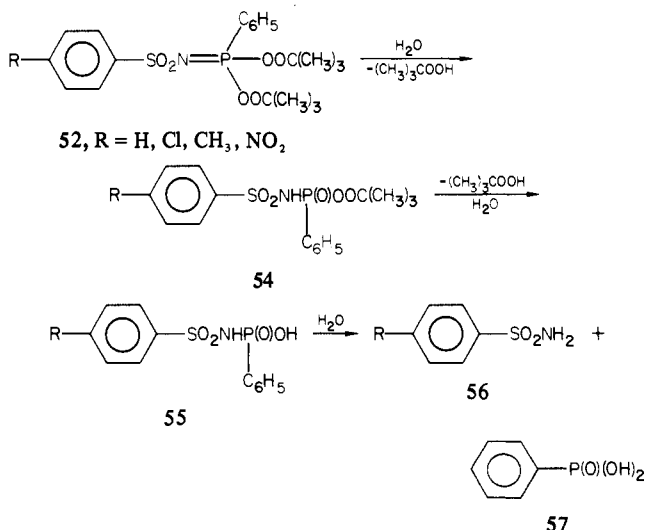
tually, atmospheric moisture is sufficient to effect the hydrolysis of **52** to **54**. Subsequent addition of a further quantity of water hydrolyzes **54** to give *tert*-butyl hydroperoxide and the corresponding phosphonic acid derivative **55**. The final stage of hydrolysis results in the formation of the arylsulfonamides **56** and phenylphosphonic acid **57**.[47]

The stability of the peroxide bond in compounds of the type **52** is further verified during hydrolysis in glacial acetic acid. With an equimolar amount of acetic

R—⟨C₆H₄⟩—SO₂NHP(O)OOC(CH₃)₃
|
C₆H₅

54

R	n^{20}D	% "active" oxygen	
		calcd	found
H	1.5069	4.33	4.34
Cl	1.5268	3.96	4.08
CH₃	a	4.40	4.28
NO₂	a	3.86	3.93

a Not reported.

acid, perester **54** is obtained, together with *tert*-butyl peroxyacetate. Excess acid leads to the formation of **57** and the *N*-acetyl derivative of sulfonamide **56**, with the elimination of another mole of *tert*-butyl peracetate.

Ammonolysis with moist ammonia results in the formation of *N*-(arylsulfonyl)-*p*-phenylphosphonic diamides **58**.[47]

52 $\xrightarrow{\text{NH}_3}{\text{H}_2\text{O}}$ R—⟨C₆H₄⟩—SO₂NHP(O)NH₂
R = H, Cl, CH₃, NO₂ |
C₆H₅

58
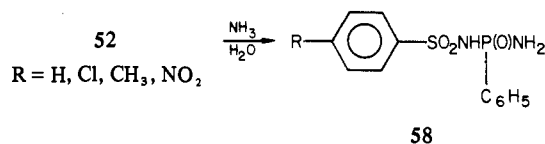
Unlike the reaction of diperoxides **52** with aqueous ammonia, which results in the conversion of the phosphine imide linkage to the phosphoroamidate moiety in **58**, the reaction of **52** with diethylamine proceeds to give (diethylamino)phenyl-*N*-(arylsulfonyl)phosphine imides **59**, R = H, CH₃, with retention of the imide

52   + (C₂H₅)₂NH $\xrightarrow{-\text{C}(\text{CH}_3)_3\text{OOH}}$
R = H, CH₃

R—⟨C₆H₄⟩—SO₂N=PN(C₂H₅)₂
|
C₆H₅

59
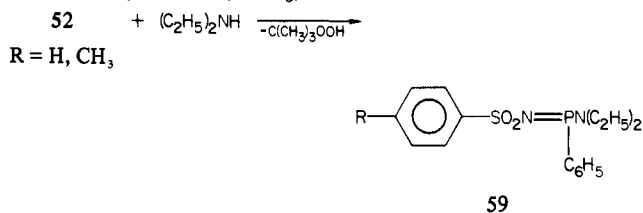
linkage, together with *tert*-butyl hydroperoxide.[51] If aniline is used instead of diethylamine, the diperoxide **52** oxidizes the aniline to give intractable resinuous products.

Another class of diperoxides containing nitrogen moieties, i.e., the phosphoranylidene derivatives **66**, are prepared analogously to the arylphosphazosulfenyls **52**.[52] Thus, the reaction of *N*-(dichlorophenyl-phosphoranylidene) derivatives of substituted vinyl amines **60** with sodium *tert*-butyl peroxide in ether under anhydrous conditions results in the formation of the substituted *N*-[bis(*tert*-butylperoxy)phenyl-phosphoranylidine]vinylamines (**61**) (Table VIII) in

R'\
   C=C(R)—N=P(C₆H₅)—Cl   + 2(CH₃)₃COONa $\xrightarrow{\text{Et}_2\text{O}}{\text{Na}_2\text{SO}_4}$
R''/ |
                          Cl

60, R = CCl₃, CF₃
R' = alkyl–OCO
R'' = alkyl–OCO, CN, alkyl–CO

R'\
   C=C(R)—N=P(C₆H₅)—OOC(CH₃)₃
R''/ |
                          OOC(CH₃)₃

61
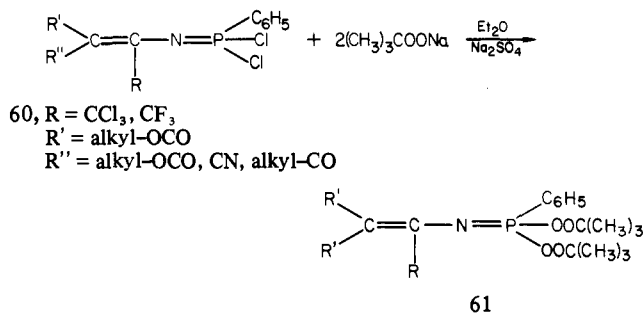
TABLE VIII. Substituted N-[Bis(tert-butylperoxy)-phenylphosphoranylidene]vinylamines (61)[52]

61

R	R'	R''	yield, %	% "active" oxygen calcd	found
CCl₃	CH₃OC(O)	CH₃OC(O)	64	5.69	5.61
CCl₃	C₂H₅OC(O)	C₂H₅OC(O)	67	5.43	5.29
CF₃	CH₃C(O)	C₂H₅OC(O)	55	6.36	6.22
CF₃	C₂H₅OC(O)	C₂H₅OC(O)	61	5.91	5.66
CCl₃	CH₃OC(O)	(CH₃)₃COC(O)	68	5.31	5.47
CF₃	C₂H₅OC(O)	(CH₃)₃COC(O)	63	5.64	5.71
CF₃	i-C₃H₇OC(O)	(CH₃)₃COC(O)	67	5.50	5.29
CCl₃	CN	C₂H₅OC(O)	63	5.91	5.83
CF₃	CN	C₂H₅OC(O)	75	6.50	6.47

TABLE IX. Substituted
N-[(tert-Butylperoxy)phenylphosphinyl] vinylamines (62)[52]

62

| R	R'	R''	agent of hydrolysis	% "active" oxygen calcd	found
CCl₃	CH₃OC(O)	CH₃OC(O)	H₂O	4.12	4.12
CF₃	CH₃C(O)	C₂H₅OC(O)	H₂O	3.80	3.50
CF₃	C₂H₅OC(O)	C₂H₅OC(O)	H₂O	3.51	3.16
CCl₃	CN	C₂H₅OC(O)	H₂O	3.52	3.34
CCl₃	C₂H₅OC(O)	C₂H₅OC(O)	H₂O	3.09	3.28
CCl₃	C₂H₅OC(O)	C₂H₅OC(O)	HOAc	3.09	3.37
CF₃	C₂H₅OC(O)	(CH₃)₃COC(O)	HOAc	3.23	2.95

61-75% yield. The hydrolysis of compounds **61**, which are undistillable, colored oils, characterized by microanalysis and IR spectra, by either water or glacial acetic acid proceeds with retention of one tert-butylperoxy linkage to give the N-[(tert-butylperoxy)phenyl-phosphinyl]vinylamines **62** in 70–75% and 67–70%


61

62
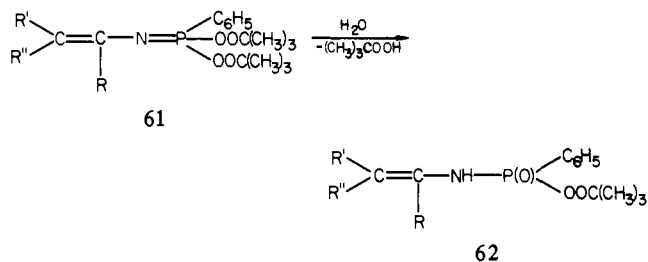
yields, respectively. In the case of aqueous hydrolysis, the byproduct is tert-butyl hydroperoxide, whereas in the case of glacial acetic acid, the reaction results in the formation of tert-butyl peroxyacetate. Compounds **62** are undistillable, colored, viscous oils (Table IX).

The reaction of diperoxides **61** with dry ammonia results in the formation of compounds **63**, with preservation of the P=N linkage. In the case of **61**, R = CH₃CO, product **63**, R = CH₃CO, is obtained in 85% yield, whereas in the case of **61**, R = CN, imide **63**, R = CN is obtained in 87% yield.

c. Miscellaneous Compounds

61, R = CH₃C(O), CN

63
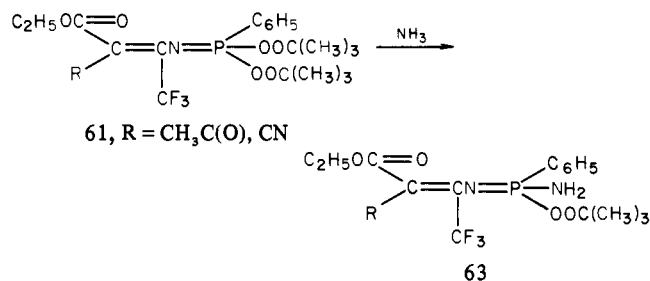
In 1971, it was reported[53] that irradiation of hexamethylphosphoric triamide (**64**) in the presence of oxygen at room temperature over a period of 65 h results in the formation of hydroperoxide **65**. Because of its

64   65
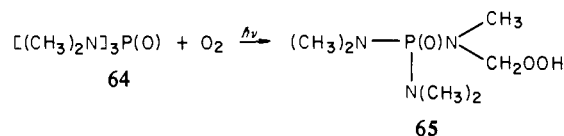
instability, compound **65** was not isolated, but, instead, was characterized through its decomposition products. Thus, compound **65** is polarographically stepwise reduced to give the hydroxy derivative **66**, which decom-

66

67
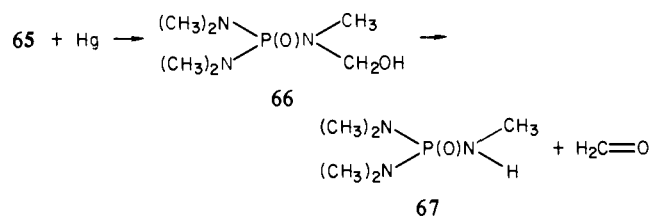
poses further to the amide **67** and formaldehyde. The peroxy linkage was further verified by the characteristic hydroperoxide infrared absorption at 835 cm⁻¹[54] and by the liberation of iodine from an acidic solution of potassium iodide in the presence of compound **65**.

Over the years, the mechanism of the biological activation of the important antitumor agent Endoxan (cyclophosphoramide; **68**) has been extensively inves-

68
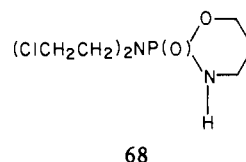
tigated.[55-59] In order to gain insight into the action of the compound **68**, numerous derivatives have been prepared, including a number of peroxides and hydroperoxides, as possible active metabolites of **68**. All of these compounds exhibit cytostatic activity in both in vivo and in vitro experiments, confirming that the reaction at the carbon α to the nitrogen in the ring of Endoxan (**68**) is responsible for the activation of the drug **68**.[55]

Ozonization of the diamidate **69** in aqueous acetone at 0 °C results in the formation of the hydroperoxide **71**, a solid melting at 107–108 °C, in approximately 10% yield. The yield is increased to 50–60% if an excess of either hydrogen peroxide or tert-butyl hydroperoxide is added to the ozonization reaction mixture to prevent dimerization and/or decomposition of **71**.

Hydroperoxide **71** presumably arises via the zwitterionic intermediate **70**.[55] The formation of **70** can be verified by conducting the reaction in the presence of either ethanol or benzyl alcohol to give the open-chain

$(ClCH_2CH_2)_2NP(O)$ with NH_2 / $OCH_2CH_2CH=CH_2$ $\xrightarrow{O_3}$

69

$[(ClCH_2CH_2)_2NP(O)$ with NH_2 / $\overset{+}{OCH_2CH_2CHOO^-}]$ $\longrightarrow$

70

$(ClCH_2CH_2)_2NP(O)$ ring with OOH

71
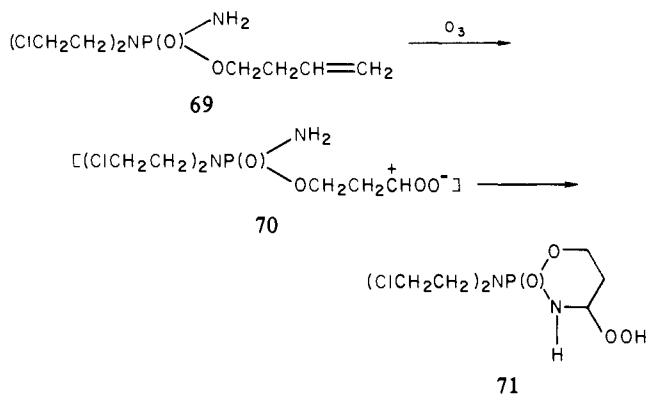
hemiacetal hydroperoxides **72**, R = C_2H_5, $CH_2C_6H_5$, in

70 + ROH $\longrightarrow$ $(ClCH_2CH_2)_2NP(O)$ with NH_2 / OCH_2CH_2CH with OOH / OR

72
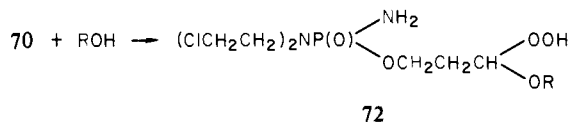
50% yield. The reaction of hydroperoxy acetate **72** with pyridine–thionyl chloride reagent proceeds to give the esters **73** in good yields. Attempted deoxygenation of

72 + $SOCl_2$ $\xrightarrow{pyridine}$ $(ClCH_2CH_2)_2NP(O)$ with NH_2 / OCH_2CH_2COR (with $\overset{O}{\parallel}$)

73, R = C_2H_5, $CH_2C_6H_5$

72 in the presence of triphenylphosphine affords no characterizable product.[55]

The reaction of compound **71** with potassium iodide results in the liberation of iodine. The reaction of **71** with thionyl chloride in pyridine results in the keto derivative **74**.[55] Similar results are achieved with other

$(ClCH_2CH_2)_2NP(O)$ ring with OOH $\xrightarrow[pyridine]{SOCl_2}$ $(ClCH_2CH_2)_2NP(O)$ ring with $=O$

71   **74**

reducing agents such as ferrous ($FeSO_4$) or cuprous (Cu_2Cl_2) ions.[56] Deoxygenation of **71** in the presence of triphenylphosphine[55] or sodium thiosulfate[56] at 0 °C results in the hydroxy derivative **75**. Hydroperoxide

71 + $(C_6H_5)_3P$ or $Na_2S_2O_3$ $\xrightarrow[0°C]{CH_2Cl_2}$ $(ClCH_2CH_2)_2NP(O)$ ring with OH

75

71 is readily regenerated from the hydroxy derivative **75** with hydrogen peroxide.

Although ozonolysis of compound **69** in aqueous acetone affords the hydroperoxide **71** as the primary product,[53] in a less polar solvent such as chloroform or dichloromethane the dimer **76** is obtained in 20%

$(ClCH_2CH_2)_2NP(O)$ with NH_2 / $OCH_2CH_2CH=CH_2$ $\xrightarrow[CH_2Cl_2 \ or \ CHCl_3]{O_3}$
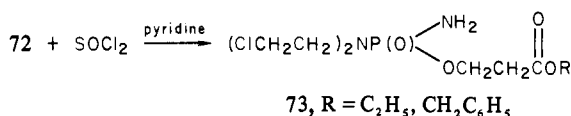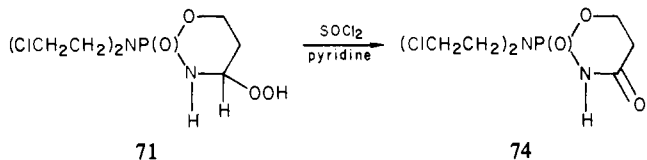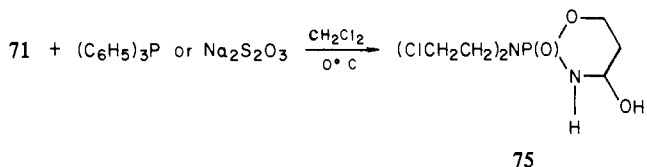
69

$(ClCH_2CH_2)_2NP(O)$ ring — O—O — ring $P(O)N(CH_2CH_2Cl)_2$

76

CHART I

$RCH=CH_2 + O_3 \longrightarrow RCH\overset{}{-}CH_2 \longrightarrow R\overset{+}{C}H—OO^- +$

69   **70**

$RCH=O \longrightarrow RCH\overset{O-O}{\underset{O}{\diagdown}}CH—R \longrightarrow$

$(ClCH_2CH_2)_2NP(O)$ ring with $OOCH—OH$ and R $\xrightarrow{-H_2O}$ **76**

R = $(ClCH_2CH_2)_2NP(O)(NH_2)OCH_2CH_2$
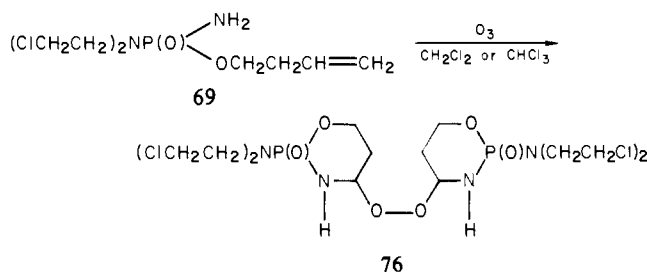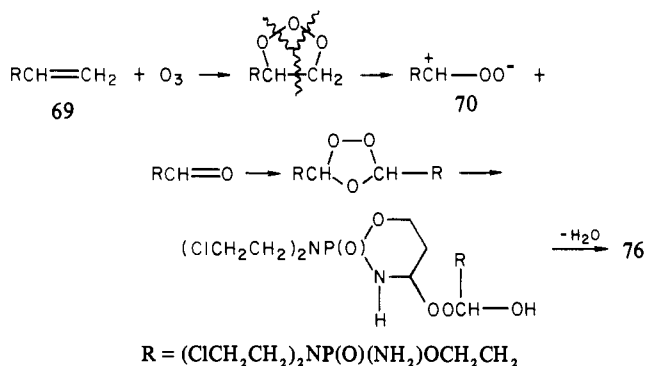
yield.[56] Only a small amount (2%) of the hydroperoxide **71** is obtained as the byproduct. The dimer **76**, a solid violently decomposing at 113–114 °C, is stable at 5 °C for nearly a month. The formation of **76** presumably occurs as shown in Chart I.[56]

Dimer **76** is also obtained in good yield by the reduction of **71** with either potassium ferricyanide or sodium bisulfite or by treatment with alkali such as sodium carbonate[56] or potassium hydroxide.[57] The dimer is formed, albeit in the low yield of 6%, by the direct oxidation of cyclophosphoramide (**68**) with Fenton's reagent (Fe^{2+}/H_2O_2).[57] A 4% yield of the hydroperoxide **71** is also obtained in this reaction. The reaction of dimer **76** with hydrogen peroxide in aqueous dimethyl sulfoxide proceeds to give, primarily, the hydroperoxide **71**, together with small amounts of the ketone **74**.[57]

Isophosphoramide (**77**) is a compound structurally

$ClCH_2CH_2NHP(O)$ ring with CH_2CH_2Cl

77
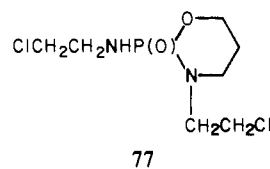
related to cyclophosphoramide (**68**). It is likewise an effective antitumor agent. Hence, the possible in vivo metabolites of **77** are also of interest.

Recently, two analogues of **77** containing the peroxide linkage, i.e., **79** and **82**, were reported.[58] Thus, ozonolysis of 3-butenyl N,N'-bis(2-chloroethyl)phosphorodiamidate (**78**) in aqueous acetone followed by treat-

$(ClCH_2CH_2NH)_2P(O)OCH_2CH_2CH=CH_2$ $\xrightarrow[2. H_2O_2]{1. O_3}$

78

$ClCH_2CH_2NHP(O)$ ring with OOH and CH_2CH_2Cl

79
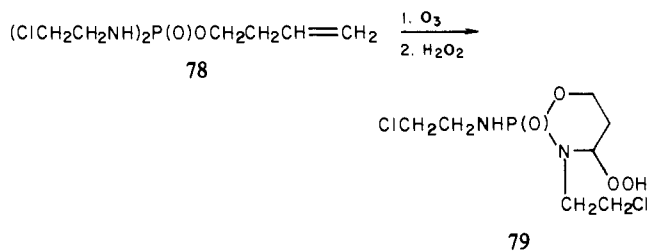
ment with 30% hydrogen peroxide results in the formation, in a 30% yield,[58] of 4-(hydroperoxy)isophosphoramide (**79**), a solid melting with violent decomposition at 113–114 °C. The radioactively labeled analogue of hydroperoxide **79** similarly is prepared in approximately 53% yield. The carbon-14 label α to the ring oxygen of **79** is introduced through the appropriately labeled precursor **78**.[59]

CHART II

$(C_6H_5)_2P(O^*)$—OO—$P(O^*)(C_6H_5)_2$

20

$(C_6H_5)_2P(O)OP(O)(C_6H_5)(OC_6H_5)$

$(C_6H_5)_2P(O)OH + C_6H_5P(O)OH$
83
OC_6H_5
84
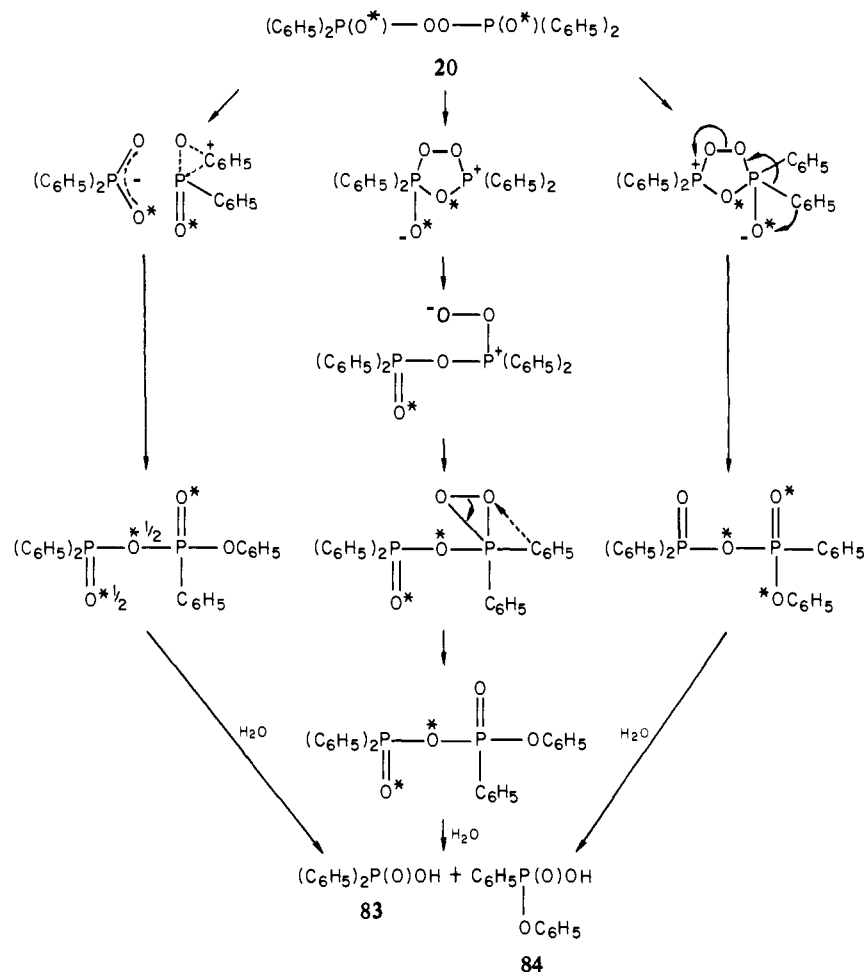
On treatment of hydroperoxide **79** with either ferrous (FeSO₄) or cuprous (Cu₂Cl₂) ions, the 4-keto derivative **80** is obtained in high yield.[58] Deoxygenation of **79** to

79 $\xrightarrow{\text{Fe}^{2+} \text{ or } \text{Cu}^+}$ ClCH₂CH₂NHP(O)

80
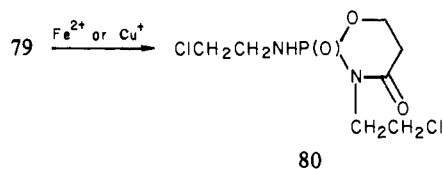
the hydroxy derivative **81** is achieved with triethyl

79 $\xrightarrow[\text{CH}_2\text{Cl}_2]{(C_2H_5O)_3P}$ ClCH₂CH₂NHP(O)

81
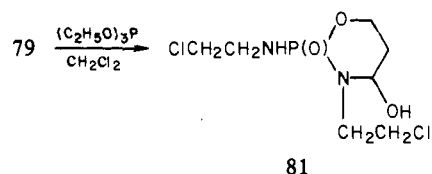
phosphite in dichloromethane at 0 °C in quantitative yield. Unlike in the case of cyclophosphoramide (**68**), treatment of hydroperoxide **79** with aqueous base such as sodium carbonate gives no corresponding peroxy dimer. Instead, the cyclized peroxide **82** is obtained in good yield.

79 + Na₂CO₃ $\xrightarrow{\text{H}_2\text{O}}$ ClCH₂CH₂NHP(O)

82
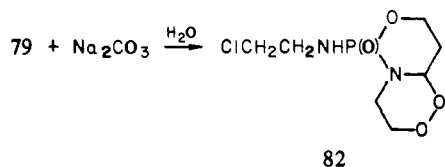
Compound **79** was found to be active in vitro against leukemia cells.[58]

B. Reactions

1. Decomposition of Bis(diphenylphosphinyl) Peroxide

Of all the bisphosphorus peroxides which have been prepared, the most extensively studied is bis(diphenylphosphinyl) peroxide (**20**). Thus, the thermal, photochemical, acid-catalyzed, and base-catalyzed decompositions of peroxide **20** were investigated. The thermal decomposition[36] of **20** yields, after hydrolysis

$(C_6H_5)_2P(O)OOP(O)(C_6H_5)_2$ →
20
$(C_6H_5)_2P(O)OH + C_6H_5P(O)(OH)OC_6H_5$
83 **84**
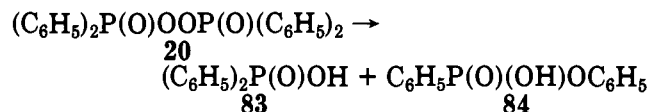
of the reaction mixture, diphenylphosphinic acid (**83**) and phenyl hydrogen phenylphosphonate (**84**). Products **83** and **84** presumably arise from the decomposition of the unstable unsymmetric anhydride **85**, the product

$(C_6H_5)_2P(O)OP(O)(C_6H_5)(OC_6H_5)$
85
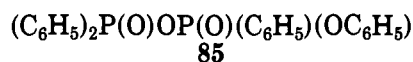
of the thermal rearrangement of peroxide **20**.[36] In chloroform, tetrachloroethane, dimethylformamide, and acetic acid, the reaction is first order with respect to the peroxide, has an energy of activation of 21.5 kcal/mol in all four solvents, and results in the formation of equimolar amounts of **84** and **85**. Three routes have been delineated for the mechanism of the thermal decomposition of peroxide **20** (Chart II).[60,61] In order to establish which route is operative in this case, the isotope-labeled bis(diphenylphosphinyl-¹⁸O) peroxide **20**

was prepared and the products were analyzed.[60,61] Thermal decomposition of isotope-labeled **20** results in products **83** and **84** in which all of the oxygen-18 labels remains on the oxo oxygens. This result is consistent only with either a concerted process or an ion-pair intermediate which would not permit a scrambling of the label.[60,61]

The decomposition of peroxide **20** by photolysis in chloroform was also studied.[36] The reaction is accelerated by ultraviolet light, and the rate is first order with respect to the peroxide.[60,61] On the basis of these results, a free-radical mechanism is proposed for the reaction.

The photochemical decomposition of oxygen-18-labeled peroxide **20** results in the formation of the anhydride **85** as detected by mass spectrometry;[60,61] **85** further decomposes to produce phenyl hydrogen phenylphosphonate (**84**) in which the phenoxy group contains virtually one-half of the ^{18}O label as compared to that of the starting material, i.e., $1.9 \pm 0.4\%$ vs. 4.6% for the latter, a finding consistent with a complete oxygen scrambling of the free radical intermediate **86**.
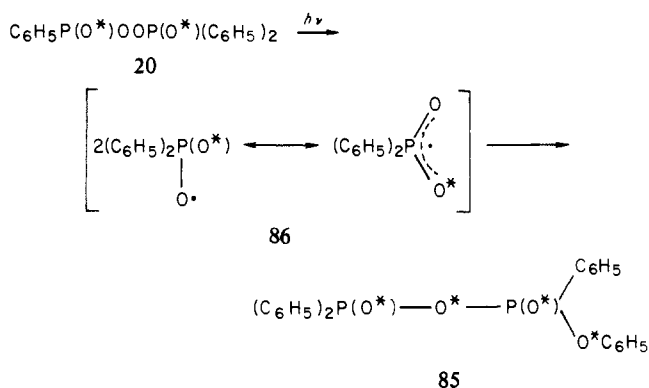
The rate of decomposition of **20** in chloroform increases with increasing concentration of pyridine. The reaction is first order with respect to the base and results in a quantitative yield of diphenylphosphinic acid (**83**), characterized as the anhydride **87**. Identical re-

sults are obtained with quinoline in place of pyridine. Since the peroxide is reduced to the acid and the amine is recovered unchanged, the solvent must undergo an oxidation reaction. However, since no such products were isolated, no mechanism for the decomposition can be proposed.[36]
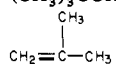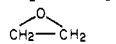
Peroxide **20** was also decomposed in chloroform and an excess of cyclohexene, with sodium hydroxide as catalyst, to give *trans*-2-hydroxycyclohexyl diphenylphosphinate (**88**) in 16% yield. It is proposed[36] that **88**
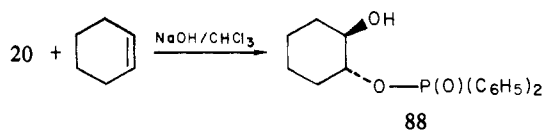
arises via an epoxide intermediate, but insufficient evidence is presented to support this hypothesis.

The effect of acid catalysis is also complex. The rate of peroxide decomposition in chloroform is increased with increasing acid strength in the series acetic, mo-

TABLE X. Products of the Reaction of Peroxide **47**, R = CH₃, $n = 1$, with Triphenylphosphine

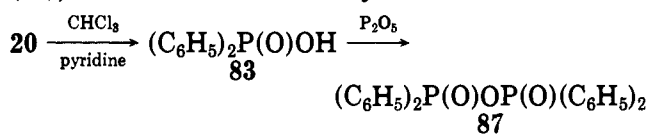| product[a]	reaction in benzene,[63] %			reaction in cumene, %
	47: Ph₃P = 1:2	47: Ph₃P = 1:3	47: Ph₃P = 1:4	47: Ph₃P = 1:2
$(CH_3)_3COH$	29.0	34.3	30.5	32.0
CH₂=C—CH₃ (CH₃)	58.0	60.0	59.3	60.0
(epoxide)	20.0	20.6	23.1	22.0
$Ph_3P(O)$	91.4	96.0	84.5	94.5
Ph_3P	b	37.0	89.5	b

[a] Also formed are acids of phosphorus and tarry material.
[b] Not reported.

nochloroacetic, dichloroacetic, and trichloroacetic acids and by increasing the concentration of the acids. The mechanism of the reaction is not straightforward, and is complicated by dimerization of the acid catalyst. Concurrent catalysis by the conjugate base is also presumed. Two moles of diphenylphosphinic acid (**83**) per mole of phenyl hydrogen phenylphosphonate (**84**) are produced, as expected for a simultaneous acid-catalyzed rearrangement and a base-catalyzed solvent oxidation. Hence, the mechanism shown in eq 1–3 is proposed for
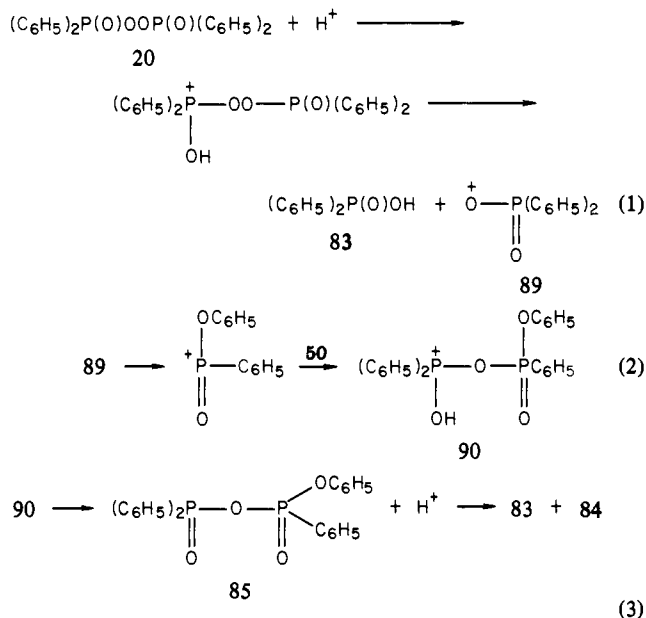
the decomposition. Since the thermal decomposition reactions are not autocatalytic, it is unlikely that the decompositions are catalyzed by the phosphorus-containing acids produced during the decomposition. However, more data are necessary in order that definitive conclusions can be made.[36]

2. With Triphenylphosphine

The decomposition reaction of the phosphonate **47**,

$$RP(O)[OCH_2CH_2OOC(CH_3)_3]_2$$
$$\textbf{47}, R = CH_3, n = 2$$
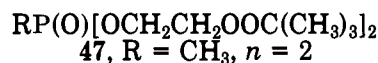
R = CH₃, $n = 2$, containing two *tert*-butylperoxy

moieties not directly attached to the phosphorus, in the presence of triphenylphosphine at 95 °C for 10 h was studied.[63] The reaction was performed with 1:2, 1:3, and 1:4 ratios of **47** to triphenylphosphine in benzene, and with a 1:2 ration in cumene. In all cases, varying amounts of *tert*-butyl alcohol, isobutylene, triphenylphosphine oxide, ethylene oxide, and acids of phosphorus, which were not identified, were formed, together with tarry material (Table X). The reaction proceeds by a nonradical mechanism, since no radical breakdown products of the *tert*-butoxy moiety, i.e., methane and acetone, are detected.

Two possible mechanisms might account for the products. In one case the formation of a complex between triphenylphosphine and the peroxide **47** is proposed. The transformation of this complex **91** to the complex **92** and fragmentation of the latter result in the mixture of phosphonylated ethylene glycol (**93**), triphenylphosphine oxide, and isobutylene. Further decomposition of the phosphonate ester **93** affords ethylene oxide and acids of phosphorus,[63] which were not characterized.

$$47, R = CH_3, n = 2$$

91

92

92 $\longrightarrow$ RP(O)(OCH$_2$CH$_2$OH)$_2$ + (CH$_3$)$_2$C=CH$_2$ + Ph$_3$P=O

93

Alternatively, a reaction of the anion fragment of **92** within the cage may be taking place to give ethylene oxide, which then leaves the cage, together with the new ion pair **94**. The reaction of species **94** proceeds to give the phosphonic acid **95**, R = CH$_3$, isobutylene, and triphenylphosphine oxide. The feasibility of the second

92

94

94 $\longrightarrow$ RP(O)(OH)$_2$ + (CH$_3$)$_2$C=CH$_2$ + Ph$_3$PO

95, R = CH$_3$

mechanism is strengthened by the observation that the amount of the acid **95** formed is approximately equal to the amount of ethylene oxide.

The *tert*-butyl alcohol presumably arises from the

TABLE XI. Products of the Thermal Decomposition of Peroxide[46] **47**, R = CH$_3$, $n = 2$

product[a]	neat, %	in cumene, %	in benzene, %
methane	40	34	50
acetone	43	35	46
isobutylene	99	77	14
tert-butyl alcohol	18	52	41
tert-butyl hydrogen methylphosphonate (**98**)	26	14	70
water	24	trace	trace

[a] The figures are expressed as the ratio of moles of product to moles of substrate × 100.

ion-pair complex **96**, R = CH$_3$. Since the *tert*-butyl

96

97
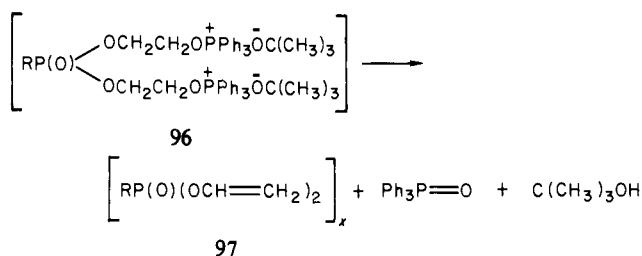
anion is a very powerful nucleophile, an abstraction of hydride from the ester portion of the complex occurs to give the divinyl ester of methylphosphonic aci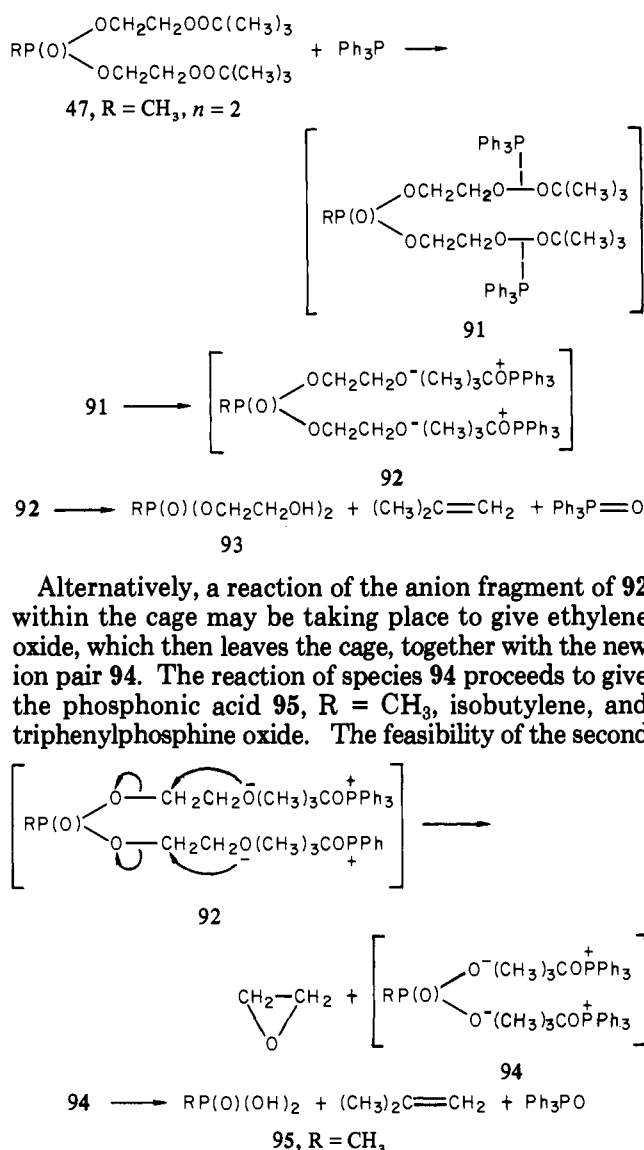d (**97**, $x = 1$), which rapidly polymerizes to give tarry material. Infrared analysis of the tarry material formed during the reaction indicates the presence of the P=O ($\nu = 1240$ cm^{-1}) and P—O—C ($\nu = 958$ cm^{-1}, 1038 cm^{-1}) linkages.

3. Thermal Decomposition

The thermal decomposition reaction of the peroxy phosphonate **47**, R = CH$_3$, $n = 2$, in the presence or absence of solvent was studied.[46] Thus, the decomposition of peroxide **47**, R = CH$_3$, $n = 2$, at 120–125 °C is complete and gives methane, acetone, isobutylene, *tert*-butyl alcohol, acidic products, and tarry material (Table XI). The radical mechanism (shown in eq 4–9),

$$CH_3(RO)P(O)OCH_2CH_2OOC(CH_3)_3 \rightarrow$$
$$47, R = CH_2CH_2OOC(CH_3)_3$$
$$CH_3(RO)P(O)OCH_2CH_2O\cdot + \cdot OC(CH_3)_3 \quad (4)$$

$$(CH_3)_3CO\cdot \rightarrow CH_3C(O)CH_3 + \cdot CH_3 \quad (5)$$

$$\cdot CH_3 + SH \rightarrow CH_4 + S\cdot \quad (6)$$

$$(CH_3)_3CO\cdot + SH \rightarrow (CH_3)_3COH + S\cdot \quad (7)$$

$$CH_3(RO)P(O)OCH_2CH_2O\cdot \rightarrow$$
$$CH_3(RO)P(O)O\cdot + [-CH_2CH_2-O-] \quad (8)$$

$$CH_3(RO)P(O)O\cdot + SH \rightarrow CH_3(RO)P(O)OH + S\cdot \quad (9)$$
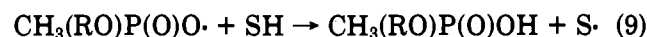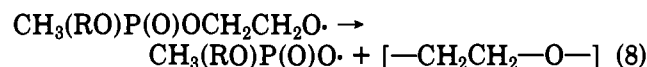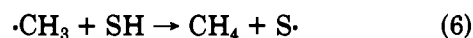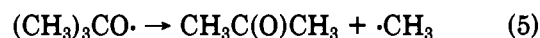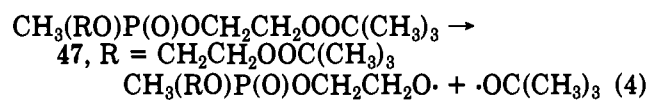
involving the participation of cumene which was used as solvent (SH), was confirmed by the isolation of the dimer of cumene. Both neat and in the presence of the solvent, the yields of methane and acetone are virtually the same. Isobutylene presumably arises from dehydration of *tert*-butyl alcohol by the phosphorus acid(s) formed during the decompositions, i.e., methylphosphonic acid (**95**, R = CH$_3$) and *tert*-butyl hydrogen methylphosphonate (**98**). Acid **98** presumably is

CH$_3$P(O)(OH)$_2$ HO(CH$_3$)P(O)OC(CH$_3$)$_3$
95   **98**
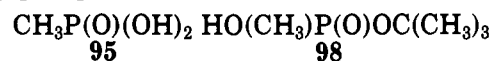
formed by the reaction of isobutylene or tert-butyl alcohol with acid 95.

The reaction is depicted as proceeding stepwise with homolytic cleavage of the peroxy linkage. However, it is impossible to rule out a simultaneous cleavage of both peroxy bonds of the peroxide 47, R = CH_3, $n = 2$. Although the mechanism as written indicates the formation of ethylene oxide, obviously, under the conditions of the experiment, the epoxide is not isolated, but results in polymeric material.

IV. Peroxy Esters

A. Preparation

1. Peroxy Phosphates

In 1959, Rieche et al. published the first report on the preparation of dialkyl peroxy phosphates 3 (R = CH_3, C_2H_5; R' = $(CH_3)_3C$) from the corresponding chloridate 21 and tert-butyl hydroperoxide in an excess of anhydrous pyridine at -10 to -20 °C (method A). Com-

method A

$$(RO)_2P(O)Cl + (CH_3)_3COOH \xrightarrow[\text{-10 to -20 °C}]{\text{pyridine}}$$
21, R = CH_3, C_2H_5
$$(RO)_2P(O)OOC(CH_3)_3$$
$$\textbf{3}$$

pound 3, R = CH_3, obtained in 65% yield prior to distillation, and in 59% yield after purification, is a low-melting solid. Peroxy ester 3, R = C_2H_5, obtained in 65-85% yield after purification, is a liquid. Both peroxy esters 3, R = CH_3 and R = C_2H_5, can be purified by careful distillation under vacuum on a small scale.[4-6] On a larger scale, decomposition usually ensues.

In 1960, Harrison and Mageli[64] reported the preparation of 3 (R = C_2H_5, n-C_4H_9, n-C_8H_{17}, C_6H_5, R' = $C(CH_3)_3$) in 76-89% yield by the reaction of the corresponding chloridate 21 (R = C_2H_5, n-C_4H_9, n-C_8H_{17}, C_6H_5) and the potassium salt of tert-butyl hydroperoxide prepared in situ from the hydroperoxide and potassium hydroxide in water (method B). In the case

method B

$$21 + K^+ \,^-OOC(CH_3)_3 \xrightarrow{H_2O} 3$$

R = C_2H_5, n-C_4H_9, n-C_8H_{17}, C_6H_5

of diethyl chlorophosphate (21, R = C_2H_5), the mixed solvent system of water and petroleum ether (bp 30-60 °C) was used. However, based on published analytical data,[64] peroxy esters 3 were obtained in crude form.
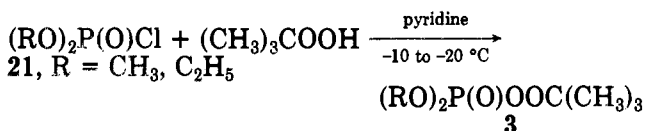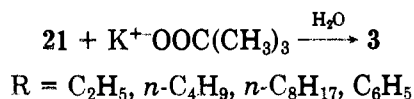
At that time, it was the experience that although the method of Rieche and co-workers[4-6] could be reproduced, it was poorly applicable to systems of R greater than propyl, and only the isopropyl derivative 3, R = i-C_3H_7, could be distilled under vacuum. Replacing pyridine with 2,6-lutidine had no effect on either the yield or the purity of the products.

An improvement in the preparation of peresters 3 came in 1967, when Sosnovsky[65] reported the development of a procedure by which compounds 3 could be prepared in larger quantities than had previously been possible. Thus, the analytically pure peroxy esters 3, R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, n-C_8H_{17}, are obtained in 30-77% yield by the reaction of the cor-

responding chlorophosphates 21 with an aqueous solution of potassium hydroxide and tert-butyl hydroperoxide in the presence of petroleum ether (bp 20-40 °C)[65-68] (method C). The choice of solvent is surpris-

method C

$$21 + C(CH_3)_3OOH \xrightarrow[\text{petroleum ether}]{\text{KOH}} 3$$

R = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, n-C_8H_{17}
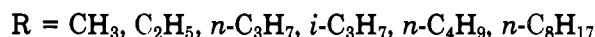
ingly critical to the success of the reaction,[66] since in experiments in which pentane, diethyl ether, or benzene are substituted for the petroleum ether, little or no product is isolated. Peroxy esters 3, R = C_6H_5, C_6H_5-CH_2, prepared by this method proved to be too unstable for complete characterization, decomposing rapidly at 0 °C and ambient temperature, respectively.

Although this method is satisfactory for the preparation of consistently pure peroxy esters, it is limited to a maximum scale of 0.2 mol. Pure peroxy esters 3 can be obtained successfully on a larger scale ranging from 0.2 to 1.0 mol if the sodium salt of tert-butyl hydroperoxide is first prepared in situ by use of the reaction of sodium hydride and tert-butyl hydroperoxide in ether, and then is treated with the phosphorochloridate 21[69,70] (method D). This method is applicable to the preparation of 3, R = C_2H_5, n-C_3H_7, i-C_3H_7,

method D

$$(CH_3)_3COOH + NaH \xrightarrow{Et_2O} [NaOOC(CH_3)_3] \xrightarrow[Et_2O]{21}$$
$$(RO)_2P(O)OOC(CH_3)_3$$
$$\textbf{3}$$
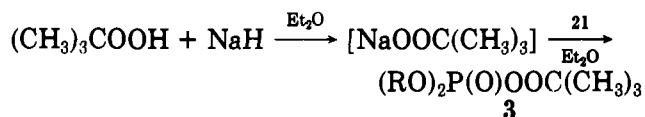
cable to the preparation of 3, R = C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, C_6H_5, c-C_6H_{11}. Unlike previously reported,[65] peroxy ester 3, R = C_6H_5, prepared by this method is stable for several days at 5 °C in ether, presumably because of the absence of trace amounts of diphenyl phosphate. The method was used for the preparation of 99 and 100, viscous, colorless oils which decompose
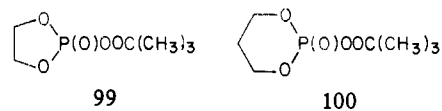
at room temperature to yield polymeric products and volatile byproducts. All attempts to prepare 101 and 102 were unsuccessful.[70] The methods of synthesis and
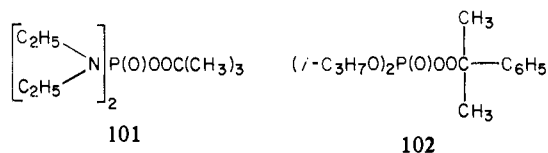
properties of tert-butylperoxy phosphates 3 are shown in Table XII.

Although most peroxy esters of phosphorus that have been prepared contain the tert-butylperoxy moiety, occasionally attempts have been to synthesize peroxy esters other than tert-butylperoxy phosphates. Thus, in 1960, Harrison and Mageli[64] reported the preparation of di-n-butyl and di-n-octyl pinanylperoxy phosphates 3 (R = n-C_4H_9, n-C_8H_{17}; R' = pinanyl), di-n-butyl, di-n-octyl and diphenyl cumylperoxy phosphates 3 (R = n-C_4H_9, n-C_8H_{17}, C_6H_5; R' = cumyl), di-n-butyl hexylperoxy phosphate 3 (R = n-C_4H_9, R' = C_6H_{13}), and 2,5-dimethyl hexane-2,5-diperoxy diphenyl and di-n-

butyl phosphates **103**, R = n-C_4H_9, C_6H_5. The per-

$$
\begin{array}{ccc}
& CH_3 & CH_3 \\
& | & | \\
& CH_3CCH_2CH_2CCH_3 & \\
& | & | \\
(RO)_2P(O)OO & & OOP(O)(OR)_2
\end{array}
$$

103, R = n-C_4H_9, C_6H_5

oxides were prepared by using the corresponding chloridates **21** and either the hydroperoxide and pyridine in petroleum ether or diethyl ether or the potassium salt of the hydroperoxide.[64] Unfortunately, the products were poorly defined and incompletely characterized.

A decade later, Maslennikov and Sergeeva[71] found the earlier reported method[64] for the preparation of dibutyl cumylperoxy phosphate (**3**, R = n-C_4H_9, R' = C-$(CH_3)_2C_6H_5$) to be unreproducible. In fact, it was found that the alleged product was a mixture of products arising from the decomposition of the peroxide **3**, R = $(RO)_2P(O)Cl$ + $NaOOC(CH_3)_2C_6H_5$ →
21, R = n-C_4H_9

$$(RO)_2P(O)OOC(CH_3)_2C_6H_5$$
3, R = n-C_4H_9, R' = $C(CH_3)_2C_6H_5$

$(RO)_2P(O)OOC(CH_3)_2C_6H_5$ →

$$(RO)_2P(O)OC(CH_3)_2OC_6H_5$$
104

104 → $(RO)_2P(O)OH$ + CH_2 = $C(CH_3)OC_6H_5$
105, R = n-C_4H_9

n-C_4H_9, R' = $C(CH_3)_2C_6H_5$. Peroxy ester **3**, R = n-C_4H_9, R' = $C(CH_3)_2C_6H_5$, is too unstable to survive even for short periods of time at -60 °C. In view of these results, the preparations of peroxy esters described in the patent[64] warrant a reinvestigation.

The only reliable report concerning the preparation of a peroxy ester with a group other than $tert$-butylperoxy was published in 1972.[72,76] The synthesis of diethyl sec-butylperoxy phosphate **3**, R = C_2H_5, R' = sec-C_4H_9, is achieved by the reaction of diethyl chlorophosphate (**21**, R = C_2H_5) with the sodium salt of

$$(RO)_2P(O)Cl + NaOOCHCH_2CH_3 \xrightarrow[0-5\ °C]{pentane} (C_2H_5O)_2P(O)OOCHCH_2CH_3$$
$$\begin{array}{cc} \textbf{21}, R = C_2H_5 & \\ & | \\ & CH_3 \end{array} \qquad \begin{array}{c} | \\ CH_3 \end{array}$$
3

sec-butyl hydroperoxide in pentane at 0-5 °C. Compound **3**, R = C_2H_5, R' = sec-C_4H_9, is extremely sensitive to hydrolysis and thermal decomposition. Thus, in nonane at 140 °C, diethyl phosphate (**105**, R = C_2H_5)

$$(C_2H_5O)_2P(O)OOCH(CH_3)CH_2CH_3 \xrightarrow{140\ °C}$$
3
$$(C_2H_5O)_2P(O)OH + CH_3COCH_2CH_3$$
105, R = C_2H_5

and 2-butanone are obtained in nearly quantitative yield.[72] The peroxy esters **3** other than $tert$-butylperoxy esters are shown in Table XIII. In most cases, the values for active oxygen are in poor agreement with calculated values. Hence, it appears that these peroxy esters were obtained in a crude form, and would warrant further investigation.

2. Peroxy Phosphonates

The first preparation of peroxy esters of phosphorus containing a P–C bond was reported in 1966. Yurzhenko and Kaspruk[75] synthesized the $tert$-butylperoxy

alkylphosphonates **106**, R = CH_3, R' = CH_3, C_2H_5, n-
method A

$$(RO)R'P(O)Cl + NaOOC(CH_3)_3 \xrightarrow{Et_2O}$$
$$(RO)R'P(O)OOC(CH_3)_3$$
106

23, R = CH_3, R' = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7

C_3H_7, i-C_3H_7, using the condensation of the corresponding alkyl alkylphosphonochloridate **23** with the sodium salt of $tert$-butyl hydroperoxide in anhydrous ether (method A). In the case that peroxides **106** were prepared by using the reaction of $tert$-butyl hydroperoxide with chloridates **23** in the presence of either pyridine or triethylamine, decomposition of the product results. Peroxides **106** cannot be synthesized by the interaction of chloridates **23** with $tert$-butyl hydroperoxide in the absence of a base.

Subsequently, other peroxy phosphonates (**106**; R = CH_3, R' = CH_2=CH,[76] R = C_2H_5, R' = C_6H_5,[74,77] R = C_2H_5, R' = C_2H_5,[78-80] R = C_2H_5, R' = $ClCH_2$,[42] and R = C_2H_5, R' = CH_2=CH[79] were prepared. Phosphonate **106**, R = R' = C_2H_5, can be synthesized from the corresponding chloridate **23** and $tert$-butyl hydroperoxide in the presence of pyridine[80] (method B).

method B

$$
\begin{array}{c}
\textbf{23} \\
(R = R' = C_2H_5)
\end{array} + HOOC(CH_3)_3 \xrightarrow{pyridine}
$$
$$(RO)R'P(O)OOC(CH_3)_3$$
106

The $tert$-butylperoxy phenylphosphonates **106**, R = H, Na, R' = C_6H_5, are prepared by using a different method.[81] The reaction of $tert$-butyl hydroperoxide with phenylphosphonic dichloride in petroleum ether, bp 80-100 °C, in the presence of a mixture of aqueous sodium hydroxide and sodium acetate results in the formation of sodium $tert$-butylperoxy phenylphosphonate (**106**; R = Na, R' = C_6H_5) in 24% yield.

$$C_6H_5P(O)Cl_2 + (CH_3)_3COOH \xrightarrow[AcONa]{NaOH/H_2O}$$
$$C_6H_5P(ONa)(O)OOC(CH_3)_3$$
106, R = Na, R' = C_6H_5

Acidification of the aqueous layer of the reaction mixture results in the isolation of the benzene-soluble hydrogen peroxy phosphonate ester **106**, R = H, R' =

$$C_6H_5P(O)(OH)OOC(CH_3)_3$$
106, R = H, R' = C_6H_5
$$C_6H_5P(O)[OOCC(CH_3)_3]_2$$
107

C_6H_5, in 26% yield. Also formed in the reaction is the diperoxy ester **107**.

Alkyl $tert$-butylperoxy alkylphosphonates **106**, R = alkyl, R' = alkyl, are also obtained in 45–68% yield by the reaction of the corresponding chloridate **23** with the potassium salt of $tert$-butyl hydroperoxide, prepared in situ from the hydroperoxide and aqueous potassium hydroxide, in the two-phase solvent system consisting of water and petroleum ether (bp 20–40 °C)[82] (method C). The details on the $tert$-butylperoxy phosphonates are collected in Table XIV. To date, no report concerning the preparation of peroxyphosphonates other than $tert$-butyl has appeared. The $tert$-butylperoxy phosphonates **106** are, in general, liquids purifiable by

TABLE XII. Preparation of *tert*-Butylperoxy Phosphates 3 [(RO)$_2$P(O)OOC(CH$_3$)$_3$]

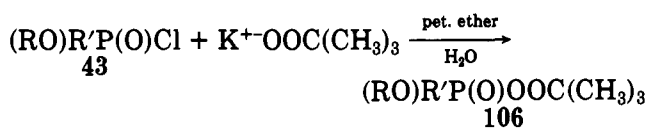| R	method of preparation	yield, %	mp or bp, °C (mm)	$n^{°}{}_D$	ref
CH$_3$	A	65 (crude)	23-25	a	6
		60 (pure)	70 (10^{-3})		
	C	53	26	1.4160^{25}	66
C$_2$H$_5$	A	95 (crude)	60-65 (10^{-2}-10^{-3})	1.419-1.421^{20}	6
	A	60-85 (pure)	75 (0.2)	a	70
	A	51	a	1.4164^{24}	70
	A	76	a	1.4163^{25}	64^b
	C	a	66-67 (0.15)	1.4169^{25}	66
	C	53	a	1.4161^{25}	66
	D^c	71	75-77 (0.1)	1.4166^{25}	69, 70
	D^d	75	75-77 (0.1)	1.4175^{25}	69, 70
n-C$_3$H$_7$	A	82.5^e	a	a	70
	C	70	85-87 (0.3)	1.4219^{25}	66
	D	81	a	1.4212^{25}	69, 70
n-C$_4$H$_9$	A	a	a	a	73
	C	77	f	1.4247^{25}	66, 74
	B^{g,h}	89	a	1.4248^{25}	64
	D	86	a	1.4251^{25}	69, 70
i-C$_3$H$_7$	A^i	33	84-86 (0.1)	1.4135^{27}	70
		27	82-85 (0.4)	a	
	A^j	a	a	a	70
	A	30	64-67 (0.1)	1.4148^{25}	66
	C	52	76-78 (0.03)	1.4145^{25}	66
	D^k	66	78-81 (0.2)	1.4142^{25}	69, 70
	D^l	77	82-85 (0.3)	1.4150^{25}	69, 70
i-C$_4$H$_9$	C^f	47	99.5-100 (0.4)	1.4200^{25}	66
	D	49	a	1.4226^{25}	69
	D	65	a	1.4226^{25}	70
n-C$_8$H$_{17}$	C^m	30	a	1.4389^{25}	66
	B^{g,n}	79	a	1.4380^{25}	64
C$_6$H$_5$	C^o	a	a	1.5133^{26}	66
	B^g	80	a	1.4996^{25}	64
	D^p	a	a	a	70
c-C$_6$H$_{11}$	D	60	a	1.4612^{25}	70
C$_6$H$_5$CH$_2$	q	a	a	a	66

^{a} Not reported. ^{b} "Active" oxygen calcd 7.08; found 6.97. Petroleum ether bp 30-60 °C was used as the additional solvent. ^{c} Reaction scale 0.18 mol. ^{d} Reaction scale 1.0 mol. ^{e} Compound decomposed on attempted distillation under vacuum. The yield is determined titrimetrically from active oxygen. ^{f} Reportedly undistillable. ^{g} Reaction was performed in the absence of petroleum ether. ^{h} Microanalysis was not within the accepted range. ^{i} In the presence of pyridine. In the presence of anhydrous magnesium sulfate, no pure 3, R = *i*-C$_3$H$_7$, was obtained. ^{j} In the presence of triethylamine. ^{k} Reaction scale 0.1 mol. ^{l} Reaction scale 0.45 mol. ^{m} Purified by chromatography on neutral alumina. ^{n} Microanalysis was within the acceptable range. ^{o} Material decomposes violently at °C. ^{p} Reportedly prepared. No details were given. ^{q} The compound was prepared by the reaction of the sodium salt of *tert*-butyl hydroperoxide and chlorophosphate 22, R = C$_6$H$_5$CH$_2$, in ether. It was too unstable to isolate. The product was identified by NMR.

TABLE XIII. Preparation of Alkyl- and Aralkylperoxy Phosphates 3 [(RO)$_2$P(O)OOR']

R	R'	method of preparation	yield, %	$n^{°}{}_D$	ref
n-C$_4$H$_9$	pinanyl	A	98^a	1.4577^{25}	64
n-C$_8$H$_{17}$	pinanyl	A	99^b	1.4593^{25}	64
n-C$_4$H$_9$	cumyl	A	90^{c,d}	1.4677^{25}	64
n-C$_8$H$_{17}$	cumyl	A	76^e	f	64
C$_6$H$_5$	cumyl	B	78^g	1.5182^{25}	64
n-C$_4$H$_9$	hexyl	A	89^h	1.4264^{25}	64
C$_2$H$_5$	*sec*-butyl	C^i	f	1.4113^{20}	72

^{a} % "active" oxygen: calcd 4.41; found 4.00. ^{b} % "active" oxygen: calcd 3.37; found 2.93. ^{c} % "active" oxygen: calcd 4.65; found 3.85. ^{d} Also reported to be too unstable to isolate, even at -60 °C.^{72} ^{e} % "active" oxygen: calcd 3.51; found 2.36. ^{f} Not reported. ^{g} % "active" oxygen: calcd 4.17; found 3.66. ^{h} % "active" oxygen: calcd 5.16; found 3.92. ^{i} The sodium salt of *sec*-butyl hydroperoxide was used; bp 20 °C (10^{-2} mm). Anal. Calcd: C, 42.6; H, 8.55; mol wt, 226. Found: C, 41.8; H, 8.60; mol wt. 214.^{72}

method C

$$\text{(RO)R'P(O)Cl} + \text{K}^{+-}\text{OOC(CH}_3)_3 \xrightarrow[\text{H}_2\text{O}]{\text{pet. ether}}$$
43

$$\text{(RO)R'P(O)OOC(CH}_3)_3$$
106

R = CH$_3$, C$_2$H$_5$, *i*-C$_3$H$_7$, *n*-C$_4$H$_9$; R' = CH$_3$, C$_2$H$_5$

distillation in vacuum. It has been our experience^{83} that the peroxy phosphonates are somewhat more stable and easier to distill than the *tert*-butylperoxy phosphates 3 of similar molecular weight.

3. Peroxy Phosphinates

The phosphinic peroxy esters **109** are generally prepared by using the condensation reaction of the corresponding phosphinic chloride **108** with the sodium salt

$$\text{RR'P(O)Cl} + \text{NaOOC(CH}_3)_3 \xrightarrow{\text{Na}_2\text{SO}_4}$$
108   **48**

$$\text{RR'P(O)OOC(CH}_3)$$
109
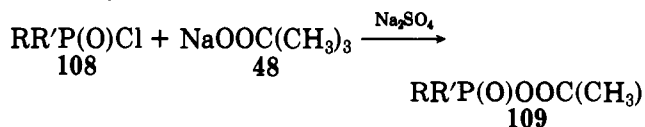
R = C$_2$H$_5$, CH$_2$=CH, ClCH$_2$CH$_2$; R' = CH$_2$=CH, ClCH$_2$CH$_2$, C$_6$H$_5$

of *tert*-butyl hydroperoxide in a neutral solvent in the presence of sodium sulfate.^{79} Although the compounds were reportedly characterized by their indices of refraction, peroxide oxygen content, and microanalysis, neither specific values nor yields were given^{79} (Table XV).

Alternatively, compounds **109** are prepared by using the reaction of *tert*-butyl hydroperoxide and phosphinic chloridate (**108**) in the presence of pyridine.^{84} Thus, the

TABLE XIV. Preparation of *tert*-Butylperoxy Phosphonates 106 [(RO)R'P(O)OOC(CH$_3$)$_3$]

R	R'	method of preparation	yield, %	mp or bp, °C (mm)	$n^{\circ C}_{D}$	ref
CH$_3$	CH$_3$	A	a	50–51 (0.02)	1.4265^{20}	75, 76
CH$_3$	C$_2$H$_5$	C	45	51.5–52 (0.10)	1.4240^{20}	82
CH$_3$	C$_2$H$_5$	A	a	56–57 (0.02)	1.4420^{20}	75
CH$_3$	C$_2$H$_5$	A	a	56–57 (0.02)	1.4282^{20}	76
CH$_3$	n-C$_3$H$_7$	A	a	64–65 (0.02)	1.4302^{20}	76
CH$_3$	n-C$_3$H$_7$	A	a	54–55 (3)	1.4437^{20}	75
CH$_3$	i-C$_3$H$_7$	A	a	46–47 (2)	1.4418^{20}	75
CH$_3$	i-C$_3$H$_7$	A	a	60–61 (0.02)	1.4266^{20}	76
CH$_3$	CH$_2$=CH	A	a	47–48 (0.02)	1.4388^{20}	76
C$_2$H$_5$	CH$_3$	C	54	51.5–52 (0.15)	1.4248^{20}	82
C$_2$H$_5$	C$_2$H$_5$	B	60	20–25 (0.005)	1.4288^{20}	80
C$_2$H$_5$	C$_2$H$_5$	A	a	a	a	78, 79
C$_2$H$_5$	CH$_2$=CH	A	a	a	a	79
C$_2$H$_5$	CH$_2$Cl	A	48	a	a	42
C$_2$H$_5$	C$_6$H$_5$	A	a	20–25 (0.005)	a	73, 78
C$_2$H$_5$	C$_6$H$_5$	A	a	a	1.4852^{20}	77
i-C$_3$H$_7$	CH$_3$	C	40	65–66 (0.15)	1.4224^{20}	82
i-C$_3$H$_7$	C$_2$H$_5$	C	68	59–60 (0.075)	1.4243^{20}	82
n-C$_4$H$_9$	CH$_3$	C	60	72–74 (0.085)	1.4227^{20}	82
n-C$_4$H$_9$	C$_2$H$_5$	C	46	74–75 (0.15)	1.4297^{20}	82
H	C$_6$H$_5$	a	26	88.5 dec	a	81
Na	C$_6$H$_5$	a	24	237 dec	a	81

^{a} Not reported.

TABLE XV. Preparation of *tert*-Butylperoxy Phosphinates 109 [RR'P(O)OOC(CH$_3$)$_3$]

R	R'	yield, %	mp, °C	ref
CH$_3$^{a}	CH$_3$	70 (crude)	21–23	84
		48 (pure)		79
C$_2$H$_5$^{b}	CH$_2$=CH	c	oil	79
C$_2$H$_5$^{b}	ClCH$_2$CH$_2$	c	oil	79
CH$_2$=CH^b	C$_6$H$_5$	c	oil	79
ClCH$_2$CH$_2$^{b}	C$_6$H$_5$	c	oil	79

^{a} Compound prepared by the reaction of the chloridate 108 with *tert*-butyl hydroperoxide in the presence of pyridine. ^{b} Compound prepared by the reaction of sodium *tert*-butoxide and chloridate 108 in the presence of sodium sulfate. ^{c} Not specified.

symmetric dimethylphosphinic peroxy ester 109 (R = R' = CH$_3$) is obtained in 48% yield following purification.

$$\text{(CH}_3)_2\text{P(O)Cl} + \text{HOOC(CH}_3)_3 \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{pyridine}}$$
108, R = R' = CH$_3$

$$\text{(CH}_3)_2\text{P(O)OOC(CH}_3)_3$$
109, R = R' = CH$_3$

The decomposition^{84} of peroxy ester 109, R = R' = CH$_3$, in the presence of trimethyltin hydride in toluene affords *tert*-butyl alcohol in 92–96% yield, the phosphorus-containing tin ester 110 in 89–92% yield, the dimer 111 of trimethyltin radicals in 5% yield, tetramethyltin, and methane in trace amounts. The reac-

$$\text{(CH}_3)_2\text{P(O)OOC(CH}_3)_3 \xrightarrow[\text{toluene}]{(\text{CH}_3)_3\text{SnH}}$$
109, R = R' = CH$_3$
$$\text{(CH}_3)_2\text{P(O)OSn(CH}_3)_3 + \text{(CH}_3)_3\text{COH} +$$
110
$$\text{(CH}_3)_3\text{Sn—Sn(CH}_3)_3 + \text{(CH}_3)_4\text{Sn} + \text{CH}_4$$
111

tion is presumed to proceed by a free-radical mechanism involving the trimethyltin radical^{84} [(CH$_3$)$_3$Sn·].

4. Miscellaneous Monoperoxy Esters

Peroxyamino phosphonates of the type 113 are obtained stepwise by using the reaction of the dichloroanhydride 112, R = CH$_3$, C$_2$H$_5$, of the corresponding alkylphosphonic acid with anhydrous ammonia in chloroform, followed by treatment of the intermediate, which is not isolated, with *tert*-butyl hydroperoxide.^{85}

$$\underset{\substack{\text{Cl}\quad\quad\text{Cl}\\112,\ R=\text{CH}_3,\ \text{C}_2\text{H}_5}}{\text{RP(O)—O—P(O)R}} \xrightarrow[\text{2. (CH}_3)_3\text{COOH/CHCl}_3]{\text{1. NH}_3\text{/CHCl}_3} \underset{\substack{\text{NH}_2\\113,\ R=\text{CH}_3,\ \text{C}_2\text{H}_5}}{\text{RP(O)OOC(CH}_3)_3}$$

Compounds 113, R = CH$_3$, C$_2$H$_5$, which can be recrystallized from benzene, are well-characterized solids, melting with decomposition. No transformations of peresters 113, R = CH$_3$, C$_2$H$_5$, were reported.^{85}

The only fluorine-containing peroxy ester of phosphorus was prepared in 1972. Although compound 115 cannot be prepared directly from trifluoromethyl hydroperoxide and the perfluorophosphorus derivative, perester 115 is obtained in 87% yield, by using the condensation of μ-oxo-bis(phosphonyl difluoride) (114; P$_2$O$_3$F$_4$) and trifluoromethyl hydroperoxide in the absence of a solvent.^{85} Perester 115, a liquid, was purified

$$\underset{114}{\text{P}_2\text{O}_3\text{F}_4} + \text{CF}_3\text{OOH} \rightarrow \underset{115}{\text{F}_2\text{P(O)OOCF}_3} + \text{F}_2\text{P(O)OH}$$

by distillation under vacuum and extensively studied^{85} as a synthetic intermediate.

5. Diperoxy Esters

In 1966, Yurzhenko and Kaspruk^{75} reported the preparation of the diperoxy esters 107, R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$, by the reaction of the corresponding alkyl phosphonic dichloride 116 with the sodium salt of *tert*-butyl hydroperoxide in hexane. At the time,

$$\underset{116}{\text{RP(O)Cl}_2} + \text{NaOOC(CH}_3)_3 \xrightarrow{\text{hexane}}$$

$$\underset{107}{\text{RP(O)[OOC(CH}_3)_3]_2}$$

R = CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, i-C$_3$H$_7$

it was found that compounds 107 cannot be distilled under vacuum due to decomposition and were characterized through their hydrolytic decomposition prod-

TABLE XVI. Preparation of Diperoxy Phosphonic *tert*-Butyl Esters 107 [RP(O)[OOC(CH₃)₃]₂]

R	yield, %	mp or bp, °C (mm)	$n^{20}C_D$	ref
CH_3[a]	b	b	1.4315[20]	75, 76
C_2H_5[a]	b	b	1.4325[20]	75, 76
C_2H_5[c]	60	b	b	80
n-C_3H_7[a]	b	b	1.4362[20]	75, 76
i-C_3H_7[a]	b	b	1.4346[20]	75, 76
c-C_6H_{11}	21	58.5-60	b	81[d]
$ClCH_2$[a]	50	b	b	42
CH_2=CH[a]	b	b	b	79
CH_2=$CHCH_2$[a]	b	b	b	79
$ClCH_2CH_2$[a]	b	b	b	79
C_6H_5[a]	b	68	b	76
C_6H_5[d]	20	61-63.5	b	81
C_6H_5CH=CH[a]	b	70	b	76
$C_6H_5C(Cl)$=CH[a]	b	b	b	79

[a] Reaction of dichloride 116 with the sodium or potassium salt of *tert*-butyl hydroperoxide in an inert solvent. [b] Not reported. [c] Reaction of dichloride 116 with *tert*-butyl hydroperoxide in the presence of pyridine. [d] Reaction of dichloride 116 in light petroleum with an aqueous mixture of *tert*-butyl hydroperoxide, sodium hydroxide, and sodium acetate.

ucts, i.e., methylphosphinic acid, acetone, methanol, and microanalysis. Subsequently, the area was expanded to include diperoxy esters 107, R = C_6H_5,[76,81] C_6H_5C-H=CH,[76] CH_2=CH,[79] CH_2=CHCH₂,[79] $ClCH_2CH_2$,[42,79] C_6H_5(Cl)C=CH,[79] c-C_6H_{11}.[81] In this work, either the sodium or potassium salt of *tert*-butylhydroperoxide was used in ether, benzene, and hexane as solvent.[76]

Peroxy esters 107 can also be prepared by using the reaction of the dichloridate 116 with *tert*-butyl hydroperoxide in the presence of pyridine.[80]

In the preparation of di-O,O-*tert*-butylphenyldiperoxy phosphonate (107, R = C_6H_5) in a two-phase system of light petroleum (bp 80-100 °C) and water with the chloridate 116, sodium hydroxide, sodium acetate, and *tert*-butyl hydroperoxide, product 107, R = C_6H_5, is obtained in only 20% yield.[81] In addition, the partially hydrolyzed compounds 106, R = Na, and 106, R = H, are also found as byproducts. Similarly, the cyclohexyl

$C_6H_5P(O)OOC(CH_3)_3$
|
ONa

106, R = Na

$C_6H_5P(O)OOC(CH_3)$
|
OH

106, R = H
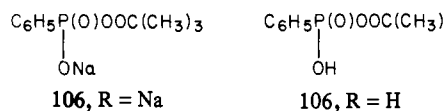
derivative 107, R = c-C_6H_{11}, is isolated in 21% yield. The data of peroxy esters 107 are collected in Table XVI.

B. Reactions

1. Peroxy Phosphates

a. Hydrolysis

At the time of their discovery, in 1959,[4-6] it was noted that peroxy phosphates 3 are very sensitive to hydrolytic conditions. Thus, the decomposition of 3, R = C_2H_5, in water occurs within a few minutes to give diethylphosphoric acid (105, R = C_2H_5), acetone, and methanol.[4,6] Further, it was found that the product
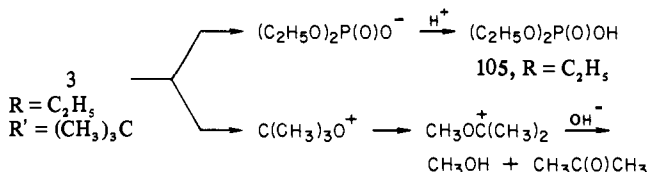
composition of the alkaline hydrolysis depends on the concentration of the alkali used.[6] Thus, in 2 N sodium hydroxide solution, phosphorus–oxygen bond cleavage predominates, and the dialkylphosphoric acid 105, R = C_2H_5, and *tert*-butyl hydroperoxide are formed.
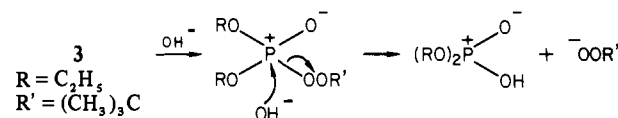
However, in dilute base, i.e., 0.1 N sodium hydroxide, oxygen–oxygen bond cleavage predominates, and the acid 105, R = C_2H_5, and acetone are formed.

Hydrolysis in dilute acid proceeds slowly, i.e., after 1 h in 2 N sulfuric acid, nearly 5% active oxygen still remains.

The sensitivity of other peroxy phosphates to hydrolytic conditions has also been reported.[64,72] Thus, the di-n-butyl cumyl peroxide 3, R = C_4H_9, R' = C(C-

105, R = n-C_4H_9

TABLE XVII. Reaction of Dialkyl *tert*-Butylperoxy Phosphates 3 with Benzene in the Presence of Aluminum Chloride

R	solvent	duration of reaction, h	reaction of R group, %	C_6H_5R, yield, %	$C_6H_5C(CH_3)_3$ yield, %	C_6H_5OH yield, %
C_2H_5	C_6H_6	0.5	33	33[a]	16	6
C_2H_5	C_6H_6	20	90	90[a]	0	14
C_2H_5	CH_2Cl_2/CH_3NO_2	4	2	2	40	<1
n-C_3H_7	C_6H_6	0.5	71.5	15 (n-C_3H_7) 40[b] (i-C_3H_7)	20	12
n-C_3H_7	CH_2Cl_2/CH_3NO_2	4	20	13 (n-C_3H_7) 7 (i-C_3H_7)	55	5
i-C_3H_7	C_6H_6	20	74	24[a]	0	12
i-C_3H_7	C_6H_6	0.5	64	52[d]	15	<1
i-C_3H_7	CH_2Cl_2/CH_3NO_2	20	90	90	56	4
i-C_3H_7	CH_2Cl_2/CH_3NO_2	3	21	21	16	2
n-C_4H_9	C_6H_5	0.5	60	0 (n-C_4H_9) 60[e] (sec-C_4H_9)	21	23
n-C_4H_9	CH_2Cl_2/CH_3NO_2	4	38	38 (n-C_4H_9) 0 (sec-C_4H_9)	40	2

[a] The diethylbenzene was formed in <1% yield. [b] The dipropylbenzene was formed in 40% yield. [c] The dipropylbenzene was formed in 50% yield. [d] The dipropylbenzene was formed in 12% yield. [e] The dibutylbenzene was formed in <1% yield.

SCHEME I

$$(RO)_2P(O)OOC(CH_3)_3 + AlCl_3 \longrightarrow [3\cdots AlCl_3 \text{ complex}]$$
$$\quad\quad\quad\quad\quad 3 \quad\quad\quad\quad\quad\quad\quad\quad\quad 117$$

$$117 \longrightarrow 2R^+ + C(CH_3)_3O^+ + P(O)(O^-)_3$$

$H_3)_2C_6H_5$, cannot be isolated following washing with dilute alkali.[64] Similarly, the instability of the *sec*-butylperoxy compound 3, $R = C_2H_5$, $R' = CH(CH_3)C$-H_2CH_3, toward hydrolytic conditions[72] was observed, although no attempts were made to characterize the decomposition products.

b. In the Presence of Aluminum Chloride

In 1971, it was reported[86] that the reaction of diisopropyl *tert*-butylperoxy phosphate (3, $R = i\text{-}C_3H_7$) in the presence of aluminum chloride results in 47% monoalkylbenzene, 10% dialkylbenzene, 8% trialkylbenzene, and 22% phenol. The accounting of alkyl

$$(i\text{-}C_3H_7O)_2P(O)OOC(CH_3)_3 \xrightarrow[\text{10 °C}]{C_6H_6/AlCl_3}$$
$$3$$
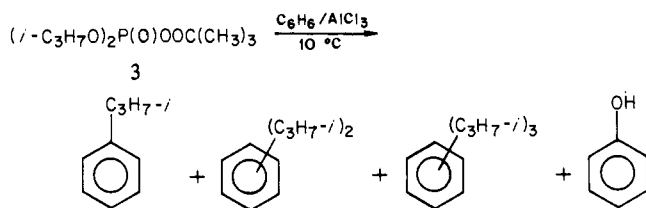
groups, as aralkane, totaled 47%.[86] Similar results were subsequently achieved with other peroxy esters 3.[87] In addition, *tert*-butylbenzene was also found (Table XVII). The products were explained by Scheme I.

The polyalkylation of benzene is virtually entirely suppressed if the excess benzene which acts as solvent is substituted by a mixture of dichloromethane and nitromethane (Table XVII). In all solvents, rearrangement of alkyl groups to the more branched carbonium ion is occurring. However, in dichloromethane/nitromethane this isomerization is greatly suppressed (Table XVII).

c. With Phenylmagnesium Bromide

The reaction of dialkyl peroxyphosphate esters 3 with
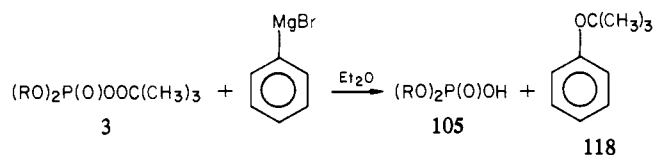
phenylmagnesium bromide affords high yields of *tert*-butyl phenyl ether (118) and moderate-to-high yields of the corresponding dialkylphosphonic acids 105[82] (Table XVIII).

TABLE XVIII. Reaction of Dialkyl Peroxy Phosphates 3 with Phenylmagnesium Bromide

perester 3, R	duration of reaction, h	reaction, temp, °C	yield of *tert*-butyl phenyl ether (118), %	yield of acid 105, %
C_2H_5	4.3	20–25	78	a
C_2H_5	1.25	0–5	82	30
$n\text{-}C_3H_7$	1.0	20–25	86	58
$i\text{-}C_3H_7$	0.7	10	60	a
$i\text{-}C_3H_7$	0.75	20–25	88	71
$n\text{-}C_4H_9$	19.5	20–25	74	a
$n\text{-}C_4H_9$	1.25	20–25	95	88

a Identified spectroscopically.

d. With Triphenylphosphine

Dialkyl *tert*-butylperoxy phosphates (3) are reduced by triphenylphosphine in ether to give the corresponding dialkyl *tert*-butyl phosphates (119) in low-to-moderate yields.[88] Thus, dimethyl *tert*-butyl

$$(RO)_2P(O)OOC(CH_3)_3 + (C_6H_5)_3P \xrightarrow{Et_2O}$$
$$3$$
$$(RO)_2P(O)OC(CH_3)_3 + (C_6H_5)_3P{=}O$$
$$\quad\quad 119 \quad\quad\quad\quad\quad\quad 120$$
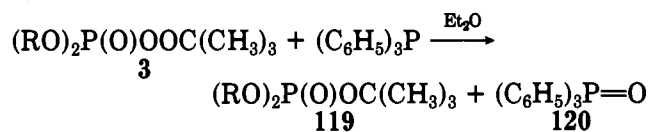
phosphate (119, $R = CH_3$) is obtained in 11% yield, whereas diethyl *tert*-butyl phosphate (119, $R = C_2H_5$) and diisopropyl *tert*-butyl phosphate (119, $R = i\text{-}C_3H_7$) are obtained in 9 and 36% yield, respectively. Also formed, as byproduct in the reaction, is triphenylphosphine oxide (120). It is difficult to remove all traces of this byproduct from the reaction mixture. Attempts to purify products 119 by distillation in the presence of triphenylphosphine and its oxide result in extensive decomposition, thereby reducing the yield of the dialkyl *tert*-butyl phosphates (119).

The reaction of the di-*n*-butylperoxy ester 3 with triphenylphosphine (118) results in the formation of the

$$(n\text{-}C_4H_9O)_2P(O)OOC(CH_3)_3 + (C_6H_5)_3P \xrightarrow{Et_2O}$$
$$\quad\quad 3 \quad\quad\quad\quad\quad\quad\quad\quad\quad 118$$
$$(n\text{-}C_4H_9O)_2P(O)OH + (C_6H_5)_3P{=}O +$$
$$\quad 105 \quad\quad\quad\quad\quad\quad\quad 120$$
$$\quad\quad (n\text{-}C_4H_9O)_2P(O)OP(O)(OC_4H_9\text{-}n)_2$$
$$\quad\quad\quad\quad\quad\quad 121$$
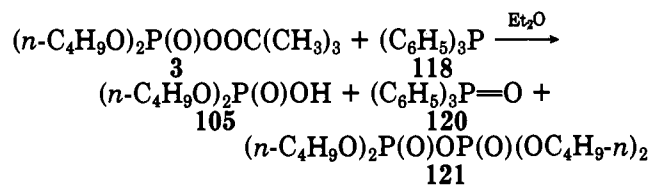
unresolvable mixture of triphenylphosphine oxide (120), di-*n*-butyl phosphate (105, $R = n\text{-}C_4H_9$), and tetra-*n*-butyl pyrophosphate (121, $R = n\text{-}C_4H_9$), as detected by thin layer chromatography with silica gel.[88]

Attempts to reduce peroxy esters 3 by other methods were unsuccessful.[88] Thus treatment of diisopropyl *tert*-butylperoxy phosphate (3, $R = i\text{-}C_3H_7$) with aqueous sodium bisulfite results, after 2–168 h, in the recovery of unreacted peroxyester 3 in 49–79% yield. The corresponding *tert*-butyl ester 119 ($R = i\text{-}C_3H_7$) is formed in only trace amounts, as determined by thin-layer chromatography.[88]

e. With Amines

The reaction of dialkyl peroxyphosphates (3, $R = C_2H_5$, $i\text{-}C_3H_7$) with cyclohexyl- and dicyclohexylamine proceeds, both in the absence and in the presence of water, to give the corresponding ammonium salt 122 and *tert*-butyl alcohol as the major products[89,90] (Table XIX).

TABLE XIX. Reaction of Dialkyl *tert*-Butylperoxy Phosphates (3) with Amines (R'R''NH)[90]

R	mol	R'	R''	mol	solvent	duration of reaction, h	temp, °C	122, yield, %	R'R''NH⁺Cl⁻ yield, %
i-C₃H₇	0.02	c-C₆H₁₁	H	0.02	C₆H₆	12	25	55	
C₂H₅	0.05	c-C₆H₁₁	H	0.1	C₆H₆	16	25	53	
i-C₃H₇	0.04	c-C₆H₁₁	H	0.05	C₆H₆	14	25	54	
i-C₃H₇	0.02	c-C₆H₁₁	H	0.02	C₆H₆	504	25	84	
i-C₃H₇	0.05	c-C₆H₁₁	H	0.1	C₆H₆	5	70	79	
i-C₃H₇	0.02	c-C₆H₁₁	H	0.04	C₆H₆	18	40	68ᵃ	
i-C₃H₇ᵇ	0.02	c-C₆H₁₁	H	0.04	C₆H₆	1	40	55ᵃ	
i-C₃H₇ᶜ	0.025	c-C₆H₁₁	H	0.05	CCl₄	168	25	57	trace
i-C₃H₇	0.025	c-C₆H₁₁	H	0.05	CCl₄	168	25	30	30
i-C₃H₇	0.025	c-C₆H₁₁	H	0.05	CCl₄	2	25	21	16
i-C₃H₇ᵈ	0.039	c-C₆H₁₁	H	0.039	CCl₄	20	25	26ᵉ	26
i-C₃H₇	0.02	c-C₆H₁₁	H	0.02	CH₃OH	9	25	32	
i-C₃H₇ᶠ	0.02	c-C₆H₁₁	H	0.02	CH₃OH	17.5	40	32	
i-C₃H₇	0.02	c-C₆H₁₁	H	0.04	CH₃OH	18	40	56	
C₂H₅	0.02	c-C₆H₁₁	c-C₆H₁₁	0.048	C₆H₆	39	25	54	
C₂H₅	0.02	c-C₆H₁₁	c-C₆H₁₁	0.02	C₆H₆	48	25	59	

ᵃ Yield of salt **122** was lowered by removal of five 0.5-mL aliquots of the reaction mixture for titration prior to workup. ᵇ Reaction was carried out in the presence of 0.002 mol of galvinoxyl. ᶜ Reaction was carried out in the presence of 0.05 mol of water. ᵈ Reaction was carried out in a glove box under dry nitrogen. ᵉ Perester 3, R = *i*-C₃H₇, was recovered in 46% yield. ᶠ Reaction was carried out in the presence of 0.01 mol of sodium methoxide.

$$(RO)_2P(O)OOC(CH_3)_3 + R'R''NH \rightarrow$$
3
$$(RO)_2P(O)O^-N^+HR'R'' + C(CH_3)_3OH$$
122

$$R = C_2H_5, i\text{-}C_3H_7, R' = H, c\text{-}C_6H_{11}, R'' = c\text{-}C_6H_{11}$$
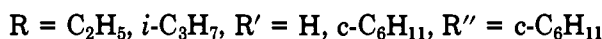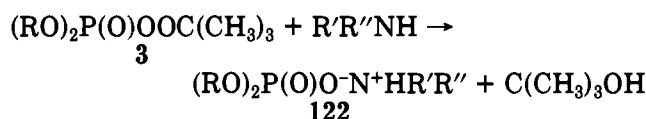
Attempts[90] to prepare the corresponding salts **122** of piperidine, phenethylamine, diphenylamine, aniline, and triethylamine failed to give crystalline products, whereas no reaction of 3, R = *i*-C₃H₇, occurred with benzylamine at 40 °C, and the unreacted peroxy ester was recovered. In addition to *tert*-butyl alcohol, in the case of the reaction of perester 3, R = *i*-C₃H₇ with cyclohexylamine, in benzene, trace amounts of cyclohexanone oxime, *N*-cyclohexylphosphoramidate **123** (R

123
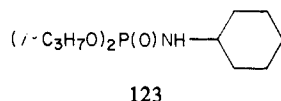
= *i*-C₃H₇), acetone, and methanol are formed. In carbon tetrachloride, moderate amounts of the amine hydrochloride salt also are detected (Table XIX). No simple mechanistic explanation could be proposed to account for the products.[90] Thus, the salts **122** are formed in the absence and in the presence of a solvent such as benzene, carbon tetrachloride, and methanol, both in the presence or absence of water. The amine appears to induce the decomposition of the peroxy ester. The rate of decomposition is accelerated in methanol as compared to nonpolar solvents. Typical free-radical initiators, i.e., azobis(isobutyronitrile), surprisingly inhibit the reaction, whereas radical traps, i.e., galvinoxyl, again surprisingly accelerate the reaction. Clearly, on the basis of the results, no simple mechanism involving proton transfer, radical decomposition, or nucleophilic displacement can be invoked to explain the products.

f. Decomposition in *n*-Nonane

By far the most extensively studied reaction of dialkyl *tert*-butylperoxy phosphates (3) is the decomposition of the peroxy ester under anhydrous conditions in *n*-nonane.[72,74,78,91-96]

In 1969, Maslennikov and co-workers reported[94] that

SCHEME II

$$(C_2H_5O)_2P(O)OOC(CH_3)_3 \xrightarrow{\Delta} (CH_3)_3CO\cdot + (C_2H_5O)_2P(O)O\cdot$$
3

$$(C_2H_5O)_2P(O)O\cdot + RH \longrightarrow (C_2H_5O)_2P(O)OH + R\cdot$$

$$(CH_3)_3CO\cdot + RH \longrightarrow (CH_3)_3COH + R\cdot$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3C(O)CH_3 + \cdot CH_3$$

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

$$2R\cdot \longrightarrow R\text{—}R$$

$$(CH_3)_3COH \longrightarrow (CH_3)_2C\text{=}CH_2 + H_2O$$

$$(C_2H_5P(O)OOC(CH_3)_3 \longrightarrow (C_2H_5O)_2P(O)OC(CH_3)_2\text{—}OCH_3$$
3

$$(C_2H_5O)_2P(O)OC(CH_3)_2OCH_3 \longrightarrow (C_2H_5O)_2P(O)OH + CH_3OC(CH_3)\text{=}CH_2$$
105

$$CH_3O\text{—}C(CH_3)\text{=}CH_2 + H_2O \longrightarrow CH_3OH + CH_3C(O)CH_3$$

$$2(C_2H_5O)_2P(O)OH \longrightarrow (C_2H_5O)_2P(O)OP(O)(OC_2H_5)_2 + H_2O$$
121

$$(C_2H_5O)_2P(O)OOC(CH_3)_3 + R\cdot \longrightarrow (C_2H_5O)_2P(O)OR + (CH_3)_3CO\cdot$$
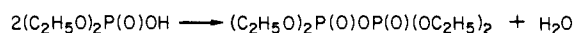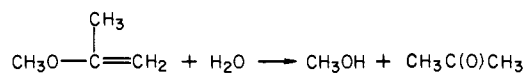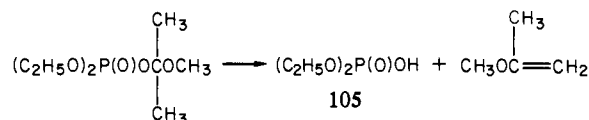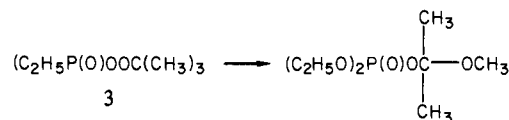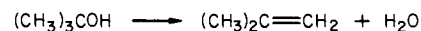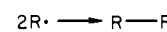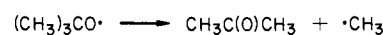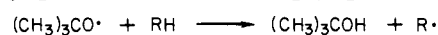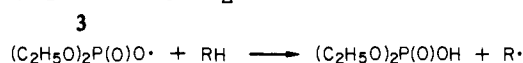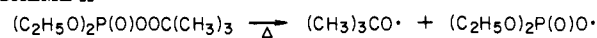
RH = solvent or another hydrogen donor substance

TABLE XX. Products of the Decomposition of Organophosphorus Peroxyesters 3 (R = C₂H₅, *n*-C₄H₉) in *n*-Nonane at 140 °C[78]

| peroxy-ester 3, R | yield, mol/mol of peroxide 3 ||||||| |
	ace-tone	*tert*-butyl alcohol	methyl alcohol	iso-meth-ane	iso-butyl-ene	acid	ester of phosphorus-containing acid
C₂H₅	0.50	0.38	0.48	0.04	0.03	0.71	0.18
C₂H₅ᵃ	0.62	0.24					
n-C₄H₉	0.48	0.50	0.47	0.02	0.03	0.75	0.19

ᵃ Reaction with a 35% of the corresponding acid 105, R = C₂H₅, added.

diethyl *tert*-butylperoxy phosphate (3, R = C₂H₅) decomposes, when in the pure state, only at above 120 °C in nonane. The products of the reaction include methane, isobutene, acetone, *tert*-butyl alcohol, iso-

TABLE XXI. Thermal Decomposition of Peresters 3 in Solution[98]

peroxyester 3, R	solvent	temp, °C	time, h	yield, %[a]					
				105	123	CH₃OH	(CH₃)₂CO	124	CH₂=CCH₃-(OCH₃) 122
C_2H_5	C_6H_6	77	24	90	4				
C_2H_5	C_6H_6	80	7	53					
C_2H_5	C_6H_6	80	22	66		27	18	26	4
$i\text{-}C_3H_7$	C_6H_6	80	4		9[b]	c	c	c	
$i\text{-}C_3H_7$	C_2H_5OH	78	3.5	59		c	c	c	c
$i\text{-}C_3H_7$	$CHCl_3$	61	5			c	c		c
$i\text{-}C_3H_7$	C_6H_5SH	110-115	2	trace[d]	trace				
$i\text{-}C_3H_7$[e]	C_6H_6	80	47	19[f]					
$i\text{-}C_3H_7$[g]	C_6H_6	80	42.5	66					

[a] The decompositions always produce intractable tar. [b] Peroxy ester 3 was recovered in 24% yield. [c] Determined qualitatively. [d] Plus 10% diphenyl disulfide. [e] Plus 20 mol % pyridinium hydrochloride. [f] Peroxy ester 3 was recovered in 8% yield. [g] Plus 20 mol % pyridine.

SCHEME III
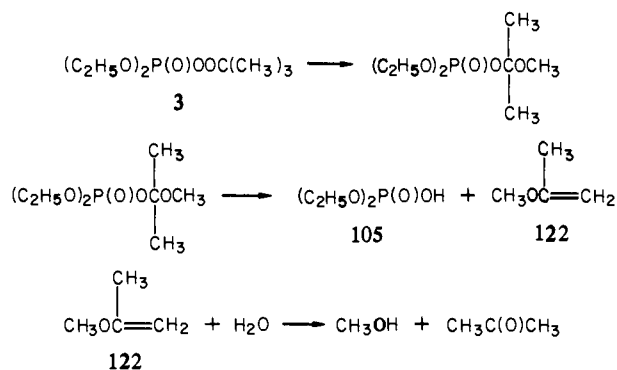
propenyl methyl ether, diethyl hydrogen phosphate (105, R = C₂H₅), and tetraethyl pyrophosphate (121, R = C₂H₅). These products presumably arise from simultaneous heterolytic and homolytic decomposition reactions of peroxy ester 3. Scheme II was proposed to account for the products.[91,94]

The homolytic decomposition reaction has zero-order kinetics with respect to the peroxy ester. The heterolytic decomposition reaction is catalyzed by diethyl hydrogen phosphate (105, R = C₂H₅).

Subsequently, the decomposition reactions of the diethyl (3, R = C₂H₅) and di-n-butyl (3, R = n-C₄H₉) compounds were further studied, the products formed in n-nonane at 140 °C were quantified[78,91] (Table XX), and rate constants as a function of temperature were determined. It was found that variations in the substituents attached to the phosphorus atom had little effect on the course of the reaction.[78,91,92] Substitution of sec-butyl and cumyl moieties in place of the tert-butyl groups causes polarization of the peroxy oxygen-oxygen bond, and thus the decomposition of these peroxy esters results only in the formation of rearranged products derived from the peroxy alkyl moiety.[78] Thus, the decomposition of diethyl sec-butylperoxy phosphate (3, R = C₂H₅, R' = sec-C₄H₉) proceeds rapidly at 140 °C to give diethyl hydrogen phosphate (105, R = C₂H₅) and acetone in virtually quantitative yield.[72] The temperature of the decomposition can be decreased by the addition of a free-radical initiation such as lauroyl peroxide.[78,95,97] This result is consistent with an induced type of decomposition, rather than a spontaneous type of decomposition.

g. Decomposition in Solvents Other Than n-Nonane

In addition to the decomposition reaction of tert-

butylperoxy phosphates 3, R = C₂H₅, n-C₄H₉, in nonane, the decomposition reaction was also studied in polar solvents.[78,91,97,98] Unlike in n-nonane, in which the decomposition proceeds by both homolytic and heterolytic cleavage of the peroxide bond, in solvents with either a high dielectric constant or favorable solvation properties, heterolytic rearrangement of 3, R = C₂H₅, occurs to give a nonperoxidic derivative, which then decomposes into diethylphosphoric acid (105, R = C₂H₅) and α-methylvinyl methyl ether (122).[97]

The decomposition of 3, R = C₂H₅, in nitrobenzene, nitromethane, n-butyl alcohol, ethyl alcohol, methyl alcohol, acetic acid, valeric acid, and water is a first-order reaction, and the composition of the final product is independent of the solvent. Diethyl phosphate (105, R = C₂H₅) is obtained in 87–94% yield, and the amounts of acetone and methanol are virtually quantitative. Scheme III is proposed to account for these products.[97]
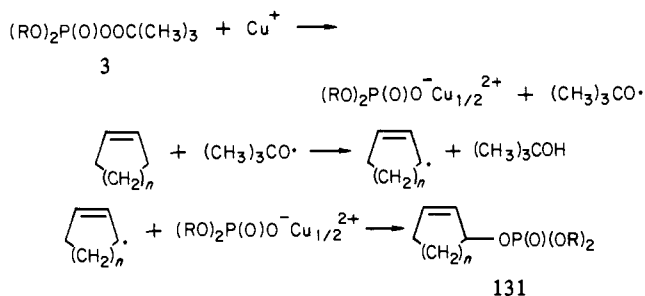
As has been noted in earlier work,[4,6] the heterolytic decomposition of peroxy phosphates is catalyzed by strong acids to afford the same products as formed in the absence of acid.

Sosnovsky and Zaret[98] found somewhat different products resulting from the decomposition of tert-butylperoxy phosphates 3, R = C₂H₅, i-C₃H₇, in solvents such as benzene, absolute ethanol, chloroform, and thiophenol (Table XXI). Thus, the decomposition reaction proceeds at elevated temperature to give the corresponding acid 105 (R = C₂H₅, i-C₃H₇), trialkyl phosphate 123 (R = C₂H₅, i-C₃H₇), methyl alcohol, acetone, 2,2-dimethoxypropane (124), and methyl isopropenyl ether (122). The triphosphate 123 presum-

$$(RO)_2P(O)OOC(CH_3)_3 \xrightarrow[\Delta]{solvent} (RO)_2P(O)OH +$$
$$\textbf{3}, R = C_2H_5, i\text{-}C_3H_7 \qquad \textbf{105}$$
$$(RO)_3P{=}O + CH_3OH + (CH_3)_2C(OCH_3)_2 +$$
$$\textbf{123}$$
$$CH_2{=}C(OCH_3)CH_3 + CH_3C(O)CH_3$$
$$\textbf{122}$$
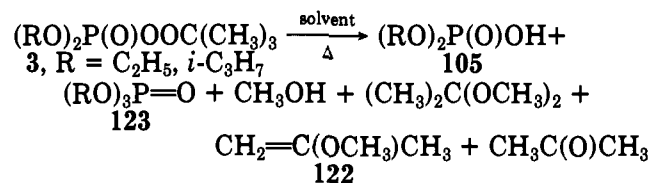
ably arises from a further reaction of diphosphate 105. As can be derived from the data shown in Table XXI, at a temperature of decomposition below 100 °C, the products are independent of the solvent, although the nature of the solvent has an affect on the rate of the decomposition of the peroxy ester. Thus, after the peroxy ester 3, R = i-C₃H₇, is boiled in absolute ethanol for 17 h, no trace of peroxy ester 3 is detected, whereas in about the same period of time, in boiling benzene,
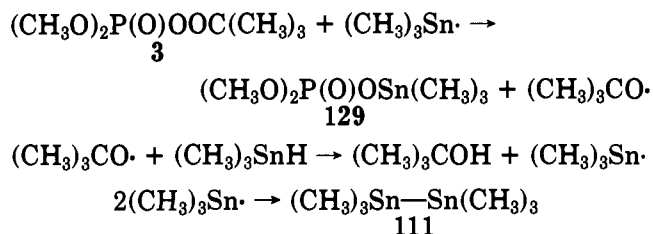
SCHEME IV

$(RO)_2P(O)OOC(CH_3)_3 + Cu^+ \longrightarrow$

  3

$(RO)_2P(O)O^-Cu_{1/2}^{2+} + (CH_3)_3CO\cdot$

$+ (CH_3)_3CO\cdot \longrightarrow$ $+ (CH_3)_3COH$

 $+ (RO)_2P(O)O^-Cu_{1/2}^{2+} \longrightarrow$ —$OP(O)(OR)_2$

  131

81% of the unreacted perester **3**, R = i-C_3H_7, is recovered.

The effect of various additives on the decomposition of peroxy esters **3** in benzene was also studied[98] (Tables XXI, XXII). Thus, introduction of 20 mol % pyridinium hydrochloride accelerates the rate of decomposition of perester **3**, R = i-C_3H_7, whereas addition of pyridine itself retards the reaction. Addition of 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (**125**) and diphenylpicrylhydrazyl (**126**) surprisingly accelerates the decomposition, while 2,6-di-$tert$-butyl-α-(3,5-di-$tert$-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy (galvinoxyl, **127**) and azobis(isobutyronitrile) (**128**) have no effect (Table XXII). In conclusion, on the basis of all these results, although it is impossible to exclude a free-radical mechanism for the decomposition of peroxy esters **3**, especially at elevated temperatures, in a nonpolar solvent, the thermal decomposition of peroxy esters **3** in the absence of solvents or in the presence of polar solvents seems to proceed predominately by an ionic mechanism.

  125   126

  127

$N\text{≡}C(CH_3)_2C—N\text{=}N—C(CH_3)_2C\text{≡}N$

  128
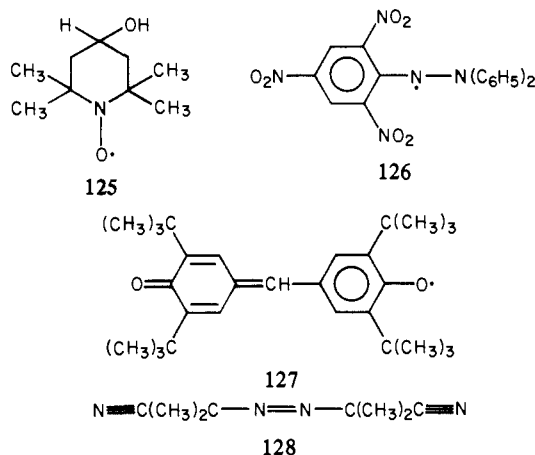
h. In the Presence of Tin Hydride and Copper Ions

The reaction of trimethyltin hydride with dimethyl $tert$-butylperoxy phosphate (**3**, R = CH_3) in toluene produces $tert$-butyl alcohol in 92–96% yield, the phosphate ester **129** containing the trimethyltin moiety in 89–92% yield, hexamethylditin (**111**) in 5% yield, and tetramethyltin and methane in trace amounts. No

$(CH_3O)_2P(O)OOC(CH_3)_3 + (CH_3)_3Sn\cdot \longrightarrow$

  3

$(CH_3O)_2P(O)OSn(CH_3)_3 + (CH_3)_3CO\cdot$

  129

$(CH_3)_3CO\cdot + (CH_3)_3SnH \longrightarrow (CH_3)_3COH + (CH_3)_3Sn\cdot$

$2(CH_3)_3Sn\cdot \longrightarrow (CH_3)_3Sn—Sn(CH_3)_3$

  111

hydrogen is evolved. The half-life of the peroxy phosphate **3**, R = CH_3, in the presence of the trimethyltin hydride is approximately 12 min.[84]

The reaction of $tert$-butylperoxy phosphates **3** with compounds containing active hydrogens, such as, cyclohexene (**130**, n = 2)[99,100] and cycloheptene (**130**, n = 3),[100] in the presence of copper ions proceeds by an oxidative phosphorylation process to give the trialkylphosphates **131** (Table XXIII). The phosphorylated cyclopentene **131**, n = 1, and cyclooctene **131**, n = 4, derivatives cannot be isolated, because of their thermal instability,[100] and only 1,3-cyclopentadiene and 1,3-

$(RO)_2P(O)OOC(CH_3)_3 +$ $\xrightarrow[80\ °C]{CuBr/C_6H_6}$

  3   130, n = 2, 3

$(RO)_2P(O)O$— $+ (CH_3)_3COH$

  131, n = 2, 3
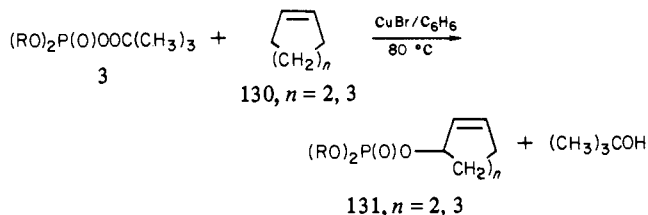
cyclooctadiene are obtained, in 92% and 38% yield, respectively. A similar reaction of peroxy ester **3**, R = i-C_3H_7, with 1-hexene in the presence of copper ion results also in the formation of a phosphorylated, unsaturated ester.[101] However, in view of the small scale of the experiment, no firm conclusion can be drawn concerning either the specific nature or the purity of the product. It is assumed that the product probably has structure **132**.

$(i\text{-}C_3H_7O)_2P(O)O—\overset{\displaystyle CH\text{=}CH_2}{\underset{\displaystyle}{CHCH_2CH_2CH_3}}$

  132
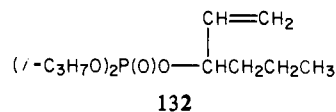
The copper ion catalyzed reaction of peroxy phosphates **3** with cycloalkenes proceeds in part via a radical mechanism, as verified by the significant retarding effect of typical free-radical scavengers such as 2,6-di-$tert$-butyl-α-(3,5-di-$tert$-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy (galvinoxyl; **127**), 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (**125**), and 2,2-diphenyl-1-picrylhydrazyl (DPPH, **126**) (Table XXIV). The mechanism shown in Scheme IV is proposed for the reaction; it involves ionic and radical species.[99]

**i. Decomposition in the Absence of Solvent**

At the time of the earliest investigations concerning the preparation of dialkyl $tert$-butylperoxy phosphates (**3**) in 1959,[4-6] the thermal instability of the peresters was observed. However, no attempts were made to identify the products of the thermal decompositions until 1966, when Sosnovsky and Zaret[73] reported in a preliminary communication that the decomposition of pure diethyl $tert$-butylperoxy phosphate (**3**, R = C_2H_5) proceeds at 70–80 °C (0.1 mm) to give an oil which was believed to be tetraethyl pyrophosphate (**121**, R = C_2H_5) in 74% yield. In an analogous manner, the decomposition of peroxide **3**, R = i-C_3H_7, was felt to afford pyrophosphate **121**, R = i-C_3H_7, in 80% yield. However, the decomposition of di-n-butyl perester **3**, R = n-C_4H_9, gave a different type of product, i.e., di-n-butyl phosphate (**105**, R = n-C_4H_9), in 55% yield. In the case that the decomposition is conducted at atmospheric pressure, extensive polymerization occurs, resulting in larger amounts of intractable products. In all cases, acetone, methyl alcohol, $tert$-butyl alcohol,[73] trialkyl phosphate

TABLE XXII. Thermal Decomposition of Peresters 3 in Benzene at 80 °C in the Presence of Additives

		percent unreacted 3 recovered after elapsed time, h											
perester 3, R	additive	0	3	4	7	9	17	20	22	25	28	44	52
i-C$_3$H$_7$	a	100							81		69	38	27
i-C$_3$H$_7$	122	100					82			65			
i-C$_3$H$_7$	120	100	96		21								
i-C$_3$H$_7$	121	100			82								
C$_2$H$_5$	a	100	77			35		0					
C$_2$H$_5$	123	100	72			34							
C$_2$H$_5$	121	100			70	20							
n-C$_4$H$_9$	a	100						10					
i-C$_4$H$_9$	a	100						14					

a Not reported.

TABLE XXIII. Reaction of Peroxy Phosphates 3 with Cycloalkenes in the Presence of Copper Ions

R	cycloalkene	131	ref
C$_2$H$_5$	(cyclopentene)	56	100
i-C$_3$H$_7$	(cyclohexene)	25	99
		71	100
n-C$_3$H$_7$	(cyclohexene)	49	100
n-C$_4$H$_9$	(cyclohexene)	50	100
i-C$_3$H$_7$	(cyclopentadiene)	a	100
i-C$_3$H$_7$	(cycloheptene)	71	100
i-C$_3$H$_7$	(cyclooctadiene)	b	100

a Only 1,3-cyclopentadiene (92%) was obtained. b Only 1,3-cyclooctadiene (38%) was obtained.

TABLE XXIV. Reaction of 3, R = i-C$_3$H$_7$, with Cyclohexene in the Presence of Copper(I) Bromide and Radical Inhibitors

inhibitor	3:inhibitor, mol:mmol	duration of reaction, min	recovery of 3, %	yield of 131, %
127	0.025:1.25	15	60	7
125	0.025:1.25	15	53	6
125	0.025:1.25	90	0	56
126	0.01:1.00	15	64	6

(123), 2,2-dimethoxypropane (124), and polymer were also found.[102] The same type of major phosphorus-containing product was isolated from the decomposition of 3 in aromatic solvents such as benzene or cumene.[102] However, these results had to be revised several years later.[98] The thermal decomposition of peroxy esters 3 proceeds under reduced pressure to give the corresponding dialkyl phosphates 105, which, on heating are readily transformed to the trialkyl phosphates 123 (Table XXV). The mixture of 105 and 123 can simu-

$$(RO)_2P(O)OOC(CH_3)_3 \rightarrow (RO)_2P(O)OH \rightarrow$$
$$\qquad\quad 3 \qquad\qquad\qquad\quad 105$$
$$(RO)_3P{=}O$$
$$123$$

late properties, such as boiling point under vacuum of the corresponding pyrophosphate,[98] and, hence, on the basis of this observation, the original[102] misinterpretation of preliminary data is explained. In addition, methyl alcohol, acetone, 2,2-dimethoxypropane (124), and methyl isopropenyl ether (122) are formed. However, no pyrophosphate, $tert$-butyl alcohol, methane, or

TABLE XXV. Products of the Thermal Decomposition of Peroxy Ester 3 in the Absence of Solvent[98]

3, R	temp, °C	pressure, mm	pyrolysis time, h	yield of 105, %	yield of 123, %
C$_2$H$_5$	80	0.2	0.17	19	b
C$_2$H$_5$	100	0.04	1.0	79	b
C$_2$H$_5$	70	0.05	0.5	74	b
C$_2$H$_5$ c	70	0.10	1.0	80	b
n-C$_3$H$_7$	102	0.05	2	39	b
i-C$_3$H$_7$	72–78	0.2	24	33	b
i-C$_3$H$_7$	80	0.1	19.5	4	20
i-C$_3$H$_7$	90–100	0.1–1.0	4	52	9
n-C$_4$H$_9$	68–72	0.1	8	a	72
n-C$_4$H$_9$ d	62–68	0.1	8	trace	59
n-C$_4$H$_9$	122–125	0.1	0.5	a	74

a Not including intractable tar. b Not isolated or detected spectroscopically. c Plus 8 mol % diethyl pyridinium phosphate. d Plus 20 mol % $tert$-butyl hydroperoxide.

SCHEME V
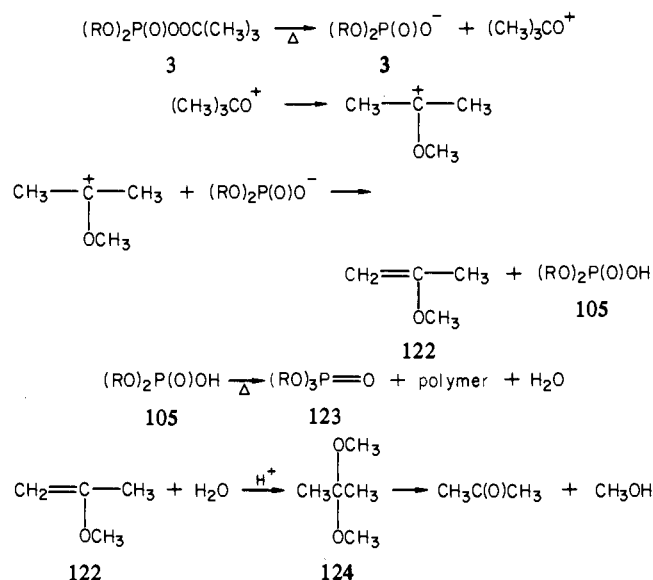
other gaseous products typical of a free-radical process are detected.[98]

The decomposition of neat diisopropyl $tert$-butylperoxy phosphate (3, R = i-C$_3$H$_7$) under nitrogen at 83 °C is accelerated by the parent phosphate 105, R = i-C$_3$H$_7$, and retarded by a base such as pyridine. The decomposition is not affected by small amounts of either $tert$-butyl hydroperoxide or azobis(isobutyronitrile) (128). On the basis of these results, the ionic mechanism shown in Scheme V is proposed[98] to account for the products of the decomposition of phosphorus peroxy esters in the absence of solvent.

TABLE XXVI. Photochemical Preparation of Cycloalk-1-en-3-yl Dialkyl Phosphates (131) in Benzene[103]

$$(RO)_2P(O)O \text{—} \underset{(CH_2)_n}{\diagdown}$$

131, $n = 1,2$

R	cycloalkene 125	n	yield, %
$i\text{-}C_3H_7$	⬠	1	36^a
C_2H_5	⬡	2	69
$n\text{-}C_3H_7$	⬡	2	61
$i\text{-}C_3H_7$	⬡	2	53
$n\text{-}C_4H_9$	⬡	2	52

a Product could not be completely purified because of thermal instability.

TABLE XXVII. Effect of Photosensitizers on the Photochemical Copper Ion Catalyzed Reaction of Peroxy Ester 3, R = i-C_3H_7[103]

3, mmol	photosensitizer, mmol	duration of reaction, h	yield of 131, %
10	none	4^a	30
10	none	8	53
10	benzene (1)	4	53
10	benzophenone (1)	4.5	66
10	acetone (1)	5	58
10	Eosin-Y^b	8	60

a Reaction was terminated after 4 h. Unreacted perester 3 was recovered in 43% yield. b 18-Crown-6 (3.1 mmol) was added to solubilize Eosin-Y.

j. Photochemical Decomposition

The decomposition of diethyl *tert*-butylperoxy phosphate (3, R = C_2H_5) in n-nonane or irradiation with a wavelength of 253.7 nm[78,96] proceeds with an 80% conversion into products. The reaction is first order in perester and is proposed to involve a radical mechanism, i.e., the homolytic cleavage of the peroxide bond, to give diethyl phosphate (105, R = C_2H_5) in 83% yield, *tert*-butyl alcohol in 61% yield, and unidentified gaseous products.[78,96] Different results are obtained in the

$$(C_2H_5O)_2P(O)OOC(CH_3)_3 \xrightarrow[n\text{-nonane}]{h\nu} (C_2H_5O)_2P(O)\cdot +$$
3

$$(CH_3)_3CO\cdot \xrightarrow{RH} (C_2H_5O)_2P(O)OH + C(CH_3)_3OH$$
105
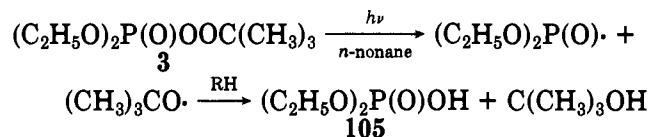
photochemically induced decomposition of peroxy phosphates 3 in the presence of cycloalkenes catalyzed by copper ions.[103] Thus, the photochemical reaction of 3 with cyclohexene (130, n = 2) in the presence of photosensitizers such as benzene, acetone, and benzophenone catalyzed by copper ions proceeds smoothly to give the phosphates 131, n = 1, 2, in moderate yields (Table XXVI). The lower temperature, i.e. 5–10 °C, as compared to the thermal reaction, is advantageous in the case of thermally unstable products 131 such as the cyclopentenyl derivative 131, R = i-C_3H_7, n = 1. Thus, in this case, phosphate 131 is obtained in 36% yield, while no phosphate 131, R = i-C_3H_7, n = 1, is isolated from the thermally induced copper ion catalyzed reaction.[100]

TABLE XXVIII. Reactions of (Trifluoromethyl)peroxyphosphoryl Difluoride (115)

reactant, mmol^a	duration of reaction (24 °C)	products
H_2O,^{b} 0.22	4 h^c	$HOPOF_2$, $(HO)_2POF$, SiF_4, CF_3OOH
H_2S,^{d} 0.23	1 d	$HOPOF_2$, POF_3, S, O_2, COF_2, CF_3OOH
HCl,^{d} 0.25	14 d	POF_3, Cl_2, O_2, HCl, COF_2, CF_3OOH
CF_3CO_2H,^{d} 0.21	1 d	CF_3CO_2H, CF_3OOPOF_2
CH_3OH,^{b} 1.22	4 h^c	CH_3OPOF_2, CF_3OOH, SiF_4^{f}
C_2F_4,^{b} 1.0	3 d	CF_3OOPOF_2, C_2F_4
CF_3OOPOF_2,^{e} 0.75	1 h	POF_3, PF_5, $P_2O_3F_4$, COF_2, CF_3OOCF_3, CF_3OOOCF_3, O_2
CF_3OF, 0.50	1 d	POF_3, COF_2, CF_3OOOCF_3, CF_3OOCF_3, O_2
$CF_2(OF)_2$,^{d} 0.25	4 h	POF_3, COF_2, $CF_2(OF)_2$, O_2
SF_5OF,^{d} 0.25	2 d	POF_3, COF_2, SF_5OF, O_2
$S_2O_6F_2$,^{b} 0.25	1 d	POF_3, COF_2, $S_2O_6F_2$, O_2

a An equimolar amount of 115 was used in each case. b 100-mL Pyrex vessel. c -196 to +22 °C. d 15-mL Pyrex vessel. e Photolyzed with 2.5-W 2537-Å UV lamp in 500-mL vessel. f An unidentified nonvolatile liquid was also obtained.

$$(RO)_2P(O)OOC(CH_3)_3 \ + \ \underset{(CH_2)_n}{\diagdown} \ \xrightarrow[h\nu, \ 5\text{-}10 \ °C]{CuBr/C_6H_6}$$
3

130, n = 1, 2

$$(RO)_2P(O) \text{—} \underset{(CH_2)_n}{\diagdown} \ + \ (CH_3)_3COH$$
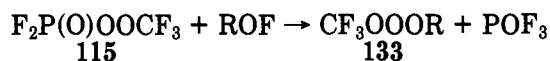
131, n = 1, 2
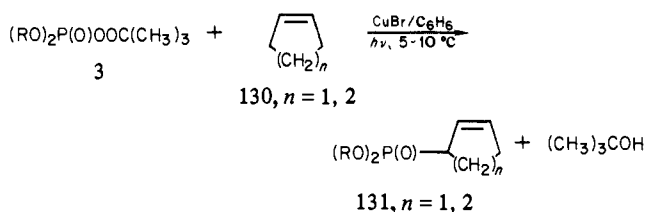
If benzene is omitted as solvent, the photolytic reaction is considerably retarded (Table XXVII). Instead of benzene, 10 mol % of other triplet sensitizers such as acetone or acetophenone can be used to accelerate the reaction. However, no effect is observed on the addition of the singlet sensitizer, Eosin-Y. Addition of radical scavengers such as galvinoxyl (127), 4-hydroxy-2,2,6,6-tetramethylpiperidinyl-1-oxy (125), and DPPH (126) in the amount of 10 mol %, effectively retards the photochemical reaction. On the basis of these results, it is concluded that the triplet-sensitized photochemical reaction of peresters 3 in the presence of copper ions proceeds via the radical-type intermediates proposed for the thermal reaction. However, the finer delineation of the individual steps of the reaction may warrant a further study.

2. Trifluoromethyl Peroxyphosphoryl Difluoride

The decomposition of trifluoromethyl peroxyphosphoryl difluoride (115) in either Pyrex or stainless steel vessels occurs slowly at 22 °C and rapidly at 115 °C to give difluorocarbonyl, phosphorus oxyfluoride, and oxygen. The reaction of peroxide 115 with CF_3OF

$$F_2P(O)OOCF_3 \xrightarrow{2 \text{ h, } 115 \text{ °C}} COF_2 + POF_3 + {}^1/_2O_2$$
115
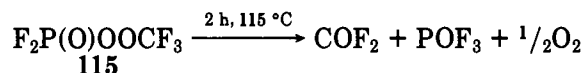
gives detectable amounts of 133, R = CF_3. In methyl

$$F_2P(O)OOCF_3 \ + \ ROF \ \rightarrow \ CF_3OOOR \ + \ POF_3$$
**115**   **133**

alcohol, difluoride 134 is formed in a low yield. The

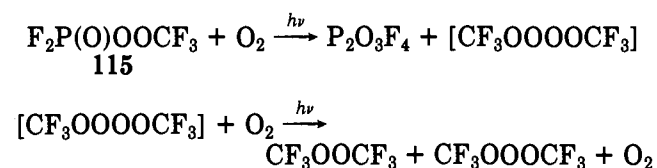**TABLE XXIX.** Products of the Reaction of **106** with Benzene in the Presence of Aluminum Chloride

101 R	101 R'	experimental method[a]	yield, % RC$_6$H$_5$	yield, % C(CH$_3$)$_3$C$_6$H$_5$	yield, % C$_6$H$_5$OH	alkyl group accounted for as aralkyls, %
CH$_3$	C$_2$H$_5$	A	40	6	7	40
CH$_3$	C$_2$H$_5$	C	0.5	35	13	0.5
C$_2$H$_5$	CH$_3$	A	69	15	9	69
C$_2$H$_5$	CH$_3$	C	0.5	44	15	0.5
C$_2$H$_5$	CH$_3$	B	95	0	0	95
i-C$_3$H$_7$	CH$_3$	A	62	11	8	62
i-C$_3$H$_7$	CH$_3$	C	53	33	17	53
i-C$_3$H$_7$	CH$_3$	C[b]	67	40	10	67
i-C$_3$H$_7$	C$_2$H$_5$	A	62	12	9	62
i-C$_3$H$_7$	C$_2$H$_5$	C	66	25	20	66
n-C$_4$H$_9$	CH$_3$	A	46.5 (n-C$_4$H$_9$) 35 (sec-C$_4$H$_9$)	2	2	83
n-C$_4$H$_9$	CH$_3$	C	17 (n-C$_4$H$_9$) 3 (sec-C$_4$H$_9$)	2	2	20
n-C$_4$H$_9$	C$_2$H$_5$	A	50 (n-C$_4$H$_9$) 35 (sec-C$_4$H$_9$)	3	2	85
n-C$_4$H$_9$	C$_2$H$_5$	C	20 (n-C$_4$H$_9$) 10 (sec-C$_4$H$_9$)	3	2	30

[a] Reaction A: ratio of AlCl$_3$:benzene:**106** = 0.034:1.34:0.01; reaction time 15 min. Reaction B: ratio of AlCl$_3$:benzene:**106** = 0.10:0.79: 0.05; reaction time 36 h. Reaction C: reaction performed in methylene chloride-nitromethane; ratio of AlCl$_3$:benzen:**106** = 0.034:1.35: 0.19; reaction time 4 h.

SCHEME VI

$$F_2P(O)OOCF_3 + CH_3OH \rightarrow CH_3OP(O)F_2$$
$$\qquad\mathbf{115}\qquad\qquad\qquad\qquad\mathbf{134}$$
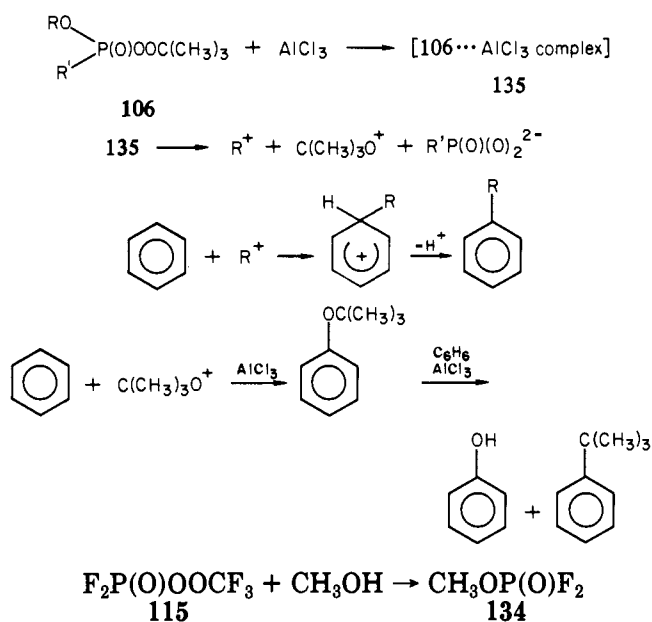
photochemical decomposition of peroxy difluoride **115** in the presence of oxygen proceeds as follows.[85]

$$F_2P(O)OOCF_3 + O_2 \xrightarrow{h\nu} P_2O_3F_4 + [CF_3OOOCF_3]$$
$$\mathbf{115}$$

$$[CF_3OOOCF_3] + O_2 \xrightarrow{h\nu}$$
$$\qquad\qquad CF_3OOCF_3 + CF_3OOOCF_3 + O_2$$

It is believed that the reaction involves the trifluoro-peroxy (CF$_3$OO·) radical intermediate rather than the trifluoroalkoxy (CF$_3$O·) radical intermediate. The results of reactions of **115** with various substrates and under varied conditions are shown in Table XXVIII.

3. Peroxy Phosphonates

a. In the Presence of Aluminum Chloride

The reaction of peroxy phosphonates **106** with

TABLE XXX. Reaction of Alkyl tert-Butylperoxy Alkylphosphonates **106** with Phenylmagnesium Bromide[105]

101 R	101 R'	yield of tert-butyl phenyl ether[a,b] (**118**), %	yield of acid **136**, %
CH$_3$	C$_2$H$_5$	99	36[c]
C$_2$H$_5$	CH$_3$	76	30[c]
i-C$_3$H$_7$	CH$_3$	81	30[c]
i-C$_3$H$_7$	C$_2$H$_5$	98	35[d]
n-C$_4$H$_9$	CH$_3$	83	43[c]
n-C$_4$H$_9$	C$_2$H$_5$	99	60[d]

[a] Yields are based on moles of perester. [b] Determined by gas chromatography. [c] Identified as the dicyclohexylamine salt and by boiling point. [d] Identified by boiling point.

benzene in the presence of aluminum chloride gives after 20 h at room temperature, products derived exclusively from carbon-oxygen (R–O) bond cleavage.[87] Under mild conditions, i.e., very short reaction times and low temperature (5 °C), phenol and tert-butyl-benzene can also be detected. Products derived from the peroxy phosphonates **106**, R = CH$_3$, C$_2$H$_5$, R' = C$_2$H$_5$, CH$_3$, are obtained in low yield (Table XXIX), presumably because of the difficulty of formation of the methyl and ethyl carbonium ions, respectively. The mechanism in Scheme VI is proposed to account for the observed products.[87] The instability of tert-butyl-benzene and tert-butyl phenyl ether in the presence of aluminum chloride is not surprising, in view of the rearrangements and dealkylation reactions which have previously been reported for the compounds under similar conditions.[104] At no time was any product detected which is derived from phosphorus-carbon bond cleavage of the peroxy derivative.

b. With Phenylmagnesium Bromide

The reaction of alkyl tert-butylperoxy alkyl-phosphonates **106** with phenylmagnesium bromide proceeds smoothly at room temperature to give tert-butyl phenyl ether (**118**) in 85–98% yield and the corresponding phosphonic acid **136**, R, R' = alkyl, in
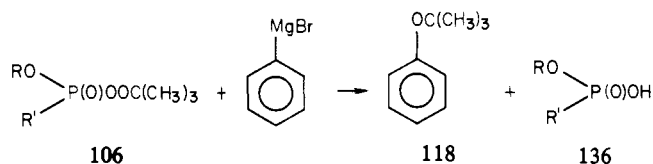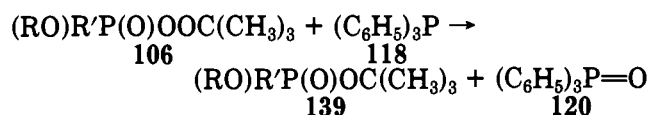
30–60% yield.[105] The reaction of nonperoxy phosphonates with the Grignard reagent has been known to give alkylated aromatic compounds.[106-108] However, the
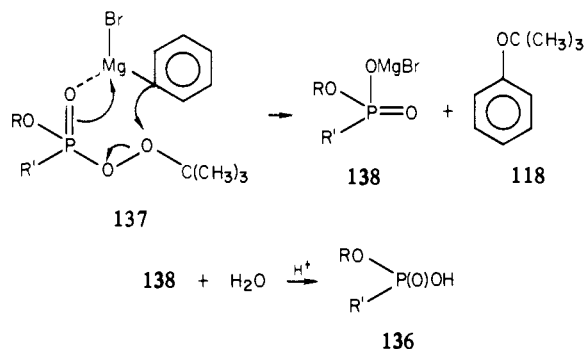
reaction of peroxy phosphonates is different, i.e., proceeding in analogy to peroxy esters of carbon,[109] presumably through the cyclic intermediates 137 to give 118 and intermediate 138 which on hydrolysis in dilute acid gives the byproduct 136. The results of the reaction of *tert*-butylperoxy phosphonates with phenylmagnesium bromide are shown in Table XXX.

c. With Triphenylphosphine

The reaction of alkyl *tert*-butylperoxy alkylphosphonates (106) with triphenylphosphine (118) gives

$$(RO)R'P(O)OOC(CH_3)_3 + (C_6H_5)_3P \rightarrow$$
$$\quad\quad 106 \quad\quad\quad\quad\quad\quad 118$$
$$(RO)R'P(O)OC(CH_3)_3 + (C_6H_5)_3P{=}O$$
$$\quad\quad 139 \quad\quad\quad\quad\quad 120$$

low-to-moderate yields of the corresponding alkyl *tert*-butyl alkylphosphonates 139 and high yields of triphenylphosphine oxide (120)[110] (Table XXXI). Unlike the reaction of *tert*-butylperoxy phosphates 3 with triphenylphosphine, which was completed within 5 h,[88] at least 20 h are required for completion of the corresponding reaction of peroxy phosphonates 106.[110] Since phosphonates 139 and phosphine oxide 120 are mutually soluble, difficulties were encountered during the isolation of the products, thereby reducing the yield of the *tert*-butyl phosphonates 139. *tert*-Butyl phosphonates 139 are only moderately stable, even on storage at –20 °C, and visible signs of decomposition are observed in a few weeks.[110]

d. With Amines

The reaction of alkyl *tert*-butylperoxy alkylphosphonates (106) with dicyclohexylamine in benzene at 60 °C in either the presence or the absence of moisture gives the corresponding dicyclohexyl-ammonium alkyl alkylphosphonates (140)[110] in 66–87%
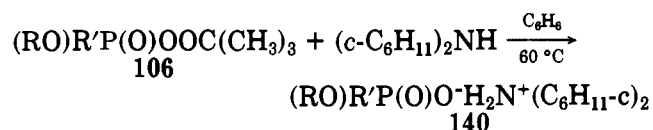
$$(RO)R'P(O)OOC(CH_3)_3 + (c\text{-}C_6H_{11})_2NH \xrightarrow[60\ °C]{C_6H_6}$$
$$106$$
$$(RO)R'P(O)O^-H_2N^+(C_6H_{11}\text{-}c)_2$$
$$140$$

TABLE XXXI. Reaction of Alkyl *tert*-Butylperoxy Alkylphosphonates (106) with Triphenylphosphine[110]

R	R'	yield of 139,[a,b] %
C_2H_5	CH_3	13
CH_3	C_2H_5	11
$i\text{-}C_3H_7$	CH_3	38
$i\text{-}C_3H_7$	C_2H_5	25
$n\text{-}C_4H_9$	CH_3	30
$n\text{-}C_4H_9$	C_2H_5	31

[a] After distillation. [b] There was also obtained triphenylphosphine oxide (120) in 74–97% yield.

TABLE XXXII. Reaction of Alkyl *tert*-Butylperoxy Alkylphosphonates (106) with Dicyclohexylamine[110]

R	R'	yield of 140,[a] %
CH_3	C_2H_5	76[b]
C_2H_5	CH_3	73[b] (87[c])
$i\text{-}C_3H_7$	CH_3	78[b]
$n\text{-}C_4H_9$	CH_3	66[b]

[a] After recrystallization from Skellysolve C (bp 90-100 °C). [b] Reaction in anhydrous benzene. [c] Reaction in a 1:1 mixture (v/v) of water and benzene.

SCHEME VII

RH = solvent
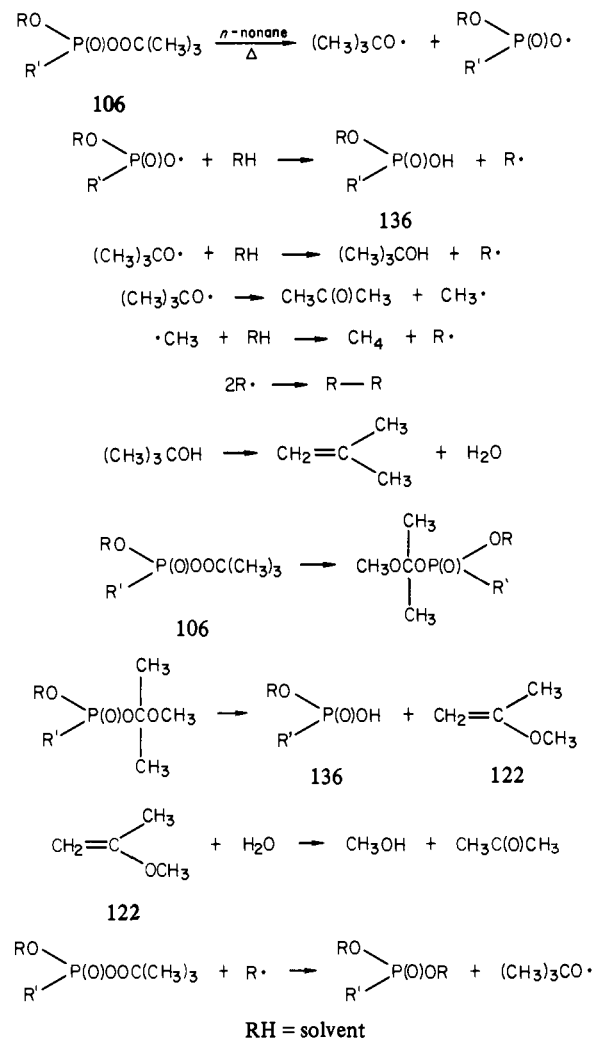
yield. The results of this reaction are shown in Table XXXII.

e. Decomposition in *n*-Nonane

The thermal decomposition of ethyl *tert*-butylperoxy

TABLE XXXIII. Results of the Decomposition of Peroxy Phosphonates 106 in Boiling Toluene[a]

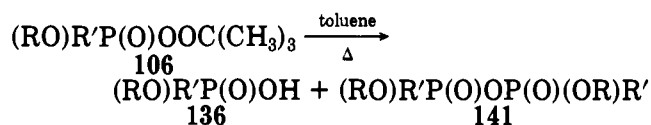| R	R'	yield of acid 136, %	yield of pyrophosphonate 141, %
CH_3	C_2H_5	0	95
C_2H_5	CH_3	13	76
i-C_3H_7	CH_3	0	86
i-C_3H_7	C_2H_5	10	80
n-C_4H_9	CH_3	0	88
n-C_4H_9	C_2H_5	10.5	88

[a] Yields are based on moles of perester.

ethylphosphonate (106, R = R' = C_2H_5) and ethyl *tert*-butylperoxy phenylphosphonate (106, R = C_2H_5, R' = C_6H_5) in *n*-nonane is a zero-order reaction and results in the formation of acetone, *tert*-butyl alcohol, isopropyl methyl ether (122), methyl alcohol, and the corresponding phosphonic acid 136.[74,78,80,91] While the addition of acetone or *tert*-butyl alcohol to the reaction mixture has no effect on the rate of the decomposition, the introduction of the corresponding phosphonic acid 136 not only increases the rate of decomposition but also reduces the energy of activation for the process from 28 to 22 kcal/mol. Furthermore, in the presence of acid 136, the yield of acetone increases and the yield of *tert*-butyl alcohol decreases, confirming the autocatalytic effect of the phosphonic acid formed during the decomposition. By analogy to the decomposition reaction of peroxy phosphates 3 in *n*-nonane, the reaction of peroxy phosphonates is suggested to proceed by concurrent homolytic and heterolytic reaction pathways, as shown in Scheme VII.[74,81,91]

Since these results closely parallel those obtained in the decomposition of dialkyl *tert*-butylperoxy phosphates 3, the effect of the phosphorus–carbon bond in compound 106 on the mode of decomposition of peroxy esters 106, under the given experimental conditions, is insignificant.

f. Decomposition in Solvents Other Than *n*-Nonane

It was shown[98] that dialkyl *tert*-butylperoxy phosphates (3) readily decompose in boiling benzene. However, in contrast to crude peroxy phosphonates, the pure compounds 106 are considerably more stable.[110] Thus, boiling of pure 106 (R = C_2H_5, R' = CH_3) in anhydrous benzene (78 °C) gives virtually no decomposition, and, after 20 h, as much as 90% of unreacted 106 is recovered. In the higher boiling toluene (110 °C), a complete decomposition is achieved after 15–20 h[110] to give 0–13% yields of the corresponding pyrophosphonates 141 and 76–95% yields of the phosphonic acids 136 (Table XXXIII).

$$(RO)R'P(O)OOC(CH_3)_3 \xrightarrow[\Delta]{toluene}$$
$$\mathbf{106}$$
$$(RO)R'P(O)OH + (RO)R'P(O)OP(O)(OR)R'$$
$$\mathbf{136} \qquad\qquad \mathbf{141}$$

Since the experiments in this case were performed on a small scale, i.e., 38 mmol, purification of the crude products by fractional distillation was difficult. The amounts of pyrophosphonate 141 and phosphonic acid 136 in the reaction mixture were estimated by infrared spectroscopy. This semiquantitative analysis is possible in view of the fact that the phosphorus–oxygen–phos-
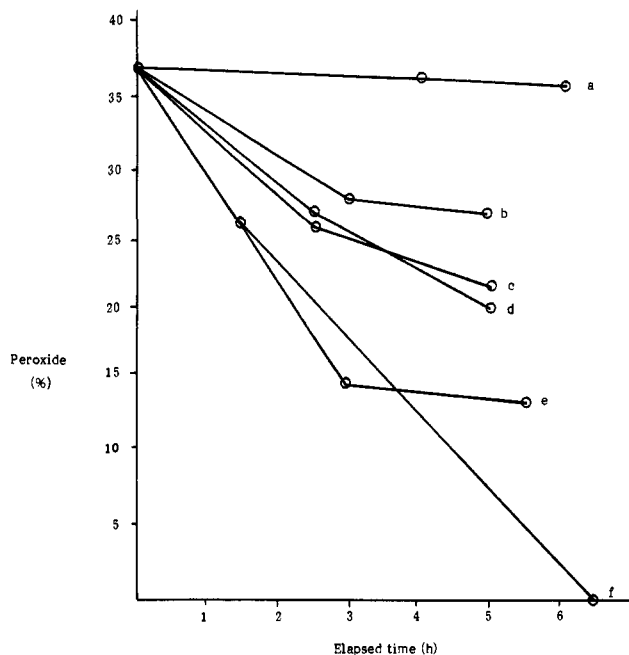

Figure 1. Effect of various additives on the rate of decomposition of peroxide 106, R = C_2H_5, R' = CH_3, in toluene. (a) Blank reaction, i.e., no additives. (b) Plus 10% by weight pyridine. (c) Plus 10% by weight of acid 136, R = C_2H_5, R' = CH_3. (d) Plus 10% by weight of salt 142, R = C_2H_5, R' = CH_3. (e) Plus 10% by weight of pyridinium hydrochloride. (f) In pyridine instead of toluene.[110]

phorus absorption of pyrophosphonate 140 is found at approximately 930 cm^{-1}, a frequency at which the other phosphonate derivatives do not absorb. In all cases, the estimated amounts of 141 and 136 were in agreement with the actual amounts of isolated products.

In addition to the pyrophosphonate 141 and acid 136, also formed during the reaction are acetone, methanol, isopropenyl methyl ether (122), and 2,2-dimethoxypropane (124). However, neither *tert*-butyl alcohol nor any gases such as methane or ethane, which would be indicative of a radical process, are found. In addition, no solvent dimer, i.e., bibenzyl, is formed. On the basis of these results, it is concluded that, in boiling toluene, peroxyphosphonates 106 decompose by a heterolytic cleavage of the peroxide bond. Addition of a small amount, i.e., 10% by weight, of the parent acid 136 slightly enhances the rate of decomposition of perester 106, R = C_2H_5, R' = CH_3. Addition of pyridinium hydrochloride greatly enhances the rate of decomposition. A small amount, i.e. 10% by weight, of pyridine itself significantly retards the rate of decomposition. However, if pyridine is used as a solvent, the rate of decomposition is greatly increased, either because of the formation of the pyridinium phosphonate 142, which
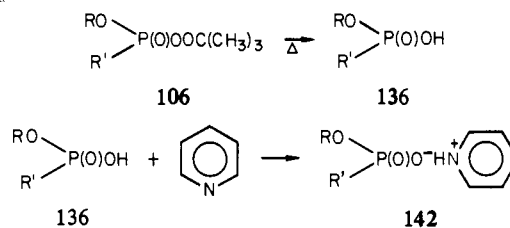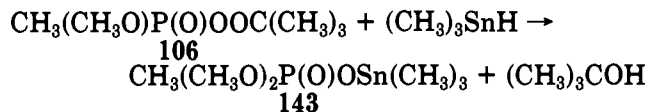

rapidly catalyzes the decomposition of 106, or because of the nucleophilic action by pyridine on the peroxide bond.[110] The results of these experiments are shown in Figure 1.

TABLE XXXIV. Reaction of Alkyl *tert*-Butylperoxy Alkylphosphonates (106) with Cyclohexene in the Presence of Copper Ions at 80 °C[100]

R	R'	yield of 144, %
C_2H_5	CH_3	50
i-C_3H_7	CH_3	53
n-C_4H_9	CH_3	65
C_2H_5	C_2H_5	58
i-C_3H_7	C_2H_5	52

TABLE XXXV. Photochemical Reaction of Alkyl *tert*-Butylperoxy Phosphonates (106) with Cyclohexene in the Presence of Copper Ions[103] at 5-10 °C

| R	R'	yield of 144, %
C_2H_5	CH_3	56
i-C_3H_7	CH_3	55
n-C_4H_9	CH_3	52
C_2H_5	C_2H_5	55
i-C_3H_7	C_2H_5	51

g. In the Presence of Tin Hydride and Copper Ions

The reaction of methyl *tert*-butylperoxy methylphosphonate (106, R = R' = CH_3) with trimethyltin radicals, derived from trimethyltin hydride, proceeds by an S_H2 reaction at room temperature, with a half-life of 12 min, to give the corresponding phosphonate containing the trimethyltin moiety (143) and *tert*-butyl

$$CH_3(CH_3O)P(O)OOC(CH_3)_3 + (CH_3)_3SnH \rightarrow$$
$$\textbf{106}$$
$$CH_3(CH_3O)_2P(O)OSn(CH_3)_3 + (CH_3)_3COH$$
$$\textbf{143}$$

alcohol in quantitative yield.[84] The reaction is retarded by hydroquinone, a well-known radical scavenger.

The reaction of peroxy phosphonates 106 with cycloolefins in benzene in the presence of copper ions proceeds, in analogy to the reaction of phosphates 3, by a mechanism involving ionic and radical species to give the corresponding phosphonate esters 144 in 50-58% yield (Table XXXIV).[100] In addition, *tert*-butyl alcohol is also formed in nearly quantitative yield. The reaction
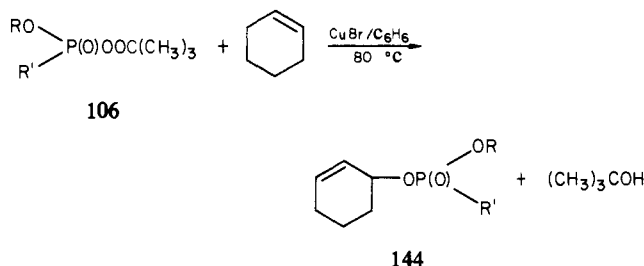
is specifically catalyzed by copper ions. Thus far, iron(II) chloride, cobalt(II) bromide, and manganese(II) chloride have been tested and found ineffective. Although the reaction proceeds slowly at room temperature, at 80 °C in benzene, the reaction is complete within minutes. A mechanism analogous to that proposed for the copper ion catalyzed reaction of peroxy phosphates 3 with olefins is proposed to account for the products.[100]

h. Photochemical Decomposition

The photochemical reaction of alkyl *tert*-butylperoxy alkylphosphonates (106) with cyclohexene in benzene as solvent in the presence of copper ions gives phosphonates 144 in 50-70% yield (Table XXXV).[103] In
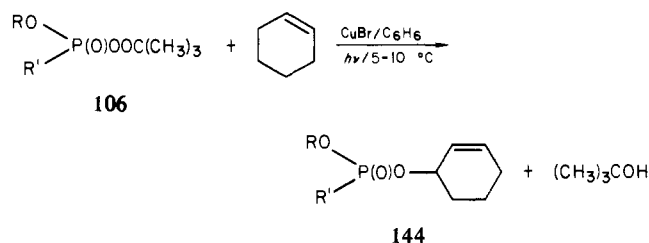

contrast to the thermal reaction, which is complete within 15 min at about 80 °C, the photochemical reaction at 5-10 °C is slower, and is completed within 4-5 h. Nevertheless, the milder reaction conditions, because of lower temperatures, make the photochemical reaction the method of choice in cases involving thermally sensitive products.[103]

4. Diperoxy Phosphonates

a. Hydrolysis

The hydrolysis of phenyl di-*tert*-butylperoxy phosphonate (107, R = C_6H_5) in boiling water gives the corresponding phenylphosphonic acid 95, R = C_6H_5 in
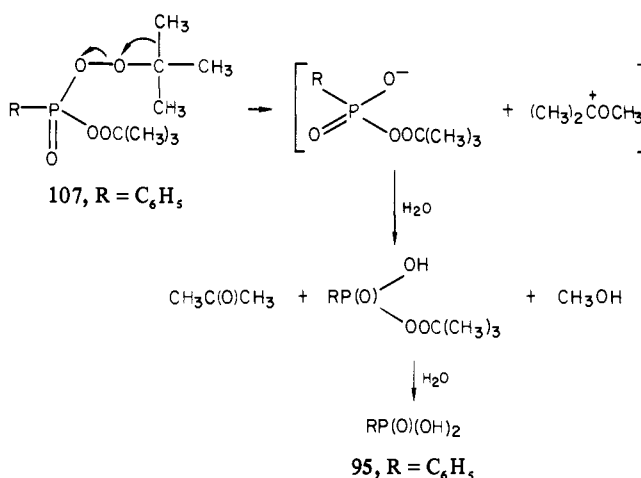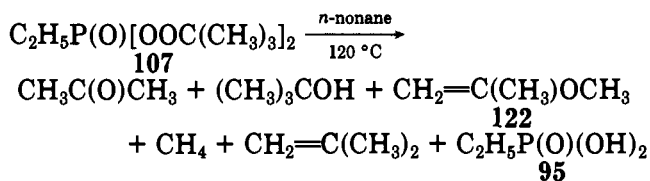

nearly quantitative yield.[81] Phosphonic acid 95 presumably arises from a heterolytic cleavage of the peroxide bond. Acetone and methyl alcohol are also formed during the reaction.

Even mildly electron-withdrawing substituents such as the phenyl moiety attached to phosphorus facilitate the hydrolysis, as evidenced by the stability of the cyclohexyl derivative 107, R = c-C_6H_{11}, as compared to the phenyl analogue 107, R = C_6H_5, under comparable conditions.

b. Decomposition in *n*-Nonane

The decomposition reaction of ethyl di-*tert*-butylperoxy phosphonate (107, R = C_2H_5) in *n*-nonane was extensively studied.[78,80,91,111] The rate of decomposition is a function of the temperature and concentration of the peroxy phosphonate. The zero-order reaction is independent of the surface of the vessel[111] and proceeds[78] by an induced decomposition to give acetone, *tert*-butyl alcohol, isopropenyl methyl ether (122), methane, isobutylene, and ethylphosphonic acid (95, R = C_2H_5).

$$C_2H_5P(O)[OOC(CH_3)_3]_2 \xrightarrow[120\ °C]{n\text{-nonane}}$$
$$\underset{\mathbf{107}}{}$$

$$CH_3C(O)CH_3 + (CH_3)_3COH + CH_2{=}C(CH_3)OCH_3$$
$$\underset{\mathbf{122}}{}$$

$$+ CH_4 + CH_2{=}C(CH_3)_2 + C_2H_5P(O)(OH)_2$$
$$\underset{\mathbf{95}}{}$$

Addition of acetone or *tert*-butyl alcohol to the reaction mixture results in no appreciable effect on the rate of the decomposition.[80] However, addition of the corresponding phosphonic acid **95**, R = C_2H_5, prior to commencement of the experiment increases the rate of the reaction. On the basis of all results, it is concluded that the decomposition of diperoxy esters **107** proceeds in analogy to the decomposition of monoperoxy phosphates **3**, i.e., by a concomittant homolytic and heterolytic mechanism.[80,91]

c. In the Presence of Tin Hydride

The reaction of cyclohexyl di-*tert*-butylperoxy phosphonate (**107**, R = c-C_6H_{11}) with an equimolar amount of tin hydride in benzene at room temperature forms the isolable peroxy ester **145**, containing one trimethyltin moiety.[84] In the case that an excess of
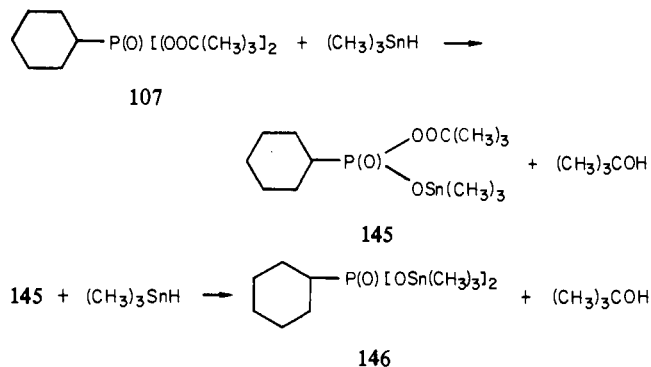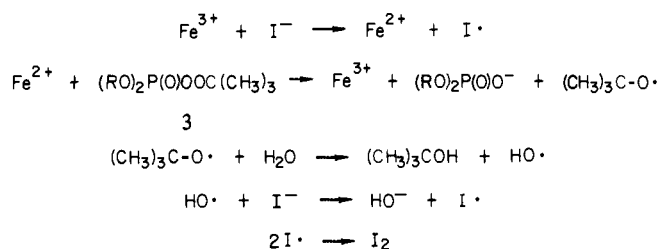

trimethyltin hydride is used, the reaction of perester **145** gives the distannyl derivative **146** in good yield.[84] The reaction of trimethyltin hydride probably proceeds by a homolytic attack of the trimethyltin hydride radical on the peroxide bond.
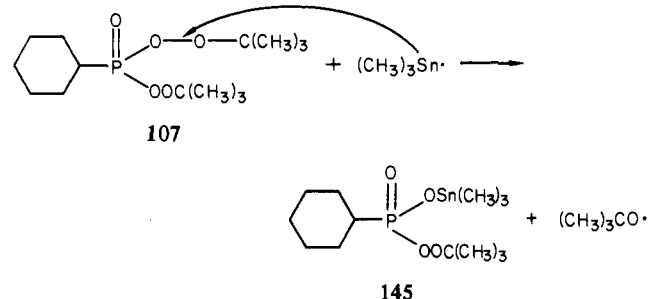

V. Analysis of Peroxides of Phosphorus

The characteristic infrared absorptions of several peroxy phosphates **3**, R = C_2H_5, n-C_4H_9, and phosphonates **106**, R = C_2H_5, R' = C_2H_5, C_6H_5, have been reported.[9,112] The strong phosphoryl P=O vibration appears in the region of 1270 cm^{-1}. The P–O–O–R' and P–OR moieties absorb at 950 cm^{-1} and 970–1015 cm^{-1}, respectively. The *tert*-butoxy [(CH$_3$)$_3$CO] group (C–O stretch) absorbs at 1150 cm^{-1}. In addition, other absorptions specific to the peroxy derivatives of phosphorus can be observed at approximately 825 cm^{-1}.

SCHEME VIII

$$Fe^{3+} + I^- \longrightarrow Fe^{2+} + I\cdot$$

$$Fe^{2+} + (RO)_2P(O)OOC(CH_3)_3 \longrightarrow Fe^{3+} + (RO)_2P(O)O^- + (CH_3)_3C\text{-}O\cdot$$
$$\underset{\mathbf{3}}{}$$

$$(CH_3)_3C\text{-}O\cdot + H_2O \longrightarrow (CH_3)_3COH + HO\cdot$$

$$HO\cdot + I^- \longrightarrow HO^- + I\cdot$$

$$2I\cdot \longrightarrow I_2$$

In the case that the peroxy derivatives contain strongly electron-withdrawing groups, the absorptions are shifted. Thus, the trifluoroperoxy phosphate **115** possesses absorptions at 1395 (ν(P=O)), 825 (ν(O—O)), 595, 495, 460 cm^{-1} (ν(PO$_2$F$_2$, CF$_3$OO)).[85]

$$F_2P(O)OOCF_3$$
$$\underset{\mathbf{115}}{}$$
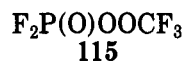
The NMR spectra of certain *tert*-butylperoxy phosphates **3**, R = alkyl, have also been reported.[68-68] The spectra of peroxy esters **3** are not the typical first-order spectra because of the contribution of the ^{31}P nucleus, with its spin of $^1/_2$, which couples very strongly to the protons of the alkyl groups.[68] Thus, for example, in the case of **3**, R = CH$_3$, the methyl groups appears as a

$$(CH_3O)_2P(O)OOC(CH_3)_3$$
$$\mathbf{3},\ R = CH_3$$
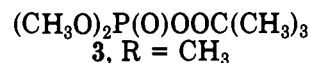
doublet instead of a triplet, with J = 11 Hz, because of the effect of ^{31}P. The influence of phosphorus on the expected chemical shifts of the protons of the alkyl groups of peroxy esters is insignificant.[88]

The determination of the active peroxy oxygen in peresters sometimes presents difficulties. The best method for determination of active oxygen content involves the titration of the iodine liberated from an excess amount of sodium iodide by a known quantity of peroxide with standardized sodium thiosulfate.[101,105,113] The analysis is performed by dissolving an excess of sodium iodide in glacial acetic acid which is purged continuously with nitrogen in the presence of 0.002% by weight anhydrous ferric chloride, which is added to catalyze the decomposition of the peroxide. The addition of starch as the indicator is optional. The liberated iodine is titrated with standardized thiosulfate solution.[101,105] The active oxygen content is calculated by using eq 10, where W = weight of samples (g), A =

$$\% \text{ active oxygen} = \frac{(A - B) \times \text{normality} \times 0.8}{W} \quad (10)$$

volume of 0.1 N sodium thiosulfate required by the sample, B = volume of 0.1 N sodium thiosulfate required by the blank. By this improved method only approximately 5 min is required for each determination.

In most cases, from the practical point of view, the density of the peroxy ester can be assumed to be 1.0 g/mL, and thus W will equal the volume of perester used.

Scheme VIII is proposed to account for the stoichiometry and products of the reaction.[113] This mechanism is analogous to that proposed for carbon peresters.[114]

VI. *References*

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