column at 150°. There was a shoulder on the peak for **20**: ir **20** $\nu_{\mathrm{CH=}}$ 3080; ν_{CH} 2980; 2930, 2850 (d); $\nu_{\mathrm{C=C}}$ 1640; bands at 1025, 932, 880, 735, and 725 cm^{-1}; nmr (**20**, Figure 3), δ 1.3–1.9 (4 protons, m, CH_2 of C_4, C_5), 2.1 (2 protons, q, J = 13, 6 Hz, $CH_2CH_2CH{=}$), 2.75 (t of d, J_{HF} = 20 Hz, CF_2CH_2CH), 4.4 (1 proton, 5 line, J = 12 and 6 Hz, CH_2CHICH_2); nmr (**21**) δ 1.8 (6 protons, t of d, J_{HF} = 20, J = 8 Hz, CF_2CH_2CHI), 4.4 [2 protons, m, $(CHI)_2$].

Reaction of 5 and 8 to Give *endo*-2-Iodo-*exo*-3-perfluorobutylnorbornane (17).—**5** (17.3 g, 0.0500 mol), **8** (4.70 g, 0.0500 mol), and ABN (0.164 g, 1.00 mmol) were processed as above and heated for 3 hr at 70.0°. Distillation gave **17**: bp 79–82° (3.5 mm), 16.7 g (76%), a single peak by glpc; ir (KBr plates) δ_{CH} 1480, 1460, 1355, 1320; ν_{CF} 1250–1200, 1130; bands at 1030, 1020, 1010, 970, 945, 925, 910, 875, 855, 790, 760, 740, 735, 685, and 650 cm^{-1}; nmr was identical with the published spectrum of perfluoropropyl homolog.[10]

Anal. Calcd for $C_{11}H_{10}F_9I$: C, 30.02; H, 2.29; I, 28.84. Found: C, 30.2; H, 2.10; I, 28.2.

Reaction of 5 and 9 to Give 5-Perfluorobutyl-*exo*- and -*endo*-7-iodonortricyclene ($11_{a,b}$).—**5** (6.93 g, 0.0200 mol), **9** (0.921 g, 0.0100 mol), ABN (0.0328 g, 0.200 mmol), and 2-butanone (10 ml) were treated as above. After 16 hr at 70° the reaction mixture was analyzed by glpc (6-ft Apiezon N column, temperature-programmed 7°/min from 110° to 180°); adducts were found at 5.75 (3.19%), 9.5 (3.26%), and $11_{a,b}$ at 10.2 and 11.2 min (48.5 and 45.0% relative areas). The small amount of the first set of peaks precluded isolation. Distillation afforded $11_{a,b}$: bp 75–78° (1.5 mm), 3.56 g (81.3%); ir (KBr plates) ν_{CH} 3040, 3020, 3000, 2980, 2955; no bands at 1600–1900; δ_{CH} 1475, 1355, 1320, 1300; ν_{CF} 1250–1150; and bands at 1050, 1035, 1025, 980, 950, 910, 900, 880, 870, 820, 740, 730, 720, 700, and 650 cm^{-1}; nmr δ 1.0–2.68 (6 protons, m, ring protons), 3.2, (1 proton, t, J_{HF} = 17 Hz, CF_2CH–; δ 3.82 (0.9 proton, s, CHI), 4.25 (0.06 proton, s, CHI). That the perfluorobutyl group was exo was indicated by the absence of coupling of proton on C-5 to adjacent protons at a 90° dihedral angle.

Anal. Calcd for $C_{11}H_8F_9I$: C, 30.16; H, 1.84; F, 39.03; I, 28.97. Found: C, 30.4; H, 1.8; I, 27.7.

Competitive Addition of 5 to 6 and 3.—A 50 ml, three-necked, pear-shaped flask fitted with a nitrogen inlet, a Dry Ice filled condenser, and a liquid sampling tube extending to the bottom of the flask, was charged with materials as listed in Table X. The flask was partly immersed in an oil bath kept at 70° and at intervals indicated in Table X, a sample (approximately 0.010 g) was removed by suction through the sample tube. The liquid in the sample tube below the "Teflon-Varibor" valve was flushed back into the reaction by external nitrogen. Samples thus obtained from three different experiments were kept in a refrigerator and analyzed by glpc as described below.

A mixture of reaction products was weighed and weight/area factors were determined from replicate analysis as indicated in Table XI.[2] Results from these experiments were mainly used as guidance for more quantitative work, as given in Table VII.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—**1**, 591-93-5; **18**, 40735-20-4; **19**, 40735-21-5; **2**, 592-42-7; A (n = 2), 40735-22-6; B (n = 2), 40735-23-7; **3**, 3070-53-9; **20**, 40735-24-8; **21**, 40735-25-9; **22a** (cis), 40735-26-0; **22b** (trans), 40735-27-1; **4**, 3710-30-3; A (n = 4), 13105-45-8; B (n = 4), 40735-29-3; **5**, 423-39-2; **6**, 592-41-6; **7**, 592-76-7; **8**, 498-66-8; **9**, 121-46-0; **11a**, 40735-30-6; **11b**, 40735-31-7; **15**, 40735-32-8; **16**, 40735-33-9; **17**, 40735-34-0.

Supplementary Material Available.—Tables IV, V, VI, IX, X and XI and Figures 3 and 4 will appear immediately following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-73-3167.

Reactions of Alkyl Phenyl Selenide with Benzoyl Peroxide

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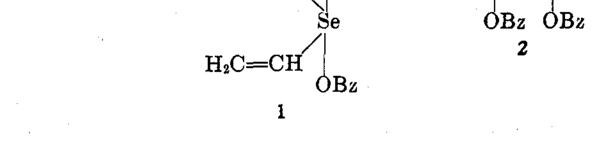
Benzoyl peroxide readily reacts with alkyl phenyl selenides in CCl_4 solution at room temperature to yield stable tetravalent selenium coordination compounds: alkylphenyldibenzoyloxyselenuranes (**4**). When refluxed in CCl_4, **4** decomposed into α-benzoyloxyalkyl phenyl selenides (**5**) and benzoic acid. Benzoyl peroxide further reacts with **5** to form stable selenium(IV) compounds: α-benzoyloxyalkylphenyldibenzoyloxyselenuranes (**9**). Upon heating, they decomposed into additional α-benzoyloxylation products (**10**). It is suggested that the reaction involves the initial decomposition of **4** into ion pairs and attack of the benzoate ion on the α hydrogen, producing a selenium-stabilized carbonium ion. Subsequently, the benzoyloxy moiety on the selenium rearranges the α position of the alkyl group and yields the benzoyloxylation product (**5a**).

Recently, we found that free-radical initiators such as benzoyl peroxide did not initiate the polymerization of phenylvinyl selenide. This failure was attributed to the addition of benzoyl peroxide on the selenium atom to give a tetravalent selenium(IV) compound (**1**).[1] Similar tetravalent selenium compounds have been known in the literature for some time.[2] Foster isolated diphenylselenium diacetate from the reaction of diphenylselenium oxide with acetic anhydride.[3] Stable cyclic tetravalent selenium compounds were also prepared by the intramolecular reactions between selenium oxide and carboxylic acid.[4–6] More recently Reich



PhSeCH=CH₂ + (BzO)₂ ⟶ 1 ⟶ 2 (1)

1

2

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(1) Y. Okamoto, R. Homsany, and T. Yano, *Tetrahedron Lett.*, 2531 (1972).

(2) For a discussion of bonding in high-valenced selenium compounds, see (a) J. I. Musher, *Ann. N. Y. Acad. Sci.*, 19252 (1972); (b) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969).

(3) D. G. Foster, *Recl. Trav. Chim. Pays-Bas*, **54**, 447 (1935).

(4) L. B. Agenas and B. Lindgren, *Acta Chem. Scand.*, **24**, 3301 (1970).

(5) R. Lesser and R. Weiss, *Ber.*, **47**, 2510 (1914).

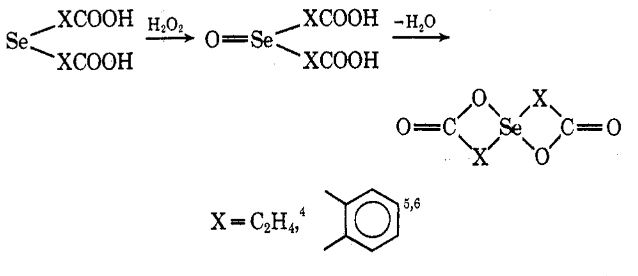
(6) B. Lindgren, *Acta Chem. Scand.*, **26**, 2560 (1972).

TABLE I

REACTION PRODUCTS OF ALKYL PHENYL SELENIDE WITH BENZOYL PEROXIDE

Compd	Chemical shift, τ (CCl_4) Alkyl protons	 Aryl protons	$n^{22}D$	Bp, °C (mm)	Yield, %
CH_3SePh, **3a**	7.80 (s, 3 H)	2.50–3.00 (m, 5 H)	1.5895	70–72 (7)	
4a	7.15 (s, 3 H)	1.95–2.90 (m, 15 H)		Mp 116	92
5a	4.20 (s, 2 H)	2.10–3.05 (m, 10 H)	1.6130	120 (0.7)	60
C_2H_5SePh, **3b**	7.35 (q, 2 H) $J = 7.5$ Hz 8.35 (t, 3 H) $J = 7.5$ Hz	2.33–2.92 (m, 5 H)	1.5745	63 (3)	
4b	6.05 (q, 2 H) $J = 7.5$ Hz 8.22 (t, 3 H) $J = 7.5$ Hz	1.80–3.05 (m, 15 H)		Mp 95–99	87
5b	3.45 (q, 1 H) $J = 7.0$ Hz 8.30 (d, 2 H) $J = 7.0$ Hz	1.85–3.05 (m, 10 H)	1.5970	122 (0.3)	60
C_4H_9SePh, **3c**	7.18 (t, 2 H) $J = 7.5$ Hz 8.10–8.90 (m, 4 H) 9.05 (t, 3 H) $J = 6.5$ Hz	2.47–2.98 (m, 5 H)	1.5605	85 (3)	
4c	6.92 (t, 2 H) $J = 7.5$ Hz 8.10–8.90 (m, 4 H) 9.05 (t, 3 H) $J = 6.5$ Hz	1.80–2.98 (m, 15 H)		Mp 75–80	82
5c	3.60 (t, 1 H) $J = 6.5$ Hz 8.00–8.90 (m, 4 H) 9.05 (t, 3 H) $J = 6.5$ Hz	1.95–3.05 (m, 10 H)	1.5855	140 (0.3)	49

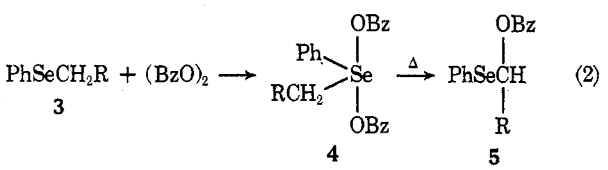
synthesized several cyclic chiral dialkoxydiaryl selenuranes.[7]



In this paper, we report the direct synthesis of the tetravalent selenium dicarboxylate by the reaction of alkyl phenyl selenides with benzoyl peroxide and the thermal decomposition products of the compounds.

Results and Discussion

In a typical reaction, a CCl_4 solution of methyl phenyl selenide (**3a**) was added dropwise to a CCl_4 solution of benzoyl peroxide. The solution was cooled using water. A slight exothermic reaction followed and a white solid precipitate was obtained. The solid was methylphenyldibenzoyloxyselenurane (yield 92%) (**4a**). **4a** was refluxed in CCl_4 for 2 hr. Upon cooling, the solution remained clear. It was washed with aqueous $NaHCO_3$, the CCl_4 solution was dried, and the solvent was evaporated. α-Benzoyloxymethyl phenyl selenide (**5a**) (60% yield) was obtained. From the $NaHCO_3$ extract, benzoic acid and a trace amount of phenylselenic acid were isolated. These results are summarized in Table I.

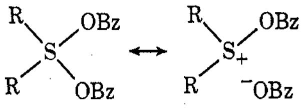


$$PhSeCH_2R + (BzO)_2 \longrightarrow Ph(RCH_2)Se(OBz)_2 \xrightarrow{\Delta} PhSeCH(OBz)R \quad (2)$$

3 **4** **5**

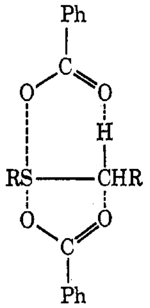
a, R = H
b, R = CH_3
c, R = C_3H_7

The thermal decomposition of benzoyl peroxide in the presence of alkyl ether[8,9] or sulfide[10] has been reported to yield the corresponding α-benzoyloxylation products. The reaction mechanisms were accounted for by the chain-reaction sequence. Recently, however, Pryor and Bickley reported that benzoyl peroxide decomposes at an accelerated rate in the presence of alkyl sulfide.[11] They showed that the sulfide makes a nucleophilic attack on the O–O bond of benzoyl peroxide to form an unstable intermediate which subsequently decomposes into α-benzoyloxy sulfide and benzoic acid. The intermediate was not isolated. The structure could be postulated to have a resonance hybrid of ionic (**6**) and covalent (**7**) characters.



6 **7**

Horner suggested that the possible mechanism for the formation of the α-benzoyloxylation product involves the cyclic structure **8**.[12] This structure is similar to one



8

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[7] H. J. Reich, *J. Amer. Chem. Soc.*, **95**, 964 (1973). The name "selenurane" for tetrasubstituted selenium(IV) compounds was used in analogy with sulfurane.

[8] W. E. Cass, *J. Amer. Chem. Soc.*, **69**, 500 (1947).

[9] P. D. Bartlett and K. Nozaki, *J. Amer. Chem. Soc.*, **69**, 2299 (1947).

[10] H. B. Henbest, J. A. W. Reid, and C. J. M. Stirling, *J. Chem. Soc.*, 1217 (1964).

[11] S. A. Pryor and H. T. Bickley, *J. Org. Chem.*, **37**, 2855 (1972).

[12] L. Horner and E. Jurgens, *Justus Liebigs Ann. Chem.*, **602**, 135 (1957).

TABLE II

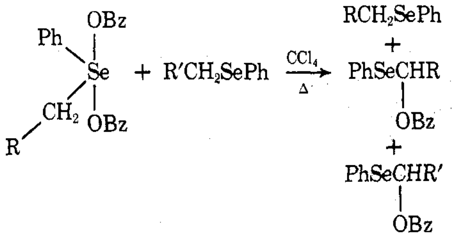
REACTION PRODUCTS OF α-BENZOYLOXYALKYL PHENYL SELENIDES WITH BENZOYL PEROXIDE

Compd	Chemical shift, τ (CCl_4) Alkyl protons	 Aryl protons	Mp, °C	Yield, %
9a	3.38 (s, 2 H)	1.50–3.05 (m, 20 H)	102	85
10a	0.20 (s, 1 H)	1.80–2.70 (m, 15 H)	121–122	54
9b	8.30 (d, 3 H) $J = 5.5$ Hz[a]	1.20–3.00 (m, 20 H)	55	77
10b	8.25 (s, 3 H)[a]	1.70–2.60 (m, 15 H)	70–74	48

[a] The proton spectra for CH were overlapped with those of aromatic protons.

proposed by Oae and Kise to rationalize an ^{18}O exchange between a sulfoxide and acetic anhydride.[13] They suggested that the exchange involves an equilibrium between a cyclic structure similar to **8** and one like **6** ⇄ **7**. Johnson and Phillips have, however, investigated the Pummerer rearrangement of sulfonium salts.[14] Their results indicate that the initial formation of an ylide is the rate-determining step; the ylide then leads to product *via* a sulfur-stabilized carbonium ion. This mechanism is supported by Pryor and Bickley.[11]

When alkylphenyldibenzoyloxyselenuranes were decomposed in the presence of different alkyl-substituted selenides, crossover products were obtained. However, methyl phenyl selenide was found to preferentially form the α-benzoyloxylation products over ethyl and n-butyl phenyl selenides.

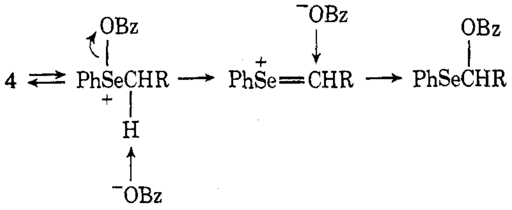


R = H, C_3H_7
R′ = H, CH_3

These results suggest that benzoate ion escapes to solution in the α-rearrangement reaction and the reaction has an intermolecular nature.

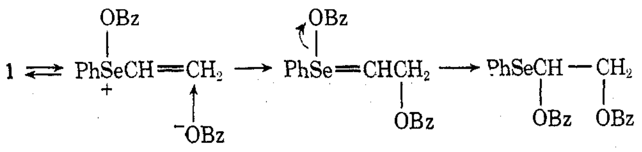
Therefore, it is likely that the reaction shown in eq 2 involves the initial formation of an ion pair and then leads to product *via* a selenium-stabilized carbonium ion as shown in Scheme I.

SCHEME I

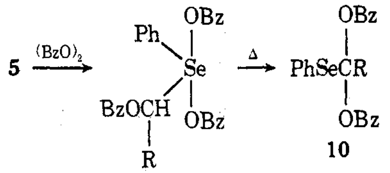


Similarly, the reaction mechanism of eq 1 can be described as shown in Scheme II.

SCHEME II



Benzoyl peroxide further reacts with **5a** and **5b** at room temperature to form corresponding stable selenium(IV) compounds: α-benzoyloxyalkylphenyldibenzoyloxyselenurane (**9**). After **9** was refluxed in CCl_4 and the reaction products were treated by a procedure similar to that described above, the additional α-benzoyloxylation products (**10**) were obtained. However, the compounds tend to hydrolyze during the treatment with the aqueous $NaHCO_3$ to form diphenyl diselenide and alkyl dibenzoates.[15] The typical results of these reactions are summarized in Table II.



9 **10**

a, R = H
b, R = CH_3

Experimental Section

All boiling points and melting points reported are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60 spectrometer with tetramethylsilane as an internal reference. Infrared spectra were recorded with a Perkin Elmer Infracord. Mass spectra were obtained on a Hitachi Perkin-Elmer Model RMU-60. Benzoyl peroxide was purchased from Matheson Coleman and Bell and was recrystallized from CCl_4–methyl alcohol. Elemental analyses and molecular weight determination were made by Schwartzkopf Laboratories, New York, N. Y.

Alkyl Phenyl Selenide.—Ethyl and n-butyl seneides were prepared by the method of Okamoto and Yano.[17] Methyl phenyl selenide was synthesized by the method previously reported in 72% yield, bp 70–72° (7 mm) [lit.[18] bp 200–201° (760 mm)].

Reactions between Alkyl Selenides (3) and Benzoyl Peroxide.—Methyl phenyl selenide (7.0 g, 0.04 mol) in 30 ml of CCl_4 was added dropwise over 20 min to a solution of benzoyl peroxide (9.5 g, 0.04 mol) in 40 ml of CCl_4. The solution was cooled using water. A slight exothermic reaction was followed by the precipitation of a white solid. The solid was identified as methylphenyldibenzoyloxyselenurane (**4a**): yield 92%; mp 116°; mol wt (benzene) 402 (calcd for $C_{21}H_{18}O_4Se$, 413); ir (CCl_4) 1680 and 1725 cm^{-1} with no absorption bands which can be attributed to benzoyl peroxide; mass spectrum m/e 171, 122, 105, and 77. The CCl_4 solution of **4a** was refluxed for 2 hr and washed with aqueous $NaHCO_3$. After the CCl_4 solution was dried and the

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[13] S. Oae and M. Kise, *Tetrahedron Lett.*, 2261 (1968).

[14] C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 682 (1969).

[15] The mechanisms of the decomposition have not been investigated. However, it may be speculated that the dibenzoates react with water to form diphenyl diselenide and alkyl dibenzoates.

$$PhSeCH(OBz)_2 + H_2O \rightarrow PhSeOH + CH_2(OBz)_2$$

$$2PhSeOH \rightarrow PhSeOOH + PhSeH^{16}$$

$$PhSeH + PhSeOH \rightarrow Ph_2Se_2 + H_2O$$

[16] K. W. Bagnall, "The Chemistry of Selenium, Tellurium and Polonium," Elsevier, Amsterdam, 1966, p 164.

[17] Y. Okamoto and T. Yano, *J. Organometal. Chem.*, **29**, 99 (1971).

[18] W. J. Pope and A. Neville, *J. Chem. Soc.*, **81**, 1553 (1902).

solvent was evaporated, benzoyloxymethyl phenyl selenide (**5a**) (7 g, yield 60%) was obtained: bp 120° (0.7 mm); $n^{20}\mathrm{D}$ 1.6130. *Anal.* Calcd for $C_{14}H_{12}O_2Se$: C, 57.70; H, 4.10; Se, 27.14. Found: C, 57.38; H, 4.10; Se, 27.15. Ir had 1720, 2982, 3022 cm^{-1}; mass spectrum *m/e* 291, 261, 122, 105, and 77. From the $NaHCO_3$ extract, benzoic acid (5.0 g) and phenylselenic acid (0.5 g) were isolated and identified. Under similar conditions, ethyl and *n*-butyl phenyl selenides were treated with benzoyl peroxide. α-Benzoyloxyethyl and butyl phenyl selenides were obtained. *Anal.* Calcd for $C_{15}H_{14}O_2Se$ (**5b**): C, 59.01; H, 4.59; Se, 25.90. Found: C, 59.25; H, 4.70; Se, 25.40. Calcd for $C_{17}H_{18}O_2Se$ (**5c**): C, 61.26; H, 5.41; Se, 23.72. Found: 61.54; H, 5.59; Se, 23.35.

Decomposition of Alkylphenyldibenzoyloxyselenuranes in the Presence of Other Alkyl Phenyl Selenides.—Alkylphenyldibenzoyloxyselenurane was prepared by the reaction of alkyl phenyl selenide with benzoyl peroxide in CCl_4. To the solution was added a different alkyl-substituted phenyl selenide. The CCl_4 solution was gradually refluxed for 2 hr. After the CCl_4 was washed with aqueous $NaHCO_3$ and then water, the CCl_4 solution was dried and the solvent was evaporated. The products were determined by nmr measurements without isolation. The results are shown in Table III.

Table III

Decomposition of Alkylphenyldibenzoyloxyselenuranes in the Presence of Other Alkyl Phenyl Selenides

Reaction system		α-Benzoyloxylation product, %	
$PhSe(OBz)_2CH_2R$ +	$PhSeCH_2R'$	$\mathrm{PhSe\underset{\underset{OBz}{\vert}}{C}HR}$	$\mathrm{PhSe\underset{\underset{OBz}{\vert}}{C}HR'}$
R	R′		
H	CH_3	92	8
C_3H_7	H	5	95
C_3H_7	CH_3	40	60

Reactions between α-Benzoyloxyalkyl Phenyl Selenides (5) and Benzoyl Peroxide.—The reactions were carried out by a procedure similar to those described in the reactions between alkyl phenyl selenides and benzoyl peroxide. Benzoyloxymethyl phenyl selenide (5.8 g, 0.020 mol) was dissolved in 60 ml of CCl_4 solution of benzoyl peroxide (5.2 g, 0.022 mol). The white solid **9a** obtained was filtered and washed with CCl_4, 9.0 g (85% yield), mp 100–102°. **9a** (8.0 g, 0.015 mol) was heated in CCl_4 for 2 hr and the solution was treated with aqueous $NaHCO_3$. After CCl_4 solutions were dried and the solvent was evaporated, dibenzoyloxymethyl phenyl selenide (**10a**) was obtained, 3.3 g (0.008 mol), yield 54%, mp 121–122°. *Anal.* Calcd for $C_{21}H_{16}O_4Se$: C, 61.16; H, 3.88; Se, 19.17. Found: C, 61.59; H, 4.10; Se, 18.80. α,α′-Dibenzoyloxyethyl phenyl selenide (**10b**) was obtained (yield 48%), mp 70–74°. *Anal.* Calcd for $C_{22}H_{18}O_4Se$: C, 62.11; H, 4.23; Se, 18.60. Found: C, 62.49; H, 4.60; Se, 18.15.

Decomposition Products of α,α′-Dibenzoyloxyalkyl Phenyl Selenide (10).—After recrystallization of **10a** from $CHCl_3$, the solvent was evaporated and the residue was treated with petroleum ether (bp 30–60°). From the petroleum ether solution, diphenyl diselenide was isolated (0.41 g), mp 57°. Its spectrum was superimposed on that of the pure compound. The petroleum ether insoluble solid was recrystallized from benzene and methylene dibenzoate was obtained (0.52 g), mp 96°, (lit.[19] mp 99°). *Anal.* Calcd for $C_{15}H_{12}O_4$: C, 70.30; H, 4.68; mol wt, 256. Found: C, 69.87; H, 4.48; mol wt, 281 (benzene). Ethylidene dibenzoate was isolated from the reaction of **9b** → **10b**, 0.45 g, mp 69° (lit.[19] mp 70°). *Anal.* Calcd for $C_{16}H_{14}O_4$: C, 71.10; H, 5.02; mol wt, 270. Found: C, 71.80; H, 5.22; mol wt, 292 (benzene).

Acknowledgment.—The authors are grateful to the Selenium-Tellurium Development Association, Inc., for the generous support of part of this work.

Registry No.—**3a**, 4346-64-9; **3b**, 17774-38-8; **3c**, 28622-61-9; **4a**, 38104-61-9; **4b**, 40902-60-1; **4c**, 40872-41-1; **5a**, 40872-42-2; **5b**, 40872-43-3; **5c**, 40872-44-4; **9a**, 40872-45-5; **9b**, 40872-46-6; **10a**, 40872-47-7; **10b**, 40872-48-8; benzoyl peroxide, 94-36-0; diphenyl diselenide, 1666-13-3; methylene dibenzoate, 5342-31-4; ethylidene dibenzoate, 4991-30-4.

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[19] R. J. P. Allen, E. Jones, and P. D. Ritchie, *J. Chem. Soc.*, 524 (1957).

The Reaction of Peroxides with Phosphines in the Presence of Water

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The reaction of alkyl- or arylphosphines with dialkyl peroxides or polyperoxides in solvent systems containing water leads to the formation of alcohols or glycols from the peroxides. The quantitative formation of phosphine oxides in this reaction provides a useful analytical tool and glc analytical methods are described. The model systems investigated are (1) the reaction of styrene and 1,3-octadiene polyperoxides with triphenylphosphine and (2) the reaction of di-*n*-hexyl peroxide, 1,2-dioxane, ascaridole, and di-*tert*-butyl peroxide with tri-*n*-butylphosphine. The latter two compounds do not give quantitative amounts of phosphine oxide.

The reaction of phosphines with peroxygen compounds to give phosphine oxides was first reported in 1927[1] when the reaction of benzoyl peroxide and triphenylphosphine was described. Horner and Jurgeleit,[2] however, were the first workers to report results of a comprehensive study of the reaction of phosphines with a variety of peroxides. They reported that dialkyl peroxides react very sluggishly with triphenyl- or triethylphosphine in hydrocarbon solvent to give the corresponding dialkyl ethers and phosphine oxides. Some of their data for tertiary peroxides was subsequently shown to be in error.[3] More recently, Denney, *et al.*,[4] reported the formation of ethanol, ethylene, ethyl ether, and tributylphosphine oxide from the reaction of diethyl peroxide and tri-*n*-butylphosphine in the absence of solvent.

The ready reduction of hydroperoxides to alcohols by phosphines has been used in oxidation chemistry as a tool in determining the structure of hydroperoxides. Quantitative measurements of the resultant alcohols and phosphine oxides can be used as analytical methods.[5]

We were interested in the analysis of various olefin autoxidation product mixtures which were expected to contain both peroxide and hydroperoxide groups.

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[1] F. Challenger and V. K. Wilson, *J. Chem. Soc.*, 209 (1927).

[2] L. Horner and W. Jurgeleit, *Justus Liebigs Ann. Chem.*, **591**, 138 (1955).

[3] R. Hiatt in "Organic Peroxides," Vol. 3, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1972, p 24.

[4] D. B. Denney, H. M. Relles, and A. K. Tsolis, *J. Amer. Chem. Soc.*, **86**, 4487 (1964).

[5] R. Hiatt in "Organic Peroxides," Vol. 3, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1972, p 71.