solvent was evaporated, benzoyloxymethyl phenyl selenide (**5a**) (7 g, yield 60%) was obtained: bp 120° (0.7 mm); n^{20}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, %	
$PhSe(OBz)_2CH_2R$ + $PhSeCH_2R'$		$PhSeCHR$	$PhSeCHR'$
		OBz	OBz
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).

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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.

(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.

(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.

Iodometric analysis of such materials in the presence of olefin and other functional groups is very unreliable owing to various interfering reactions. It was, therefore, of interest to establish the reactivity and reaction products of a number of model peroxide systems. This paper deals with the reaction of several polyperoxides and dialkyl peroxides with tri-*n*-butyl- and triphenylphosphine. We have demonstrated that this reduction in the presence of solvent systems containing water leads to the nearly exclusive formation of alcohols and phosphine oxides as products. Glc methods for the determination of the major reaction products have been developed.

Results and Discussion

Polyperoxides.—Styrene and 1,3-octadiene polyperoxides were chosen as model systems because they are representative of olefin polyperoxides in general and because they were readily available without major by-products from the oxidation of the respective olefins.

Styrene polyperoxide in styrene was prepared by the reaction of styrene with oxygen (70 psig) in the presence of AIBN at 50° as described by Miller and Mayo.[6] They have shown that these conditions lead to styrene polyperoxide containing sytrene and oxygen in nearly 1:1 ratio with only small amounts of monomeric oxidation products. Table I shows results of the analysis of styrene polyperoxide with triphenylphosphine.

TABLE I

STYRENE POLYPEROXIDE DETERMINATIONS[a]

Run no.	Styrene convn,[b] %	O_2 uptake,[c] mol × 10^2	Ph_3PO,[d] mol × 10^2	Solvent
1	8.3	3.20	3.10	Acetone
2	10.8	4.34	4.17	Acetone
3	10.8	4.34	4.34	Benzene
4	10.8	4.34	4.13	Aqueous acetone[e]
5	13.9	5.27	5.26	Acetone

[a] A 2–3-g portion of polyperoxide solution with twice the stoichiometric amount of Ph_3P (calculated from O_2 absorption) in 4 ml of solvent in a sealed Diels–Alder tube under N_2 for 12–24 hr at ambient temperature. [b] Based on 1 mol of styrene converted per mol of O_2 absorbed. [c] By weight gain. [d] Determined by glc using internal standard. [e] A 0.25-ml portion of H_2O, 4 ml of acetone.

The utility of this method for the analysis of styrene polyperoxide is apparent. The products from the polyperoxide reaction are 1-phenylethane-1,2-diol and styrene oxide, depending on conditions (Table II).

TABLE II

PRODUCTS FROM THE REACTION OF STYRENE POLYPEROXIDE WITH TRIPHENYLPHOSPHINE

		Products[a]	
Run no.	Solvent	Glycol, mol %	Epoxide, mol %
1[b]	Benzene[c]	None	58
2	Acetone (4 ml)–H_2O (0.25 ml)	88	None
3	Acetone[c]	28	55

[a] Products by glc using internal standard based on moles of styrene polyperoxide as computed from O_2 absorption; small amounts of benzaldehyde were also observed. [b] A small amount of 1-phenylethane-1,2-diol was observed early in the reaction; it, however, disappeared ultimately. [c] Reagent grade.

(6) A. A. Miller and F. R. Mayo, *J. Amer. Chem. Soc.*, **78**, 1017 (1956).

The presence or absence of water during the reduction has a major influence on product formation. It was shown that the epoxide, once formed, is not converted to glycol under the reaction conditions. The glycol and epoxide were isolated from the reaction mixtures by silica gel chromatography or distillation for comparison with authentic samples. The rate of reaction can be qualitatively followed by glc by monitoring the disappearance of the benzaldehyde peak from the thermolysis of unreacted polyperoxide in the glc injection port.

Conjugated dienes are known to react with oxygen by both 1,2 and 1,4 addition to give polyperoxides.[7] Although the polyperoxide from 1,3-octadiene has not been reported in the literature, we experienced no difficulty in its synthesis by the method used with styrene at 50°. An ir spectrum of the polyperoxide isolated by evaporation of unreacted octadiene in a stream of nitrogen showed no significant carbonyl absorption, an indication that little polyperoxide had decomposed during the synthesis. Table III shows some representative analytical data.

TABLE III

1,3-OCTADIENE POLYPEROXIDE DETERMINATIONS[a]

Run no.	1,3-Octadiene conversion, %	O_2 uptake,[b] mol × 10^2	Ph_3PO,[c] mol × 10^2	Solvent	Time, hr
1	6.3	2.04	1.46	Acetone–H_2O	20
1a	6.3	2.04	1.97	Acetone–H_2O	72
2	9.5	3.20	3.05	Acetone–H_2O	72

[a] A 2–3-g portion of polyperoxide solution with twice the stoichiometric amount of Ph_3P in 4 ml of acetone, 0.25 ml of H_2O in a sealed Diels–Alder tube under N_2 at ambient temperature. [b] By weight gain. [c] Determined by glc using internal standard.

In one semiquantitative experiment 2.00 g (1.66×10^{-3} mol of active O_2) of oxidate was treated with 3.11×10^{-3} mol of tri-*n*-butylphosphine in 6 ml of acetone and 0.25 ml of water in the presence of benzophenone as internal standard. Successive glc analyses showed that the ratio of phosphine to phosphine oxide remained constant after 12 hr, indicating that the butylphosphine is much more reactive than triphenylphosphine.

The major reduction products in this system were studied in some detail. They were shown to be 2-octene-1,4-diol (**1**), 3-octene-1,2-diol (**2**), and 1-octene-3,4-diol (**3**), by a combination of mass, ir, nmr, and C, H analyses and comparison with the same compounds produced by $NaAlH_2(OCH_2CH_2OCH_3)_2$ reduction of the polyperoxide. In addition, **2** and **3** were synthesized by reaction of 1,3-octadiene with *m*-chloroperbenzoic acid and hydrolysis of the epoxide and glycol ester. A typical product analysis (duplicate runs) is shown in Table IV. In addition to the glc peaks attributed to diols, some smaller and lower eluting peaks were also observed and are probably due to small amounts of monools present. As_2O_3 titration of a sample containing 2.04×10^{-2} mol total O_2 by weight gain gave 0.95×10^{-3} mol of active oxygen as hydroperoxide (4.6% of the total).

Dialkyl Peroxides.—Di-*n*-hexyl peroxide was pre-

(7) O. L. Magelli and C. S. Sheppard in "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, p 52.

TABLE IV

TRIPHENYLPHOSPHINE REDUCTION OF 1,3-OCTADIENE POLYPEROXIDE[a]

	Sample A	Sample B
Active O_2 in aliquot, mol × 10^3 [b]	1.66	1.66
Ph_3P, mol × 10^3	3.83	3.82
Products by glc, mol × 10^3		
Ph_3PO	1.61	1.54
Ph_3P + Ph_3PO	3.75	3.71
1,4-diol (1)	0.76	0.76
1,2-diol (2)	0.35	0.33
3,4-diol (3)	0.12	0.10
Total diols	1.23	1.19

[a] A 2-g solution of polyperoxide in 1,3-octadiene, 4 ml of acetone, 0.25 ml of water, 72 hr under nitrogen in a sealed Diels–Alder tube. [b] By weight gain (oxygen uptake).

TABLE V

REDUCTION OF DI-*n*-HEXYL PEROXIDE WITH TRI-*n*-BUTYLPHOSPHINE[a]

Run no.	1	2	3[b]
	Reactants, mol × 10^3		
$(n\text{-}C_6H_{13})_2O_2$	1.03	1.00	1.05
n-Bu_3P	1.90	1.94	1.89
	Solvents, ml		
Acetone	8.0		
Water	0.4		
Benzene		8.0	8.0
	Products, mol × 10^3		
n-Hexyl alcohol	2.00	1.52	0.50
n-Hexyl ether		0.08	0.49
n-Bu_3PO	1.08	1.07	0.96

[a] Reaction carried out at ambient temperature under N_2 for 7 days in a sealed bulb or Diels–Alder tube. [b] Benzene and n-Bu_3P dried over 3A molecular sieve.

pared by the known method.[8] Table V illustrates the results obtained in the reduction of di-n-hexyl peroxide with n-Bu_3P in acetone–water and benzene. We were surprised to find n-hexyl alcohol as the major product in moist benzene (run 2); using benzene and Bu_3P (dried over 3 A molecular sieve) gave the expected ether as the major product (run 3), indicating that traces of moisture can have a significant effect on the relative amounts of ether and alcohol formed even in benzene solvent.

The effect of moisture in these systems is also shown in Table VI, where it is demonstrated that the maximum amount of alcohol is formed very soon with increasing amounts of ether as the reaction progresses and the

TABLE VI

PRODUCTS OF THE REACTION OF TRI-*n*-BUTYLPHOSPHINE WITH DI-*n*-HEXYL PEROXIDE AS A FUNCTION OF TIME[a]

	Time, hr				
	0	0.5	18	91	189	266
	Reactants, mol × 10^3					
n-Hexyl peroxide	1.05					
n-Bu_3P	1.89					
n-Bu_3PO	0.19					
	Products, mol × 10^3					
n-Hexyl alcohol		0.49	0.47	0.58	0.50	0.59
n-Hexyl ether		0.17	0.18	0.39	0.49	0.59
n-Bu_3PO (corrected)		0.50	0.54	0.80	0.95	0.95
n-Bu_3P + n-Bu_3PO		1.98	1.90	2.07	2.00	1.95

[a] Conditions are identical with those of run 3, Table V.

(8) F. Welch, H. R. Williams, and H. S. Mosher, *J. Amer. Chem. Soc.*, **77**, 551 (1955).

water present is used up. Some n-hexyl alcohol is observed as decomposition product when n-hexyl peroxide is injected into the glc instrument under conditions similar to those used in the analysis. Some of the reaction products observed may have been formed in the glc instrument. The proportion of these materials would be a maximum at low reaction times.

1,2-Dioxane was prepared by the method of Criegee and Müller.[9] Reduction of this material with n-Bu_3P in benzene without added water gave about an equal mixture of tetrahydrofuran and 1,4-butanediol in 6 days at room temperature. A similar reduction except in a 95:5 acetone–water mixture for 7 days gave essentially only 1,4-butanediol. Experiments using Ph_3P instead of n-Bu_3P indicated reaction rates ~25 times slower at ambient temperature.

Di-*tert*-butyl peroxide was shown to be virtually unreactive toward n-Bu_3P at 50°. Peroxide (1×10^{-3} mol) and n-Bu_3P (1.97×10^{-3} mol) in acetone (8 ml) and water (0.4 ml) were allowed to react for 10 days at 50° in a sealed Diels–Alder tube under nitrogen. Only 0.14×10^{-3} mol of n-Bu_3PO and no *tert*-butyl alcohol or di-*tert*-butyl ether was observed.

Ascaridole was shown to react sluggishly at 50°. Ascaridole (3.92×10^{-3} mol) and n-Bu_3P (5.31×10^{-3} mol) were allowed to react in acetone (6 ml) and water (0.25 ml) for 160 hr in a sealed bulb under nitrogen at 50°. The yield of n-Bu_3PO was 85% and the yield of p-menthene-1,4-diol was 23% based on ascaridole. The structure of the 1,4-diol was ascertained by comparison with an authentic sample of correct melting point and spectral properties obtained by reduction of ascaridole with $NaAlH_2(OCH_2CH_2OCH_3)_2$ in benzene. The reaction was sluggish at 50°; better results were obtained at 75°. Horner and Jurgeleit[2] have reported the reduction of ascaridole to the corresponding 1,4-endo oxide by Ph_3P at 100°. However, it has been found more recently[10] that 3,4-epoxy-p-menth-1-ene is the product of this reduction under Horner's conditions.

Mechanism.—Careful recent kinetic studies by Hiatt, *et al.*,[11,12] on the reaction of hydroperoxides with phosphines have confirmed earlier suggestions[2] that such peroxide reductions are nucleophilic displacements rather than free-radical reactions. However, reactions of alkoxy and alkylperoxy radicals with trivalent phosphorus compounds are also well known.[13]

Pentavalent phosphorus intermediates are involved in the reactions of trialkylphosphines[4,14] and trialkyl phosphites[15] with dialkyl peroxides.

The results of this work are generally consistent with such a nucleophilic displacement mechanism.

Equation 1 illustrates the formation of the pentavalent phosphorus intermediate (I), which in the pres-

(9) R. Criegee and G. Müller, *Ber.*, **89**, 238 (1956).

(10) A. W. P. Jarvie, C. G. Moore, and D. Skelton, *J. Polym. Sci., Part A-1*, **9**, 3105 (1971).

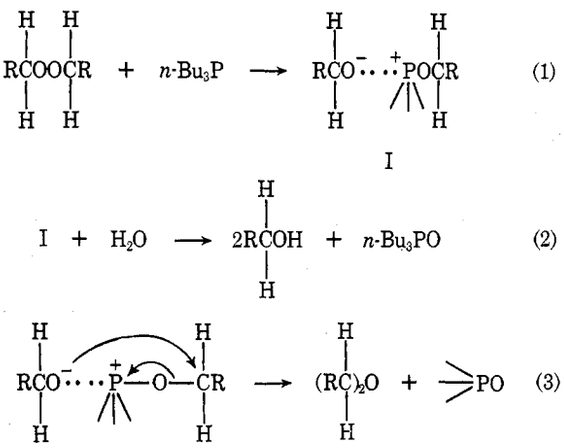
(11) R. Hiatt, R. J. Smythe, and C. McColeman, *Can. J. Chem.*, **49**, 1707 (1971).

(12) R. Hiatt and C. McColeman, *ibid.*, **49**, 1712 (1971).

(13) K. U. Ingold and B. P. Roberts, "Free Radical Substitution Reactions," Wiley-Interscience, New York, N. Y., 1971, p 118.

(14) (a) D. B. Denney and N. Gershman Adin, *Tetrahedron Lett.*, 2569 (1966); (b) D. B. Denney, *et al.*, *J. Amer. Chem. Soc.*, **91**, 5243 (1969); (c) B. C. Chang, *et al.*, *ibid.*, **93**, 4004 (1971); (d) D. B. Denney, *et al.*, *ibid.*, **94**, 245 (1972); (e) C. D. Hall, *et al.*, *ibid.*, **94**, 9264 (1972).

(15) (a) D. B. Denney and H. M. Relles, *ibid.*, **86**, 3897 (1964); (b) D. B. Denney and S. T. D. Gough, *ibid.*, **87**, 138 (1965); (c) D. B. Denney and D. H. Jones, *ibid.*, **91**, 5821 (1969).



ence of water is hydrolyzed (eq 2) to give alcohols or in an anhydrous medium (eq 3) forms ethers. The ether-forming reaction must be largely intramolecular in the case of styrene polyperoxide reacting with Ph_3P because the major product is styrene oxide. (Thermal decomposition of styrene polyperoxide gives almost exclusively benzaldehyde and formaldehyde.[16]) The apparent initial formation of alcohols in the reduction of dialkyl peroxides by tri-*n*-butylphosphine in benzene in the absence of added water could be attributed to the presence of moisture in the solvent or the phosphine, especially in view of runs 2 and 3, Table V; however, determination of the exact amount of alcohol due to the presence of moisture or due to the reaction sequence suggested by Denney, *et al.*,[4] must await further experimental clarification.

Experimental Section

Infrared spectra were obtained on a Perkin-Elmer Model 137 sodium chloride spectrophotometer. Glc determinations were carried out on Perkin-Elmer Model 900 or Varian Aerograph A90P3 instruments. All melting points are corrected.

Polyperoxides.—Both styrene and 1,3-octadiene polyperoxide were prepared in an apparatus consisting of a 60 × 75 mm Pyrex thick wall bulb with a capillary neck attached to an oxygen reservoir and 100-psi test gauge with a 53 × 1/16 in. stainless steel tube *via* a nylon ferrule and Swagelok fitting. The bulb was immersed in an Eberbach constant-temperature shaking bath using a YSI Model 74 Thermistemp temperature controller at 50°. Pressure drops were converted to volume (STP) by a calibration curve making the appropriate temperature correction for fluctuations in the oxygen reservoir temperature.

In a typical oxidation a solution of 0.0921 g of AIBN (Aldrich, twice recrystallized) in 41.7708 g of freshly distilled styrene was placed in the reactor bulb. The system was flushed twice with oxygen and then pressured to 70 psig. A pressure drop from 67.9 to 16.9 psig in 940 min corresponded to a weight gain of 1.3879 g of oxygen. Conversion of styrene was 10.8% assuming 1 mol of oxygen per mol of sytrene. Polyperoxide solutions in monomer were stored in a brown bottle at −10°.

The reduction of styrene polyperoxide by Ph_3P can be qualitatively followed by observing the disappearance of PhCHO (from polyperoxide pyrolysis) and the appearance of Ph_3PO peaks by glc as a function of time. Styrene oxide is quantitatively determined on a 5 ft × 0.25 in. 17% Carbowax 20M on AW Chromosorb P column using methyl caprate as internal standard. Styrene glycol, Ph_3P, and Ph_3PO are determined using a 1 ft × 0.25 in. 10% GE SE-30 silicone rubber on AW Chromosorb P column with benzophenone as internal standard. In analyses for Ph_3PO, the column must be preconditioned by injection of a sample containing Ph_3PO prior to the first quantitative determination. 1-Phenylethane-1,2-diol was trapped from the glc effluent and recrystallized from CCl_4, mp 64° (lit.[17] mp 67–68°), ir identical with that of authentic sample.

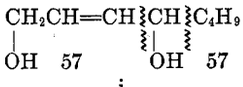
Styrene oxide was prepared from the polyperoxide as follows. Styrene polyperoxide in styrene (30 g, 0.03 mol of peroxide) was treated with Ph_3P (8.7 g, 0.033 mol) under N_2 for 5 hr at room temperature and 2 days in the refrigerator. The product was distilled and a fraction, bp 40–50° (0.5 mm), was collected; this sample was fractionated through a 2-ft microcolumn using 5 g of methyl pentadecanoate as chaser. Styrene oxide [2.1 g, 58% on polyperoxide, bp 42° (2 mm)] was collected. Both glycol and epoxide were also isolated from Ph_3P-reduced samples of polyperoxide by silica chromatography.

1,3-Octadiene polyperoxide was prepared in the apparatus described previously. A cis–trans mixture of 1,3-octadiene (from Chemical Samples Co.) was distilled and a center cut was collected. The distillate was shown to be 95+% trans by nmr and was uniform by capillary glc on a 150 ft × 10 mil squalane column at room temperature.

The reduction of 1,3-octadiene polyperoxide by Ph_3P requires ~72 hr at ambient temperature. Ph_3P and Ph_3PO were determined as before. The glycols were determined on a 5 ft × 0.25-in. Carbowax 20M (5%) on Percopak T column using benzophenone as internal standard. Response factors for the glycols were determined using the individual glycols trapped from the glc effluent.

The reduction of 1,3-octadiene polyperoxide by Ph_3P in aqueous acetone or by $NaAlH_2(OCH_2CH_2OCH_3)_2$ in benzene resulted in the same mixture of major product peaks (glc) identified as glycols. In order of elution, peak 1 was 1-octene-3,4-diol (**3**), and peaks 2 and 3 were 3-octene-1,2-diol (**2**) and 2-octene-1,4-diol (**1**), respectively. Some lower eluting peaks are presumed to be monools but were not specifically identified owing to the small amounts present. For compounds **1**, **2**, and **3** the C, H analyses were low in C owing to the presence of 3–4% water (observed by nmr).

2-Octene-1,4-diol (**1**) had ir 3300, 2900, 1460, 1075, 1010, 975 cm^{-1}; mass spectrum *m/e* 113 $(M - CH_2OH)^+$, 85 $(C_5H_9O)\cdot^+$, 69 $(HOCH{=}CHCH{=}CH)\cdot^+$, 57 (i), 31 $(CH_2OH)\cdot^+$;



i

nmr ($CDCl_3$, T60) δ 0.85 (m, 3 H, methyl), 1.4 (m, 6 H, methylene), 3.5 (s, 2 H, –OH), 4.1 (m, 3 H, methine plus methylene), 5.8 (m, 2 H, nonterminal olefinic).

3-Octene-1,2-diol (**2**) had ir 3300, 2900, 1450, 1065, 1025, 970, 875 cm^{-1}; mass spectrum *m/e* 144 $(M^+, C_8H_{16}O_2)$, 113 $(M - CH_2OH)^+$, 95 (*m/e* 113 − H_2O), 69, 57; nmr ($CDCl_3$) δ 0.9 (m, 3 H, methyl), 1.4 (m, 4 H, methylene), 2.0 (m, 2 H, $CH_2CH{=}CH$), 3.6 (m, 4.1 H, OH, CH_2 next to OH), 4.2 (1 H, methine), 5.6 (m, 1.9 H, nonterminal olefin).

1-Octene-3,4-diol (**3**) had ir 3300, 2900, 1450, 1100, 1030, 990, 920, 830 cm^{-1}; mass spectrum *m/e* 87 $(HOCHC_4H_9)\cdot^+$, 69 (*m/e* 87 − H_2O), 58 (base peak), 57 $(CH_2{=}CHCHOH)\cdot^+$; nmr ($CDCl_3$) δ 0.9 (m, 3 H, methyl), 1.3 (5.9 H, methylene), 2.4 (2 H, –OH), 3.6 (1 H, methine adjacent to OH), 4.0 (1 H, methine), 5–6 (2.8 H, vinyl).

The 1,2 and 3,4 glycols were also synthesized from 1,3-octadiene by oxidation with *m*-chloroperbenzoic acid in $CHCl_3$ followed by hydrolysis of the epoxide and benzoate esters. The products isolated by glc trapping had the same spectral properties as the compounds obtained from the polyperoxide.

Dialkyl Peroxides.—*n*-Hexyl peroxide was prepared from *n*-hexyl methanesulfonate by the method of Mosher, *et al.*,[8] in 17% yield. The peroxide had bp 64° (0.3 mm), $n^{20}D$ 1.4244 (lit.[8] $n^{20}D$ 1.4248). Among the products of the reduction of *n*-hexyl peroxide by *n*-Bu_3P, *n*-hexyl alcohol was identified by trapping from the glc effluent and by silica gel chromatographic separation and spectral comparison with an authentic sample. *n*-Hexyl ether was separated by silica chromatography as a mixture with *n*-Bu_3P. The chromatographic results demonstrate that the products are not formed in the glc instrument. In some reduction runs using Bu_3P in acetone, aldol condensation products of acetone were also observed.

Glc analyses were carried out on a 5 ft × 0.25 in. Carbowax 20M (5%) on Percopak T column with 2-dodecanone or *n*-hexadecane as internal standards. The order of elution with increas-

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(17) R. C. Weast, "Handbook of Chemistry and Physics," 45th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1964, p C-310.

ing temperature is *n*-hexyl alcohol, *n*-hexyl ether, *n*-Bu_3P, internal standard, and *n*-Bu_3PO.

1,2-Dioxane was prepared by the method of Criegee[9] in 18% yield. The product had bp 49° (67 mm) [lit.[9] bp 61–62° (110 mm)]; $n^{20}D$ 1.4261 (lit.[7] $n^{20}D$ 1.4262). Ir, mass, and nmr spectra confirm the structure. 1,4-Butanediol was trapped from the glc effluent of a reduced sample of 1,2-dioxane for comparison with an authentic sample.

The best column for quantitative glc analysis of the components of a reduced sample of 1,2-dioxane was a 10 ft × 0.25 in. Carbowax 20M (16.7%) on AW Chromosorb P (60–80 mesh); 2-dodecanone was used as internal standard.

Di-*tert*-butyl peroxide was obtained from Lucidol and was 99.9% pure by glc.

Ascaridole was obtained from K & K. The reduction product, *p*-menthene-1,4-diol, was prepared by hydride reduction. Ascaridole (1.7 g, 1.01×10^{-2} mol) in 30 ml of benzene was refluxed with $NaAlH_2(OCH_2CH_2OCH_3)_2$ (2.86×10^{-2} mol) for 2 hr. On cooling, 50 ml of water was added, benzene was removed on a Rotavapor, and the aqueous phase was extracted with four 300-ml portions of 1:1 ether–*n*-pentane. Removal of the solvent provided 1.8 g of residue which on two crystallizations from cyclohexane gave 1.6 g of crystals: mp 80–81° (lit.[18] mp 82°); nmr ($CDCl_3$) δ 0.8–1.0 (2 d, 6 H, methyl), 1.25 (s, 3 H, methyl), 1.5–2.0 (m, 5 H, methylene + methine), 2.3 (1 H, OH), 2.7 (1 H, OH), 5.4–5.9 (2 d, 2 H, olefinic); the OH resonance is shifted by addition of D_2O and CF_3CO_2H. The glycol as a mixture with *n*-Bu_3PO was also obtained by chromatograpic separation of a Bu_3P-reduced sample of ascaridole on basic alumina (Alcoa, pH 9).

The product mixture from *n*-Bu_3P reduction was analyzed by glc on a 5 ft × 0.25-in. Carbowax 20M (5%) on Percopak T column using methyl heptanoate as internal standard. The order of elution was internal standard, *n*-Bu_3P, ascaridole decomposition peaks, 1,4-diol, and *n*-Bu_3PO.

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Registry No.—**1**, 40735-15-7; **2**, 40735-16-8; **3**, 40735-17-9; styrene polyperoxide, 27379-77-7; triphenylphosphine, 603-35-0; 1,3-octadiene polyperoxide, 40742-13-0; *n*-hexyl peroxide, 3903-89-7; tributylphosphine, 998-40-3; 1,2-dioxane, 5703-46-8; *tert*-butyl peroxide, 110-05-4; ascaridole, 512-85-6; styrene oxide, 96-09-3; *p*-menthene-1,4-diol, 40735-19-1.

Reactions of 2-Acyloxyisobutyryl Halides with Nucleosides. III.[1] Reactions of Tubercidin and Formycin

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The reaction of tubercidin with 2-acetoxyisobutyryl halides gives exclusively the 2′-*O*-acetyl-3′-halo-3′-deoxy-β-D-xylofuranosyl nucleoside (**3**) substituted at the 5′ position with a trimethyldioxolanone moiety. Treatment of **3** with methanolic ammonia rapidly removed both the acetyl and dioxolanone groups to give crystalline 4-amino-7-(3-deoxy-3-halo-β-D-xylofuranosyl)-pyrrolo[2,3-*d*]pyrimidines (**4**) which could be converted to 2′,3′-anhydrotubercidin with sodium methoxide. Catalytic hydrogenolysis of the 3′-bromo nucleoside (**4b**) gave 3′-deoxytubercidin while similar treatment of the bromo acetate (**3b**) gave both 3′-deoxytubercidin and 2′,3′-dideoxytubercidin. Similar reactions of formycin with 2-acetoxyisobutyryl bromide gave both 2′-*O*-acetyl-3′-bromo-3′-deoxy-β-D-xylofuranosyl and 3′-*O*-acetyl-2′-bromo-2′-deoxy-β-D-arabinofuranosyl nucleosides (**9** and **10**) substituted at the 5′ position as 2-acetoxyisobutyryl esters. The acetyl and acetoxyisobutyryl esters could be sequentially removed by treatment with ammonia and catalytic hydrogenolysis of the appropriate compounds gave 2′-deoxy-, 3′-deoxy-, and 2′,3′-dideoxyformycin. Treatment of **9** and **10** with sodium methoxide gave 2′,3′-anhydroformycin.

Several recent papers from this laboratory have described the reactions of 2-acetoxyisobutyryl halides (**1**) with uridine[4] and adenosine.[1] These studies, based upon earlier work by Mattocks, showed that simple cis vicinal diols react with **1** to form trans halo acetates *via* intermediate acetoxonium ions. In the case of the reaction of **1** with uridine the major products proved to be derivatives of 3′-*O*-acetyl-2′-deoxy-2′-halouridine, the unusual cis configuration of the acetyl and halo functions being explained by interaction of the C_2 carbonyl group of the uracil ring with the intermediate 2′,3′-acetoxonium intermediate.[4] On the other hand, the reaction of adenosine with **1** led predominantly to the formation of 2′-*O*-acetyl-3′-deoxy-3′-halo and 3′-*O*-acetyl-2′-deoxy-2′-halo nucleosides with the D-xylo and D-arabino configurations in a ratio of roughly 10:1.[1] These products were entirely to be expected on the assumption that the intermediate 2′,3′-acetoxonium ion was opened by halide attack without participation of the purine ring. The halo nucleosides obtained from adenosine and **1** were shown to be useful intermediates for the preparation of 3′-deoxy- and 2′,3′-dideoxyadenosine as well as of 2′,3′-anhydroadenosine.

In recent years numerous nucleoside antibiotics have been isolated from nature.[5] Analogs of adenosine have been particularly prevalent in this class and antibiotics such as 4-amino-7-(β-D-ribofuranosyl)pyrrolo-[2,3-*d*]pyrimidine (**2**, tubercidin) and 7-amino-3-(β-D-ribofuranosyl)-pyrazolo[4,3-*d*]pyrimidine (**8**, formycin) have been widely studied.[5,6] The interesting spectrum of biological activities shown by tubercidin and formycin has made the chemical modification of these molecules an attractive exercise and has led to both work on total synthesis[7] and to preparation of a variety of

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