tions 5 (63%) and 4 (60%). Fraction 2 was composed of about 80% of another component. Infrared analysis of all the fractions showed strong bands characteristic of nitro groups (6.15–6.18 and 7.50 μ). That none of the 4–5 components was an olefin or nitrite ester was demonstrated by the fact that the gas chromatogram of fraction 5 was not changed either qualitatively or quantitatively by prolonged (24 hr.) shaking with aqueous potassium permanganate or concentrated sulfuric acid.

Reactions in a Hot Tube.—Passage of excess nitric oxide (2.5 ml./sec.) and 5*H*-octafluoropentanoic acid through a quartz-packed tube (described in ref. 1) at temperatures from 200–390° gave, at lower temperatures, mainly gaseous degradation products boiling below 0°. From 7*H*-dodecafluoroheptanoic acid and excess nitric oxide at 360°, a trace of $H(CF_2)_4CF{=}CF_2$ was isolated.

When 7*H*-dodecafluoroheptanoic acid and a nitric oxide–air mixture[1] were passed through a reaction tube packed with quartz-chips and heated at 350°, there was obtained a 10% yield of 6*H*-1-nitrododecafluorohexane. The infrared absorption spectrum and g.c. retention time of this compound were essentially identical with those observed for the same nitrofluoro alkane obtained by synthesis in an autoclave.

Autoxidation of 2-Alkenyldioxolanes and 2-Alkenyl-1,3-dioxanes

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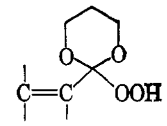
Eleven 2-alkenyldioxolanes and two 2-alkenyl-1,3-dioxanes were autoxidized under different conditions. Terminal products, such as peroxides, hydroperoxides, spirocyclic peroxides, α,β-unsaturated esters, and polymers, were isolated and identified. A mechanism which accounts for these products is presented.[2]

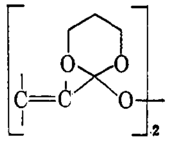
This paper describes the autoxidation of 2-alkenyldioxolanes and 2-alkenyl-1,3-dioxanes. While the literature on the autoxidation of hydrocarbons is voluminous[3-5] little has been reported on the autoxidation of acetals. Criegee[6] and Lederer oxidized 2-methyldioxolane with molecular oxygen and isolated di(2-methyldioxolan-2-yl) peroxide. Rieche, *et al.*,[7] autoxidized 2-phenyldioxolane and obtained 2-hydroperoxy-2-phenyldioxolane. No work on the autoxidation of 2-alkenyl-1,3-cyclic acetals has been reported in the literature.

We wish to report our findings on the autoxidation of a number of 2-alkenyl-1,3-cyclic acetals. The cyclic acetals (Table I) were autoxidized with (1) oxygen alone, (2) oxygen + a trace of Co(II), and (3) oxygen + a trace of *p*-toluenesulfonic acid. Five types of products were isolated and identified (a–e, col. 2).

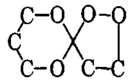
(a) Hydroperoxide



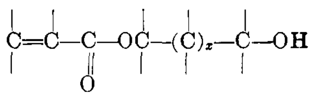
(b) Peroxide



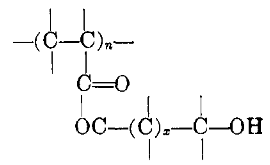
(c) Spirocyclic peroxide



(d) α,β-Unsaturated esters



(e) Complex polymers of α,β-unsaturated esters (where x = 0 or 1)



The principal product or products obtained from autoxidation of the cyclic acetals of Table I are summarized in Table II. Oxidations conducted in the absence of additives gave either hydroperoxides or spirocyclic peroxides. In the presence of Co(II) the products were generally α,β-unsaturated ester and polymer; in a few cases spirocyclic peroxide was the main product. Two oxidations conducted in the presence of *p*-toluenesulfonic acid also gave spirocyclic peroxides.

Thus, oxidation of 2-vinyl-4-methyldioxolane (I) in the absence of additives gave 2-hydroperoxy-2-vinyl-4-methyl dioxolane (XIV) and di(2-vinyl-4-methyldioxolan-2-yl) peroxide (XV). When the oxidation was conducted in the presence of a catalytic amount of cobaltous ion the products were 2-hydroxypropyl acrylate (XXV) and polymer XXVI.[8] Oxidation of I in the presence of toluenesulfonic acid gave the spirocyclic peroxide, 2-methyl-1,4,6,7-tetraoxaspiro-[4.4]nonane (XXXV), as the major product.

The reaction scheme (see eq. 1–5) accounts for the formation of the observed products in the case of 2-vinyl-4-methyldioxolane (I) (p. 287).

Reactions 2, 3, and 4 of this scheme comprise the free-radical sequence accounting for the formation of the hydroperoxide (XIV). Coupling reactions 5 and 6

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[1] To whom any correspondence should be addressed.

[2] E. J. Burrell, Radiation Physics Laboratory, Engineering Department, E. I. du Pont de Nemours and Co., Wilmington, Del., has examined the kinetics and has measured the absolute reaction rate constants for every significant step for the cobalt-catalyzed autoxidation of 2-vinyl-4(4-hydroxybutyl)dioxolane using pulse radiolysis. His work is summarized in another paper which has been submitted to the *Journal of Chemical Physics*.

[3] K. U. Ingold, *Chem. Rev.*, **61**, 563 (1961).

[4] W. A. Waters, *Progr. Org. Chem.*, **5**, 1 (1961).

[5] F. R. Mayo, *Ind. Eng. Chem.*, **52**, 614 (1960).

[6] R. Criegee, "Methoden der Organische Chemie," Vol. III, 4th Ed., Georg Thieme Verlag, Stuttgart, 1952, p. 23.

[7] A. Rieche, E. Schmitz, and E. Beyer, *Ber.*, **91**, 1935 (1958).

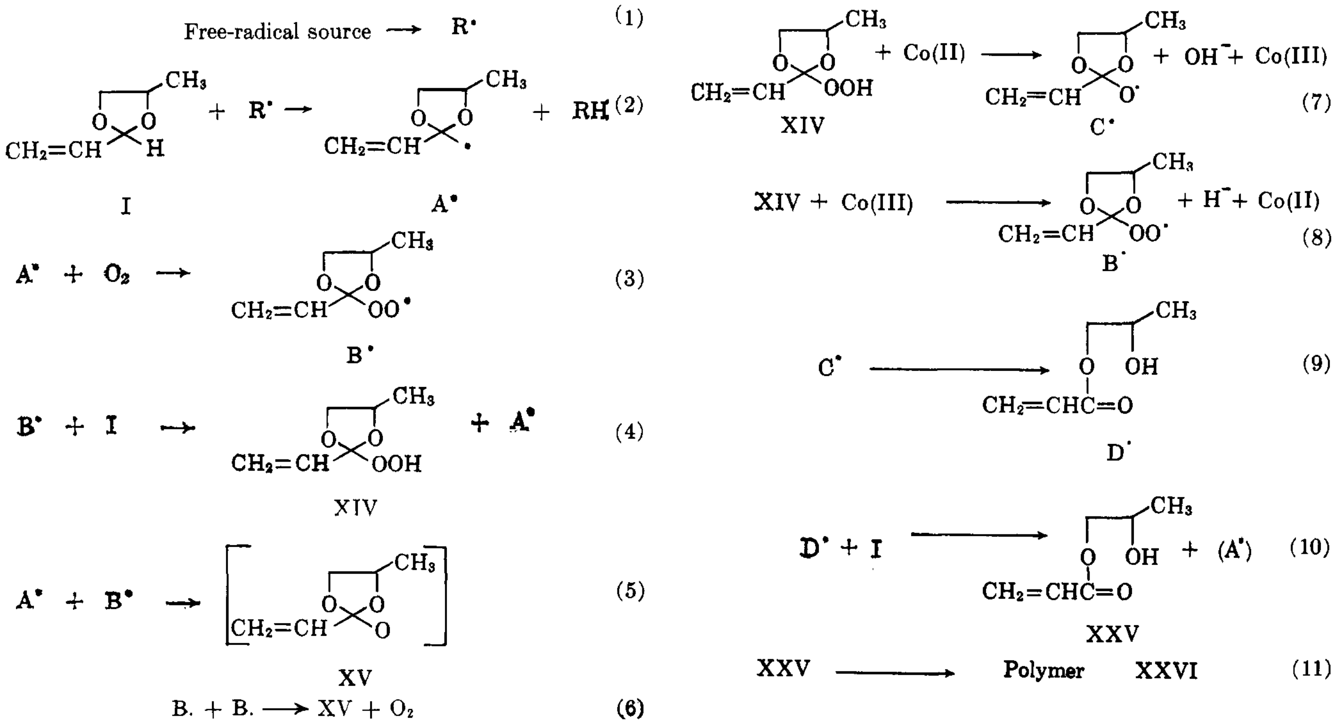
[8] Fractionation of polymer XXVI by gradient elution through acid-washed alumina with benzene, ether, and finally ethanol gave five fractions with molecular weights ranging from 530 to 1050. The structure of the polymer is much more complex than one would suspect from the infrared spectra of the fractions which were all substantially the same as poly(2-hydroxypropyl acrylate). Elemental analyses (C, H, and O) and functional group determinations (OH and ester equivalent), although close, do not correspond to the values for poly(2-hydroxypropyl acrylate). The presence of such groups as hydroperoxy, peroxy, and dioxolanyl in the various fractions were demonstrated by qualitative tests.

TABLE I

2-ALKENYLDIOXOLANES AND -1,3-DIOXANES OXIDIZED

	Dioxolane	Yield,[b] %	B.p.[c] (mm.), °C.	n^{25}_D	Oxidation procedure[a] O_2 only	O_2 + Co(II)	O_2 + acid[d]
I	2-Vinyl-4-methyl	45	122 (760)	1.4211	A	B	A
II	2-Vinyl-4,5-dimethyl	68	94 (180)	1.4238	A	A	
III	2-Vinyl-4,4-dimethyl	42	126 (760)	1.4171	A	A	A
IV	2-Vinyl-4,4,5-trimethyl	70	76 (80)	1.4213	A	A	
V	2-Vinyl-4,4,5,5-tetramethyl	77	89 (80)	1.4289	A	B	
VI	2-Propenyl-4-methyl	47	76 (50)	1.4330	A	B	
VII	2-Propenyl-4,5-dimethyl	80	105 (100)	1.4345	A	A	
VIII	2-Propenyl-4,4,5,5-tetramethyl	91	102 (50)	1.4381	A	A	
IX	2-Isopropenyl-4-methyl	55	78 (90)	1.4279	A	B	
X	2-Isopropenyl-4,5-dimethyl	80	93 (100)	1.4300	A	A	
XI	2-Isopropenyl-4,4,5,5-tetramethyl	90	90 (51)	1.4352	A	A	
	1,3-Dioxane						
XII	2-Vinyl-4,4,6-trimethyl	91	65 (12)	1.4362	A	B	
XIII	2-Vinyl-4,4,6,6-tetramethyl	56	68 (16)	1.4384		A	

[a] See Experimental section. [b] Based on glycol. [c] Uncorrected. [d] p-Toluenesulfonic acid.



terminate the chain sequence and produce the dioxolanyl peroxide (XV).

When Co(II) is present another free-radical chain sequence involving the hydroperoxide (XIV) is possible. Hydroperoxide decomposition by Co(II) and Co(III) (reactions 7 and 8) has been the subject of many investigations.[9,10] These reactions explain the catalytic behavior of Co(II) in the oxidation. The driving force for the isomerization of radical C· to radical D· (eq. 9) is the formation of the conjugated acrylate double bond.

Because the acrylate is easily polymerized by free radicals (reaction 11) most of it was converted to the terminal product, polymer XXVI and gave a low (1:9) ester to polymer product ratio (See Table I). The more highly substituted 2-vinyl-4,5-dimethyldioxolane (II) and 2-vinyl-4,4,5-trimethyldioxolane (IV), which are oxidized to bulkier and, therefore, less reactive acrylates, gave substantially higher ester to polymer ratios, 1:3 and 1:1, respectively. The 2-isopropenyl-1,3-cyclic acetals also gave higher (1:2 or greater) ester to polymer ratios because they oxidize to methacrylates which polymerize less readily than acrylates.[11] Finally, 2-propenyl-4-methyldioxolane (VI) which oxidizes to a crotonate, a monomer class well-known for its sluggishness in addition polymerizations,[12] gave the highest (2:1) ester to polymer ratio.

An exothermic reaction occurred when a trace of Co(II) butyl phthalate was added to a toluene solution fo 2-hydroperoxy-2-vinyl-4-methyldioxolane (XIV). The infrared spectrum of the resultant polymer was substantially identical with polymer XXVI which formed during oxidation of acetal I and with poly(2-hydroxypropyl acrylate) obtained by polymerizing an authentic sample of ester XXV. These results support the reaction sequence 7–11.

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(9) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 103.

(10) A. G. Davies, "Organic Peroxides," Butterworth and Co., London, 1961, p. 177.

(11) G. M. Burnett, "Mechanism of Polymerization Reactions," Interscience Publishers, Inc., New York, N. Y., 1954, p. 232.

(12) T. Alfrey, J. J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 49–52.

TABLE II

SUMMARY OF PRINCIPAL PRODUCTS FROM AUTOXIDATION OF 2-ALKENYLDIOXOLANES AND -1,3-DIOXANES

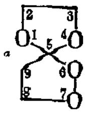
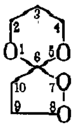
	Dioxolane oxidized	Principal product					
		O_2 only		O_2 + Co(II)[a]		O_2 + acid[b]	
I	2-Vinyl-4-methyl	XIV XV	Hydroperoxide Peroxide	XXV XXVI	Ester Polymer (1:9)	XXXV	Cyclic peroxide
II	2-Vinyl-4,5-dimethyl	XVI	Hydroperoxide	XXVII XXVIII	Ester Polymer (1:3)		
III	2-Vinyl-4,4-dimethyl	XVII	Hydroperoxide			XXXVI	Cyclic peroxide
IV	2-Vinyl-4,4,5-trimethyl	XVIII	Cyclic peroxide	XXIX	Ester (1:1) Polymer		
V	2-Vinyl-4,4,5,5-tetramethyl	XIX	Cyclic peroxide	XIX	Cyclic peroxide		
VI	2-Propenyl-4-methyl	XX	Cyclic peroxide	XXX	Ester (2:1) Polymer		
VII	2-Propenyl-4,5-dimethyl	XXI	Cyclic peroxide		Ester[c]		
VIII	2-Propenyl-4,4,5,5-tetramethyl	XXII	Cyclic peroxide	XXII	Cyclic peroxide		
IX	2-Isopropenyl-4-methyl		Hydroperoxide[c]	XXXI	Ester (1:2) Polymer		
X	2-Isopropenyl-4,5-dimethyl		Hydroperoxide[c]		Ester[c]		
XI	2-Isopropenyl-4,4,5,5-tetramethyl	XXIII	Cyclic peroxide	XXXII	Ester Polymer (1:1)		
XII	2-Vinyl-4,4,6-dimethyl	XXIV	Cyclic peroxide	XXXIII	Ester (1:1) Polymer		
XIII	2-Vinyl-4,4,6,6-tetramethyl			XXXIV	Cyclic peroxide		

[a] Arabic numerals in parentheses indicate weight ratio of monomeric ester to polymer. [b] p-Toluenesulfonic acid. [c] By inference from infrared spectrum.

TABLE III

NEW SPIROCYCLIC PEROXIDES

	1,4,6,7-Tetraoxaspiro-[4.4]nonanes[a]	Yield,[b] %	B.p.[c] (mm.), °C.	$n^{25}D$	Empirical formula	Carbon, %		Hydrogen, %		Mol. wt.		Peroxide[d]	
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
XVIII	2,2,3-Trimethyl-	47	55 (0.5)	1.4412	$C_8H_{14}O_4$							19.5	19.6
XIX	2,2,3,3-Tetra-methyl-	72	58 (0.3)	1.4468	$C_9H_{16}O_4$	57.43	58.20	8.57	8.87	188	179	18.5	17.5
XX	2,8-Dimethyl-	61	51 (0.4)	1.4415	$C_7H_{12}O_4$	52.49	53.66	7.55	8.16	160	161	21.2	17.5
XXI	2,3,8-Trimethyl-	56	60 (1.1)	1.4408	$C_8H_{12}O_4$	55.16	56.78	8.10	8.71	174	171	19.5	16.4
XXII	2,2,3,3,8-Penta-methyl-	78	56 (0.2)	1.4432	$C_{10}H_{18}O_4$	59.39	60.34	8.97	9.20	202	196	16.8	12.5
XXIII	2,2,3,3,9-Penta-methyl-	72	66 (0.3)	1.4486	$C_{10}H_{18}O_4$	59.39	59.55	8.97	9.15	202	198	16.9	15.9
XXXV	2-Methyl-	22	50 (0.7)	1.4425	$C_6H_{10}O_4$	49.31	48.86	6.89	6.78	146	146	23.3	21.3
XXXVI	2,2-Dimethyl-	67	39 (0.4)	1.4365	$C_7H_{12}O_4$	52.49	52.55	7.55	7.38	160	158	21.2	17.5
	1,5,7,8-Tetraoxaspiro-[4.5]decanes[e]												
XXIV	2,2,4-Trimethyl-	37	58 (0.6)[f]		$C_9H_{16}O_4$	57.43	57.90	8.57	8.81			18.1	18.5
XXXIV	2,2,4,4-Tetra-methyl-	70	63 (0.6)	1.4501	$C_{10}H_{18}O_4$	59.39	60.12	8.97	9.21	202	181	16.9	17.0

[a]  [b] Based on O_2 consumed. [c] Uncorrected. [d] As % H_2O_2. [e] . [f] M.p. 34–38°.

Although the spirocyclic peroxides of Table III, may form *via* a free-radical route,[13] an ionic route[14–17] is indicated, because in the oxidation of acetals I and III merely adding a trace of p-toluenesulfonic acid changed the major product from hydroperoxide to spirocyclic peroxide, Table II. Consistent with this observation is the mechanism shown in eq. 12–14, p. 289.

Addition of p-toluenesulfonic acid to crude 2-hydroperoxy-2-vinyl-4,4-dimethyldioxolane (XVII) produced a mild exotherm and a decrease in the 3.0-μ (hydroperoxy OH) band in the infrared. Further, all unoxidized cyclic acetals were neutral to moist pH paper while all oxidized acetals were acid with pH values of 2–4. The acids produced in seven of eleven of the oxidations (conducted in the absence of additives) were sufficient to cyclize the hydroperoxide. Like the acetals I and III, the acetals IX and X could undoubtedly be made to yield spirocyclic peroxides rather than hydroperoxides by acidifying with p-toluenesulfonic acid prior to oxidation.

The data (Table IV) abstracted from Table II makes it apparent that spirocyclic peroxide formation becomes progressively more difficult as the 2-alkenyl substituent is changed from propenyl to vinyl to isopropenyl.

A multiplicity of methyl groups on the ring carbon atoms favors cyclic peroxide formation. Thus, cyclic acetals V, VIII, and XV have four methyl substituents

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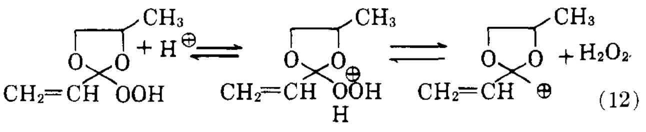
(13) A. V. Tobolsky and R. V. Mesrobian, "Organic Peroxides," Interscience Publishers, Inc., New York, N. Y., 1954, p. 179.

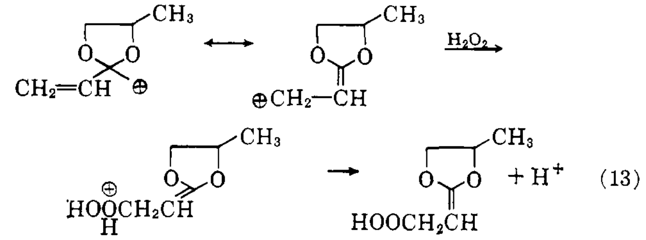
(14) G. B. Payne, *J. Org. Chem.*, **23**, 310 (1958).

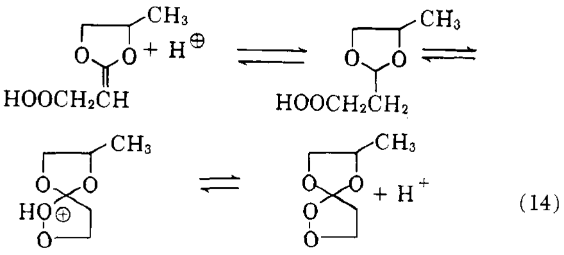
(15) R. Criegee and G. Paulig, *Ber.*, **88**, 712 (1955).

(16) A. Rieche, E. Schmitz, *et al.*, *ibid.*, **93**, 2443 (1960).

(17) A. Rieche, E. Schmitz, *et al.*, *Angew. Chem.*, **72**, 635 (1960).







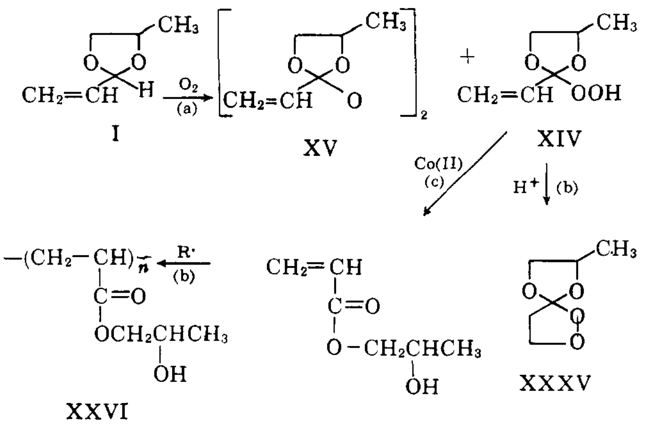
XVIII

TABLE IV

Acetal	2-Alkenyl group	No. of ring methyl substituents	Principal product
VI	Propenyl	1	Cyclic peroxide
VII	Propenyl	2	Cyclic peroxide
VIII	Propenyl	4 (Co^{+2})	Cyclic peroxide
I	Vinyl	1	Hydroperoxide
II	Vinyl	2	Hydroperoxide
IV	Vinyl	4 (Co^{+2})	Cyclic peroxide
IX	Isopropenyl	1	Hydroperoxide
X	Isopropenyl	2	Hydroperoxide
XI	Isopropenyl	4 (Co^{+2})	Ester

and each gave a cyclic peroxide, even when oxidations were conducted in the presence of Co(II). Perhaps the methyl groups shield the hydroperoxy group and make the hydroperoxides less reactive towards Co(II) (reaction 7). The opportunity for hydroperoxide cyclization (reactions 12 and 15) is increased and spirocyclic peroxides, rather than esters or polymers, become the principal product.

The following is a schematic representation of the product interrelationships for oxidation of 2-vinyl-4-methyldioxolane and is believed applicable to the 2-alkenyl-1,3-cyclic acetals generally.



Initial products are peroxide and hydroperoxide. Because the latter product can react further by two alternative reaction paths, one acid- and the other Co(II)-catalyzed, several different terminal products are possible. Spirocyclic peroxide is the principal product when Co(II) is absent and the reaction environment is sufficiently acid. α,β-Unsaturated ester and polymer are generally the terminal products when Co(II) is present. The ratio of ester to polymer obtained depends upon the susceptibility of the ester to addition polymerization.

Experimental

Preparation of 2-Alkenyldioxolanes and -1,3-dioxanes.—The acetals (Table I) used in this study were prepared by refluxing toluene solutions of α,β-unsaturated aldehydes (20 molar % excess) with appropriate diols in the presence of a catalytic amount of acid.[18] Oxalic acid was employed in the preparation of compounds III, VI, and IX; *p*-toluenesulfonic acid was used in the remaining preparations. Water of reaction was distilled azeotropically as formed and collected in a Dean-Stark trap. The reaction mixtures were washed with 5% sodium hydroxide solution, dried over anhydrous magnesium sulfate, and fractionated. The compounds prepared are listed in Table I.

Autoxidation of Cyclic Acetals. Procedure A. 2-Hydroperoxy-2-vinyl-4-methyldioxolane (XIV) and Di(2-vinyl-4-methyldioxolan-2-yl) Peroxide (XV) from I.—To a 500-ml. flask equipped with a stirrer, a thermometer, and a reflux condenser attached to a 1-l. gas buret was charged 2-vinyl-4-methyldioxolane (114 g., 1 mole). The stirrer was started and the apparatus evacuated to 10-mm. pressure and then filled with oxygen (atmospheric pressure). The reaction temperature was raised gradually until an oxygen absorption rate of about 2 l./hr. was achieved at about 85°. This temperature was maintained until 6.3 l. (0.28 mole) of oxygen was absorbed. After cooling, unchanged dioxolane (83.2 g., 0.62 mole) was recovered by distillation at 20° (1 mm.). The residue was fractionated to give 2-hydroperoxy-2-vinyl-4-methyldioxclane (XIV, 18.5 g.); b.p. 64–66° (0.15 mm.); maximum pot temperature, 105°; infrared spectrum, hydroperoxy OH, 3.0, and 2-vinyl-1,3-cyclic acetal bands at 10.2 and 10.6 μ.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.90; O, 43.79; mol. wt., 146. Found: C, 49.27; H, 7.41; O, 43.70; mol. wt., 152.

The colorless liquid residue from the distillation was di-(2-vinyl-4-methyldioxolan-2-yl) peroxide.

Anal. Calcd. for $C_{12}H_{18}O_6$: C, 55.80; H, 7.02; H_2 no. (for 2C=C and —O—O—), 0.0232; peroxide oxygen as % H_2O_2, 13.1. Found: C, 55.89; H, 7.10; H_2 no., 0.0232; peroxide oxygen as % H_2O_2, 12.9.

The hydroperoxide (XIV) reacted exothermically with a trace of Co(II) butyl phthalate to give a polymer whose infrared spectrum was substantially identical with that of poly(2-hydroxypropyl acrylate). Upon treatment with water, the hydroperoxide gave hydrogen peroxide and 2-hydroxypropyl acrylate (identified by infrared). The peroxide (XV) did not react with water or Co(II) and was considerably more stable towards heat than the hydroperoxide.

Autoxidation of Cyclic Acetals. Procedure B. 2-Hydroxypropyl Acrylate (XXV) and Polymer XXVI from I.—To a 190-mm. diameter crystallizing dish placed in a vacuum desiccator was added 2-vinyl-4-methyldioxolane (25 g., 0.22 mole) and 1.25 ml. of Co(II) butyl phthalate in toluene (10 mg. of Co(II)/ml.). The desiccator was evacuated to 30 mm. and filled with oxygen to atmospheric pressure. After standing under oxygen at room temperature for 6 hr. the contents of the dish were mixed with hydroquinone. Six runs were made in this manner, combined, and permitted to stand for 24 hr. The composite was filtered and fractionated through a short Vigreux column to yield polymer XXVI (47 g.) and a liquid (16 g.), b.p. 55–58° (0.5 mm.). Redistillation of the latter product gave additional polymer and 2-hydroxypropyl acrylate (6 g.), b.p. 49° (0.4 mm.). The infrared spectrum of the ester was identical with that of an authentic sample of 2-hydroxypropyl acrylate.

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[18] R. F. Fischer and C. W. Smith, *J. Org. Chem.*, **25**, 319 (1960).

TABLE V

α,β-UNSATURATED ESTERS

	Ester	Yield,[a] %	B.p.[b] (mm.), °C.	n^{25}D	Sapon. equiv. Calcd.	Sapon. equiv. Found	C=C (g. of H_2/g.) Calcd.	C=C (g. of H_2/g.) Found	OH, % Calcd.	OH, % Found
XXV	2-Hydroxypropyl acrylate	10	49 (0.4)		130	129		*c*		*d*
XXVII	1-Methyl-2-hydroxypropyl acrylate	30		1.4428		*e*		*c*		*d*
XXIX	1,2-Dimethyl-2-hydroxypropyl acrylate	45	50 (0.4)	1.4410	158	169		*c*		*d*
XXX	2-Hydroxypropyl crotonate	72	81 (1.2)	1.4537	144	144	0.0139	0.0142	11.8	11.9
XXXI	2-Hydroxypropyl methacrylate	30	57 (0.5)	1.4460	144	145		*f*	11.8	11.4
XXXII	1,1,2-Trimethyl-2-hydroxypropyl methacrylate	50	60 (0.3)	1.4482		*e*		*f*		*d*
XXXIII	1,1,3-Trimethyl-3-hydroxybutyl acrylate	40	42 (0.2)	1.4432	172	175	0.0117	0.0119	8.00	8.21
XXXVII	2-Methyl-2-hydroxypropyl acrylate		40 (0.3)	1.4420		*e*		*c*		*d*

[a] Based on O_2 consumed. [b] Uncorrected. [c] Acrylate C=C doublet at 6.1 and singlet at 12.2 μ (infrared). [d] Alcohol OH at 2.8 μ (infrared). [e] Ester C=O at 5.8 μ (infrared). [f] Methacrylate C=C singlet at 6.1 and 12.2 μ (infrared).

Anal. Calcd. for $C_6H_{10}O_3$: sapon. equiv., 130. Found: sapon. equiv., 129 and 130.

The infrared spectrum of the polymer (XXVI) produced upon work-up of the oxidation mixture was substantially identical with poly(2-hydroxypropyl acrylate) obtained by heating 2-hydroxypropyl acrylate with a catalytic amount of benzoyl peroxide.

2-Methyl-1,3,5,7-tetraoxaspiro[4.4]nonane (XXXV) from I.—2-Vinyl-4-methyldioxolane (57 g., 0.5 mole) containing *p*-toluenesulfonic acid (0.2 g.) reacted with oxygen (8 g., 0.25 mole) at 85° by procedure A. The oxidized mixture gave unconverted dioxolane (24 g.) and a moderately viscous oil (41 g.) on stripping at 25–30° (0.3 mm.). The oil was dissolved in benzene (70 ml.) and stirred vigorously with 10% caustic solution while cooling with an ice bath. The organic phase upon fractional distillation yielded polymer (11 g.) and the cyclic peroxide, 2-methyl-1,4,6,7-tetraoxaspiro[4.4]nonane (XXXV, 8 g.); b.p. 50° (0.7 mm.); n^{25}D 1.4425.

Anal. Calcd. for $C_6H_{10}O_4$: C, 49.31; H, 6.89; mol. wt., 146; peroxide oxygen as % H_2O_2, 23.3. Found: C, 48.86; H, 6.89; mol. wt., 146, 146; peroxide oxygen as % H_2O, 21.9, 20.7.

2-Hydroperoxy-2-vinyl-4,5-dimethyldioxolane (XVI) from II.—Oxygen (12 g., 0.37 mole) was added to 2-vinyl-4,5-dimethyldioxolane at 90° (procedure A). Unconverted dioxolane was removed by heating at 30–50° (1 mm.). The residue (64 g.) was a water white liquid whose infrared spectrum showed strong absorption at 3.0 μ. The crude product reacted exothermically with Co(II) butyl phthalate to give polymer and with water to give hydrogen peroxide and an acrylate ester.

Anal. Calcd. for $C_7H_{15}O_4$: peroxide oxygen as % H_2O_2, 21.2. Found: peroxide oxygen as % H_2O_2, 16.9.

Presumably the product is a mixture of hydroperoxide XVI and peroxide. No attempt was made at separation because of the possible explosion hazard.

1-Methyl-2-hydroxypropyl Acrylate (XXVII) from II.—By procedure A, 2-vinyl-4,5-dimethyldioxolane (92 g., 0.79 mole) containing Co(II) (40 mg.) as Co(II) butyl phthalate absorbed 11 g. (0.34 mole) of oxygen at 35°. The oxidized mixture, after standing 24 hr. over hydroquinone (10 g.), gave upon distillation starting acetal (38 g.), crude ester (23 g.), and polymer XXVIII (45 g.). The crude ester was taken up in benzene (25 ml.) and washed with 5% caustic solution. After drying and removal of volatiles by heating at 50° (0.5 mm.) for 30 min. a pale yellow oil (16 g.) was obtained, n^{25}D 1.4428. The oil was identified as a hydroxyalkyl acrylate (XXVII) by inference from its infrared spectrum: strong band at 3.0 (OH), strong doublet at 6.1, and singlet at 12.2 μ which are characteristic of acrylates. Further, the oil gave a polymer when it was heated with a small amount of benzoyl peroxide. The infrared spectrum of this polymer was nearly identical with the spectrum of the polymer XXVIII isolated from the oxidation mixture.

2-Hydroperoxy-2-vinyl-4,4-dimethyldioxolane (XVII) from III.—2-Vinyl-4,4-dimethyldioxolane (102 g., 0.8 mole) reacted with oxygen (12 g., 0.36 mole) by procedure A. Elimination of unchanged dioxolane from the reaction mixture by heating at 30–40° (0.5 mm.) gave 55 g. of crude 2-hydroperoxy-2-vinyl-4,4-dimethyldioxolane (XVII). The product absorbed strongly at 3.0 μ (hydroperoxy OH) in the infrared. It ignited when heated on a hot plate and reacted exothermically when mixed with a small quantity of Co(II) butyl phthalate. Because of the possible explosion hazard, no attempt was made to purify the product.

2-Methyl-2-hydroxypropyl Acrylate (XXXVII) by Hydrolysis of Crude 2-Hydroperoxy-2-vinyl-4,4-dimethyldioxolane (XVII).—Crude XVII (56 g.) was stirred with water (58 ml.) while cooling in an ice bath. Sodium chloride (20 g.) was added and the mixture extracted with benzene (50 ml.). The organic layer was washed with saturated sodium chloride solution, dried over anhydrous magesium sulfate, and fractionally distilled to obtain 2-methyl-2-hydroxypropyl acrylate (20 g., XXXVII); b.p. 40° (0.3 mm.); n^{25}D 1.4420; infrared, 2.9 (OH), 5.8 (ester C=O), 6.1 and 6.2 doublet and 12.2 μ singlet (acrylate C=C).

Anal. Calcd. for $C_7H_{12}O_3$: ester equiv., 144. Found: ester equiv., 142.

2,2-Dimethyl-1,4,6,7-tetraoxaspiro[4.4]nonane (XXXVI).—Fifty-six grams (0.44 mole) of 2-vinyl-4,4-dimethyldioxolane (III) was acidified with toluenesulfonic acid (0.1 g.) and allowed to absorb 7 g. (0.22 mole) of oxygen at 95° according to procedure A. The resulting mixture on fractionation gave unconverted dioxolane (25.5 g., 0.147 mole), nonvolatile peroxidic material (8 g.), and spirocyclic peroxide, 2,2-dimethyl-1,4,6,7-tetraoxaspiro[4.4]nonane (24 g., XXXVI), b.p. 39° (0.4 mm.), n^{25}D 1.4365.

Anal. Calcd. for $C_7H_{12}O_4$: C, 52.49; H, 7.55; mol. wt., 160; peroxide oxygen as % H_2O_2; 21.2. Found: C, 52.55; H, 7.38; mol. wt., 157, 158; peroxide oxygen as % H_2O_2, 18.6.

The remaining 2-alkenyl-1,3-cyclic acetals (IV–XIII) of Table I were oxidized either by procedure A or B. The oxidized mixtures were freed of unchanged acetal by heating at 30–40° (1 mm.) and the crude products examined by infrared. If the examination indicated that the principal product was ester or cyclic peroxide, the concentrates were worked up. Pertinent data on the products isolated and identified are summarized in Table III (cyclic peroxides) and Table V (esters). If hydroperoxide was indicated, confirmatory tests such as peroxide titer, behavior towards heat, and Co(II) butyl phthalate were run.

Analysis of Peroxide Content in Cyclic Peroxides.—The methods[19] normally used for determining peroxide were found to be highly unreliable in the case of cyclic peroxides. After a brief study the following method was adopted.

Approximately 0.2 g. of sample and 1.0 g. of sodium iodide were added to 10 ml. of acetic anhydride, blanketed with nitrogen heated on the steam bath for 15 min., and allowed to stand 6 hr. at room temperature. The mixture was diluted with 50 ml. of distilled water and titrated with standard sodium thiosulfate to a colorless end point. Peroxide as per cent hydrogen peroxide was calculated as follows.

$$\frac{\text{ml. of thiosulfate} \times \text{normality} \times 34 \times 100}{\text{wt. of sample} \times 2 \times 1000} = \text{peroxide as } \%\ H_2O_2$$

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[19] A. V. Tobolsky and R. V. Mesrobian, "Organic Peroxides" Interscience Publishers, Inc., New York, N. Y., 1954, pp. 52–54.