melting point 216–217° (uncorrected). Several recrystallizations from ethanol yielded material of m.p. 217.0–217.5°.

Anal. Calcd. for $C_{24}H_{25}N_5O_7$: C, 58.17; H, 5.09; N, 14.14. Found: C, 57.88; H, 5.15; N, 14.14.

Examination of the infrared spectrum, taken in a potassium bromide pellet, of the above analyzed compound, m.p. 217.0–217.5°, revealed the presence of a carbonyl group absorption peak at 1640 cm.$^{-1}$ No peak was present in the 1660 cm.$^{-1}$ region.

Several attempts were made to separate the original mixture of pyridones by chromatographic means. Use of alumina of various activities in combination with different eluents gave only a limited separation of products. It was observed that, in general, 1-(3,4-dimethoxyphenethyl)-3-ethyl-4-(carboxaldehyde diethylacetal)-2-pyridone was more readily displaced from an alumina column than its isomer.

B. In a second run similar to that described above the yield of mixed pyridones was 3.26 g. (84%). An exception to the procedure employed in the first run was that the potassium ferricyanide oxidation was allowed to proceed without interruption for a period of 12 hr. An infrared spectrum of the resultant oil, taken in chloroform solution, showed absorption peaks at 1645 cm.$^{-1}$ and 1660 cm.$^{-1}$ of approximately equal intensity.

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LAWRENCE, KAN.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, RESEARCH AND ENGINEERING DIVISION, MONSANTO CHEMICAL CO.]

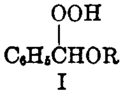
Autoxidative Formation and Chemical Properties of α-Alkoxybenzyl and α-Alkoxyallyl Hydroperoxides[1]

DEXTER B. SHARP AND TRACY M. PATRICK, JR.

Received May 5, 1960

Alkyl benzyl ethers and alkyl allyl ethers autoxidize readily at 100° in liquid phase to α-alkoxybenzyl and α-alkoxyallyl hydroperoxides, respectively. Conversion of the former to the corresponding aromatic aldehyde is effected by reduction; ferrous ion catalyzes *gem*-dehydration to the carboxylate ester. *gem*-Dehydration of α-alkoxyallyl hydroperoxide gives low yields of acrylate ester; a concomitant polymerization of the monomer in the presence of peroxide limits the yields of this potential acrylate synthesis.

Clover[2] reported the autoxidation of benzyl ethers and an allyl ether in the presence of light. He exposed ether samples at ordinary temperature to oxygen for prolonged periods, and reported development of active oxygen, hydrolysis of the peroxidic intermediate to hydrogen peroxide, and isolation of secondary products which were derived by oxidation of the activated methylene group. Clover suggested that the primary product of oxidation of a benzyl ether amounted to addition of an oxygen molecule, and formulated it as an α-alkoxybenzyl hydroperoxide (I). Milas[3] proposed a different intermediate.

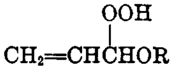


$$C_6H_5\overset{\displaystyle OOH}{\overset{|}{C}}HOR$$

I

As a part of a liquid phase oxidation program at this laboratory, the preparation of I by more efficient means and its decomposition to benzaldehyde appeared worthy of investigation as a possible route to aromatic aldehydes. *gem.*-Dehydration of I would also constitute an interesting route to arylcarboxylate esters.

Similar considerations were applied to oxidation of an allyl ether, which presumably would give α-alkoxyallyl hydroperoxide (II).

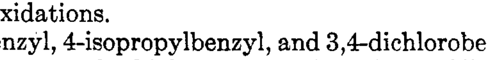


$$CH_2{=}CH\overset{\displaystyle OOH}{\overset{|}{C}}HOR$$

II

Compound II is of interest as a possible precursor for an acrylic ester *via gem*-dehydration.

Liquid-phase autoxidation at 100° of a series of alkyl benzyl ethers gives, in the more successful cases, the corresponding α-alkoxybenzyl hydroperoxides in 33–56% yields (Table III). Time periods of three to six hours were required to reach the maximum hydroperoxide value. In these oxidations, as well as in oxidations of the alkyl allyl ethers (Table III), exothermic decompositions occasionally resulted in loss of hydroperoxide. In this work none of these decompositions was explosive in nature; however, adequate shielding was used for all oxidations.



Benzyl, 4-isopropylbenzyl, and 3,4-dichlorobenzyl ethers gave the highest conversions (20–23%) and yields (42–56%) of the corresponding α-alkoxy-

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[1] Presented before the Organic Division, American Chemical Society, New York Meeting, September 8–13, 1957.

[2] A. M. Clover, *J. Am. Chem. Soc.*, **46**, 419 (1924).

[3] N. A. Milas, *J. Am. Chem. Soc.*, **53**, 221 (1931).

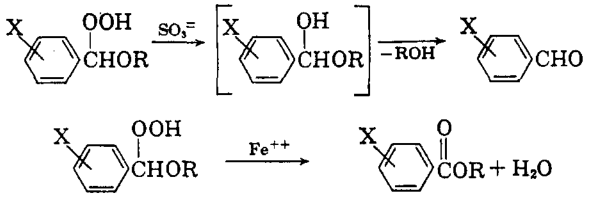
benzyl hydroperoxides. Total ether consumed was around 40% in these cases. Usually, these substituent groups have no adverse effect on the course of an autoxidation.

On the other hand, two methoxyl-substituted benzyl ethers, 4-methoxy-, and 3,4-dimethoxybenzyl methyl ethers, give only 3–5% conversions and 20–22% yields of their corresponding hydroperoxides with 20–30% consumption of ether. This might be attributed to a limited antioxidant action by these "methylated" phenols.

Finally, three of the ethers give virtually no hydroperoxide, the 2-thenyl, 1-naphthylmethyl, and 4-nitrobenzyl methyl ethers. The first of these gave a small hydroperoxide buildup, and traces of thiophene-2-carboxaldehyde were isolated on sulfite reduction of the oxidation mixture; 75% of the ether was recovered unchanged. An 82% recovery of 1-naphthylmethyl methyl ether was obtained, along with a 34% yield of methyl 1-naphthoate, based on consumed ether. The 4-nitrobenzyl methyl ether was least affected, 88% recovery being obtained; of consumed ether, 32% appeared as 4-nitrobenzoic acid.

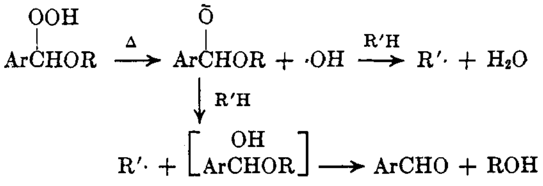
In these examples of sluggish oxidations one can conjecture as follows. It has been suggested already that the methoxyl compounds are behaving as antioxidants in part. One can suggest that the thienyl ether is also inhibitory, perhaps by an oxidation of the sulfur atom, causing a break in oxidation chains. It seems characteristic that naphthalene compounds in general autoxidize slowly, perhaps attributable to direct ring oxidation to naphthols or naphthoquinones; this would constitute an auto-inhibition effect. Finally, the low degree of oxidation of the nitro compound might be due to a diminution in electron availability because of the powerful electron-withdrawing effect of this group; this would tend to reduce the oxidizability of this ether.

The decompositions of the hydroperoxides in these benzyl ether oxidation mixtures were effected by sulfite reduction to the aldehyde (Table IV),[4] and by ferrous-ion catalyzed *gem*-dehydration to arylcarboxylate ester (Table V).[5]



Based on consumed ether, benzaldehyde (52% yield) from unsubstituted benzyl alkyl ethers and anisaldehyde (33% yield) from *p*-methoxybenzyl methyl ether (Table IV) constitute the better results obtained in the aldehyde route. In spite of relatively facile oxidations and high hydroperoxide content, the 4-isopropylbenzyl methyl and the 3,4-dichlorobenzyl methyl ether oxidation mixtures gave low aldehyde yields on sulfite treatment; apparently, dehydration to esters was favored during these attempted reductions. On the other hand, all but the methoxyl-substituted ethers gave good yields of arylcarboxylate ester when each oxidation mixture was treated with aqueous ferrous sulfate (Table V).

The attempts to reduce the hydroperoxides to aldehydes resulted, in several instances, in isolation of appreciable quantities of corresponding ester and acid. One should consider that various alternative hydroperoxide decomposition modes are undoubtedly proceeding during the oxidations, in addition to existence of such paths during the subsequent treatments of the oxidation mixtures. Probable paths involve homolytic scission of the peroxidic moiety; this leads to initiation of new oxidation chains during the first step of this sequence, by virtue of radical formation.

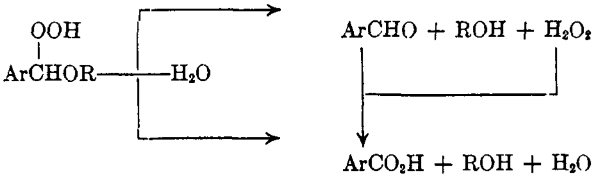


$$\overset{\text{OOH}}{\text{ArCHOR}} \xrightarrow{\Delta} \overset{\dot{\text{O}}}{\text{ArCHOR}} + \cdot\text{OH} \xrightarrow{\text{R'H}} \text{R'}\cdot + \text{H}_2\text{O}$$

$$\downarrow \text{R'H}$$

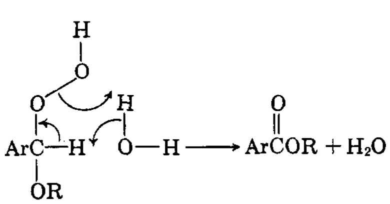
$$\text{R'}\cdot + \left[\overset{\text{OH}}{\text{ArCHOR}}\right] \longrightarrow \text{ArCHO} + \text{ROH}$$

A second decomposition route could be hydrolytic in nature, wherein water displaces hydroperoxy or alkoxy group to give, respectively, hydrogen peroxide and aldehyde, or alcohol and carboxylic acid.



$$\overset{\text{OOH}}{\text{ArCHOR}} \xrightarrow{\text{H}_2\text{O}} \text{ArCHO} + \text{ROH} + \text{H}_2\text{O}_2 \longrightarrow \text{ArCO}_2\text{H} + \text{ROH} + \text{H}_2\text{O}$$

Finally, water might lead to carboxylate ester by the following concerted cyclic *gem*-dehydration.



It is obvious that aldehyde formed during oxidation would be oxidized readily to carboxylic acid.

In alkyl allyl ethers, the combined effect of vinyl and alkoxy groups on the methylene moiety results in rapid hydroperoxide buildup when these ethers are subjected to the action of molecular oxygen. The allyl ethers oxidize two to three times faster than do the benzyl ethers (Table III).

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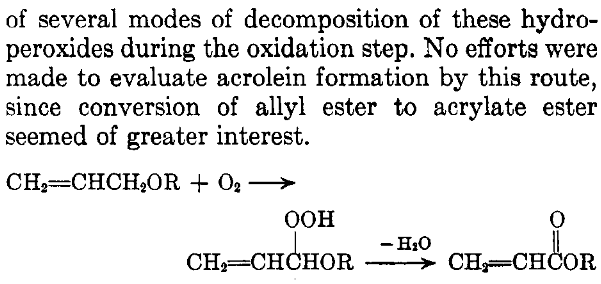
[4] F. G. Eichel and D. F. Othmer, *J. Ind. Eng. Chem.*, **41**, 2623 (1949).

[5] N. A. Milas, R. L. Peeler, and O. L. Mageli, *J. Am. Chem. Soc.*, **76**, 2322 (1954).

Temperature control was somewhat more difficult than with the benzyl ethers. A lachrymatory liquid which condensed from the oxygen stream exiting from the oxidation was identified as acrolein by derivative formation. This attests to the coexistence of several modes of decomposition of these hydroperoxides during the oxidation step. No efforts were made to evaluate acrolein formation by this route, since conversion of allyl ester to acrylate ester seemed of greater interest.

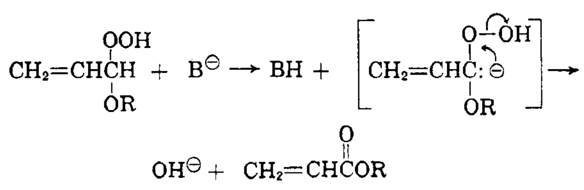


$$CH_2{=}CHCH_2OR + O_2 \longrightarrow CH_2{=}CH\overset{OOH}{C}HOR \xrightarrow{-H_2O} CH_2{=}CH\overset{O}{\overset{\|}{C}}OR$$

Obviously, formation of acrylate monomer in the presence of its peroxidic precursor poses a difficult problem. The best yield of acrylate (27%) was obtained by decomposition of α-butoxyallyl hydroperoxide with hot aqueous ferrous sulfate with simultaneous steam distillation of the monomeric butyl acrylate (Table VI).

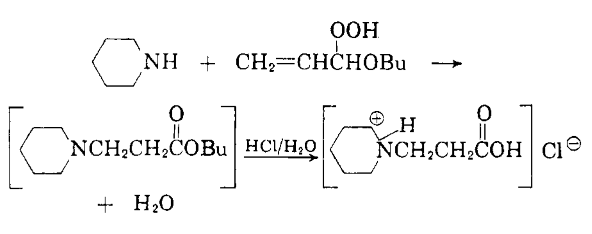
A number of other methods were tried in efforts to improve the yield of acrylate. In all attempts using aqueous media, high material losses were encountered. Attempts to use powdered solid ferrous sulfate were unsuccessful. Decompositions of ionic nature were attempted, specifically with basic catalysts,[6] and by acylation.[7]

The former allegedly could proceed as follows:

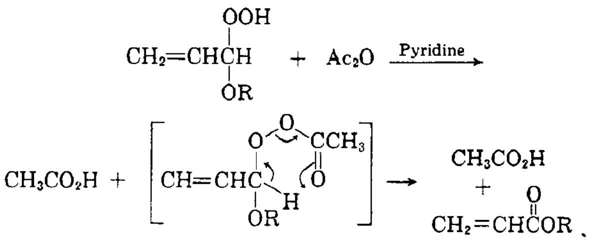


$$CH_2{=}CH\underset{OR}{\overset{OOH}{C}}H + B^{\ominus} \longrightarrow BH + \left[CH_2{=}CH\underset{OR}{\overset{O-OH}{C}}{:}\ominus\right] \longrightarrow OH^{\ominus} + CH_2{=}CH\overset{O}{\overset{\|}{C}}OR$$

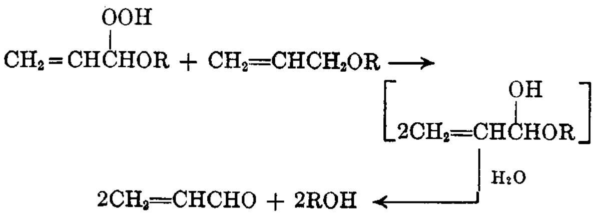
N,*N*-Dimethylbenzylamine and *N*-methylmorpholine in benzene gave only trace amounts of acrylate. Tertiary amines were used to avoid formation of β-aminopropionate compounds *via* Michael addition of secondary or primary amines to the acrylate. Piperidine alone, and potassium hydroxide in butanol, gave no isolable butyl acrylate. The piperidine decomposition gave a good yield of β-(*N*-piperidino)propionic acid, isolated as its hydrochloride.



Criegee's acylation method[7] gave some acrylate, perhaps *via* the cyclic intermediate shown.



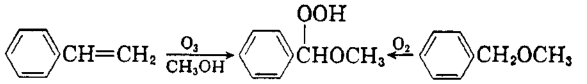
In most of these runs, the high-boiling organic by-product showed antifoamant properties which are characteristic of low molecular weight polybutyl acrylate. No further identification was attempted. It is to be noted in Table VI that two runs were made with hydroperoxide 68–71% concentrates. These solutions were obtained by vacuum stripping of unchanged allyl butyl ether. The pot temperature was not allowed to exceed 35°, and the concentrations were effected without incident. This was done to remove allyl ether which it was thought might be oxidized by the hydroperoxide as follows.



$$CH_2{=}CH\overset{OOH}{C}HOR + CH_2{=}CHCH_2OR \longrightarrow \left[2CH_2{=}CH\overset{OH}{C}HOR\right] \xrightarrow{H_2O} 2CH_2{=}CHCHO + 2ROH$$

This could lead to high losses during the decomposition step. However, these concentrates gave little or no acrylate ester even when "ionic" reagents were used under anhydrous conditions.

One final comment is of interest. The α-alkoxybenzyl hydroperoxides should have the structure of one cleavage product of an ozonide formed in alcohol; for example, α-methoxybenzyl hydroperoxide should be identical with a cleavage product of styrene when ozonolysis of styrene is run in methanol.[8]



It would be of interest to attempt to isolate the α-alkoxybenzyl hydroperoxide from each type of oxidation and prove that they are identical.

EXPERIMENTAL

Alkyl arylmethyl ethers. These were prepared in 57–90% yields by addition of the corresponding chloromethyl compound to alcoholic potassium hydroxide. The products were isolated by standard procedures and purified by distillation. Table I summarizes these preparations, and Table II lists the properties of the products, along with analyses.

Alkyl allyl ethers. Allyl butyl ether was prepared by a 2-hr. reaction at 75° of allyl chloride (918 g.) with 1-butanol (740 g.) containing potassium hydroxide (660 g.); an azeotrope of allyl butyl ether and 1-butanol distilled about 110°, and resulted in lower yields of alcohol-free ether when distillation alone was used for purification. Treatment of flash-

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(6) N. Kornblum and H. E. DeLaMare, *J. Am. Chem. Soc.*, **73**, 880 (1951).

(7) R. Criegee, *Forts. Chem. Forsch.*, **1**, 508 (1950).

(8) R. Crigee, *Ann.*, **583**, 1 (1953).

TABLE I

PREPARATION OF ALKYL ARYLMETHYL ETHERS

No.[a]	R	RCH_2Cl, G.	CH_3OH, Ml.	KOH, G.	Conditions[a]		Yield,[b] %
					Temp.	Time, Hr.	
1	C_6H_5	255	400	150	85	1.0	92
2	2-C_4H_3S	577	1000	250	75	1.5	78
3	1-$C_{10}H_7$	153	200	51	75	1.5	74
4	4-*i*-PrC_6H_4	337	750	117	75	2.0	67
5	3,4-$Cl_2C_6H_3$	180	500	57	60	2.0	66
6	4-$NO_2C_6H_4$	304	1000	112	60	2.2	42[c]
7	C_6H_5[d]	288	720[d]	150	130	6.5	57[d]
8	4-$CH_3OC_6H_4$[e]	300	750	130	65	1.0	90[f]
9	3,4-$(CH_3O)_2C_6H_3$	144	500	54	75	3.0	67

[a] For reference to Table II. [b] Based on chloromethyl compound. [c] Also isolated 45.7% yield of 4,4′-dinitrostilbene, m.p., 283–286°, listed[9] 286°. [d] 2-Ethylhexanol instead of methanol, benzyl 2-ethylhexyl ether formed. [e] Chloromethyl compound prepared by treatment of 4-methoxybenzyl alcohol with concentrated hydrochloric acid by method of Quelet and Allard[10]; the chloromethyl compound was used without purification. [f] Yield based on initial 4-methoxybenzyl alcohol.

TABLE II

ALKYL ARYLMETHYL ETHER PROPERTIES

No.[a]	B.P., Mm.	d_4^{20} (av.)	n_D^{25} (av.)	Calcd.		Found	
				C, %	H, %	C, %	H, %
1	56.0–59.0/12	0.977	1.5022	—	—	—	—
2	66.7–68.4/16	1.077	1.5180	56.21	6.29	56.35	6.70
3	150.5–156.0/16	0.715	1.6040	83.68	7.02	82.40	6.85
4	104.0–106.5/16	0.936	1.4966	80.43	9.82	81.65	9.36
5	126.5–127.2/16	1.270	1.5402	50.29	4.22	50.21	4.34
6[b]	60–90/0.1	—	1.5450	57.48	5.43	57.41	5.29
7[c]	150.0–151.8/17	0.904	1.4820	81.76	10.98	82.19	11.14
8	113.0–115.0/17	1.026	1 5126	71.02	7.95	71.06	8.02
9	139.0–139.5/13	—	1.5258	65.91	7.75	66.05	7.78

[a] Refers to numbers in Table I. [b] Nitrogen, %: Calcd., 8.28; found, 8.32. 8.40. [c] Benzyl 2-ethylhexyl ether.

distilled product-azeotrope mixture with maleic anhydride, followed by water and aqueous alkali washes gave alcohol-free ether: physical constants, b.p. 117.5–117.8°, d_4^{20} 0.780, and n_D^{25} 1.4039 (lit.,[11] b.p. 117.8–118.0/763 mm., d_4^{20} 0.7829, n_D^{20} 1.4057).

Similarly, allyl 2-ethylhexyl ether was prepared by addition of allyl chloride (328 g.) to 2-ethylhexanol (520 g.) in which metallic sodium (92 g.) had been dissolved; reaction temperature was 140°, time was 3 hr., and yield was 42% plus 323 g. of azeotrope containing 10% alcohol (by hydroxyl group analysis). Allyl 2-ethylhexyl ether has the following properties: b.p. 81.5–82.0°/15 mm., d_4^{20} 0.805, and n_D^{25} 1.4256.

Anal. Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.74; H, 13.01.

Oxidations. A 125-ml. capacity, cylindrical, glass reactor equipped with a hollow, gas-dispersing stirrer, a sample withdrawal tube and a reflux condenser in series with a Dry Ice-cooled trap was used for the oxidations of these ethers. Cylinder oxygen was the oxidant. Using 100-g. samples of ether, most runs were made at 100°; several of the ethers were run at higher temperature if they oxidized slowly. Solid sodium bicarbonate (3–6% by wt.) was added to these runs to reduce acid formation. The progress of a run was followed by withdrawal of samples at arbitrary time intervals and immediate analysis of these samples for hydroperoxide by iodimetric means.[12] Plots of hydroperoxide against time gave the typical S-curve for a radical chain oxidation.

The oxidations of alkyl benzyl ethers and of alkyl allyl ethers are summarized in Table III, showing temperature used and the time required to reach the maximum hydroperoxide. Hydroperoxide conversions are based on hydro-

TABLE III

AUTOXIDATION OF BENZYL AND ALLYL ETHERS[a]

RCH_2OCH_3

R	Temp.	Time, hr.	Maximum % $RCH(OOH)OCH_3$	
			Conv.	Yield
C_6H_5	100	4.0	22.2	56.0
2-C_4H_3S[b]	100	6.0	2.2	11.9
1-$C_{10}H_7$	100	5.0	0.0	0.0
	160	1.0		
4-*i*-PrC_6H_4	100	5.5	20.1	54.2
3,4-$Cl_2C_6H_3$	100	3.0	21.1	45.2
4-$NO_2C_6H_4$	100	2.5	0.0	0.0
	150	2.5		
C_6H_5[c]	100	5.0	22.8	41.8
4-$CH_3OC_6H_4$	100	3.5		
	130	1.0	6.5	22.3
3,4-$(CH_3O)_2C_6H_3$	100	6.0	4.2	20.0
$CH_2{=}CHCH_2OR$				
R=				
n-C_4H_9	100	2.2	17.8	56.3
2-Ethylhexyl	100	4.1	15.0	33.1

[a] Sodium bicarbonate (3.0 g.) added to each run to neutralize acids formed. [b] 2-Thienyl. [c] Benzyl 2-ethylhexyl ether.

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(9) A. G. Green, A. H. Davis, and R. S. Horsfall, *J. Chem. Soc.*, 91, 2076 (1907).

(10) R. Quelet and J. Allard, *Bull. Soc. Chim.*, [5], 4, 1468 (1937).

(11) E. A. Talley, A. S. Hunter, and E. Yanovsky, *J. Am. Chem. Soc.*, 73, 3528 (1951).

(12) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, 19, 974 (1947).

TABLE IV

REDUCTION OF α-ALKOXYBENZYL HYDROPEROXIDES

$RCH(OOH)OCH_3$

	Ether,[a] Wt. %	Products, Yield %[b]		
		RCHO	RCO_2CH_3	RCO_2H
C_6H_5	60.3	52.5	17.8	4.6
$2\text{-}C_4H_3S$[c]	75.0	8.5	0.0	0.0
$4\text{-}i\text{-}PrC_6H_4$	62.9	2.0	67.3	7.4
$3,4\text{-}Cl_2C_6H_3$	54.0	8.3	19.7	10.5
C_6H_5[d]	45.8	23.3	28.6[d]	18.5
$4\text{-}CH_3OC_6H_4$	70.9	33.5	9.4	5.0
$3,4\text{-}(CH_3O)_2C_6H_3$	79.0	4.9	0.0	0.0
$4\text{-}NO_2C_6H_4$	88.0	0.0	0.0	32.0

[a] Ether recovered. [b] Over-all yield from starting ether. [c] 2-Thienyl. [d] Benzyl 2-ethylhexyl ether, ester is 2-ethylhexyl benzoate.

peroxide analyses, and the yields are based on consumed ether as determined by the quantity of unchanged ether recovered after the subsequent decomposition step.

Decompositions of α-alkoxyarylmethyl hydroperoxides. In the alkyl benzyl ether series, reduction of the hydroperoxide to the aldehyde was accomplished by treating the oxidation mixture with aqueous sodium sulfite with vigorous stirring for 16 hr. at room temperature. Such treatment of an oxidized sample of benzyl methyl ether is typical. A 100-g. sample of benzyl methyl ether containing 6.8 g. of sodium bicarbonate was oxidized for 4 hr. at 100°, at which time the concentration of α-methoxybenzyl hydroperoxide was 26.6%. The 110-g. oxidation mixture was diluted with hexane and stirred with 52 g. of sodium sulfite in 200 ml. of water for 16 hr. The layers were separated. The organic layer was extracted with a solution of 25 g. of sodium bisulfite in 200 ml. of water. To the bisulfite extract was added 75 g. of potassium carbonate, and the mixture was extracted with hexane. Distillation gave 18.1 g. of benzaldehyde with b.p., 68°/16 mm., d_4^{20} 1.022, n_D^{25} 1.5418 (lit.,[13] b.p. 179.5°, d_4^{15} 1.0504, $n_D^{17.6}$ 1.54629). The bisulfite-extracted organic layer from the reduction was then distilled, giving 60.3 g. of benzyl methyl ether, b.p. 60–63°/14 mm., n_D^{25} 1.5030, and 8.0 g. of methyl benzoate, b.p. 63–83°/14 mm., n_D^{25} 1.5130 (lit.,[14] b.p. 80°/11.5 mm., n_D^{15} 1.5205).

The original sulfite solution was acidified with dilute sulfuric acid and gave 1.4 g. of benzoic acid, m.p. 119–120° (listed,[14] 122°). These quantities of products represent the following over-all conversions and yields:

	Conv., %	Yield, %
α-Methoxybenzyl hydroperoxide	22.2	56.0
Benzaldehyde	20.7	52.5
Methyl benzoate	7.0	17.8
Benzoic acid	1.8	4.6

Note that the benzaldehyde yield from hydroperoxide is 93%.

Data for reductions of the other ethers are summarized in Table IV, wherein aldehyde, ester and acid yields are listed, and recovered ether quantity is shown; these yields are for the two step sequence.

Illustrative of the *gem*-dehydration of an α-alkoxybenzyl hydroperoxide is the following experiment. A 100-g. portion of benzyl methyl ether containing 3.4 g. of sodium bicarbonate was oxidized 6 hr. at 100° to a 21.9% concentration of the hydroperoxide; 4.3 g. of analytical samples had been withdrawn. The remaining mixture weighed 101.3 g. The mixture was diluted with hexane and extracted with water. The aqueous extract gave on acidification 2.8 g. of benzoic acid, m.p. 119–119.5°. The hexane solution was then added dropwise in 1 hr. to 10 g. of ferrous sulfate heptahydrate in 100 ml. water at 75° with vigorous stirring. The organic layer was separated, dried, and distilled giving 53 g. of benzyl methyl ether, b.p. 59–61°/13 mm., n_D^{25} 1.5031, and 34.9 g. of methyl benzoate, b.p. 74.5–83.0°/13 mm., n_D^{25} 1.5167 (lit.,[14] b.p. 80°/11.5 mm., n_D^{15} 1.5205). The amounts of ether, methyl benzoate and acid represent the following yields, based on original charge of ether:

	Conv., %	Yield, %
α-Methoxybenzyl hydroperoxide	19.7	41.5
Methyl benzoate	31.4	66.8
Benzoic acid	5.6	11.9

Data for ester formation from the other ethers are summarized in Table V.

TABLE V

GEM-DEHYDRATION OF α-ALKOXYBENZYL HYDROPEROXIDES

$RCH(OOH)OCH_3$

R	Ether,[a] Wt. %	Products, RCO_2CH_3	Yield, %[b] RCO_2H
C_6H_5	53.0	66.8	11.9
$1\text{-}C_{10}H_7$[c]	81.7	34.0	2.7
$4\text{-}i\text{-}PrC_6H_4$	60.5	57.0	8.6
$3,4\text{-}Cl_2C_6H_3$	62.4	50.8	9.2

[a] Recovered ether. [b] Over-all yield from starting ether. [c] Products isolated directly from oxidation mixture without the "dehydration" step.

Decomposition of α-alkoxyallyl hydroperoxides. With the α-alkoxyallyl ethers, *gem*-dehydration was the only mode of decomposition studied, although acrolein was identified as a minor oxidation product collected in a cold-trap in exit gas stream. The 2,4-dinitrophenylhydrazone was prepared, m.p. 162–164° (lit.,[14] 165°). Methods of converting the α-butoxyallyl hydroperoxide to butyl acrylate included treatment of oxidation mixtures with aqueous ferrous sulfate, with bases, with acid, and with acetic anhydride. The highest yield (27%) of monomeric butyl acrylate was obtained from an aqueous ferrous sulfate system at reflux, steam distilling the acrylate as formed to reduce its polymerization. A 104.2-g. sample of oxidized allyl butyl ether con-

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TABLE VI

GEM-DEHYDRATION OF α-BUTOXYALLYL HYDROPEROXIDE

Perox. Concn., %	Catalyst	Solv.	Temp.	Yield, % Butyl Acrylate	High Boiler, Wt. %	Loss, Wt. %
31.3	$FeSO_4$	H_2O	100	27.4	0.0	23
12.8	$FeSO_4$	H_2O	20	12.8	11.6	26
71.0	$FeSO_4$	H_2O	100	12.8	5.9	12
17.9	Ac_2O, pyr.	—	30	11.9	7.4	42
67.7	$C_9H_{13}N$[a]	C_6H_6	25	1.6	12.9	31
12.9	KOH	BuOH	25	0.0	24.0	0.0
16.6	H_2SO_4	HOAc	80	5.7	10.9	10.5
11.4	$C_5H_{11}N$[b]	—	40	[c]	11.0	33

[a] *N,N*-Dimethylbenzylamine. [b] Piperidine. [c] No acrylate obtained; workup yielded 0.11 mole of β-(*N*-piperidino)propionic acid, yield *ca.* 30%.

taining 21.3% α-butoxyallyl hydroperoxide was added dropwise to a vigorously boiling solution of 20 g. of ferrous sulfate heptahydrate and 2.0 g. of hydroquinone in 500 ml. of water. Steam distillate was collected rapidly during the half-hour addition time, and thereafter until the distillate no longer contained oily drops. The distillate organic layer was separated, 0.1 g. of hydroquinone was added, the layer was dried 3 hr. over Drierite, then distilled at reduced pressure. There was collected 68 g. of allyl butyl ether, b.p. 38.5–48.0°/40 mm., d_4^{20} 0.787–0.791, n_D^{25} 1.4031–1.4050, and 9.5 g. of butyl acrylate, b.p. 63.0–68.0°/40 mm., d_4^{20} 0.895–0.900, n_D^{25} 1.4160–1.4168 (listed,[13] b.p. 145–146° (nomograph interpolation gives b.p. 62°/40 mm.), d_4^{20} 0.898, n_D^{20} 1.4185). Residue and other losses amounted to 23% of the original charge to the oxidation.

Various modifications of the so-called ionic dehydrations were tried,[6,7] with little success. The essentials of these experiments are summarized in Table VI. Several of these runs were with hydroperoxide concentrates, up to 71% obtained by vacuum stripping to 35° maximum.

The piperidine experiment is of interest, since a 30% yield of "acrylate" was recovered as a Michael addition product, namely, β-(*N*-piperidino)propionic acid. In this case 34 ml. of piperidine was added to 90.5 g. of oxidized allyl butyl ether containing 11.4 wt. % α-butoxyallyl hydroperoxide. Extraction of the organic layer with aqueous hydrochloric acid gave, on reduction in volume, 21 g. of a solid, m.p. 189–195°, which recrystallized well from ethanol, m.p. 215–217°.

Anal. Calcd. for $C_8H_{16}ClNO_2$: C, 49.61; H, 8.33; Cl, 18.31; N, 7.23; neut. equiv., 193.5. Found: C, 49.87; H, 8.00; Cl, 17.84; N, 7.13; neut. equiv., 190, 191; sapon. equiv., 196, 189.

The calculated structure is β-(*N*-piperidino)propionic acid hydrochloride; this compound gives an immediate and copious precipitate of silver chloride when added to aqueous silver nitrate. The organic layer was distilled giving 42 g. recovery of ether and 10 g. of residue.

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Reduction of Azobenzenes by Benzoin

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4-Dimethylaminoazobenzene and related compounds as well as azobenzene are reduced by benzoin in the absence of catalysts and solvents to amines, while benzoin is oxidized to benzil, the final products being azomethine compounds formed by condensation of amines with benzil. There were some indications that the amines were produced through disproportionation, but not by direct reduction, of hydrazo compounds formed at the first stage of reduction.

In an attempt to synthesize azo derivatives of indole from aromatic aminoazo compounds and α-hydroxy ketones, it was found that the reaction did not lead to the expected products, but resulted in reduction of azo compounds, if benzoin was used as a hydroxy ketone.

Recently a variety of organic as well as biochemical reagents have been utilized for the reduction of azo compounds,[1–4] but no example of reduction by benzoin seems to have been reported. Although aromatic nitro compounds are reduced by benzoin the reduction stops at azoxy or azo stage,[5] and benzoin is ineffective for chlorophyll- or pheophytin-sensitized photochemical reduction of 2′-carboxy-4-dimethylaminoazobenzene.[2] In this

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