THE FREE RADICAL CHEMISTRY OF CYCLIC ETHERS—IV

THE FREE RADICAL REARRANGEMENT OF EPOXIDES[1,2]

T. J. WALLACE[3] and R. J. GRITTER
Department of Chemistry, University of Connecticut, U.S.A.

Abstract—The t-butyl peroxide induced free radical addition of propylene oxide, styrene oxide, 1,2-epoxybutane, 1,2-epoxyoctane, and 1,2-epoxy-3-phenoxypropane to 1-octene has been studied in the temperature range of 125 to 200°. Ketones were among the products identified from the reactions studied. These results indicate that the chain transfer atom is the alpha tertiary hydrogen atom on the epoxide ring. The products also indicate that the intermediate epoxy radicals initially formed rearrange to alpha keto radicals before adding to the olefin. A mechanistic path for this general reaction is outlined and discussed. With propylene oxide, a secondary reaction involving opening of the epoxide ring by intermediate acetonyl radicals to produce 5-hydroxy-2-hexanone was observed. In addition, the reactivities of the above epoxides, 4-methyl-3,4-epoxy-2-pentanone, trimethylene oxide, tetrahydrofuran and tetrahydropyran toward t-butoxy radicals have been determined in order to ascertain how ring size affects the rate of hydrogen atom abstraction in this series of compounds.

INTRODUCTION

In the past, studies on the free radical chemistry of epoxides have been limited to vapor phase decomposition reactions with most of the research being on ethylene oxide and its mercury-sensitized[4,5] and dimethyl mercury-catalyzed decomposition.[6] The thermal decomposition of ethylene oxide was first reported by Heckert and Mack[7] and Fletcher[8,9] later showed that the first step involved decomposition to acetaldehyde. In the mercury-photosensitized and dimethyl mercury-catalyzed decompositions of ethylene oxide it was suggested that methyl radicals abstracted a hydrogen atom from the epoxide to produce an unstable intermediate, $C_2H_3O\cdot$, which reacted further to give mainly carbon monoxide and some propionaldehyde.[5,6] Finally, in the mercury-sensitized decomposition of *trans*-butylene oxide isobutyraldehyde, acetaldehyde, propionaldehyde, and methyl ethyl ketone were among the products identified.[5] This complex reaction apparently involved some type of free radical rearrangement, since both aldehydes and a ketone were formed.

[1] Part III, T. J. Wallace and R. J. Gritter, *J. Org. Chem.* **27**, 3067 (1962).
[2] A preliminary communication concerning part of this work has appeared, R. J. Gritter and T. J. Wallace, *J. Org. Chem.* **26**, 282 (1961). The free radical reaction of an epoxide with peroxide was first attempted in the laboratory of Professor W. H. Urry, University of Chicago.
[3] Present address: Esso Research and Engineering Company, Process Research Division, Exploratory Research Section, Linden, New Jersey.
[4] R. J. Cvetanovic, *Canad. J. Chem.* **33**, 1684 (1955).
[5] R. J. Cvetanovic and J. C. Doyle, *Canad. J. Chem.* **35**, 605 (1957).
[6] R. Gomer and W. A. Noyes, *J. Amer. Chem. Soc.* **72**, 101 (1950).
[7] W. W. Heckert and E. Mack, *J. Amer. Chem. Soc.* **51**, 2706 (1929).
[8] C. J. Fletcher, *J. Amer. Chem. Soc.* **58**, 534 (1936).
[9] C. J. Fletcher and G. K. Rollefson; *J. Amer. Chem. Soc.* **58**, 2135 (1936).

The present study was undertaken to determine the products and to clarify the mechanism of the peroxide induced free radical reactions of various epoxides. To ascertain what intermediate free radicals were formed, the reactions were done in the liquid phase in the presence of 1-octene. In addition, it was also desirable to determine the relative reactivities of epoxides toward t-butoxy radicals in comparison to other cyclic ethers in order to assess the effect of ring size on the reactivity of cyclic ethers.

RESULTS

The t-butyl peroxide induced free radical addition of various epioxides to 1-octene has been studied in the temperature range of 125–200°. With the exception of propylene oxide, ketones were identified as the major products from each reaction. No aldehydes could be detected by chemical methods in any of the reactions. The conditions used and the products identified from each epoxide are summarized in Table 1. In the one instance where product identification could not be made (1,2-epoxy-3-phenoxypropane), a reaction did occur, but the results indicate a mixture of 2:1 and 3:1 addition products were formed. The three reactions of propylene oxide listed in Table 1 are significant, since two products are formed by two competing free radical reactions. The predominance of 2-hendecanone or 5-hydroxy-2-hexanone appears to be temperature dependent. However, in all cases the yield of the hydroxy ketone was low.

TABLE 1. REACTION CONDITIONS USED AND PRODUCTS IDENTIFIED FROM THE
EPOXIDES STUDIED

Epoxide (moles)	1-Octene (mole, % conv.)	t-Butyl peroxide (mole)	Time (hr) Temp.	(% Yield[a], conv. %[b])	Residue (g, mol. wt.)
1,2-Epoxyoctane (2·0)	0·40, 48·9	0·06	3 145°	7 hexadecanone (7,7, 16·1)	10·1, 538
1,2-Epoxybutane (2·0)	0·40, 40·7	0·06	3 145°	3-dodecanone (4·2, 9·4)	25·3, 466
Propylene oxide (I) (3·0)	0·20, 0	0·015	17 125°	5-hydroxy-2-hexanone[c] (1·8)	2·3, 640
Propylene oxide (II) (2·0)	0·20, 39·3	0·03	2 150°	5-hydroxy-2-hexanone[c] (1·8) 2-hendecanone (3·2, 8·2)	11·2, 324
Propylene oxide (III) (2·0)	0·10, 50·8	0·12	1 200°	5-hydroxy-2-hexanone[c] (0·4) 2-hendecanone (23·4, 70)	10·2, 349
Styrene oxide (2·0)	0·20, 23·6	0·03	3 150°	capriphenone (6·6, 28·4)	6

[a] Based on the total amount of 1-octene used.
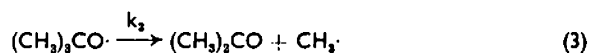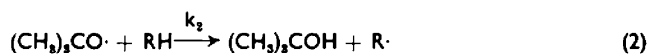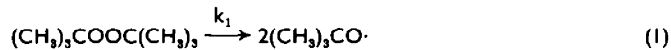[b] Based on the amount of 1-octene converted to product.
[c] Yield based on the amount of propylene oxide used.

All products were identified by gas chromatography. The products, the authentic compounds, and equal mixtures of the products and authentic compounds had identical retention times when chromatographed under the same conditions. In only one

instance, propylene oxide (Run III), could a solid derivative of the product be prepared. This is not surprising since high molecular weight ketones in which the carbonyl function is beyond the 3-position are highly resistant to derivitization. The authentic compounds were prepared by radical and ionic techniques. Capriphenone and 2-hendecanone were prepared by the free radical addition of acetophenone and acetone, respectively, to 1-octene. 7-Hexadecanol and 3-dodecanol were prepared from heptaldehyde and propionaldehyde using the appropriate Grignard reagents. The alcohols were oxidized to their respective ketones in a dichromate-acetic acid media.

Many reactions of propylene oxide are not included, since no definite products could be identified. Irradiation of propylene oxide with a U.V. light source for periods of 96 and 168 hours produced essentially no reaction. Irradiation of the epoxide in the presence of t-butyl peroxide for 42 hours gave a trace of high molecular weight telomer. Similar results were obtained when an equimolar mixture of benzene and propylene oxide were irradiated in the presence of t-butyl peroxide. The reaction of propylene oxide with benzoyl peroxide produced a high melting telomer. It was also determined that propylene oxide would not undergo reaction at 150° in the absence of peroxide. Thus, a wall reaction is not involved in the formation of the epoxy radicals.

In order to determine the effect of ring size on the reactivity of cyclic ethers a study on the reactivity of various epoxides and cyclic ethers towards t-butoxy radicals was undertaken at $135 \pm 1°$ using the gas chromatographic technique described in the experimental section. This is illustrated by the general reaction of t-butyl peroxide with an active hydrogen compound (RH).

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{k_1} 2(CH_3)_3CO\cdot \tag{1}$$

$$(CH_3)_3CO\cdot + RH \xrightarrow{k_2} (CH_3)_3COH + R\cdot \tag{2}$$

$$(CH_3)_3CO\cdot \xrightarrow{k_3} (CH_3)_2CO + CH_3\cdot \tag{3}$$

$$2R\cdot \xrightarrow{k_4} \text{Termination} \tag{4}$$

From the above reaction sequence the rate of formation of t-butyl alcohol is given by:

$$\frac{d[ROH]}{dt} = k_2 [RH] [(CH_3)_3CO\cdot] \tag{5}$$

and the rate of formation of acetone is given by:

$$\frac{d[Acetone]}{dt} = k_3 [(CH_3)_3CO\cdot] \tag{6}$$

integrating (5) and (6) and dividing (5) by (6) we obtain:

$$\frac{[ROH]}{[Acetone]} = \frac{k_2 [RH]}{k_3} \tag{7}$$

or

$$\frac{\text{Observed Ratio}}{[RH]} = k_2/k_3 \tag{8}$$

Thus, the reactivities toward t-butoxy radicals were obtained by dividing the concentration of reactant (moles/liter) into the observed alcohol:acetone ratios according to

equation (8). Similar studies have been carried out by Williams et al.[10] and Brook.[11] The reactivity studies are summarized in Table 2 and have been calculated relative to benzene. The results indicate that the 5- and 6-membered cyclic ethers undergo hydrogen atom abstraction most readily. Trimethylene oxide, propylene oxide, and

TABLE 2. RELATIVE REACTIVITIES OF EPOXIDES AND CYCLIC ETHERS TOWARD
TERT-BUTOXY RADICALS[a]

Reactant	Moles/liter of reactant	Mole ratio of reactant/ peroxide	Ratio of t-butyl alcohol/acetone	k_2/k_3[b]	k_2/k_3 relative to benzene
Benzene	10·00	49·6	0·32	0·032	1·0
Trimethylene oxide	12·63	50·3	0·57	0·045	1·4
Tetrahydrofuran	10·95	50·9	5·10	0·47	15·7
Tetrahydropyran	8·92	46·1	4·00	0·45	15·0
1,2-Epoxy-3- phenoxypropane	6·58	51·9	1·20	0·18	6·0
1,2-Epoxybutane	10·46	51·9	0·84	0·08	2·7
1,2-Epoxyoctane	5·41	49·5	1·16	0·21	7·0
4-Methyl-3,4- epoxy-2-pentanone	7·71	46·4	0·76	0·10	3·3
Styrene oxide	4·10	47·6	1·40	0·34	10·6
Propylene oxide	12·65	53·2	0·45	0·035	1·1

[a] All volumes were corrected for expansion using calibrated volumetric ampoules.
[b] $k_2/k_3 = $ [t-C_4H_9OH]/[acetone] [reactant].

1,2-epoxybutane are similar to benzene in reactivity. 1,2-Epoxyoctane and 1,2-epoxy-3-phenoxypropane are intermediate in reactivity while styrene oxide, which contains a benzylic hydrogen, was the most reactive epoxide.

DISCUSSION OF RESULTS

The t-butyl peroxide induced addition of epoxides to 1-octene appears to occur by a free radical chain mechanism which also involves a free radical rearrangement. Since only ketones and no aldehydes were identified as products, the chain transfer atom is presumably the tertiary hydrogen atom alpha to the oxygen atom. It should also be noted that in the absence of olefin the peroxide induced decomposition of propylene oxide and 1,2-epoxybutane did not lead to either propionaldehyde or butyraldehyde.[12] Thus, hydrogen atom abstraction appears to occur preferentially at the tertiary position. This has also been observed by Walling and Fredricks[13] in their studies on the low temperature radical reactions of chlorine and t-butyl hypochlorite with propylene oxide. The products also indicate that the intermediate epoxy radicals undergo decyclization to alpha keto radicals before the olefin addition step. Chain termination probably occurs by disproportionation since the I.R. spectra of the products showed a trace of carbon-carbon unsaturation at 6·15 μ. The following

[10] A. L. Williams, E. A. Oberright, and W. T. Brooks, J. Amer. Chem. Soc. 78, 1190 (1956).
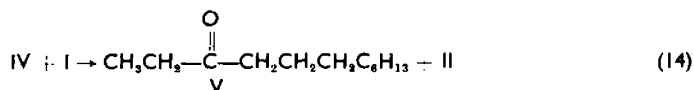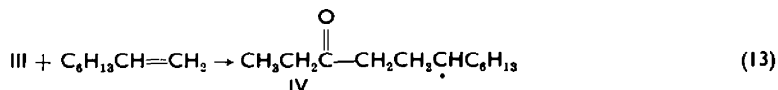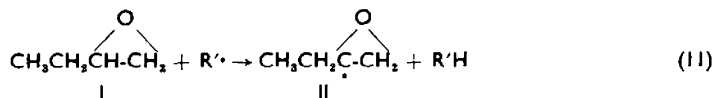[11] J. H. T. Brook, Trans Faraday Soc. 53, 327 (1957).
[12] E. C. Sabatino, Ph. D. Dissertation, University of Connecticut (1963).
[13] C. Walling and P. S. Fredricks, J. Amer. Chem. Soc. 84, 3326 (1962).

reaction scheme with 1,2-epoxybutane is typical:

$$ROOR \rightarrow 2\ RO\cdot \tag{9}$$

$$RO\cdot + R'H \rightarrow ROH + R'\cdot \tag{10}$$

where $R'H$ = olefin

$$CH_3CH_2\overset{O}{\overset{/\backslash}{CH\text{-}CH_2}} + R'\cdot \rightarrow CH_3CH_2\overset{O}{\overset{/\backslash}{\underset{\cdot}{C}\text{-}CH_2}} + R'H \tag{11}$$

$$I \qquad\qquad II$$

$$II \rightarrow CH_3CH_2\overset{O}{\overset{\Vert}{-}C}-CH_2\cdot \tag{12}$$

$$III$$

$$III + C_6H_{13}CH\!\!=\!\!CH_2 \rightarrow CH_3CH_2\overset{O}{\overset{\Vert}{C}}-CH_2CH_2\underset{\cdot}{C}HC_6H_{13} \tag{13}$$

$$IV$$

$$IV + I \rightarrow CH_3CH_2\overset{O}{\overset{\Vert}{-}C}-CH_2CH_2CH_2C_6H_{13} + II \tag{14}$$

$$V$$

$$2\ IV \rightarrow \text{Termination} \tag{15}$$

Since the yields of the 1:1 addition products are low, the chain transfer step (Eq. 14) probably does not occur to any appreciable extent.

The rearrangement of the intermediate epoxy radicals to keto radicals was suggested by the products reported in the vapor phase decomposition studies on epoxides.[4-9] These results are in agreement with recent data obtained from the peroxide induced decomposition of cyclic acetals[14,15] and the peroxide induced addition of 4-, 5- and 6-membered cyclic ethers to 1-octene.[1] The last series of compounds also yielded ketones as products apparently by a rearrangement to aldehydo radicals before the olefin addition step. The rearrangement of the intermediate epoxy radicals (Eq 11) is also consistent with the conclusion of Walling and Fredricks[13] who have suggested that the ring opening reaction predominates at higher temperatures. As shown in Table 1, this is especially true in the case of propylene oxide. The present results are also similar to those obtained with acyclic ethers, since butyl ether in the presence of 1-octene and t-butyl peroxide yielded 4-dodecanone as one of the major products.[16] The ketone arises by decomposition of the intermediate ethereal radicals to butyl radicals and butyraldehyde. The latter then adds to 1-octene by a free radical chain reaction. In addition, Aldridge et al.[17] have recently shown that the peroxide induced decomposition of dimethoxymethane resulted in the formation of methyl formate. They found that at least 80% of the intermediate ethereal radicals were formed at the methylene position. Thus, it appears that the formation of carbonyl derivatives from ethereal radicals is energetically favorable. In the case of the epoxides, preferential attack on the carbon atom of the ring is apparently due to the greater electron density around the oxygen atom which stabilizes the initially formed epoxy radicals to some extent. Undoubtedly, some radical attack does occur on other parts

[14] E. S. Huyser, *J. Org. Chem.* **25**, 1820 (1960).

[15] E. S. Huyser and Z. Garcia, *J. Org. Chem.* **27**, 2716 (1962).

[16] C. H. McDonnel, Ph.D. Dissertation, University of Chicago (1954).

[17] C. L. Aldridge, T. B. Zachry, and E. A. Hunter, *J. Org. Chem.* **27**, 47 (1962).

of the molecule but this appears to be minor. Any products or telomers resulting from such attack may be present in the higher boiling fractions.

The formation of 5-hydroxy-2-hexanone from propylene oxide, though in low yield, is significant since it represents a new type of free radical reaction in which acetonyl radicals add to the epoxide ring to give an alkoxy radical. Details of this reaction and its generality with other active hydrogen compounds have been discussed previously.[2] Further work on this type of reaction is in progress. A similar reaction scheme has been invoked to explain the opening of the cyclopropane ring of spiropentane in the presence of chlorine atoms.[18]

The reactivity studies on the cyclic ethers indicate that the ease of hydrogen atom abstraction by t-butoxy radicals is $5 \approx 6 \gg 4 > 3$. This is in good agreement with the results of Gordon and Smith[19] and Hart and Wyman[20] who found that the ease of radical formation from cycloalkanes and bis-cycloalkylformyl peroxides decreased markedly in going from the cyclohexyl to the cyclopropyl group. This is apparently due to the enhanced bond strengths of the carbon-hydrogen bonds in the epoxides and trimethylene oxide and can be considered as follows: the bond angles in the 3- and 4-membered rings are considerably less than the normal carbon-carbon bond angles of $109°$; therefore, the p-character of the carbon-hydrogen bond is diminished and the s-character is increased so that the bond approaches sp^2 hybridization. The formation of the epoxy and trimethyleneoxy radicals would be analogous to the difficult formation of a vinyl radical from ethylene or a phenyl radical from benzene in which the carbon-hydrogen bonds are sp^2 in character. For this reason, propylene oxide, 1,2-epoxybutane and trimethylene oxide are comparable to benzene in reactivity.

The high molecular weight epoxides are of interest because of their greater reactivity. Abstraction of a hydrogen atom from styrene oxide results in a benzyl type radical which is stabilized by resonance. The stability of this radical may inhibit the formation of the acetophenyl radical, thus accounting for the low yield of capriphenone obtained. A phenoxy group appears to stabilize the intermediate epoxy free radical to some extent. The reactivity of 1,2-epoxyoctane is high because of the long alkyl chain which apparently is attacked to a considerable extent by t-butoxy radicals. The low reactivity of 4-methyl-3,4-epoxy-2-pentanone is noteworthy for it indicates that a carbonyl group does not activate the hydrogen atom on the epoxide as well as a phenyl group.[21] The greater reactivity of tetrahydrofuran and tetrahydropyran partly explains the higher yields of ketonic products previously obtained from these compounds in comparison to trimethylene oxide and the epoxides.[1]

<div align="center">EXPERIMENTAL[22]</div>

Reagents. The following materials were distilled through a 14 in. column equipped with a tantalum-wire spiral before use: t-butyl peroxide (Lucidol Corp., b.p. 40° at 65 mm, n_D^{20} 1·3893); acetone (commercial grade, b.p. 56°, n_D^{20} 1·3618); t-butyl alcohol (commercial grade, b.p. 83°, n_D^{20}

[18] D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Amer. Chem. Soc.* **82**, 2368 (1960).
[19] A. S. Gordon and S. R. Smith, *J. Phys. Chem.* **66**, 521 (1962).
[20] H. Hart and D. P. Wyman, *J. Amer. Chem. Soc.* **81**, 4891 (1959).
[21] C. Walling, *J. Phys. Chem.* **64**, 166 (1960).
[22] All m.p.'s and b.p.'s are uncorrected. The elemental analyses were determined by Gellar Laboratories, Bardonia, N.Y. and Drs. Weiler and Strauss, Microanalytical Laboratory, Oxford, England.

1·3878); propionaldehyde (Eastman Co. technical grade, b.p. 49°, n_D^{20} 1·3635); heptaldehyde (Matheson Co., b.p. 68–70° at 47 mm, n_D^{20} 1·4272); 1-octene (Matheson, Coleman, and Bell, b.p. 121° n_D^{20} 1·4088); styrene oxide (Dow Chemical Co., b.p. 64° at 6 mm, n_D^{20} 1·5359); propylene oxide (Fischer Scientific Co., b.p. 36°, n_D^{20} 1·3658); trimethylene oxide (K & K Labs., b.p. 46°, n_D^{20} 1·3662); 1,2-epoxy-3-phenoxypropane (Matheson, Coleman and Bell, b.p. 61–62° at 0·50 mm, n_D^{20} 1·5305); tetrahydrofuran (Matheson, Coleman and Bell, b.p. 64–66°, n_D^{20} 1·4061); tetrahydropyran (Matheson, Coleman and Bell, b.p. 86–88°, n_D^{20} 1·4209); benzene (commercial grade, b.p. 80°, n_D^{20} 1·5014); 1,2-epoxyoctane (Matheson, Coleman and Bell, b.p. 74–75° at 45 mm, n_D^{20} 1·4144); mesityl oxide (Eastman Co., yellow label, b.p. 138°, n_D^{20} 1·4099); 1-propanol (Fischer Scientific Co., b.p. 97–98°, n_D^{20} 1·3855); cyclohexane (Fischer Scientific Co., b.p. 81°, n_D^{20} 1·4290); and toluene (commercial grade, b.p. 111°, n_D^{15} 1·4981). With the exception of 1,2-epoxybutane all other reagents were used without further purification after ascertaining that they were sufficiently pure.

A mixture of isomeric epoxybutanes (Dow Chemical Co.) was distilled through an 80-plate concentric tube Podbielniak column (Model No. 2208). 2,3-Epoxybutane distilled at 56–57° (n_D^{20} 1·3815) and 1,2-epoxybutane distilled at 58·5–59° (n_D^{20} 1·3832). The isomers were further characterized by their I.R. spectra. The spectra of each isomer was not an exact fingerprint and the 1,2-epoxybutane had the weakest C-methyl band at 7·25 microns.

Preparation of 4-methyl-3,4-epoxy-2-pentanone

This was prepared in 44·2% yield from the base catalyzed reaction of hydrogen peroxide with mesityl oxide according to the method of Payne[23] (b.p. 61–62° at 20 mm, n_D^{20} 1·4235, mol. wt. 114, calcd. 115, reported b.p.[23] 60–62° at 20 mm, n_D^{20} 1·4238).

The free radical reaction of 1,2-epoxyoctane with 1-octene and t-butyl peroxide

Two moles of 1,2-epoxyoctane (256 g), 0·40 mole 1-octene (48·8 g) and 0·06 mole of t-butyl peroxide (10 ml) were placed in a flask equipped with a condenser and mercury bubbler. The reaction mixture was deaerated with nitrogen and heated at 145° for 3 hr. The reaction mixture was then distilled through a 14 in. tantalum-wire spiral column to remove the peroxide decomposition products, unreacted epoxide, and 1-octene. The remainder was distilled through a Metroware column under red press (0·10 mm) to remove the 1:1 adduct from the telomer. The 1:1 product was redistilled through an 8 in. tantalum-wire spiral column to give 7·41 g 7-hexadecanone (b.p. 82° at 0·10 mm, n_D^{20} 1·4432, 7·7% yield based on 1-octene, mol. wt. 242, calc. 240). An I.R. spectrum of the product (γ_{max} 5·85 μ) was similar to that of an authentic sample of 7-hexadecanone. A residue (10·1 g n_D^{20} 1·4700, mol. wt. 535) remained. The product failed to give a positive ketone test with 2,4-dinitrophenylhydrazine solution and hydroxylamine hydrochloride-indicator solution.[24] (Found: C, 80·02; H, 13·10; Calc. for $C_{16}H_{32}O$: C, 79·92; H, 13·48%.) Attempts to isolate a semicarbazone were unsuccessful. Previous workers also failed to report a solid derivative of this compound.[25]

The structure of the ketone was established by gas chromatography. A gas chromatogram of the product (10 ft 30% silicone column, 216°, 10 lb. He) and a mixture of the two gave a major peak with a retention time of 17 min and a very slight peak after 24 min. A sample of 7-hexadecanone made by an unequivocal synthetic method and a mixture of the two gave a peak with a retention time of 17 min under the same conditions.

The free radical reaction of 1,2-epoxybutane with 1-octene and t-butyl peroxide

Two moles of 1,2-epoxybutane (144 g), 0·40 mole 1-octene (48·8 g) and 0·06 mole of t-butyl peroxide (10 ml) were placed in a deaerated Parr autoclave and heated at 145° for 3 hr. The reaction mixture was distilled in the previously described manner to yield 3·43 g 3-dodecanone (b.p. 65° at 0·15 mm, n_D^{20} 1·4425, mol. wt. 200, calc. 184, γ_{max} 5·85 μ, 3·0 μ). A residue (25·3 g, n_D^{20} 1·4705, mol. wt. 466) remained. A hydroxylamine hydrochloride-indicator test[24] was negative and a semicarbazone could not be obtained. A gas chromatogram of the product (10 ft. 30% silicone column, 194°, 5 lb. He) gave a peak with a retention time of 26 min and a slight peak after 29 min. A gas chromatogram of a sample of 3-dodecanone prepared by an unequivocal synthetic method and a mixture of the two

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

[24] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds* p. 120. John Wiley, New York, N.Y. (1956).

[25] F. Whitmore, J. N. Cosby, W. S. Sloatman, and D. G. Clarke, *J. Amer. Chem. Soc.* **64**, 1801 (1942).

also gave a peak with a retention time of 26 min under the same conditions. The higher boiling material was probably ketonic telomer since the I.R. spectra of the product and authentic material were very similar. From the relative peak heights the assumed 1:1 adduct contains 90% 3-dodecanone (3·10 g, 4·2% yield based on 1-octene). (Found: C, 77·92; H, 12·86; Calc. for $C_{12}H_{24}O$: C, 78·15; H, 13·13%.)

The free radical reaction of styrene oxide with 1-octene and t-butyl peroxide

Two moles of styrene oxide (240 g), 0·20 mole 1-octene (22·4 g) and 0·03 mole t-butyl peroxide (5 ml) were placed in a deaerated flask equipped with condenser and mercury bubbler and heated at 150° for 3 hr. The reaction mixture was distilled as before to give 3·10 g capriphenone (b.p. 120–128° at 0·50 mm, n_D^{20} 1·4975, mol. wt. 250, calc. 232). A residue (6 g) was recovered. An I.R. spectrum of the product (γ_{max} 5·85 μ) was similar to an authentic sample of capriphenone. A gas chromatogram of the product (10 ft. silicone column, 235°, 10 lb. He) gave one major peak with a retention time of 10 min (2·5 in.) and two minor peaks with retention times of 9 min and 13 min. A chromatogram of an authentic sample of capriphenone and a mixture also gave a peak with a retention time of 10 min under the same conditions. The relative peak heights indicate the product was about 95% pure (2·95 g, 6·6% yield based on 1-octene).

The free radical reaction of 1,2-epoxy-3-phenoxypropane with 1-octene and t-butyl peroxide

One mole of 1,2-epoxy-3-phenoxypropane (150 g), 0·10 mole 1-octene (11·2 g) and 0·03 mole of t-butyl peroxide were placed in a flask equipped with a condenser and a mercury bubbler, deaerated with nitrogen and heated at 150° for 5 hr. The reaction mixture was distilled to give 4·45 g of solid material (b.p. 170–200° at 1 mm). A residue (3·50 g) remained. The solid was recrystallized 4 times from pet ether (m.p. 83°, mol. wt. 527, γ_{max} 5·85 μ). This product appears to be a mixture of 2:1 (mol. wt. 486) and 3:1 (mol. wt. 598) addition products.

The free radical reaction of propylene oxide with 1-octene and t-butyl peroxide

Run I. Three moles of propylene oxide (174 g), 0·20 mole of 1-octene (22·4 g) and 0·015 mole t-butyl peroxide (2·5 ml) were placed in a deaerated stainless steel bomb and heated at 125° in a silicone oil bath for 17 hr. The reaction mixture was distilled to give 2·62 g of product (b.p. 60–90° at 0·10 mm, n_D^{20} 1·4520, mol. wt. 120·7, calc. 116·2). A residue (2·33 g, mol. wt. 640) remained in the pot. An I.R. spectrum of the product (γ_{max} 3·0, 5·85 μ) suggested the product was an hydroxyketone (5-hydroxy-2-hexanone).

Elemental analysis of the product was inconclusive and since no solid derivative of the product could be isolated, gas chromatography was used as a proof of structure. A gas chromatogram of the product (197°, 10 ft 30% silicone column, 5 lb. He) yielded a major peak after 3·75 min and a minor peak after 4 min. A gas chromatogram of an authentic sample of 5-hydroxy-2-hexanone gave a peak with a retention time of 3·75 min under the same conditions. An equal mixture of the two gave one peak and the peak height was essentially doubled. This evidence in addition to the I.R. indicates the major product to be 5-hydroxy-2-hexanone and the relative peak heights indicate about 80% purity (2·1 g, 0·6% yield). Attempts to isolate or identify the minor component were unsuccessful.

Run II. Two moles of propylene oxide (116 g), 0·20 mole of 1-octene (22·4 g) and 0·03 mole of t-butyl peroxide (5 ml) were placed in a deaerated Parr bomb and heated at 150° for 2 hr. The reaction mixture was distilled through a 14 in. tantalum-wire spiral column to give 5·34 g of product (b.p. 62–70° at 0·26 mm, n_D^{20} 1·4368, mol. wt. 211). A residue of 11·2 g (n_D^{20} 1·4595, mol. wt. 324) remained. An I.R. spectrum of the product (γ_{max} 3·0, 5·85 μ) indicated the presence of an hydroxyketone. A hydroxylamine hydrochloride-indicator test was negative and a semicarbazone could not be isolated from the mixture. A gas chromatogram of the mixture (10 ft silicone column, 195°, 5 lb. He) gave two major peaks with retention times of 4 min and 28 min and a slight peak at 10 min. Separate chromatograms of 5-hydroxy-2-hexanone and 2-hendecanone gave peaks with the respective retention times of 4 min and 28 min under the same conditions. A chromatogram on two separate mixtures of the product fraction with the authentic compounds also gave peaks at 4 min and 28 min, the peak heights being increased in each mixture. From the relative peak heights the ratio of 5-hydroxy-2-hexanone to 2-hendecanone was 4:1 or 4·27 g of 5-hydroxy-2-hexanone (2% yield based on epoxide) and 1·07 g of 2-hendecanone (3% yield based on 1-octene). The peak at 10 min was not identified.

Run III. Two moles of propylene oxide (116 g), 0·10 mole of 1-octene (11·2 g) and 0·12 mole of t-butyl peroxide (20 ml) were placed in a deaerated Parr bomb and heated at 200° for 1 hr. Distillation of the reaction mixture in the previously described manner yielded 4·80 g of product (b.p. 50–57° at 0·26 mm, n_D^{20} 1·4370, mol. wt. 175·6 calc. 170, γ_{max} 3·0, 5·85 μ). A residue (10·2 g n_D^{20} 1·4622, mol. wt. 349) remained. Gas chromatographic analysis under the same conditions used in Run II yielded the same retention times for each product and indicated that the ratio of the ketone to hydroxyketone was 4:1 or 3·84 g 2-hendecanone (23·4% yield based on 1-octene) and 0·96 g 5-hydroxy-2-hexanone (0·4% yield based on epoxide). After 3 attempts a semicarbazone of 2-hendecanone was isolated. m.p. 118–120° (reported m.p.[26] 119–121°). A mixed m.p. was not depressed.

The preparation of 5-hydroxy-2-hexanone

5-Hydroxy-2-hexanone was synthesized according to the method of Adams and Vanderwerf[27] and obtained in 52·8% yield (b.p. 40–42° at 0·50 mm, n_D^{25} 1·4330, mol. wt. 112, calc. 116, reported b.p.[27] 79–82° at 16 mm, n_D^{25} 1·4312).

Determination of the relative reactivities

Tetrahydrofuran, tetrahydropyran, cyclohexane, benzene, and toluene were distilled through an 80-plate concentric tube Podbielniak column before use. The other compounds studied were distilled through a 14 in. column equipped with a tantalum-wire spiral before use.

The following procedure was used for each compound studied: about a 50:1 molar ratio of reactant to t-butyl peroxide was weighed in a glass ampoule on an analytical balance. All samples were cooled in a carbon tetrachloride-chloroform dry ice bath, flushed with argon, and sealed. The samples were placed in an oil bath at 135 ± 1° for 40 hr which corresponds to at least 98% decomposition of the peroxide. After cooling in the above mentioned cooling bath, the seals were broken, and the contents analyzed by gas chromatography to obtain the necessary rate constant ratios. It was previously determined that the ratios were accurate to 1%.

Gas chromatography conditions employed in relative reactivity studies

The gas chromatographic unit (Aerograph Master A-100, Wilkins Instrument and Research Inc., Walnut Creek, Calif.) was equipped with a Speedomax Graphic Recorder (Model S 60,0000 Series, Leeds and Northrup Co., Philadelphia, Pa. 1 m.v.). The recorder was equipped with a Disc Integrator (Model K 3-1, Disc. Instrument Co., Santa Anna, Calif.). The unit was operated under the following conditions: (10 ft. 10% Ucon Polar column, 5 lb. He, 200 m.a., 89°).

[26] H. D. Dakin, *J. Amer. Chem. Soc.* **44**, 47 (1910).
[27] R. M. Adams and C. D. Vanderwerf, *J. Amer. Chem. Soc.* **72**, 4368 (1950).