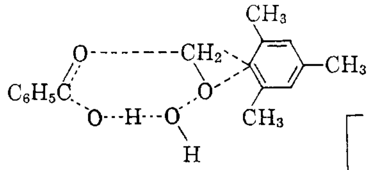
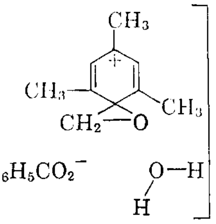


A



B

water molecule (equation 3), but may react with other nucleophiles in the system, benzoic acid in this instance.

Also, formation of III precludes extensive participation of equation 4 as a chain propagation step[7,8]

$$\text{II} + \text{Mes CH}_2\text{OOH} \longrightarrow \text{Mes OCH}_2\text{OH} + \text{Mes CH}_2\text{O}^+ \quad (4)$$

in the decomposition.

Experimental

Decomposition Experiments.—The thermal decompositions of I were conducted in an inert atmosphere as previously described.[1] For the acid-catalyzed decomposition, 120 mg. of I in 5 ml. of aqueous ethanol was decomposed with 0.1 ml. of concentrated hydrochloric acid at room temperature for 16 hr. After dilution with water and solvent extraction, there was obtained 97 mg. of a white solid which was mainly mesitol.

2,4,6-Trimethylbenzyl Hydroperoxide (I).—The Grignard reagent was prepared in *ca.* 70% yield from the slow addition of 16.8 g. (0.1 mole) of 2,4,6-trimethylbenzyl chloride in 200 ml. of ether to 10.1 g. of magnesium and 100 ml. of ether at 0°. A portion of the Grignard solution (80 ml., *ca.* 0.019 mole) was added over a period of 2 hr. to 100 ml. of ether which was continuously saturated at −78° with a stream of dry oxygen. The mixture was warmed to 0°, poured into ice water and acidified to pH 8.5–9 with carbon dioxide gas. The ether layer was separated and extracted with ice-cold sodium hydroxide solution. After acidification with carbon dioxide, ether extraction, and solvent evaporation, there remained *ca.* 1 g. of a peroxidic solid. Two recrystallizations from methylcyclohexane gave 0.4 g. (0.0024 mole, 13% yield) of white solid,[11] melting at 84–89° with slight decomposition.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H. 8.49; active oxygen, 9.64%. Found: C, 72.6; H, 8.3; active oxygen, 9.5%.

Material of comparable purity was obtained in much higher yield by chromatography of the base extract on a Cellulose–dimethylformamide[5] column. One recrystallization from methylcyclohexane gave a 30% yield of material melting at 86–89°.

Mesitoxymethyl Benzoate (III).—A mixture of 0.46 g. of 2,4,6-trimethylbenzyl hydroperoxide and 1.24 g. of benzoic acid was heated to 134° for 3 hr. After the product was extracted with sodium carbonate solution, there remained 0.59 g. of an oil which solidified on standing. Recrystallization from pentane gave m.p. 71.5–71.7°.

Anal. Calcd. for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71; sapon. equiv., 270. Found: C, 75.6; H, 6.9; sapon. equiv., 274.

From saponification of 0.12 g. of III, there were isolated 60 mg. of mesitol, m.p. 72.5–73.0°, mixture m.p. with authentic mesitol, 73.0–73.5°; and 40 mg. of benzoic acid, m.p. 118–123°. The acidified aqueous solution yielded a 2,4-dinitrophenylhydrazone, m.p. 165–166.5°, alone and mixed with authentic formaldehyde 2,4-dinitrophenylhydrazone.

Acknowledgment.—The author is indebted to L. C. Jennings for much of the experimental work, to N. F. Chamberlain and his associates for the n.m.r. spectra and their interpretation, and to Dr. F. C. Stehling and co-workers for the MS analyses.

[11] R. Hüttel, H. Schmid, and H. Ross, *Ber.*, **92**, 699 (1959), report the synthesis of an oil which is *ca.* 70% I.

The Free Radical Chemistry of Cyclic Ethers. III. A Free Radical Rearrangement Reaction[1]

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Received January 22, 1962

The mechanism of the *tert*-butyl peroxide-induced free radical addition of four-, five-, and six-membered cyclic ethers to 1-octene has been clarified. Ketones in addition to ethers were identified as the major products from all reactions studied. Thus, the chain transfer atom is the hydrogen atom alpha to the oxygen atom. The products also suggest that the intermediate alpha-ethereal radicals undergo decyclization. The infrared spectra show a trace of carbon-carbon unsaturation indicating that disproportionation is the chain termination step. The mechanistic implications of these results are discussed.

Previous work on the free radical chemistry of four-, five- and six-membered cyclic ethers has been limited to thermal decomposition and ultraviolet initiated reactions. In 1937, Kuchler and Lambert[3] demonstrated that the homogeneous thermal decomposition of *p*-dioxane proceeds mainly by a chain reaction. A similar study was carried out by Klute and Walters[4] on the thermal decomposition

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[1] Part II and a previous communication on this work have appeared, T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **26**, 5256 (1961).

[2] Present address: Esso Research & Engineering Company, Process Research Division, Linden, New Jersey. Abstracted from the Ph.D. dissertation of T. J. Wallace, June, 1960.

[3] L. Kuchler and J. Lambert, *Z. physik. Chem.* (Leipzig), **B37**, 285 (1937).

[4] C. H. Klute and W. Walters, *J. Am. Chem. Soc.*, **68**, 506 (1946).

TABLE I

REACTION CONDITIONS USED AND PRODUCTS ISOLATED FROM THE CYCLIC ETHERS STUDIED

Reactant (moles)	1-Octene, moles, % conv.	*tert*-Butyl peroxide, mole	Time, hr. temp., deg.	Product, % yield,[a] conv. %[b]	Residue, g., mol. wt.
Tetrahydrofuran (1.3)	0.25, 52	0.03	2 150	4-Dodecanone 41, 79	6, 475
Tetrahydrofuran (2.0)	.20, 35	.06	5 150	4-Dodedanone and 2-octyltetrahydrofuran 12, 67	18.1
Tetrahydrofuran (0.626)	.32	.0003	24 135	4-Dodecanone and 2-octyltetrahydrofuran	. . .
Tetrahydrofuran (0.626)	.0604	.0003	24 135	4-Dodecanone and 2-octyltetrahydrofuran	. .
Tetrahydropyran (1.5)	.20, 79	.06	2 150	5-Tridecanone 39, 49	9
Tetrahydropyran	.154, 40	.03	2 150	5-Tridecanone and 2-octyltetrahydropyran 10, 25	5.5
Trimethylene oxide	.20, 25	.03	2 145	3-Hendecanone 14, 65	19, 578

[a] Based on the total amount of 1-octene used. [b] Based on the amount of 1-octene converted to product.

of tetrahydrofuran at about 550°. Recently, reactions involving the isomerization and dehydrogenation of 2-methyltetrahydrofuran at 300–400° over platinum and other metals on activated charcoal were studied.[5] The reaction appears to have some radical character since 2-pentanone was obtained in 65–70% yields. A similar reaction occurred when *m*-dioxane was passed over pumice.[6]

The photoreaction of *p*-dioxane has been studied by Pfordte,[7] who isolated the dimer of *p*-dioxane indicating that the alpha carbon-hydrogen bond undergoes homolytic cleavage under these conditions. This is also true in the case of acyclic ethers.[8] In the photochemical chlorination of tetrahydrofuran, alpha carbon-hydrogen bond cleavage also occurs to give 2-chloro- and 2,5-dichlorotetrahydrofuran.[9] Based on these studies, one would expect that the alpha carbon-hydrogen bonds in cyclic ethers would be most reactive toward *tert*-butoxy radicals and intermediate alkyl radicals. The present study was undertaken to confirm this assumption and also to identify the intermediate radicals resulting from hydrogen atom abstraction.

Results

The *tert*-butyl peroxide-induced free radical addition of four-, five-, and six-membered cyclic ethers to 1-octene has been studied in the temperature range of 145 to 150°. In the case of tetrahydrofuran and tetrahydropyran; 4-dodecanone and 2-octyltetrahydrofuran, and 5-tridecanone and 2-octyltetrahydropyran were found to be the 1:1 addition products, respectively, with the ketone the dominant product. With trimethylene oxide the main product was 3-hendecanone. The individual reaction conditions and product yields are summarized in Table I. All compounds were identified by gas chromatography and infrared by comparison to authentic samples of each ketone. With the exception of 4-dodecanone, it was not possible to isolate solid derivatives of the products.

Authentic 4-dodecanone was prepared by the free radical addition of butyraldehyde to 1-octene according to the method of Kharasch, Urry, and Kuderna.[10] Authentic 3-hendecanone and 5-tridecanone were prepared by the free radical addition of 1-propanol and 1-pentanol to 1-octene to give 3-hendecanol and 5-tridecanol, respectively. The alcohols were then oxidized to the respective ketones in dichromate–acetic acid solution. The yields obtained and the reaction conditions employed are summarized in Table II.

TABLE II

COMPOUNDS SYNTHESIZED BY FREE RADICAL METHODS

Reactant (moles)	1-Octene, mole, % conv.	*tert*-Butyl peroxide, mole	Time, hr. temp., deg.	Product (% yield[a])
Butyraldehyde (2.0)	0.40, 69	0.06	2 145	4-Dodecanone (65)
1-Pentanol (2.0)	0.40, 69	0.06	20 130	5-Tridecanol (55)
1-Propanol (2.0)	0.40, 92	0.06	3 145	3-Hendecanol (41)

[a] Based on the amount of 1-octene converted to product.

Discussion of Results

The fact that ketones were identified as products from every reaction indicates that the alpha hydrogen atom in each cyclic ether is the chain transfer atom, and the formation of both ether and

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(5) F. Belskii, N. I. Shuikin, and N. A. Karakhanov, *Dokl. Akad. Nauk. S.S.S.R.*, **138**, 831 (1961).

(6) C. S. Rondestredt, Jr., and C. J. Mantell, *J. Am. Chem. Soc.*, **82**, 6419 (1960).

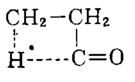
(7) K. Pfordte, *Ann.*, **625**, 30 (1959).

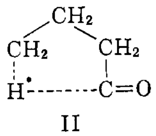
(8) K. Pfordte and G. Leuschner, *ibid.*, **643**, 1 (1961).

(9) H. Gross, *Angew. Chem.*, **72**, 268 (1960).

(10) M. S. Kharasch, W. H. Urry, and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

ketone indicates that some additional reactions are occurring beside the normal olefin addition reaction. The ketones would suggest that one of two possible reaction sequences was involved in these reactions. The first sequence would demand that most of the initial cyclic ethereal radicals undergo decyclization in a manner similar to that proposed by Huyser.[11] This is followed by an intramolecular hydrogen atom transfer *via* intermediates I, II, and III to give aldehydo radicals before addition to 1-octene occurs. This mechanism has been outlined in greater detail in an earlier communication.[2] The second sequence would involve an attack of intermediate free radicals on most of the 2-octylether to give an intermediate radical which decyclizes and chain transfers to give the ketonic products. The second possibility would involve the following additional reactions.


I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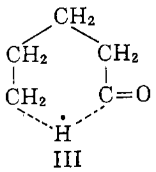
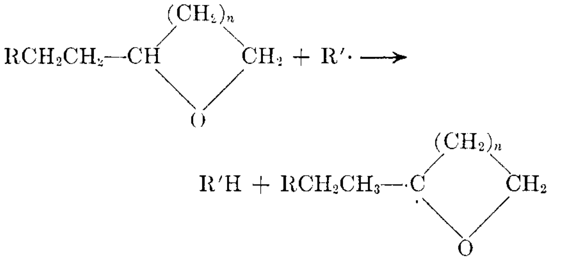
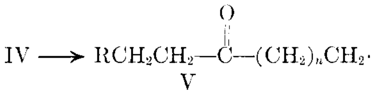

III

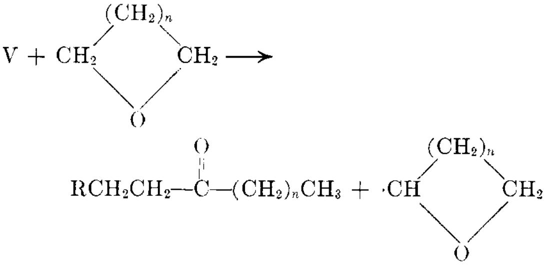

(1)

IV



$$IV \longrightarrow RCH_2CH_2-\overset{O}{\overset{\|}{C}}-(CH_2)_nCH_2\cdot \qquad (2)$$

V


(3)

In addition to the bands for the ketone and ketone and ether, the infrared spectra of the products showed a trace of carbon-carbon unsaturation indicating that chain termination probably occurs by disproportionation.

Abstraction of the alpha hydrogen atoms by *tert*-butoxy radicals and alkyl radicals was expected for the ethers since it is known that acyclic and cyclic ketones, alcohols, and amines all undergo hydrogen atom abstraction at the alpha position.[12] However, the decyclization of the intermediate radicals by electron shifts and the possibility of simultaneous intramolecular hydrogen atom abstruction are unique in cyclic systems of this general type under the reaction conditions employed. Hence, these warrant further discussion.

The decyclization of the intermediate ethereal radicals was suggested by the work of Huyser[11] and of McDonnell[13] who found that butyl ether not only adds to 1-octene at the alpha position but also readily rearranges by an electron shift to give butyraldehyde and butyl radicals (equation 4).

$$C_3H_7\underset{\cdot}{C}HOC_4H_9 \longrightarrow C_3H_7CHO + C_4H_9\cdot \qquad (4)$$

In the presence of excess either and peroxide fragments, these intermediates then add to 1-octene to give 4-dodecanone and dodecane in competing free radical chain reactions. In the cyclic ethers, decyclization should be even more facile once the initial cyclic radical is formed since the carbon-carbon bond angles are deformed from the normal bond angle of 109°. This fact, as well as the nonbonded hydrogen interactions that are present, should make the relative ease of decyclization 4 > 5 > 6 for each cyclic ethereal radical.

Intramolecular transfer reactions similar to those proposed above have been suggested for other free radical reactions and have recently been summarized bp Barton.[14] Barton has brought out that the transition state for rearrangements of this type was usually a six-membered ring, which has also been found to be so in other systems by DeTar,[15] Greene,[16] Rust,[17] and Jenner.[18] However, a transition state involving a five-membered ring has been suggested by Gordon and McNesby[19] and Pritzkau and Dietzsch[20] and a four-membered ring intermediate has been described by both Voevodskii and his co-workers[21] and Reutov and Shatkina.[22] Gordon found that the 1-pentyl radicals formed 2-pentyl radicals and Pritzkau suggested that the predominance of β-attack of free radicals on acids was possibly due to the formation of carboxy radicals which give an intramolecular H-transfer to form the new radical. Reutov found that the 1-

$$RCH_2CH_2CO_2\cdot \longrightarrow R\underset{\cdot}{C}HCH_2CO_2H \qquad (5)$$

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

[12] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, 1957.

[13] C. H. McDonnell, Ph.D. dissertation, University of Chicago, 1954.

[14] D. H. R. Barton and L. R. Morgan, *J. Chem. Soc.*, 622 (1962).

[15] D. F. DeTar and D. I. Relyea, *J. Am. Chem. Soc.*, **76**, 1202 (1954).

[16] F. Greene, *ibid.*, **83**, 2196 (1961).

[17] F. F. Rust and D. O. Collmer, *ibid.*, **76**, 1505 (1954).

[18] E. L. Jenner, *J. Org. Chem.*, **22**, 1031 (1962).

[19] A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **31**, 853 (1959).

[20] W. Pritzkau and K. Dietzsch, *Ber.*, **93**, 1733 (1960).

[21] V. V. Voevodskii, *et al.*, *Dokl. Akad. Nauk. S.S.S.R.*, **81**, 215 (1951).

[22] O. A. Reutov and T. N. Shatkina, *ibid.*, **133**, 381 (1960). See also *Chem. Abstr.*, **54**, 8583c (1960).

propyl-1-C^{14} radical isomerizes to give 4% of the 1-propyl-3-C^{14} radical in carbon tetrachloride, and Voevodskii found that the 1-propyl radical undergoes deuterium exchange at the terminal positions indicating a cyclic radical intermediate is formed in which the terminal positions are equivalent. They suggest that this is due to the nonlinear carbon chain in propane; thus hydrogen transfer from the terminal methyl group is more favored than that from the central carbon atom. They also suggest that the ease of transfer increases with the chain length since the cyclic intermediate becomes more stable. This also seems to be true in the cyclic ethers since the yield of 3-hendecanone from trimethylene oxide is relatively low in comparison to the yields obtained from the five- and six-membered rings.

The data discussed above and the results obtained in the present study are support for both sequences and for a chain mechanism, for appreciable amounts of 2:1 addition products and higher telomers are formed. The latter fact is especially true in the case of trimethylene oxide and is analogous to previous work with butyl ether.[13] These results are significant because they indicate that the alpha carbon-hydrogen bonds in ethers do not act as chain transfer agents as well as those in aldehydes in which 1:1 addition predominates.[10] The absence of aldehyde in the products isolated could possibly be due to this high reactivity of aldehydes toward free radical attack and would be support for the intramolecular mechanism proposed. However, when the results are considered in totality, the second mechanism cannot be ruled out completely. It is anticipated that a determination of the relative reactivities of various cyclic ethers toward *tert*-butoxy radicals may shed further light on this phase of the work.

Experimental

Reagents.—The following materials were distilled through a 14-in. silvered column equipped with a tantalum-wire spiral: *tert*-butyl peroxide (Lucidol Corp., b.p. 40° at 65 mm., $n^{20}\mathrm{D}$ 1.3893); butyraldehyde (Fisher Scientific Co., b.p. 83°, $n^{20}\mathrm{D}$ 1.3843); propionaldehyde (Eastman Co., b.p. 49°, $n^{20}\mathrm{D}$ 1.3635); 1-octene (Matheson, Coleman and Bell, b.p. 121°, $n^{20}\mathrm{D}$ 1.4088); trimethylene oxide (K and K Laboratories, b.p. 46°, $n^{20}\mathrm{D}$ 1.3662); tetrahydrofuran (Matheson, Coleman and Bell, b.p. 64–66°, $n^{20}\mathrm{D}$ 1.4061); tetrahydropyran (Matheson, Coleman and Bell, b.p. 86–88°, $n^{20}\mathrm{D}$ 1.4061); and 1-propanol (Fischer Scientific Co., b.p. 97–98°, $n^{20}\mathrm{D}$ 1.3855).

The Free Radical Reactions of Tetrahydrofuran with 1-Octene and *tert*-Butyl Peroxide.—In a Parr autoclave were placed 1.32 moles of tetrahydrofuran, 0.25 mole of 1-octene (28 g.), and 0.03 mole of *tert*-butyl peroxide (5 ml.). The autoclave was then deaerated, sealed, heated to 150°, and maintained at this temperature for 2 hr. by a Thermocap Relay (Niagra Electron Labs, Andover, New York). The reaction mixture was distilled through a 14-in. column equipped with a tantalum-wire spiral to remove the peroxide decomposition products and unchanged 1-octene. No butyraldehyde was present in these fractions. The remainder was distilled through a Metroware column under reduced pressure to separate the 1:1 adduct from the telomeric products.

The 1:1 adduct was redistilled through a 14-in. tantalum-wire spiral column and 18.7 g. of 4-dodecanone was isolated (b.p. 65–66° at 0.10 mm., $n^{20}\mathrm{D}$ 1.4428, mol. wt., 183.5, calcd. 184.3, 41% yield based on 1-octene).

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.15; H, 13.13. Found: C, 77.99; H, 13.01.

An infrared spectrum of the product indicated a strong carbonyl band at 5.85 μ. A hydantoin prepared according to the method of Speer[23] was isolated after two attempts and melted at 112–114° (reported m.p., 114–115°).[24] A mixture melting point with an authentic sample was not depressed. A total residue of 6 g. was obtained ($n^{20}\mathrm{D}$ 1.4650, mol. wt. 475.5).

When the reaction was carried out with 2.0 moles (144.0 g.) of tetrahydrofuran, 0.2 mole of 1-octene (22.4 g.), and 0.06 mole of peroxide (10 ml.) in the same container for 5 hr. at 150°, both 4-dodecanone and 2-octyltetrahydrofuran were obtained as the products in 67% yield based on conversion. The ketone was the predominant product.

Two similar reactions were run with 0.616 mole of tetrahydrofuran (4.44 g.), 0.0003 mole (50 ul.) of *tert*-butyl peroxide, and one with 0.32 mole (3.59 g.) of 1-octene and the other with 0.0604 mole (0.716 g.) of 1-octene at 135° for 24 hr. These were run in an attempt to get a different ratio of ether to ketone. Gas chromatography showed that the ratio of ether to ketone in the former was 1:5 and in the latter was 1:4.5. There was no significant difference.

The Synthesis of 4-Dodecanone.—Two moles of butyraldehyde (144 g.), 0.40 mole of 1-octene (48.8 g.), and 0.06 mole of *tert*-butyl peroxide (10 ml.) were placed in a deaerated Parr autoclave, heated to 145:, and maintained at this temperature for 6 hr. by a Thermocap Relay. The reaction mixture was distilled as above to yield 35.4 g. of 4-dodecanone (b.p. 48–50° at 0.10 mm. $n^{20}\mathrm{D}$ 1.4318, 48.1% yield, reported b.p. 65° at 0.25 mm., $n^{20}\mathrm{D}$ 1.4318.[12] A hydantoin prepared according to the method of Speer[23] melted at 114–115° (reported m.p. 114–115°).[12] A residue (16.3 g., $n^{20}\mathrm{D}$ 1.4551) remained in the pot.

The Free Radical Reactions of Tetrahydropyran with 1-Octene and *tert*-Butyl Peroxide.—One and one-half moles of tetrahydropyran (129.0 g.), 0.20 mole of 1-octene (22.4 g.), and 0.06 mole of *tert*-butyl peroxide (10 ml.) were heated to 150° in a deaerated autoclave and maintained at this temperature for 6 hr. by a Thermocap Relay. The reaction mixture was treated as above to remove 1:1 adduct from the telomer. The 1:1 adduct was redistilled through an 8-in. tantalum-wire spiral column under reduced pressure to yield 14.8 g. of presumed 5-tridecanone (b.p. 60–62° at 0.15 mm., $n^{20}\mathrm{D}$ 1.4400, 39% yield based on 1-octene, mol. wt. 199, calcd. 198). About 9 g. of residue ($n^{20}\mathrm{D}$ 1.4641) wa obtained. An infrared spectrum of the 1:1 adduct indicated a ketone was present by the band at 5.85 μ.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.77; H, 13.23. Found: C, 79.15; H, 13.29.

Since several attempts to isolate derivatives of the ketone were unsuccessful, gas chromatography was used to prove the structure. A gas chromatogram (Wilkens Instrument and Research Inc., Recorder by Varian Associates) of the adduct (10-ft. silicone column, 183°) yielded a peak with a retention time of 34 min. (8.5 in.). A pure sample of 5-tridecanone had the same retention time when chromatographed under the same conditions. An equal mixture of the 1:1 adduct and 5-tridecanone gave a single peak with the same retention time. Thus, the 1:1 adduct is 5-tridecanone.

When the reaction was carried out with 1.54 moles of tetrahydropyran (132.0 g.), 0.154 mole of 1-octene (17.24 g.), and 0.3 mole of *tert*-butyl peroxide (5.0 ml.), a mixture of products was produced. This mixture was shown to be composed of the 2-octyl ether and 5-tridecanone by infrared

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[23] R. J. Speer and H. R. Henze, *J. Am. Chem. Soc.*, **64**, 522 (1942).

[24] M. S. Kharasch, J. L. Rowe, and W. H. Urry, *J. Org. Chem.*, **16**, 1905 (1951).

and gas chromatographic analysis. Another reaction which used a larger concentration of olefin—10 ml. of tetrahydropyran, 10 ml. of 1-octene, and 0.3 ml. of peroxide—also yielded the mixture of products.

The Preparation of 5-Tridecanone.—Two moles of 1-pentanol (176.3 g.), 0.40 mole of 1-octene (48.8 g.), and 0.06 mole of *tert*-butyl peroxide (10 ml.) were placed in a flask equipped with a condenser and mercury bubbler. The flask was deaerated, heated to 130°, and maintained at this temperature for 20 hr. by a Thermocap Relay. The reaction mixture was distilled as before to produce 33.5 g. of 5-tridecanol (b.p. 60° at 0.16 mm., n^{20}_{D} 1.440, 41.4% yield). A residue (8.5 g., n^{20}_{D} 1.4640) remained in the pot.

In a flask equipped with reflux condenser and stirrer was placed 0.074 mole of potassium dichromate (22 g.). A mixture of 0.074 mole of tridecanol (15 g.), 0.67 mole of acetic acid (40 g.), and 40 ml. of water was added with stirring over an interval of 0.5 hr. The reaction mixture was heated at 50–53° for 3.5 hr., allowed to cool, sodium bicarbonate was added to neutralize the acid, and the organic layer was removed by ether extraction. After removal of the ether, the remainder was distilled through an 8-in. tantalum-wire spiral column and 9.0 g. of 5-tridecanone (b.p. 64–66° at 0.5 mm., n^{20}_{D} 1.4412, 60.1% yield, mol. wt. 202, calcd. 198) was obtained. No derivatives have been reported for this compound. Several attempts to make a semicarbazone were unsuccessful, even though the infrared spectrum showed a strong carbonyl peak. The usual ketone test reagents also gave negative tests.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.77; H, 13.23. Found: C, 78.35; H, 13.28.

The Free Radical Reaction of Trimethylene Oxide with 1-Octene and *tert*-Butyl Peroxide.—One mole of trimethylene oxide (58 g.), 0.20 mole of 1-octene (22.4 g.), and 0.03 mole of *tert*-butyl peroxide (5 ml.) were placed in a deaerated autoclave heated to 145° and maintained at this temperature for 6 hr. by a Thermocap Relay. The reaction mixture was treated in the previously described manner to give 6.50 g. of product (n^{20}_{D} 1.4490, b.p. 60–65 at 0.35 mm., mol. wt. 124, calcd. 116) which was thought to be 3-hendecanone. A residue (19 g., mol. wt. 578) was obtained. An infrared spectrum of the product showed a strong carbonyl band, a slight hydroxyl band, and a slight carbon-carbon unsaturation band. Several attempts to make a semicarbazone were unsuccessful and a positive carbonyl test could not be obtained with hydroxylamine hydrochloride indicator test solution.[25] Proof of structure was established by gas chromatography. A gas chromatogram of the product (5 μl., 10-ft. silicone column, 197°, 5 lb. helium, 200 ma. and a 1-mv. span on the recorder) gave a major peak with a retention time of 20 min. (7.5 in.) and two minor peaks with a retention time of 8 min. (2 in.) and 30 min. (11.25 in.). A gas chromatogram of authentic 3-hendecanone gave a peak with a retention time of 20 min. under the same conditions. A gas chromatogram of an equal mixture of the product and 3-hendecanone (10 μl.) gave a peak with a retention time of 20 min. and the peak height was doubled; thus, the major product is 3-hendecanone. The relative areas indicate the previously distilled material contains approximately 80% 3-hendecanone (5.30 g., 14% yield based on 1-octene). An attempt to isolate any alcohol that might have formed as a side product was made, but none could be obtained.

The Preparation of 3-Hendecanone.—Two moles of 1-propanol (120 g.), 0.40 mole of 1-octene (48.8 g.), and 0.06 mole of *tert*-butyl peroxide (10 ml.) were placed in a Parr autoclave. The reaction mixture was deaerated with argon before the bomb was sealed, heated to 145°, and maintained at this temperature for 3 hr. by a Thermocap Relay. The autoclave was cooled to 15°, the reaction mixture was removed and distilled to produce 25.8 g. of 3-hendecanol (n^{20}_{D} 1.4387, b.p. at 0.15 mm., yield 33%, reported b.p. 117° at 20 mm.,[26] n^{20}_{D} 1.4367) was obtained. A residue (20 g., n^{20}_{D} 1.4660) remained.

In a Morton flask equipped with a reflux condenser and dropping funnel was placed 0.058 mole of potassium dichromate (17.05 g.). To this a precooled mixture (0 to 5°) of 0.058 mole of 3-hendecanol (10 g.) and 40 ml. of glacial acetic acid was added over 0.5 hr. The reaction mixture was allowed to warm to room temperature and subsequently heated to 56° and kept at this temperature for 2 hr. by a Thermocap Relay. The reaction mixture was neutralized with sodium bicarbonate, extracted with ether, and the ether extract evaporated to remove the ether. The high boiling material was distilled through an 8-in. tantalum-wire spiral column under reduced pressure to give 6.0 g. of 3-hendecanone (n^{20}_{D} 1.4300, b.p. 46° at 0.10 mm., reported b.p. 104° at 11 mm.,[26] n^{20}_{D} 1.4295). An infrared spectrum showed a strong carbonyl band at 5.85 μ and a weak hydroxyl band at 3 μ. A semicarbazone melted at 90–91° (reported m.p. 90°).[26]

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