m.p., 104–109°. Recrystallization from 100 ml. of cyclohexane gave 11.3 g. (79%) of 2,5-di-*n*-octylhydroquinone, m.p. 109.0–109.5°. An additional recrystallization from 80 ml. of hexane gave 8 g. of pure product, m.p. 110.5–111.5°. Literature[3] m.p. 109.5–110.5°.

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[CONTRIBUTION FROM THE BALLISTIC RESEARCH LABORATORIES]

Reaction of *t*-Butyl Peroxide with Acetals

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The decomposition of *t*-butyl peroxide in 1,1-diethoxybutane and in 1,1-diisopropoxybutane has been studied in the liquid phase. From the ethyl acetal the major products are ethane, *t*-butyl alcohol, acetaldehyde, ethyl butyrate, ethyl *n*-butyl ether, *n*-butyraldehyde, and 4,5-diethoxyoctane. From the isopropyl acetal the corresponding isopropyl derivatives were obtained. On the basis of the products obtained and their yields a mechanism is proposed which involves the abstraction of a hydrogen atom by a *t*-butoxy radical from a carbon atom of the acetal which is adjacent to oxygen. The new radical which is thus formed decomposes to yield an alkyl radical and a carbonyl-containing compound.

$$R_2\dot{C}OEt \longrightarrow R_2C{=}O + Et^{\cdot}$$

The object of this work was to determine the mode of reaction between alkoxy radicals and acetals. To this end, *t*-butyl peroxide was decomposed in the acetal at 120–140° at an initial concentration of 10 mole % peroxide. On the basis of the products formed a reasonable mechanism is presented which accounts for the experimental results and which is consistent with the known reactions of alkoxy radicals.

From the decomposition of *t*-butyl peroxide in 1,1-diethoxybutane a complex mixture of products was obtained which was successfully separated and analyzed by means of gas chromatography. The results are shown in Table I. The variation in yields from run to run was about ±5%.

TABLE I
PRODUCTS FROM THE DECOMPOSITION OF *t*-BUTYL PEROXIDE IN 1,1-DIETHOXYBUTANE

Compound	Yield[a] Observed	Yield[a] Calcd.
Methane	0.32	0.32
Ethane	1.07	1.25
Butane	0.09	0.09
Acetaldehyde	2.86	2.86
Acetone	0.32	0.32
t-Butyl alcohol	1.7	1.61
n-Butyraldehyde	0.54	0.54
Ethyl *n*-butyl ether	0.61	0.61
Ethyl butyrate	0.92	0.90
4,5-Diethoxyoctane	0.88	0.88

[a] The yield is expressed in moles per mole of peroxide decomposed.

The following reactions satisfactorily account for the products and the observed yields:

$$\underset{1}{(t\text{-BuO})_2} \longrightarrow \underset{2}{2t\text{-BuO}^{\cdot}}$$

$$\underset{0.9}{t\text{-BuO}^{\cdot}} + \underset{0.9}{C_3H_7CH(OC_2H_5)_2} \longrightarrow$$

$$\underset{0.9}{t\text{-BuOH}} + \underset{0.9}{C_2H_7\dot{C}(OC_2H_5)_2}\quad \text{I}$$

$$\underset{0.9}{C_3H_7C(OC_2H_5)_2} \longrightarrow \underset{0.9}{C_3H_7COOC_2H_5} + \underset{0.9}{C_2H_5^{\cdot}}$$

$$\underset{0.72}{t\text{-BuO}^{\cdot}} + \underset{0.72}{C_3H_7CH(OC_2H_5)_2} \longrightarrow$$

$$\underset{0.72}{t\text{-BuOH}} + \underset{0.72}{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}\quad \text{II}$$

$$\underset{1.25}{C_2H_5^{\cdot}} + \underset{1.25}{C_3H_7CH(OC_2H_5)_2} \longrightarrow$$

$$\underset{1.25}{C_2H_6} + \underset{1.25}{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}\quad \text{II}$$

$$\underset{2.9}{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3} \longrightarrow$$

$$\underset{2.9}{CH_3CHO} + \underset{2.9}{C_3H_7CH(OC_2H_5)^{\cdot}}\quad \text{III}$$

$$\underset{.54}{C_3H_7CH(OC_2H_5)^{\cdot}} \longrightarrow \underset{.54}{C_3H_7CHO} + \underset{.54}{C_2H_5^{\cdot}}$$

$$\underset{0.61}{C_3H_7CH(OC_2H_5)^{\cdot}} + \underset{0.61}{C_3H_7CH(OC_2H_5)_2} \longrightarrow$$

$$\underset{0.61}{C_3H_7CH_2OC_2H_5} + \underset{0.61}{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}$$

$$\underset{1.76}{2C_3H_7CH(OC_2H_5)^{\cdot}} \longrightarrow$$

$$\underset{0.88}{C_3H_7CH(OC_2H_5)CH(OC_2H_5)C_3H_7}$$

$$\underset{0.32}{t\text{-BuO}^{\cdot}} \longrightarrow \underset{0.32}{CH_3COCH_3} + \underset{0.32}{CH_3^{\cdot}}$$

$$\underset{0.32}{CH_3^{\cdot}} + \underset{0.32}{C_3H_7CH(OC_2H_5)_2} \longrightarrow$$

$$\underset{0.32}{CH_4} + \underset{0.32}{C_3H_7CH(OC_2H_5)O\dot{C}HCH_3}$$

$$\underset{0.18}{2C_2H_5^{\cdot}} \longrightarrow \underset{0.09}{C_4H_{10}}$$

The arabic numbers under each reactant and product were so chosen that the yield of each product would be as close as possible to the yield observed and that each unstable intermediate formed in a particular step would be completely consumed in a subsequent step. The calculated yield of products obtained in this way which are listed in Table I can be seen to check very well with the observed yield.

The only products derived from the *t*-butoxy radical are *t*-butyl alcohol, methane, and acetone which indicated that the butoxy radical reacts either by hydrogen abstraction from the acetal or by decomposition to yield methyl radical and acetone. It does not combine with another radical. The fact that acetone and methane are obtained in equivalent amounts is evidence that they are derived from the same radical. The sum of the yields of acetone and *t*-butyl alcohol 2.02 checks well with the moles of *t*-butoxy radicals, 2.0, formed from the decomposition of a mole of peroxide. The yield of acetone, 0.32 mole, is comparable to the yield of acetone, 0.39 mole, obtained by previous workers[1] from the decomposition of *t*-butyl peroxide in cumene at 125°.

The *t*-butoxy radical always abstracts a hydrogen from a carbon atom which is adjacent to oxygen. This susceptibility to transfer, of hydrogen atoms on carbon adjacent to oxygen, has also been demonstrated in reactions of radicals derived from benzoyl peroxide with alcohols and aldehydes.[2] The abstraction of a hydrogen from the aldehydic carbon yields radical I which decomposes to give an ethyl radical and ethyl butyrate. The abstraction of hydrogen from methylenic carbon gives radical II which decomposes to give acetaldehyde and radical III. Radical III reacts in three ways: (1) It can decompose to give an ethyl radical and butyraldehyde, (2) It can dimerize to give 4,5-diethoxyoctane, and (3) It can abstract a hydrogen from the solvent to yield ethyl *n*-butyl ether. The hypothesis that these various products are derived from radical II in the manner shown is substantiated by the fact that the yield of acetaldehyde is equal to the sum of yields of butyraldehyde, plus ethyl butyl ether plus twice the yield of diethoxyoctane. There are four hydrogens on methylenic carbon available for abstraction and one hydrogen on the aldehydic carbon. If these hydrogens were of equal reactivity the ratio of acetaldehyde to ethyl butyrate in the products would be 4. The fact that this ratio is actually 3.3 indicates that the hydrogen on the aldehydic carbon is slightly more reactive than the hydrogen on the methylenic carbon. Although, in the sequence of reactions shown above, the hydrogen on the aldehydic carbon is abstracted only by *t*-butoxy radicals (step 2) whereas the alkyl radicals abstract only the hydrogen on methylenic carbon (steps 5, 8, and 11), it is not our intention to imply that the relative reactivities of these hydrogen atoms is any different for reaction with alkyl than for reaction with butoxy radicals.

Several experiments were performed in which *t*-butyl peroxide was decomposed in butyraldehyde diisopropyl acetal. These reactions were carried out at a temperature range which was 10 to 20° higher than the reactions with the diethyl acetal, hence the results are not strictly comparable. The following products and yields were obtained: methane 0.64, propane 1.90, propylene 0.09, acetone 2.25, *t*-butyl alcohol 2.0, butyraldehyde 0.33, isopropyl *n*-butyl ether 0.36, isopropyl butyrate 0.7 and 4,5-diisopropoxyoctane 0.30. The material balance in this reaction is not as good as that obtained in the reaction with the ethyl acetal. It is evident, however, that the same sequence of reactions occurs in both cases. Replacement of the ethyl acetal by isopropyl acetal results in the formation of propane instead of ethane, acetone instead of acetaldehyde, isopropyl butyrate instead of ethyl butyrate, isopropyl butyl ether instead of ethyl butyl ether, and diisopropoxyoctane instead of diethoxyoctane.

The conclusion to be drawn from the above results is that the attack by an alkoxy or an alkyl radical upon an acetal results in the transfer of hydrogen and the production of a new radical with its odd electron on a carbon atom adjacent to oxygen. This new radical can decompose to yield an alkyl radical and a carbonyl-containing molecule. These reactions can be represented as follows:

$$\mathrm{X^{\cdot} + R_2'CHOR \longrightarrow XH + R_2'\dot{C}OR} \qquad (1)$$

$$\mathrm{R_2'\dot{C}OR \longrightarrow R_2'CO + R^{\cdot}} \qquad (2)$$

This type of radical decomposition, which does not appear to have been previously reported, yields the same products as the decomposition of the isomeric alkoxy radical:

$$\mathrm{R_2'RCO^{\cdot} \longrightarrow R_2'CO + R^{\cdot}} \qquad (3)$$

The inability of vinyl ethers to yield homopolymers of high molecular weight when the reaction is catalyzed by free radical initiators[3] has been vaguely attributed to their electron-rich double bonds and to a low degree of resonance. A more plausible reason is the occurrence of reaction 2. The free radical polymerization of vinyl ethyl ether would be propagated by the step

$$\mathrm{RCH_2{-}\dot{C}HOEt + CH_2{=}CHOEt \longrightarrow RCH_2CH(OEt)CH_2{-}\dot{C}HOEt}$$

in which the radical intermediate has its odd electron on a carbon atom adjacent to oxygen. Since this radical can also react according to equation 2 the growth of the polymer is effectively halted.

EXPERIMENTAL

The decompositions were carried out by heating a solution of *t*-butyl peroxide (0.01 mole) in the acetal (0.1 mole) in an apparatus which consisted of a reaction flask, a 12-inch

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[1] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 1336 (1948).

[2] A. V. Tobolsky and R. B. Mesrobian, *Organic Peroxides*, Interscience, N. Y. (1954), p. 84.

[3] C. E. Schildknecht, *Vinyl and Related Polymers*, John Wiley and Sons, N. Y., 1952, p. 593.

Vigreux column, a still-head containing a cold-finger reflux condenser, a dry ice trap and a liquid nitrogen trap. The system was first purged with helium and a slow stream of helium was maintained during the reaction. The reaction flask was heated so as to maintain a slow reflux at the base of the Vigreux column but the temperature in the still-head did not exceed 30°. The temperature of the reaction mixture in the runs with diethoxybutane was initially 120° and rose to 140° during the course of the reaction. The temperature of the runs with diisopropoxybutane was about 10° higher. After 4 to 5 hr. of heating the reaction flask was allowed to cool and the flow of helium was increased to ensure the complete transfer of volatile products to the traps. At the conclusion of a run the contents of the liquid nitrogen trap were transferred to an evacuated 1-l. flask and brought to atmospheric pressure with helium. The gaseous products were analyzed with a mass spectrometer. The dry ice trap was connected to an evacuated flask and allowed to come to room temperature. The contents were thus separated into a gaseous and a liquid fraction. The gaseous fraction which was analyzed by means of gas chromatography and the mass spectrometer was at least 98% acetaldehyde. The reaction mixture was distilled at atmospheric pressure through a 12-inch Vigreux column until the temperature reached the boiling point of the acetal. The distillate was combined with the liquid fraction of the dry ice trap and analyzed by means of a Perkin-Elmer "Fractometer" using their column "A" which is supplied with the instrument. Helium was used as the carrier gas. The temperature was 50° and the pressure was 25 p.s.i. The chromatogram from the run with the ethyl acetal contained a number of well-separated bands which were identified as acetaldehyde, acetone, ethanol, *t*-butyl alcohol, *n*-butyraldehyde, ethyl *n*-butyl ether, *t*-butyl peroxide, ethyl butyrate, and the acetal in that order. The ethyl alcohol was not a reaction product but was an impurity of the acetal. The products were identified by trapping each fraction from the gas chromatography apparatus in a Dry Ice trap and transferring the condensate to an infrared cell and obtaining the infrared spectrum. The identification of each fraction was confirmed by showing that the retention time in the gas chromatogram of the known material was identical with the unknown in the reaction mixture. For quantitative analysis of the reaction mixture, a synthetic mixture was made which contained equal molecular amounts of the different substances which were found to be present. This mixture was run on the fractometer and the peak heights measured. It was found that the relative peak heights were independent of the sample size. Dividing each relative peak height of the chromatogram of the unknown mixture by the corresponding relative peak height of the known mixture gave the relative amounts of each constituent of the reaction mixture. To convert these relative amounts to absolute concentrations it was necessary to determine the concentration of any one of the constituents. For this purpose the concentration of *t*-butyl peroxide was determined from the intensity of its infrared band at 11.4 microns using a calibration curve that had previously been prepared using solutions of *t*-butyl peroxide in carbon tetrachloride in a 0.1-mm. cell. This band was chosen because there was no interference from the other constituents. The residue from the distillation of the reaction mixture was further distilled at reduced pressure. The unreacted acetal distilled at 55° to 60° at 40 mm. and a high boiling product (0.8 gram) was obtained, b.p. 72–76° at 2 mm. Its infrared curve showed no bands due to hydroxyl or carbonyl groups.

Anal. Calcd. for $C_{12}H_{26}O_2$: C, 71.29; H, 12.87; mol. wt. 202. Found: C, 71.12; H, 12.75; mol. wt. 196.

In a similar manner the decomposition of the diisopropyl acetal yielded 0.6 gram of a product, b.p. 75–80° at 2 mm.

Anal. Calcd. for $C_{14}H_{30}O_2$: C, 73.04; H, 13.04; mol. wt. 230. Found: C, 72.88; H, 12.70; mol. wt. 224.

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[CONTRIBUTION NO. 243 FROM THE DEPARTMENT OF CHEMISTRY, TUFTS UNIVERSITY]

Conversion of 4-Bromo-2-heptene to Conjugated Diene[1]

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4-Bromo-2-heptene has been converted to a mixture of 1,3- and 2,4-heptadiene by dehydrobromination with *s*-collidine and by the Hofmann exhaustive methylation procedure. The mixtures obtained by the two procedures differed both in the ratio of structural isomers and in the distribution of geometrical isomers.

For another study a straight-chain, unsymmetrical, conjugated diene without terminal unsaturation was desired. Not many such dienes are recorded in the literature, and of those that have been reported the usual method of preparation (dehydration of an allylic alcohol prepared from a Grignard reagent and an α,β-unsaturated aldehyde) leaves the structure assignment somewhat doubtful. For instance, 2,4-heptadiene has been reported at least ten times. The boiling point reported for this diene has varied from 103° to 109.7°, and agreement of literature values for the refractive index is no better. Dumoulin[3] carried out a permanganate oxidation on his 2,4-heptadiene, and the acids obtained led him to conclude that the diene contained some of the 1,3-isomer. He appears to be the only worker to have indicated that the 2,4-heptadiene might contain some of the 1,3-diene. Owens[4] did some work on the dehydration of *n*-butylvinylcarbinol which indicated that a mixture of structural isomers was obtained. The distillation curve of the dehydration product

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(1) Presented before the Division of Organic Chemistry, ACS, Atlantic City Meeting, September, 1956.

(2) From the master's thesis of J.A.S. and work of F.L.G.

(3) J. Dumoulin, *Compt. rend.*, **182**, 974 (1926).

(4) G. R. Owens, Ph.D. thesis, Ohio State University, 1937.