[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

# THE CHEMISTRY OF HYDROPEROXIDES. X. THE ADDITION OF FREE ALKOXY RADICALS TO CONJUGATED SYSTEMS

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Many investigators (1), on the basis of indirect evidence, have postulated the formation of alkoxy (RO·) free radicals in the course of the decomposition of hydroperoxides by ferrous salts. Direct evidence of existence of such radicals in the aqueous phase has been obtained by carrying out the decompositions in the presence of butadiene and other olefins at 0°. The products identified are accounted for by reaction sequences of the type indicated in equations 1 to 4.

1. $ROOH + Fe^{++} \rightarrow RO\cdot + FeOH^{++}$
2. $RO\cdot + H_2C{=}CHCH{=}CH_2 \rightarrow (ROC_4H_6)\cdot$
3. $2\ (ROC_4H_6)\cdot \rightarrow (ROCH_2CH{=}CHCH_2{-})_2$ (A)
4. $2\ (ROC_4H_6)\cdot \rightarrow ROCH_2CH{=}CHCH_2CH(CH{=}CH_2)CH_2OR$ (B)

Dimers A and B are formed in about 85 and 15% yields, respectively.

The yields of dimers A and B vary somewhat with the nature of the hydroperoxide. With butadiene the best yield (85%) was obtained with *tert*-butyl hydroperoxide. $\alpha$-Cumyl hydroperoxide and hydrogen peroxide gave 65% and 23% of the dimeric products, respectively.

*Proof of structure of dimers A and B.* The analysis and molecular weight of dimer A are consistent with the assigned empirical formula. Ozonolysis followed by oxidation with hydrogen peroxide gave succinic acid (75%). Upon hydrogenation of A with Adams' catalyst, the calculated amount of hydrogen gas was taken up. This material when hydrolyzed gave an octanediol which melted at 62° and did not depress the melting point of an authentic sample of 1,8-octanediol. Furthermore, the bisphenylurethan of the 1,8-octanediol obtained in this study did not depress the melting point of the authentic bisphenylurethan of 1,8-octanediol.

Ozonolysis of dimer B gave formaldehyde and an acid of neutral equivalent of 106 {probably $HO_2CCH[CH_2OC(CH_3)_3]CH_2CO_2H$} but no succinic acid. Hydrogenation of the compound followed by hydrolysis with acetic and perchloric acids gave the diacetate of a glycol, $(CH_3COO)_2C_8H_{16}$ (Sapon. equiv. Calc'd 115.0. Found 119.0). Hydrolysis of the diacetate gave a diol, $C_8H_{18}O_2$. The bis-diphenylurethan and dinitrobenzoate of the diol melted at 71–72° and 61–62°, respectively. These derivatives do not correspond in melting point to those recorded for the 1,8-octanediol, or 2,3-diethylbutane-1,4-diol. We conclude, therefore, that the diol obtained by us must be 2-ethylhexane-1,6-diol.

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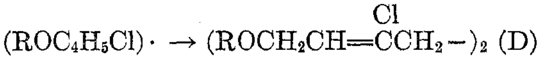
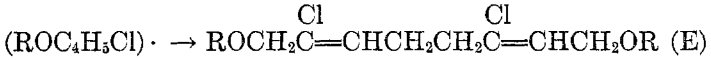
[1] The work reported in this paper was done in connection with the Government Research Program in synthetic rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

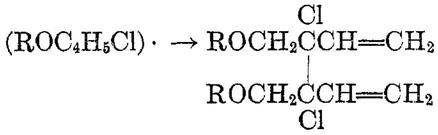
*Addition of free tert-butoxy radicals to chloroprene and isoprene.* When *tert*-butyl hydroperoxide is treated with ferrous salts in the presence of chloroprene or isoprene, dimeric products are formed. That the major reaction product is not formed by dimerization or combination of two free radicals indicated in equations 9 and 10 is surmised by the fact that the compound upon ozonolysis gives an excellent yield (75%) of succinic acid. However, the formation of succinic acid does not permit differentiation between compounds C, D, and E formed in the following manner:

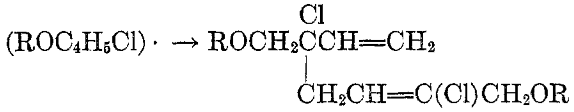
5. $\mathrm{RO\cdot + CH_2{=}CClCH{=}CH_2 \rightarrow (ROC_4H_5Cl)\cdot}$

6. 
$\mathrm{2\ (ROC_4H_5Cl)\cdot \rightarrow (ROCH_2\overset{Cl}{C}{=}CHCH_2-)_2\ (C)}$

7. 
$\mathrm{2\ (ROC_4H_5Cl)\cdot \rightarrow (ROCH_2CH{=}\overset{Cl}{C}CH_2-)_2\ (D)}$

8. 
$\mathrm{2\ (ROC_4H_5Cl)\cdot \rightarrow ROCH_2\overset{Cl}{C}{=}CHCH_2CH_2\overset{Cl}{C}{=}CHCH_2OR\ (E)}$

9. 
$$\mathrm{2\ (ROC_4H_5Cl)\cdot \rightarrow \begin{array}{l} ROCH_2\overset{Cl}{C}CH{=}CH_2 \\ \quad\quad\quad | \\ ROCH_2\underset{Cl}{C}CH{=}CH_2 \end{array}}$$

10. 
$$\mathrm{2\ (ROC_4H_5Cl)\cdot \rightarrow \begin{array}{l} ROCH_2\overset{Cl}{C}CH{=}CH_2 \\ \quad\quad\quad | \\ \quad\quad\quad CH_2CH{=}C(Cl)CH_2OR \end{array}}$$

Fortunately, in the case of isoprene an unequivocal choice of the initial attack of the free alkoxy radical on the conjugated system is possible. Isolation of succinic acid upon ozonolysis of the dimer indicates that the reaction must take the course outlined in equations 11 and 12 to the exclusion of reactions similar to 7 and 8.

11. $\mathrm{RO\cdot + CH_2{=}C(CH_3)CH{=}CH_2 \rightarrow (ROC_5H_8).}$

12. $\mathrm{2\ (ROC_5H)_8\cdot \xrightarrow{Dimerizes} [ROCH_2C(CH_3){=}CHCH_2-]_2\ (F)}$

The dimer F formed from isoprene is of interest in another connection. The formation of the compound A is represented as arising from dimerization of two free radicals (equation 3). One might argue, however, that the product arose from addition of the free radical $\mathrm{ROCH_2CH{=}CHCH_2\cdot}$ to a butadiene molecule followed by termination with a hydroperoxide molecule and/or a free $\mathrm{RO\cdot}$ radical. If that were the case the dimer from the isoprene reaction would give upon ozonolysis a keto acid, and not succinic acid. The same argument would apply to other formulations. One should mention, perhaps, an unlikely formulation that might give rise to a compound which upon ozonolysis would give succinic acid, namely, the addition of the free radical $\mathrm{(ROC_5H_8)\cdot}$ to isoprene in a manner indicated in equation 13, which then terminates with a free RO· radical or by reaction with the hydroperoxide to give compound G.

13. $(ROC_5H_8)\cdot + CH_2{=}CHC(CH_3){=}CH_2 \xrightarrow[OOH]{R}$

$ROCH_2C(CH_3){=}CHCH_2CH_2CH{=}C(CH_3)CH_2OR$ (G)

The reaction represented in equation 13 is contrary to well established facts of addition of free radicals to an isoprene molecule, and the structure of polyisoprene polymers. We conclude, therefore, that the compounds A, B, C, and F arise from an addition of the free RO· radicals to the conjugated olefins and dimerization of the thus formed free radicals.

The lower yields of dimers when α-cumyl hydroperoxide was added to butadiene, under the experimental conditions imposed, could arise from many causes: (a) slower rate of addition of the free α-cumyloxy as compared with a free *tert*-butoxy radical, (b) greater instability of the free α-cumyloxy radicals (rearrangement, etc.), and (c) the rate of interaction of the free RO· radicals with ferrous salts. In our estimation, however, the important difference is to be sought in the ability of α-cumyloxy radicals to undergo a chain reaction (2) of the following type which competes with the addition reaction.

14. $C_6H_5(CH_3)_2CO\cdot + C_6H_5(CH_3)_2COOH \rightarrow C_6H_5COCH_3 + CH_3OH + C_6H_5(CH_3)_2CO\cdot$

It is the ability of free RO· to undergo this type of chain decomposition that is the determining factor insofar as yields are concerned when different RO· radicals (*i.e.*, HO·, α-tetralyl O·, etc.) add to conjugated systems. With free alkoxy radicals of the type $(C_6H_5)_3CO\cdot$ the rate of rearrangement to $(C_6H_5O)(C_6H_5)_2C\cdot$ (and dimerization of this radical) as compared with the rate of addition of the free RO· radical to the olefin may be the factor which determines whether addition would take place.

## EXPERIMENTAL

*Reagents. α-Cumyl hydroperoxide.* Commercial α-cumyl hydroperoxide (Hercules Powder Co.) was purified by the procedure described previously (3). Analysis (by titration) indicated the material to be of high degree of purity (98–100%).

*tert-Butyl hydroperoxide.* Pure *tert*-butyl hydroperoxide (99–100%) was obtained by distillation of a commercial sample (Lucidol Co.) through a glass helices-packed column at 28 mm. The fraction boiling 43°/28 mm. was collected. Acetic acid was the solvent used in the titrations (4).

*Isoprene.* Isoprene (99%) was obtained from the Phillips Petroleum Co. It was distilled (prior to use) to remove inhibitor (b.p. 33.8–34.1°).

*The reaction of tert-butyl hydroperoxide with butadiene in the presence of a ferrous salt.* Into a one-liter three-necked flask equipped with a Dry Ice condenser, mercury-seal stirrer, and a dropping-funnel was placed 150 ml. of distilled water, urea (100 g.) (as an anti-freeze), and *tert*-butyl hydroperoxide (16.2 g.; 0.18 mole). The flask was cooled in an ethanol-Dry Ice bath to −12° and butadiene (100 g.) added to it. The air in the apparatus was displaced by nitrogen gas and to the well-stirred mixture ferrous ammonium sulfate hexahydrate, dissolved in 250 ml. of water, was added over a period of three hours while the mixture was vigorously agitated. For complete disappearance of the hydroperoxide, 71 g. (0.18 mole) of the iron salt was required. The reaction mixture was extracted with three 300-ml. portions of low-boiling ligroin (b.p. 30–60°). The combined ligroin layer was washed with water, dried over sodium sulfate, and then filtered. The residue remaining after removal of the ligroin was distilled at reduced pressure (0.1 mm.). The major portion of the residue boiled in the range of 60–80°. This fraction weighed 20.5 g. (86% yield on the basis of the *tert*-butyl hydroperoxide used). The remainder of the hydroperoxide was converted to *tert*-butyl alcohol and acetone. The fraction boiling at 60–80°/0.1 mm. was distilled using a short Vigreux column and the following fractions were collected: Fraction I, 57–59°/0.05 mm. (3.1 g.) $n_D^{20}$ 1.4432 (17%); Fraction II, 60–65°/0.05 mm. (2.3 g.) $n_D^{20}$ 1.4448 (13%); Fraction III, 65–70°/0.05 mm. (12.6 g.) $n_D^{20}$ 1.4485 (70%). Fraction III (compound A) gave the following results on analyses.

*Anal.* Calc'd for $(CH_3)_3CO(C_8H_{12})OC(CH_3)_3$: C, 75.60; H, 11.83; Mol. wt., 254.
Found: C, 75.17; H, 11.60; Mol. wt. (cryoscopic), 257.

*Identification of fraction III (compound A) (1,8-bis-tert-butoxy-2,6-octadiene).* Fraction III (2.5 g.), dissolved in absolute ethanol (60 ml.), was hydrogenated at atmospheric pressure in the presence of $PtO_2$ (50 mg.). The uptake of hydrogen ceased after absorption of 469 ml. (STP). The catalyst was collected and the filtrate subjected to distillation at reduced pressure. The fraction boiling at 65°/0.1 mm. (2 g.; 80%; $n_D^{20}$ 1.4301) was collected.

*Anal.* Calc'd for $(CH_3)_3CO(C_8H_{16})OC(CH_3)_3$: C, 74.42; H, 13.18.
Found: C, 74.86; H, 13.40.
Hydrogenation equiv.; Calc'd for $C_{16}H_{30}O_2$: 127. Found: 121.5.

*The hydrolysis of hydrogenated fraction III.* Hydrogenated fraction III (see above) (2.0 g.) dissolved in glacial acetic acid (15 ml.) was treated with 1.5 g. of 70% perchloric acid. The mixture was allowed to stand six days at room temperature during which time a deep brown color developed. The mixture was poured into a separatory-funnel, water added, and the whole extracted with ether. The ether layer was washed twice with water, then sodium bicarbonate solution (5%), dried (over sodium sulfate) and the ether removed. The residue, octanediol diacetate, distilled at 103°/0.1 mm. (0.8 g.; 42%). Loebl (5) reports the boiling point of octanediol-1,8-diacetate as 163–168°/11 mm.

The saponification equivalent of the octanediol diacetate thus obtained agreed well with the calculated value (Calc'd for $CH_3CO_2C_8H_{16}O_2CCH_3$: 115. Found: 117.8).

The reaction mixture obtained by saponification of the octanediol diacetate was extracted with ether, the ether layer washed with water, dried (over sodium sulfate) and the ether removed by distillation. The residue was dissolved in a small volume of benzene, and low-boiling ligroin (30–60°) was added until a faint cloudiness appeared and the whole cooled. A crystalline material (65% on the basis of starting material) separated which melted at 62°. This material did not depress the melting point of an authentic sample of 1,8-octanediol prepared by reduction of suberic acid with lithium aluminum hydride. 1,8-Octanediol is reported (6) to melt at 62°.

The bisphenylurethan of the 1,8-octanediol (prepared in this study) melted at 172–173°. It did not depress the melting point of the bisphenylurethan (7) of an authentic sample of 1,8-octanediol, the reported m.p. being 172–172.5°.

*Identification of the tert-butoxy group in compound A (fraction III).* Fraction III (1.5 g.) was mixed with 2 g. of thioglycolic acid and 30 ml. of 2 *N* hydrochloric acid. The mixture was stirred and heated under reflux for 18 hours. After cooling, the reaction mixture was extracted with ether. The ether layer was washed thoroughly with water to remove unreacted thioglycolic acid. The *tert*-butylthioglycolic acid was extracted with sodium hydroxide solution (5%). The alkaline solution was extracted with ether, the ether layer discarded, and the solution acidified (Congo Red paper) with 2 N hydrochloric acid. It was then extracted with ether. The ether layer, after being washed with water and dried (over sodium sulfate), was removed and the residue distilled using a micro still (8).

*Anal.* Calc'd for $(CH_3)_3CSCH_2COOH$: Neutral equiv., 148. Found: 145.3.

*The preparation of S-tert-butylthioglycolic acid anilide.* The sodium salt of *tert*-butylthioglycolic acid (0.13 g.), prepared in the manner described above, was heated with aniline

(1 g.) and concentrated hydrochloric acid (0.3 ml.) in an oil-bath kept at 150–160° for 1 hour. The mixture was poured into 50 ml. of water and evaporated to dryness. The residue was taken up in ligroin (30–60°). On evaporation of the solvent, a small amount of a viscous oil was obtained. The oil crystallized slowly to give a solid which melted at 79–79.5°. No depression in the melting point was noted when this sample was admixed with an authentic sample of the anilide prepared from *tert*-butanol and thioglycolic acid (9).

*The ozonolysis of compound A (fraction III).* Fraction III (2.5 g.) in anhydrous ethyl acetate was ozonized at −80° with a stream of oxygen containing ozone delivered at the rate of approximately 0.6 millimole of ozone per minute. The ozone was passed in for 41 minutes. The ethyl acetate was removed by distillation at reduced pressure and to the residual ozonide 100 ml. of aqueous hydrogen peroxide (4%) was added and the mixture heated at 90–100° for six hours. The excess hydrogen peroxide was decomposed with platinum black. The platinum was collected and the aqueous filtrate distilled under reduced pressure (Distillate 1). The residue (1 g., 74% of calculated amount) thus obtained melted at 183–184°. This, when mixed with an authentic sample of succinic acid showed no depression in the melting point. The *p*-bromophenacyl ester of the succinic acid obtained by ozonolysis melted at 206–207°, and did not depress the melting point of *p*-bromophenacyl ester of an authentic sample of succinic acid.

Distillate 1 contained acetone, which was probably formed by oxidation of a fragment containing a *tert*-butoxy group, *i.e.*, $(CH_3)_3COCH_2CO_2H$, and a small amount of an acid, which had a neutral equivalent of 132.5, which corresponds to that of *tert*-butoxyacetic acid (Calc'd neutral equiv., 132).

*Identification of fraction I (Compound B). Hydrogenation of fraction I.* Fraction I (1.02 g.) was dissolved in absolute ethanol (40 ml.), $PtO_2$ (90 mg.) was added to it, and the mixture was hydrogenated. The hydrogen uptake was 222 ml. at 24°/747 mm. The catalyst was collected and the ethanol was removed at reduced pressure. The residue was distilled and the fraction boiling at 55°/0.1 mm. was collected.

Hydrogenation equiv.; Calc'd for $C_{16}H_{30}O_2$: 127. Found: 135.

The hydrogenated material obtained above (1.9 g.) was dissolved in glacial acetic acid (15 ml.) and 2.2 g. of 70% perchloric acid was added to it. The solution was allowed to stand at 50° for 29 hours, during which time a deep brown color developed. The product was isolated in the manner described previously for the hydrolysis product of fraction III. The diacetate of the octanediol here obtained boiled at 85°/0.1 mm. (1.0 g.; 60% yield).

The diacetate thus obtained was treated with alkali (saponification equivalent: Calc'd for $CH_3COO(C_8H_{16})OCOCH_3$: 115. Found: 119.4), and the reaction mixture extracted with ether. The ether layer was washed with water, dried (over sodium sulfate) and the ether removed by distillation. The residue was distilled and the fraction boiling at 86–89°/0.1 mm. ($n_D^{20}$ 1.4599) was collected (0.38 g.; 60% of calculated amount).

*Anal.* Calc'd for $C_8H_{18}O_2$: C, 65.75; H, 12.33.
Found: C, 66.72; H, 12.78.

The *bisphenylurethan* of this glycol, after crystallization from high-boiling ligroin, melted at 71–72°. The bisphenylurethan of 2,3-diethylbutanediol-1,4 melted at 94–96° (the glycol was prepared by treating $\alpha,\alpha'$-diethylsuccinic acid with lithium aluminum hydride; b.p. 82–83°/0.1 mm.). However, this bisphenylurethan was different from the one obtained from the glycol in question.

Ozonolysis of fraction I (Compound B), and oxidation of the resulting ozonide with hydrogen peroxide gave formic acid and a high-boiling acid (Calc'd for $C_9H_{16}O_5$: neutral equiv., 106. Found: 102). The yield of the acid was 65%.

The data presented suggest the structure $[ROCH_2CH{=}CHCH_2CH(CH_2OR)(CH{=}CH_2)]$ for fraction I.

*Pyrolysis of compounds A and B.* A mixture of compounds A and B (b.p. 60–80°/0.1 mm.) (55 g.) containing approximately 80–85% of A was distilled through a column (vacuum-jacketed and packed with glass helices; 150 cm × 1.0 cm) at reduced pressure (0.6–1.0 mm.). A number of fractions were collected. The fraction which boiled at 82°/0.6 mm. (20 g., $n_D^{20}$

1.4403) was shown to be a mixture of the starting materials containing some of the compound described below. The residue (25 g.) was distilled through a short Vigreux column and the fraction (20.4 g.) boiling at 85–90°/0.1 mm. ($n_D^{20}$ 1.4505) was collected.

*Anal:* Calc'd for $C_{12}H_{22}O_2$: C, 72.72; H, 11.12; Mol. wt., 198.
Found: C, 72.74; H, 11.32; Mol. wt., (cryoscopic) 245.

The analyses agree with the empirical formula $(CH_3)_3CO(C_8H_{12})OH$ for the compound. Furthermore, the fact that upon ozonolysis 84% of succinic acid is formed indicates that the structure of the compound in question is as follows:

$$(CH_3)_3COCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OH$$

As would be expected from a compound of this structure some formaldehyde is formed during ozonolysis (10). Furthermore, when the material is hydrogenated and then hydrolyzed one obtains some octanediol-1,8 as well as octanol-1. (The 3,5-dinitrobenzoate of this alcohol melted at 60° and did not depress the melting point of the 3,5-dinitrobenzoate obtained from an authentic sample of octanol-1.)

*The reaction of α-cumyl hydroperoxide with butadiene and ferrous pyrophosphate. 1.* A ferrous pyrophosphate suspension was prepared by dissolving ferrous sulfate heptahydrate (44 g.) in 900 ml. of redistilled water, then adding sodium pyrophosphate decahydrate (100 g.), and making the volume up to one liter with distilled water. The air in the flask was displaced by nitrogen gas and the mixture heated in a water-bath at 60° for 40 minutes. The following compounds, in the order listed, were added to a citrate bottle: 125 ml. (0.02 mole of ferrous ion) of ferrous pyrophosphate suspension, butadiene (30 g.; 0.55 mole), and α-cumyl hydroperoxide (10 g.; 0.065 mole). The bottle was capped and placed in a bath at 4° and rotated for 24 hours. After this time, additional ferrous pyrophosphate suspension (62.5 ml.; 0.01 mole) was added and the bottle again rotated in the 4°-bath for 20 hours. The loss of α-cumyl hydroperoxide was 35% at the end of 24 hours and 51% at the end of 48 hours.

The reaction mixture was extracted with benzene, the benzene solution was dried (sodium sulfate), and benzene was removed at reduced pressure. The residue was distilled at reduced pressure (0.1 mm.) and the mixture of α-cumyl hydroperoxide, acetophenone, and the α-cumyl alcohol collected. These materials were identified in the usual way.

The residues from six experiments performed as described above were combined and distilled in a molecular still. The following fractions were collected:

Fraction A, 60–65°, 2.17 g., $n_D^{20}$ 1.5040; *Anal.* C, 82.44, H, 10.10; Mol. wt., 244;
Fraction B, 65–95°, 1.91 g., $n_D^{20}$ 1.5066; *Anal.* C, 84.27,[2] H, 9.97;[2] Mol. wt., 258;
Residue A, 9.47 g.; *Anal.* C, 82.27, H, 9.14, Mol. wt., 377;
Calc'd for $C_6H_5C(CH_3)_2O(C_8H_{12})OC(CH_3)_2C_6H_5$: C, 82.54; H, 9.00; Mol. wt., 378.

*2. Hydrolysis of residue A (bis-α-cumyloxyoctadiene).* Residue A (1.8 g.) was mixed with concentrated hydrochloric acid (20 ml.) and heated on a steam-bath under a reflux condenser for five hours. Water (20 ml.) was then added and the volatile materials removed by distillation at reduced pressure. The distillate was extracted with 50 ml. of low-boiling ligroin. The ligroin layer was washed with 5% sodium bicarbonate solution and water until the aqueous phase was free of chloride ion. The ligroin layer was dried (sodium sulfate) and the ligroin was removed under reduced pressure leaving a liquid residue of 1.6 g.

One gram of this material was treated with thioglycolic acid (1 g.) and 2 *N* hydrochloric acid (40 ml.). The mixture was stirred and refluxed for 3 hours. After cooling, the reaction mixture was extracted with ether (75 ml.) and the ether layer thoroughly washed with water to remove unreacted thioglycolic acid. The ether solution was then extracted with 5% sodium hydroxide solution. The alkaline solution was washed with ether and the ether rejected and the alkaline solution acidified with 2 *N* hydrochloric acid. The acid solution was extracted with ether. The ether solution was washed with water and dried. After removal of the ether a solid material (1 g.), which crystallized from ligroin in white needles,

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[2] That these products rapidly absorb oxygen is shown by the fact that a duplicate analysis after standing in air for a few hours was: C, 80.83; H, 9.81.

m.p. 62–63°, was obtained. There was no depression of melting point when this material was mixed with authentic sample of S-α-cumylthioglycolic acid which was prepared from α-cumyl alcohol and thioglycolic acid.

*Anal.* Calc'd for $C_{11}H_{14}O_2S$: Neutral equiv., 210. Found: Neutral equiv., 209.

The hydrolysis procedure, as an independent step, may be omitted. Thus, residue A, and the hydrogenated compound formed from it, gave S-α-cumylthioglycolic acid when heated with thioglycolic acid in the presence of hydrochloric acid.

*3. Ozonolysis of residue A (bis-α-cumyloxyoctadiene).* Residue A (5 g.) dissolved in anhydrous ethyl acetate (300 ml.) was ozonized at −80° in a stream of ozone, delivered at the rate of approximately one millimole per minute, for 69 minutes. Ethyl acetate was removed at reduced pressure, 3% hydrogen peroxide (100 ml.) was added to the residue, and the whole was heated on a steam-bath for several hours. The excess hydrogen peroxide was decomposed with platinum black and the platinum black collected. The filtrate was extracted with ether. The presence of both phenol (m.p. 42.5°; 2,4,6-tribromophenol, m.p. 88°, no depression in melting point when mixed with authentic 2,4,6-tribromophenol) and acetophenone, (2,4-dinitrophenylhydrazone, m.p. 234°, no depression in melting point when mixed with the authentic 2,4-dinitrophenylhydrazone of acetophenone) in the ether layer was demonstrated. From the aqueous layer succinic acid was obtained; the crude acid had m.p. 177–179°. The succinic acid was further identified by the preparation of its *p*-bromophenacyl ester. The ester thus obtained did not depress the melting point of an authentic sample of the *p*-bromophenacyl ester of succinic acid.

The analysis of residue A, the ease of hydrolysis of the α-cumyloxy group, and the formation of succinic acid suggest that residue A has the following structure:

$$C_6H_5(CH_3)_2COCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2OC(CH_3)_2C_6H_5$$

This assumption was further substantiated by the results obtained on hydrogenation of this substance.

*Hydrogenation of residue A (bis-α-cumyloxyoctadiene).* Residue A (4.6 g.) was dissolved in a mixture of *n*-heptane and acetic acid, $PtO_2$ (50 mg.) was added, and the mixture was hydrogenated. The uptake of hydrogen was 111% calculated on the basis of a dicumyloxyoctadiene. After removal of the catalyst and the solvent, the hydrogenated material was distilled in a Hickman still at $10^{-3}$ mm. The fraction distilling at 110–140° (bath temperature) was collected, dissolved in a small volume of benzene, and low-boiling ligroin added to it until the appearance of a slight cloud. It was then allowed to stand. Octamethylenediol-1,8 separated in long white needles (m.p. 59.5–61°). There was no depression in melting point when the octamethylenediol-1,8 thus prepared was mixed with an authentic sample (prepared by reduction of suberic acid with lithium aluminum hydride). Furthermore, the bisphenylurethan of the glycol obtained in this study did not depress the melting point of the bisphenylurethan of an authentic sample of octamethylenediol-1,8.

*4. The hydrogenation of fraction A (α-cumyl hydroperoxide butadiene adduct).* Fraction A (4.1 g.) (Mol. wt., 244) was dissolved in glacial acetic acid (65 ml.), PtO2 (30 mg.) was added, and the mixture was hydrogenated at 26° and 750 mm. The total uptake of hydrogen was 861 ml.; Calc'd for $C_{17}H_{24}O$ [Mol. wt., 244 (two double bonds)]: 856 ml. The catalyst was collected, water was added to the acetic acid filtrate, and the whole was extracted with ether. The ether solution was washed successively with water, sodium bicarbonate solution (5%), and water, dried (sodium sulfate), and the ether was removed. The residue was distilled in a molecular still and the fraction boiling at 60–70°/$10^{-5}$ mm. was collected (3.5 g.; 86% of calc'd amount).

*The formation of S-α-cumylthioglycolic acid from the hydrogenated fraction A.* The hydrogenated fraction A (see above, 1 g.) was treated with 2 *N* hydrochloric acid (50 ml.) and thioglycolic acid (1 g.). The mixture was stirred and refluxed for three hours. The reaction mixture was worked up in the manner previously described. Crystallization from ligroin gave S-α-cumylthioglycolic acid which melted at 63° (0.46 g., 54%).

*Anal.* Calc'd for $C_{11}H_{14}O_2S$: Neutral equiv., 210. Found: Neutral equiv., 208.

*5. Ozonolysis of fraction A.* Fraction A (0.657 g.) was ozonized in anhydrous ethyl acetate at −80°. Ozone was delivered at the rate of approximately 0.6 mmole per minute for ten minutes. The ethyl acetate was removed under reduced pressure, 3% hydrogen peroxide (25 ml.) was added to the residue, and the mixture was warmed on a steam-bath for four hours. The excess hydrogen peroxide was decomposed with platinum black. The platinum was removed and the aqueous solution distilled under reduced pressure. The residue was crude succinic acid (0.1 g., 30%) which melted at 174–175° (m.p. 184° after sublimation). The identity of the succinic acid was confirmed by the methods previously described.

The analyses of fraction A, hydrolysis, hydrogenation, and ozonolysis are consistent with the following formulation for this compound:

$$C_6H_5(CH_3)_2CO(C_4H_6)_2H$$

*The reaction of α-cumyl hydroperoxide with butadiene and ferrous ammonium sulfate.* To a mixture of urea (100 g.), water (100 ml.), α-cumyl hydroperoxide (27.7 g., 0.18 mole), and butadiene (54 g., 1 mole) cooled to −10° was added dropwise ferrous ammonium sulfate hexahydrate (72 g. dissolved in 200 ml. of water). The addition of the ferrous salt solution required 3.5 hours. The reaction mixture was worked up in the usual way. After removal of solvent the residue was distilled as follows: 1. 60–70°/0.5 mm., 5.3 g., which consisted of 3.2 g. of acetophenone [14.8% on hydroperoxide (determined as 2,4-dinitrophenylhydrazone)] and 2.1 g. of α-cumyl alcohol [(determined as the thioglycolic acid derivative), 8.6% on hydroperoxide]; 2. 50–60°/$10^{-5}$ mm., 0.7 g.; 3. 60–70°/$10^{-5}$ mm., 3.5 g., $n_D^{20}$ 1.5075; 4. 70–100°/$10^{-5}$ mm., 13.2 g., $n_D^{20}$ 1.5290; 5. residue 6.0. From ozonolysis, hydrogenation, molecular weights, and elementary analysis it was ascertained that fractions 3, 4, and 5 were mixtures of partially pyrolyzed di-α-cumyloctadiene dimer.

*The reaction of tetralin hydroperoxide with butadiene and ferrous pyrophosphate.* No adduct with butadiene was formed when α-tetralyl hydroperoxide was substituted for α-cumyl hydroperoxide in the experiment previously described. α-Tetralone (identified as the 2,4-dinitrophenylhydrazone) was the main reaction product.

*The reaction of hydrogen peroxide with butadiene and ferrous salts.* Into a flask equipped with an efficient stirrer and two dropping-funnels was placed methanol (100 ml.) and butadiene (54 g.). The flask was placed in a bath maintained at −10° throughout the reaction. Ferrous ammonium sulfate (72 g.) dissolved in water (200 ml.) and hydrogen peroxide (6.8 g.; 90%) were added dropwise from each of the funnels at such a rate that ferrous ion was always in slight excess in the reaction flask. The reaction products were extracted with three 200-ml. portions of ether. The presence of formaldehyde (31% on the basis of $H_2O_2$ used) in the water solution was demonstrated. The ether solution was washed with water, dried (sodium sulfate) and the ether removed. The residue (3 g.) was dissolved in 80 ml. of absolute ethanol and hydrogenated in the presence of $PtO_2$ (50 mg.). After the absorption of hydrogen has ceased, the platinum was collected and the ethanol removed by distillation at reduced pressure. The hydrogenated residue was dissolved in benzene (2 ml.) and to the solution ligroin (2 ml.) was added. Upon cooling the mixture a solid (octanediol-1,8, m.p. 60–63°) material (0.6 g.) separated. This material did not depress the melting point of an authentic sample of octanediol-1,8.

From the mother liquor was obtained an oil, presumably a diol isomeric with the one isolated. It was not further investigated.

*The reaction of tert-butyl hydroperoxide with isoprene and ferrous salt. A.* Into a two-liter three-necked flask equipped with a stirrer, condenser, and a dropping-funnel was placed water (200 ml.), methanol (200 ml.), *tert*-butyl hydroperoxide (32.4 g., 0.36 mole), and freshly distilled isoprene (120 ml.). The flask was cooled in an ethanol-Dry Ice bath to −10°. To the well stirred mixture, a water solution of ferrous ammonium sulfate hexahydrate (144 g., 0.36 mole; in 400 cc. of water) was added over a period of three hours. The air in the apparatus had been displaced by nitrogen gas. Test for the hydroperoxide indicated that all of the hydroperoxide had been used up. The isoprene layer was then separated from the aqueous layer. The aqueous layer was extracted three times (250-ml. portions) with petroleum ether. The isoprene layer and the petroleum ether extracts were combined, washed with two 150-ml. portions of water, and dried over sodium sulfate. Petroleum ether and isoprene were removed by distillation at reduced pressure. The residue was distilled and four fractions were collected: Fraction I, 40–55°/0.02 mm., 2.3 g., $n_D^{20}$ 1.4423, Mol. wt., 226; Fraction II, 56–65°/0.02 mm., 5.4 g., $n_D^{20}$ 1.4463, Mol. wt., 248; Fraction III, 69–80°/0.02 mm., 10.7 g. (21%), $n_D^{20}$ 1.4519, Mol. wt., 273; Fraction IV, 50–55°/$10^{-5}$ mm., 6.3 g., (13%), $n_D^{20}$ 1.4562, Mol. wt., 280.

Only fractions III and IV were investigated.

*Anal.* Fraction IV. Calc'd for $C_{18}H_{34}O_2$: C, 76.6; H, 12.0.
*Found:* C, 77.2; H, 12.0.

The molecular weight and the analyses of Fraction IV suggested that the compound in question might be 1,8-di-*tert*-butoxy-2,7-dimethyl-2,6-octadiene. Additional corroboration of this assumption was sought by performing experiments (*B*), (*C*), and (*D*).

*B. Hydrogenation of (1,8-di-tert-butoxy-2,7-dimethyl-2,6-octadiene) fraction IV.* Fraction IV (3.0 g., 10.65 mmoles) dissolved in absolute ethanol (60 ml.) was hydrogenated in the presence of $PtO_2$ (50 mg.). The hydrogen uptake was 555 ml. at 27°/751 mm. which corresponds to 20.2 mmoles of hydrogen (95% of calc'd amount). The catalyst was collected and the solvent removed from the filtrate. The residue was distilled at reduced pressure and the fraction boiling at 62–70°/0.05 mm.; $n_D^{20}$ 1.4356; 2.8 g.;(90% of calc'd) was collected.

*Anal.* Calc'd for $C_{18}H_{38}O_2$: C, 75.5; H, 13.3.
Found: C, 76.0; H, 13.4.

*C. Hydrolysis of (1,8-di-tert-butoxy-2,7-dimethyl octane) hydrogenated fraction IV.* The hydrogenated material obtained as described in (*B*) (2.0 g.) was dissolved in glacial acetic acid (15 ml.) and perchloric acid (1.5 g. of 70%) was added to it. The mixture was allowed to stand several days at room temperature during which time a deep brown color developed. The mixture was transferred to a separatory-funnel, water (200 cc.) was added to it, and the whole was extracted with ether. The ether layer was washed with water and sodium carbonate solution (5%), and dried (sodium sulfate). The ether was removed by distillation at reduced pressure and the residue distilled in a molecular still (bath temperature at 103°). To the distillate alcoholic potassium hydroxide was added and the whole warmed gently. Water was then added and the mixture was extracted with ether. The ether extract was washed with water and dried over sodium sulfate. After removal of ether, the residue was distilled in a micro-still (65–70°/0.05 mm.).

*Anal.* Calc'd for $C_{10}H_{22}O_2$: C, 69.0; H, 12.65.
Found: C, 69.91; H, 13.32.

The *3,5-dinitrobenzoate* of this glycol melted at 161–163° and the diphenylurethan at 129–130°.

*D. Ozonolysis of (1,8-di-tert-butoxy-2,7-dimethyl-2,6-octadiene) fraction IV.* Fraction IV (2.8 g.) was ozonized in ethyl acetate at −80° in a stream of ozone delivered at the rate of approximately 0.6 mmole per minute for 40 minutes. The ethyl acetate was removed under reduced pressure and to the residue aqueous hydrogen peroxide (50 ml.; 10%) was added and the mixture was warmed on a steam-bath for three hours. The excess hydrogen peroxide was decomposed with platinum black. Succinic acid (72% of calc'd) was obtained after removal of the water at reduced pressure. The succinic acid was identified by its melting point, and the fact that it did not depress the melting point of an authentic sample. The melting point of the *p*-bromophenacyl ester of the succinic acid obtained in this study did not depress the melting point of an authentic sample.

The following additional products were isolated and identified from the ozonolysis reaction: (a) acetic acid (*p*-bromophenacyl ester, m.p. 85°; *p*-nitrobenzyl ester, m.p. 77–78°; these derivatives did not depress the melting point of authentic samples); (b) hydroxyacetone (2,4-dinitrophenylosazone, m.p. 297°), and (c) a trace of formaldehyde (chromotropic acid test).

*Hydrogenation of fraction III.* Fraction III (2.8 g.) in 50 ml. of ethanol was treated with 50 mg. of Adams' catalyst and hydrogen at 24° and 750 mm.; 604 ml. (22.3 mmoles) of hydrogen was absorbed, (Calc'd for two double bonds: 20.0 mmoles of hydrogen). After removal of the ethanol, 1.3 g. (46%) of hydrogenated products were recovered, $n_D^{20}$ 1.4356.

*Ozonolysis of fraction III.* Fraction III (2.8 g.) in ethyl acetate (200 ml.) was ozonized at −80°. After working up the ozonide in the usual fashion there was isolated succinic acid, 0.2 g. (17%); acetic acid (not determined quantitatively), and unidentified carbonyl compounds.

*The reaction of tert-butyl hydroperoxide with chloroprene and ferrous salt.* Into a two-liter three-necked flask equipped with a stirrer, condenser, and dropping-funnel was placed methanol (150 ml.), water (100 ml.), chloroprene (88 g.; 1 mole), and 32.4 g. (0.36 mole) of *tert*-butyl hydroperoxide. The reaction flask was placed in an ethanol-Dry Ice bath (maintained at −15°). To the vigorously stirred mixture, ferrous ammonium sulfate (144 g., 0.36 mole) dissolved in water (400 ml.) was added over a period of four hours. The reaction mixture was extracted with ether, washed with water, and dried (sodium sulfate). The ether was removed at reduced pressure, leaving a viscous liquid residue (13.5 g.) which was subjected to molecular distillation in a Hickman still. The main fraction (8 g.) boiled at 60°/$10^{-5}$mm. ($n_D^{20}$ 1.4870).

*Anal.* Calc'd for $C_{16}H_{28}Cl_2O_2$: Cl, 21.98; Mol. wt., 323.

Found: Cl, 21.6; Mol. wt., 343.

Fraction II: Residue 5.3 g. This residue was not investigated.

*The ozonolysis of fraction I.* Fraction I (1.5 g.) dissolved in 300 ml. of ethyl acetate was ozonized at −80° in a stream of ozone delivered at the rate of approximately 0.6 mmole of ozone per minute, for 16 minutes. The ethyl acetate was removed at reduced pressure (10 mm.), and the residue treated with hydrogen peroxide (10%). The succinic acid was isolated and identified as described previously. A nearly quantitative yield of the acid was obtained.

## SUMMARY

Free alkoxy radicals add to butadiene, isoprene, and chloroprene to give free radicals which then dimerize. The structures of these dimeric products have been established.

CHICAGO 37, ILLINOIS

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