sodium methoxide (17.3 g., 0.32 mole) in 250 ml. of cyclohexene under a nitrogen atmosphere. During the course of the addition of the ester, the reaction temperature rose to 45° and subsequently the reaction mixture assumed a gel-like consistency. The reaction mixture was warmed to about 65° when an exothermic reaction occurred and the mixture refluxed without external heating for about 30 min. After the reaction temperature had dropped to 40°, the reaction was maintained at 40° for 10 hr. by external heating and then the mixture was heated to and maintained at 60° for 24 hr. The reaction was quenched by the addition of 200 ml. of water, the phases were separated, and the organic phase was extracted with three 100-ml. portions of *n*-pentane. The combined organic phases were dried over Drierite. After removing the *n*-pentane and the cyclohexene, a small residue remained, which on distillation gave 0.6 g. (2.4%) of methyl oxalate, b.p. 159–161° at 735 mm., m.p. 53–54°. The infrared spectrum of this ester was superimposable on that of an authentic sample of methyl oxalate.

Polymeric Peroxide of 2,5-Dimethyl-2,4-hexadiene and a New Selective Reduction of Its Peroxide Linkage

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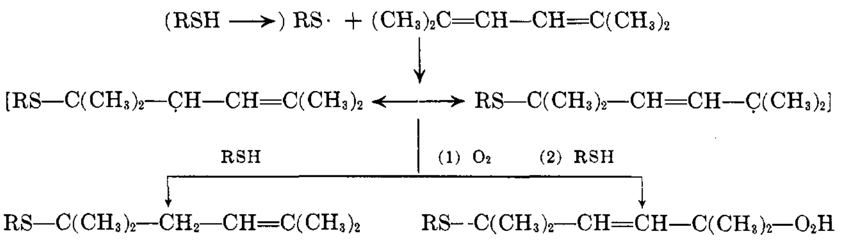
The autoxidation of 2,5-dimethyl-2,4-hexadiene affords in good yield the corresponding *trans*-1,4-polyperoxide as the only detectable product. This appears to be the first completely selective autoxidation of an acyclic conjugated diene. The *trans*-1,4 structure of the polyperoxide was established by infrared and n.m.r. analysis and by the results of reduction reactions. Catalytic hydrogenation of the polyperoxide produced 2,5-dimethylhexane-2,5-diol in high yield. During base-catalyzed reduction with an aromatic thiol, on the other hand, only the peroxide linkages were cleaved to yield *trans*-2,5-dimethyl-3-hexene-2,5-diol in 75% yield. The latter reaction represents a new method for the selective reduction of the O–O bond in polyperoxides containing olefinic linkages.

Previous reports from this laboratory have indicated that there is a correlation between the structure of a conjugated diene and the course of its free-radical reactions.[3] If the initial allylic-radical intermediate enters into a reaction requiring significant activation energy, the thermodynamically more stable products are formed.[4–6] If, on the other hand, the allylic radical undergoes a reaction requiring little or no activation energy, the thermodynamically less stable products are produced.[4,7] Typical examples of this principle are thiol addition and thiol co-oxidation reactions[4] (see Scheme I).

Scheme I



The autoxidation of conjugated dienes to form polymeric peroxides resembles the above-mentioned co-oxidation reaction in its second propagation step. In both cases, an allylic radical intermediate combines with the oxygen diradical in a step of negligible activation energy. One might therefore anticipate similar product orientations for the two reactions. However, to the best of our knowledge, completely selective autoxidation reactions of acyclic conjugated dienes have never been observed.

In studying the autoxidation of 1,3-butadiene, Handy and Rothrock[8] showed that both 1,2- and 1,4-addition of oxygen occurred. In a series of papers, Kern and co-workers reported the autoxidation of chloroprene,[9,10] isoprene,[11] and 2,3-dimethyl-1,3-butadiene.[11–13] They arrived at the conclusion that isoprene and 2,3-dimethyl-1,3-butadiene each form 1,2-polyperoxides. However, their published data do not prove that these were the sole reaction products. In a later study Kawahara[14] indeed found that the autoxidation of 2,3-dimethyl-1,3-butadiene is a more complex reaction and specifically mentioned that 1,4-addition may also occur.

A polymeric peroxide of 2,5-dimethyl-2,4-hexadiene had also been reported previously by Harper and co-workers.[15] Although these workers suggested a 1,4-

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[2] Analytical Research Division.

[3] For a summarized treatment of this subject see A. A. Oswald and K. Griesbaum, "Free Radical Addition of Thiols to Diolefins and Acetylenes," in "Organic Sulfur Compounds," N. Kharasch, Ed., Pergamon Press, Inc., New York, N. Y., in press.

[4] A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, **27**, 2439 (1962).

[5] A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962).

[6] A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 1262 (1963).

[7] A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 2355 (1963).

[8] C. T. Handy and H. S. Rothrock, *J. Am. Chem. Soc.*, **80**, 5306 (1958).

[9] W. Kern, H. Jockusch, and A. Wolfram, *Makromol. Chem.*, **16**, 81 (1955).

[10] See also A. L. Klebanskii and R. M. Sorokina, *Zh. Prikl. Khim.*, **35**, 2735 (1962).

[11] W. Kern and A. R. Heinz, *Makromol. Chem.*, **16**, 81 (1955).

[12] W. Kern and J. Stallmann, *ibid.*, **7**, 199 (1951).

[13] W. Kern, A. R. Heinz, and J. Stallmann, *ibid.*, **16**, 21 (1955).

[14] F. K. Kawahara, *J. Am. Chem. Soc.*, **79**, 1447 (1957).

[15] S. H. Harper, H. W. B. Reed, and R. A. Thompson, *J. Sci. Food Agr.*, **2**, 94 (1951).

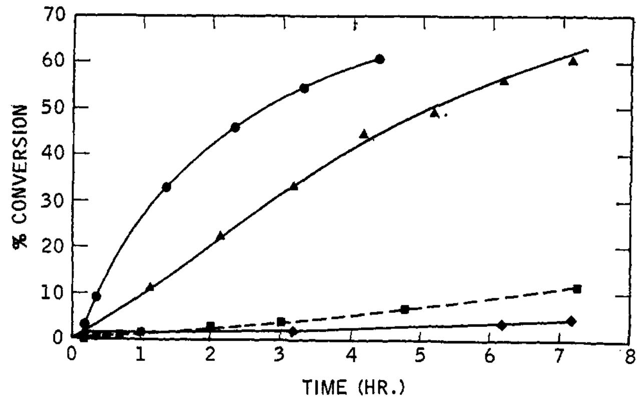


Fig. 1.—Autoxidation of 2,5-dimethyl-2,4-hexadiene under different conditions: ●, no solvent, ultraviolet irradiation; ▲, 0.35 *M* benzene solution, ultraviolet irradiation; ■, no solvent, no irradiation; ◆, 0.35 *M* benzene solution, 10 min. of ultraviolet irradiation.

structure for their polyperoxide, they did not produce any experimental evidence for it. Furthermore, they did not report any yields, so that no conclusions could be drawn as to the selectivity of their autoxidation reaction. Since it was found recently in this laboratory that 2,5-dimethyl-2,4-hexadiene could be co-oxidized in an exclusively *trans*-1,4 manner,[4] it seemed probable that the autoxidation of this same diene might indeed exhibit a similar selectivity. Therefore, we examined the latter reaction in more detail.

Selective reduction of O–O bonds in polyperoxides containing olefinic unsaturation have been achieved in moderate yields, using lithium aluminum hydride[8,14] as reducing agent. Catalytic hydrogenation with Adams catalyst,[15] on the other hand, has been claimed to attack the C=C– rather than the O–O bonds. Mayo and Miller[16] found that hydrogen sulfide or mercaptans under weakly basic conditions are good reducing agents for styrene polyperoxide. However, similar reactions with polyperoxides containing olefinic bonds have apparently remained unexamined. Recently we found that thiols in the presence of catalytic amounts of amines can be used for the selective reduction of unsaturated hydroperoxides.[17] This prompted us to try a similar thiol method for the reduction of unsaturated dialkyl polyperoxides.

Results

Autoxidation of the Diene.—The autoxidation of 2,5-dimethyl-2,4-hexadiene (I) was carried out on the neat liquid and in benzene solution. The degree of conversion was followed by quantitative n.m.r. analyses of the reaction mixtures. This method allowed us at the same time to check the selectivity of the reaction towards the formation of a uniform product.

The fastest rates were observed for the ultraviolet-catalyzed autoxidation of the undiluted diene. Within 3 hr., 52% of the diene had reacted to form the polyperoxide II with essentially complete selectivity (Fig. 1). The rate of this reaction dropped continually with increasing conversion. This might be explained by a gradual decrease of the oxygen diffusion due to the increasing viscosity of the reaction mixture. At a conversion level of 60%, the reaction mixture became heterogeneous as the polyperoxide began to separate as a colorless semisolid.

Autoxidation of the undiluted diene in the absence of ultraviolet initiation proceeded at a much slower rate. The reaction had a pronounced induction period of 10–15 min. and reached a conversion of only 4% after 3 hr. (*cf.* 52% conversion in the former case).

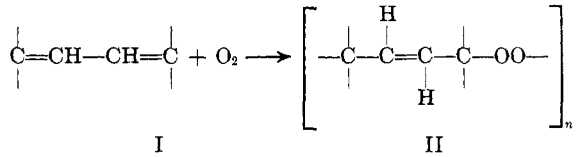
Autoxidation of the diene in a 0.35 *M* benzene solution showed some marked differences. The ultraviolet-catalyzed reaction proceeded at a slower, but more constant rate than that of the undiluted diene. Both these effects may be due to the dilution of the reaction mixture. When the ultraviolet irradiation was discontinued, on the other hand, the autoxidation rate decreased abruptly. The noninitiated oxidation in benzene solution, did not show any detectable conversion even after 20 hr.

Polyperoxide of the Diene.—The peroxide was usually prepared by ultraviolet light catalyzed autoxidation of the undiluted diene. The pure polyperoxide could be isolated from the reaction mixtures in up to 84% yield, the remainder being the unchanged diene.

After recrystallization from methanol, the polyperoxide II, m.p. 62–65°, had an average molecular weight of 1520, corresponding to 10–11 repeating units. It was very insensitive towards shock, flashed quite moderately when heated over an open flame, and was only slowly reduced by sodium iodide in acetic acid at room temperature. However, on heating in sodium iodide–acetic acid, about 90% of the calculated active oxygen could be detected.

The n.m.r. spectrum of the polyperoxide (Table I) showed only two signals with the relative intensities of 1:6, thus demonstrating the presence of only one compound, the 1,4-autoxidation product. The shift of the double bond during the reaction from the α- to the β-position relative to the methyl groups changed the spectrum characteristically. While the methyl groups in the diene appeared as two separate signals resulting from the *cis* and *trans* position relative to the olefinic protons, they were all equivalent in the polyperoxide due to free rotation around the C–C single bonds and gave rise to a sharp singlet, shifted to higher field by about 0.45 p.p.m. The olefinic protons appeared as a sharp singlet also shifted to higher field compared to the corresponding signal in the conjugated diene. These changes are in full agreement with results obtained on analogous olefinic compounds.[18]

The *trans* configuration of the polyperoxide was indicated by a strong infrared absorption band at 10.2 μ^{19a} and a very weak absorption at 5.95 μ^{19b} (Table II). This assignment was further supported by reduction experiments and by n.m.r. studies as discussed below.



$$\overset{|}{\underset{|}{C}}{=}CH{-}CH{=}\overset{|}{\underset{|}{C}} + O_2 \longrightarrow \left[-\overset{|}{\underset{|}{C}}-\overset{H}{\overset{|}{C}}=\underset{\underset{H}{|}}{C}-\overset{|}{\underset{|}{C}}-OO- \right]_n$$

I II

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(16) F. R. Mayo and A. A. Miller, *J. Am. Chem. Soc.*, **78**, 1023 (1956).

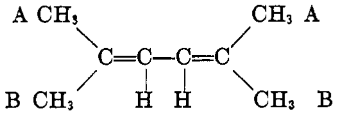
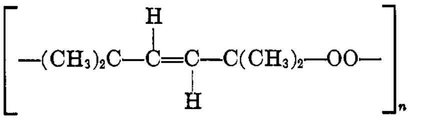
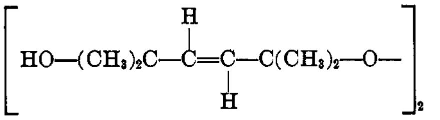
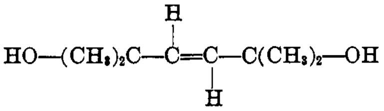
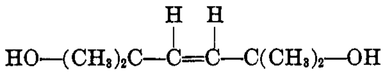
(17) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *J. Org. Chem.*, **28**, 2351 (1963).

(18) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 244.

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1959, (a) p. 45, (b) p. 36, (c) p. 96.

TABLE I

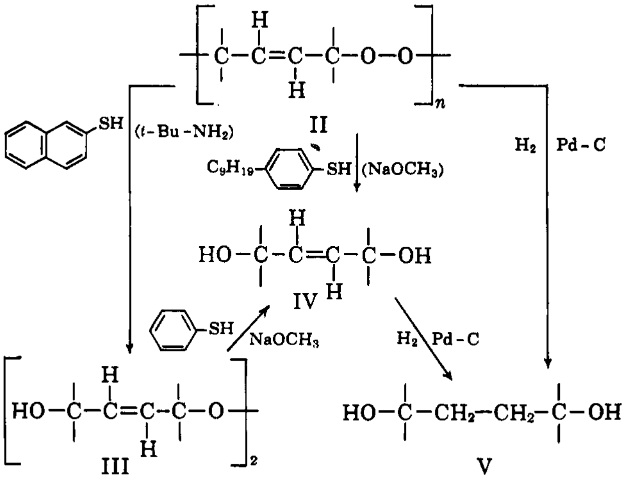
PARAMETERS OF N.M.R. SPECTRA OF 2,5-DIMETHYL-2,4-HEXADIENE AND ITS OXIDATION PRODUCTS[a]

Compound	Chemical shifts of structural units[b]			
	$-\overset{CH_3}{\underset{CH_3}{C}}-$	$=\overset{H}{C}-$	$-CH_2-CH_2-$	O—H[c]
 $\overset{A\,CH_3}{\underset{B\,CH_3}{}}\!>C=\underset{H}{C}-\underset{H}{C}=C<\!\overset{CH_3\,A}{\underset{CH_3\,B}{}}$	A: 1.73[d] B: s 1.78	s 5.97[e]		
 $\left[-(CH_3)_2C-\overset{H}{C}=\underset{H}{C}-C(CH_3)_2-OO-\right]_n$	s 1.30	s 5.70		
 $\left[HO-(CH_3)_2C-\overset{H}{C}=\underset{H}{C}-C(CH_3)_2-O-\right]_2$	s 1.30	s 5.68		3.50
 $HO-(CH_3)_2C-\overset{H}{C}=\underset{H}{C}-C(CH_3)_2-OH$	s 1.32	s 5.80		s 2.82
 $HO-(CH_3)_2C-\overset{H}{C}=\overset{H}{C}-C(CH_3)_2-OH$	s 1.40	s 5.35		s 1.50
$HO-(CH_3)_2C-CH_2-CH_2-C(CH_3)_2OH$	s 1.23		s 1.58	s 2.20

[a] $CDCl_3$ as a solvent. [b] Downfield from tetramethylsilane, internal reference; p.p.m.; s = singlet. [c] The positions of these signals may vary with the nature of the solvent and the concentration. [d] Unresolved doublet, assigned the *trans*-methyl group since it shows a remote splitting ($J \backsim 0.5$ c.p.s.) by the *trans*-vinyl protons (L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Inc., New York, N. Y., 1959, p. 85); the *cis*-methyl group signal shows no coupling and appears as a sharp singlet. [e] Broadened owing to coupling to the *trans*-methyl groups.

All these data suggested that the autoxidation of 2,5-dimethyl-2,4-hexadiene occurred in a selective *trans*-1,4 manner.[20]

Reduction of the Polyperoxide.—The proposed *trans*-1,4 structure of the polyperoxide II was further proven by the following series of reduction reactions.



Catalytic hydrogenation on palladium–charcoal under pressure reduced both the C=C- and the O–O bonds to give 2,5-dimethylhexane-2,5-diol (V) in almost quantitative yield.

t-Butylamine-catalyzed reduction with 2-naphthalenethiol attacked the O–O bonds selectively. This reaction, however, did not produce the anticipated unsaturated diol IV, but instead only the partially reduced product III as evidenced from its positive peroxide test with sodium iodide in acetic acid. The infrared spectrum of this compound (m.p. 58–59°) had a strong OH absorption at 3.0 μ.[19c] The n.m.r. spectrum showed three singlets with the relative intensities of approximately 1:2:12, corresponding to the hydroxy, vinyl, and methyl protons, respectively. The presence of a strong infrared band (in carbon tetrachloride solution) at 9.68 μ that was not present in the spectrum of either II or IV convinced us that III was not an eutectic mixture of the diol IV and the starting polyperoxide II. Furthermore, a synthetic mixture of the polyperoxide II and the diol IV exhibited an n.m.r. spectrum in which all signals characteristic of the individual components clearly were separated. On the basis of this evidence and the relative intensities of the n.m.r. signals, structure III is suggested for this partially reduced product. The successful further reduction of III with thiophenol in the presence of a base to form *trans*-2,5-dimethyl-3-hexene-2,5-diol furnished additional proof for this structure.

Complete reduction of the peroxy linkages of the polyperoxide II was achieved by using a stronger base as catalyst and higher reaction temperatures. When a mixture of the polyperoxide, 4-nonylthiophenol, and catalytic amounts of sodium methylate was heated under vacuum, a rapid exothermic reaction occurred at 130–140°. This reaction yielded 75% of *trans*-2,5-dimethyl-3-hexene-2,5-diol (IV). The residue contained 4-nonylphenyl disulfide, indicating that the following reaction took place.

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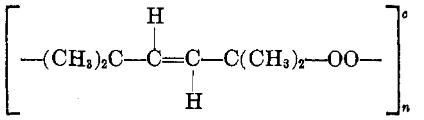
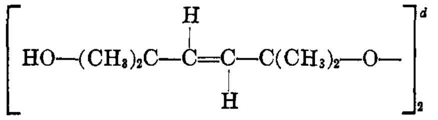
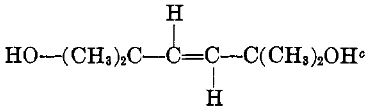
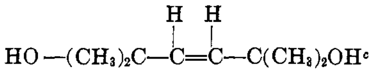
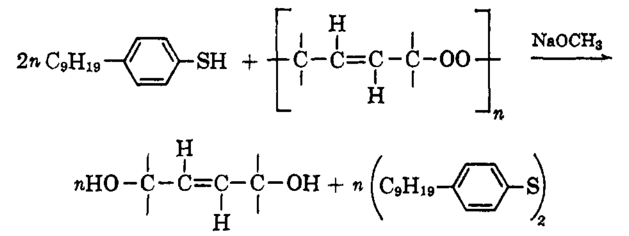
[20] From here on, methyl groups are represented by unsatisfied bonds in the formula.

TABLE II

INFRARED SPECTRA OF 2,5-DIMETHYL-2,4-HEXADIENE AND ITS OXIDATION PRODUCTS[a]

Compound	Stretching region			—C(CH₃)₂—	Other				
	OH	=C—H	C=C	deformation					
$(CH_3)_2C{=}CH{-}CH{=}C(CH_3)_2$[b]	...	3.30 m	6.15 m	7.22 s 7.27 s				8.54 m	
 $\left[-(CH_3)_2C-\overset{H}{C}=\underset{H}{C}-C(CH_3)_2-OO-\right]_n$[c]	...	3.31 i	5.95 w	7.27 s 7.36 s	7.75 m	7.97 s		8.55 s	8.82 vs
 $\left[HO-(CH_3)_2C-\overset{H}{C}=\underset{H}{C}-C(CH_3)_2-O-\right]_2$[d]	3.00 vs	3.31 i		7.26 s 7.35 s	7.75 m	7.95 s		8.55 i	8.80 vs
 $HO-(CH_3)_2C-\overset{H}{C}=\underset{H}{C}-C(CH_3)_2OH$[c]	3.00 vs	3.31 w	6.12 w	7.30 s 7.37 s	7.83 s			8.14 s	8.85 vs
 $HO-(CH_3)_2C-\overset{H}{C}=\overset{H}{C}-C(CH_3)_2OH$[c]	3.00 vs	3.30 i 3.30	6.05 w	7.25 s 7.35 s	7.68 m	7.99 w	8.32 m	8.45 s	8.64 vs
$HO-(CH_3)_2C-CH_2-CH_2-C(CH_3)_2OH$[c]	3.05 vs	...	...	7.27 s 7.33 s	7.64 m	7.77 s	8.00 s	8.30 s	8.70 vs

[a] Characteristic absorption peaks: vs, very strong; s, strong; m, medium; w, weak; i, inflection. [b] No solvent. [c] KBr pellet.



The structure of the diol (IV) was established by subsequent catalytic hydrogenation to form 2,5-dimethylhexane-2,5-diol (V), and by its n.m.r. spectrum (Table I). Its *trans* configuration[21] was confirmed by agreement of its melting point[22,23] and the position of typical infrared bands[23] with those reported for authentic samples.

We realized that the exclusive formation of a *trans*-diol in the selective reduction reaction did not necessarily prove the proposed *trans* configuration of the polyperoxide II, since isomerization could occur under the conditions of the reduction reaction. To exclude the possible intermediacy of a *cis*-diol, we prepared the corresponding *cis*-2,5-dimethyl-3-hexene-2,5-diol and treated it under the same conditions. No isomerization was observed. Since there is no apparent reason to assume that *cis–trans* isomerization of a *cis*-polyperoxide would occur more easily than that of a *cis*-diol, we feel that this experiment adds strong support to the proposed *trans* configuration of the polyperoxide II.

This was further substantiated by a comparison of the n.m.r. spectra of all of our products with that of the *cis*-diol (Table I). From the fact that both the methyl and the vinyl proton signals of the dimeric peroxide III appeared as singlets, it was evident that the change from the structural unit of a $(CH_3)_2C{-}O{-}O$ to that of a $(CH_3)_2C{-}OH$ group does not exert a noticeable chemical shift of these signals (the same is true for *t*-butyl alcohol and *t*-butyl hydroperoxide). A change of the configuration at the double bond, however, does give rise to a significant chemical shift, as can be seen by a comparison of the spectra of *cis*- and *trans*-2,5-dimethyl-3-hexene-2,5-diol (Table I). The perfect correspondence of the signals of the polyperoxide II with those of the *trans*- rather than those of the *cis*-2,5-dimethyl-3-hexene-2,5-diol supports, therefore, anew the *trans* configuration of the polyperoxide II.

Infrared studies demonstrated that the OH absorption bands of both *trans*- and *cis*-2,5-dimethyl-3-hexene-2,5-diol shifted to lower wave lengths upon dilution (Table III). This would indicate that the hydroxyl groups of the *cis*-diol do not form strong intramolecular hydrogen bridges. Molecular models showed that steric crowding of the methyl groups might well prevent the hydroxyl groups from assuming a conformation that would allow strong intramolecular hydrogen bonding.

TABLE III

RESULTS OF HYDROGEN BONDING STUDIES BY INFRARED SPECTROSCOPY OF THE STEREOISOMERIC 2,5-DIMETHYL-3-HEXENE-2,5-DIOLS

Concentration, mole/l.	Cell size, mm.	Wave length (μ) of OH stretching band[a]	
		cis-Diol[b]	*trans*-Diol[c]
1.0	0.096	3.0 vs	2.93 vs and 2.77 m
0.1	0.98	3.08 vs	2.89 m and 2.76 s
0.01	10.0	3.08 m and 2.90 s	2.87 w and 2.76 s
0.005	10.0	...	2.90 w

[a] vs, very strong; s, strong; m, medium; w, weak. [b] Due to the limited solubility in CCl_4 the 1 M solution was prepared in $CHCl_3$ and subsequently diluted with CCl_4. [c] The 1.0 and 0.1 M solutions were run in $CHCl_3$; the 0.01 M solution was obtained by diluting the former with CCl_4.

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[21] The configuration of this diol has been a controversial issue in the literature for a long time. See, *e.g.*, (a) R. Johnson and O. H. Johnson, *J. Am. Chem. Soc.*, **62**, 2615 (1940); (b) I. Zalkind, *ibid.*, **63**, 2282 (1941); (c) R. Johnson, *ibid.*, **63**, 2282 (1941).

[22] K. Alder and H. V. Brachel, *Ann.*, **608**, 195 (1957).

[23] I. N. Nazarov, L. D. Bergel'son, L. P. Badenkova, and B. V. Lopatin, *Zh. Obshch. Khim.*, **28**, 1132 (1958).

characteristic peaks above 7.5 μ, including C—O stretching and =C—H deformation absorption peaks									
	9.47 s	10.13 m					11.88 vs	12.25 m	15.05 m
		10.20 s					11.38 s	12.98 m	
	9.68 vs		10.35 s				11.35 m		
	9.91 m	10.20 vs	10.39 vs	10.73 m		10.98 m	11.98 w	12.94 s	14.85 m
		10.28 s	10.44 s	10.76 m		11.36 m	11.98 m	12.15 m	13.59 m
9.09 vs	9.72 w	10.14 w	10.34 m	10.74 s	10.82 s	10.96 vs		12.73 m	13.23 m

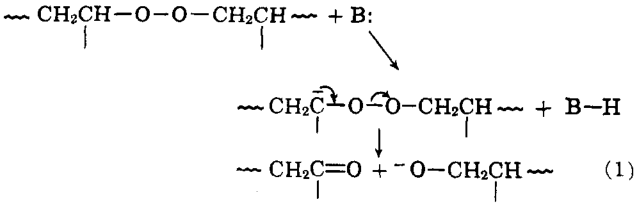
[d] In CCl_4 solution.

Discussion

The formation of an exclusively 1,4-polyperoxide is the first example of an entirely selective copolymerization of oxygen and an acyclic conjugated diene. It extends the scope of our previous hypothesis[7] concerning the course of conjugated diene-free radical reactions, *i.e.*, the intermediate allylic radical combines with the oxygen diradical at the more substituted allylic position.

The selective reduction method described above represents a new synthetic tool for the conversion of an unsaturated dialkyl polyperoxide to the corresponding unsaturated diol. The high yields and the lack of *cis–trans* isomerization under these conditions suggest that this method may also be useful as an analytical tool for the structural elucidation of similar unsaturated autoxidation products. An inherent advantage of this method over others is the fact that the reduction products can in any given case be removed from the reaction mixture as soon as they are formed. This is possible since the starting polyperoxides are higher boiling materials than their reduction products and because the reducing thiol is converted to its higher boiling disulfide. The only essential criterion is, therefore, to select a thiol that is higher boiling than the anticipated reduction product(s).

There are several obvious reaction paths that may be generally envisaged for the cleavage of peroxide linkages under the conditions employed.[24a,b] Mayo and Miller[16] proposed that the first step in base-catalyzed cleavage reactions may involve the abstraction of a proton at the α-carbon atom. Subsequent cleavage would then lead to a carbonyl compound and an alcohol, *e.g.*, see eq. 1.



$$\sim CH_2CH{-}O{-}O{-}CH_2CH\sim + B: \longrightarrow \sim CH_2\overset{\frown}{C}{-}O{-}\overset{\frown}{O}{-}CH_2CH\sim + B{-}H \longrightarrow \sim CH_2C{=}O + {}^{-}O{-}CH_2CH\sim \quad (1)$$

Since all the α-carbon atoms in the polyperoxide II are substituted by methyl groups, this reaction path can be precluded in our case.

A second possibility is the homolytic cleavage of the peroxy bond and subsequent hydrogen abstraction from a thiol to form alcohol and disulfide. Since our

$$RO{-}OR \longrightarrow 2RO\cdot \xrightarrow{2R'SH} 2ROH + R'SSR'$$

reduction reactions occurred at rather high temperatures, such a homolytic cleavage of the peroxide cannot be excluded. However, it is hard to recognize the role of the base in a reaction of this type. Therefore, we would like to advance another proposal for the course of our base-catalyzed peroxide reduction, shown below.

$$\begin{array}{lcl} R'S^- + RO{-}OR & \longrightarrow & R'S{-}OR + RO^- \\ R'S^- + R'S{-}OR & \longrightarrow & R'S{-}SR' + RO^- \\ \hline 2R'S^- + RO{-}OR & \longrightarrow & R'S{-}SR' + 2RO^- \end{array}$$

The first step in this reaction course involves a nucleophilic substitution at oxygen by the thiolate ion to form an alkoxide ion and a sulfenate ester. Subsequent displacement of a second alkoxide ion—this time at sulfur—by another thiolate ion leads to the observed reaction products, *viz.*, alcohol and disulfide. The latter step would be analogous to the well-known reduction of hypoiodite to iodine by the iodide ion.

Experimental

Materials.—2,5-Dimethyl-2,4-hexadiene from Matheson was practical grade. It was redistilled before use. 2,5-Dimethyl-3-hexyne-2,5-diol and 2,5-dimethylhexane-2,5-diol from Matheson were recrystallized before use. The "4-nonylthiophenol" from Pitt-Consol was a mixture of isomeric 4-nonylthiophenols.

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[24] A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers) Ltd., London, 1961: (a) p. 128, (b) p. 165.

Methods of Analyses.—The infrared spectra were recorded on a Baird spectrophotometer, Model B. The hydrogen bonding studies were made using a calcium fluoride prism. The nuclear magnetic resonance spectra were recorded on a Varian Model A-60 proton resonance spectrometer.

Method of Autoxidation.—The autoxidation was generally carried out in a round-bottom flask, equipped with a condenser, a magnetic stirrer, and a sintered glass inductor. The reaction flask in each case was placed into a temperature controlled (15 ± 1°) water bath. For the ultraviolet-initiated reactions, quartz flasks were used, while the uncatalyzed reactions were carried out in darkened Pyrex flasks. In cases where only intermittent irradiation was used, the quartz flask was darkened and the ultraviolet lamp was removed while the oxygenation was continued. As a source for the ultraviolet light, a 100-w. Hanovia utility lamp was used. The oxygen flow rate was in each case adjusted so that one bubble of gas left the reaction mixture per second.

For a comparison of the relative autoxidation rates under different conditions, samples were taken from the reaction mixtures at regular time intervals and analyzed by n.m.r. spectroscopy. The results of these experiments are summarized in Fig. 1.

Preparation of the Polyperoxide II.—The freshly distilled diene I (122 g., 0.1 mole) was autoxidized under ultraviolet irradiation. After 2–5 min. the mixture in the reaction flask exhibited a faint yellow color which disappeared within the next hour. After 4–5 hr. 60% of the diene was converted and the peroxide began to precipitate as a white semisolid. The oxygenation was continued overnight without further ultraviolet irradiation to yield a sticky, colorless mass. Infrared and n.m.r. analysis of this crude mixture demonstrated that it consisted only of the polyperoxide and the unreacted diene. The crude mixture was recrystallized from methanol and *n*-heptane to yield 133.3 g. (84%) of the polyperoxide II, m.p. 62–65°.

Anal. Calcd. for $(C_8H_{14}O_2)_n$: C, 67.57; H, 9.92. Found: C, 67.42; H, 10.56; mol. wt. (cryoscopic in *p*-bromotoluene), 1520, *i.e.*, n = 10–11.

The active oxygen content was determined by reduction of the polyperoxide by a saturated solution of sodium iodide in glacial acetic acid at 60° under nitrogen atmosphere, and subsequent titration of the iodine liberated. The titration value was corrected by running a blank sample under the same conditions.

Anal. Calcd. for active oxygen: 11.25. Found: 10.0 (89% of the theory).

Catalytic Hydrogenation of the Polyperoxide II.—A mixture containing 10 g. (0.07 mole) of the polyperoxide and 0.5 g. of a 10% palladium-on-charcoal catalyst in 70 ml. of tetrahydrofuran reacted for 22 hr. under approximately 10 atm. of hydrogen pressure at 24°. The catalyst was removed by filtration and the solvent was evaporated to yield 8.9 g. (90%) of the essentially pure (according to its infrared spectrum) saturated diol V. It was recrystallized from a mixture of ether and *n*-pentane to yield colorless crystals, m.p. 87–88°. Mixture melting point (86–87°) and comparison of the infrared and n.m.r. spectra with those of an authentic sample established identity.

Partial Reduction of the Polyperoxide II.—A solution containing 12.8 g. (0.08 mole) of 2-naphthalenethiol, 5.68 g. (0.04 mole) of the polyperoxide II, and 0.28 g. (0.004 mole) of *t*-butylamine in 100 ml. of tetrahydrofuran was heated to reflux overnight. The reaction mixture was poured into twice its volume of methanol and kept in the refrigerator for a day. The di(2-naphthyl) disulfide by-product was filtered and the mother liquor cooled to −70°. The dimeric peroxide III precipitated as a colorless solid, m.p. 58–59°.

Selective Reduction of the Dimeric Peroxide III.—A mixture of 10 g. (0.35 mole) of the dimeric peroxide III, 38.5 g. (0.35 mole) of benzenethiol, and 5.9 g. (0.1 mole) of sodium methoxide was placed into a flask, equipped with a 10-cm. Vigreux column. The mixture was heated under vacuum (1 mm.) while it was stirred. At a bath temperature of 120°, an exothermic reaction occurred. The reduction product distilled together with some benzenethiol. After recrystallization from ether, 8 g. (80%) of *trans*-2,5-dimethyl-3-hexene-2,5-diol (IV) was obtained, m.p. 93–94°.

Selective Reduction of the Polyperoxide II.—A mixture of 20 g. (0.14 mole) of the polyperoxide and 1.35 g. (0.025 mole) of sodium methoxide in an excess (95 g., 0.4 mole) of isomeric 4-nonylthiophenol was treated as in the previous case. A vigorous reaction occurred at a bath temperature of 140°. The product distilled between 95–97° at 2 mm. Recrystallization from ether afforded 15 g. (75%) of the diol IV, m.p. 93–94°.

The residue in the distillation flask was a dark brown oil. The unchanged 4-nonylthiophenol was removed from it by methanol extraction. The residue thereof was a mixture of isomeric di(4-nonylphenyl) disulfides, as shown by the comparison of its infrared and n.m.r. spectra with those of an authentic sample.

Preparation of Isomeric Di(4-nonylphenyl) Disulfides.—To a solution of 45.2 g. (0.2 mole) of the isomeric 4-nonylthiophenol and 0.73 g. (0.01 mole) of *t*-butylamine in 100 ml. of methanol, 9 g. (0.01 mole) of *t*-butyl hydroperoxide was added dropwise with stirring. The temperature was kept below 20° by an ice bath. The disulfide separated from the methanol solution as a slightly yellow oil. It was washed three times with 25-ml. portions of methanol to remove the unchanged hydroperoxide. Then the oil was separated and the methanol traces were removed by vacuum distillation to yield 38 g. (84%) of the crude disulfide. A sample of the isomeric disulfide was distilled, b.p. 210–220° (0.3 mm.). A narrow boiling fraction of the distillate (b.p. 215–216° at 0.3 mm.) was used for its characterization. N.m.r. analysis established that the signals of the aliphatic *vs.* aromatic protons were in the correct ratio. The ratio of the CH_3 *vs.* CH_2 proton signals, on the other hand, was higher than expected, thus indicating that the side chains consisted of isomeric nonyl groups. This probably explains why the disulfide did not crystallize.

Anal. Calcd. for $C_{30}H_{46}S_2$: C, 76.53; H, 9.84; S, 13.62. Found: C, 76.54; H, 9.58; S, 13.78.

Catalytic Hydrogenation of the Unsaturated Diol IV.—A mixture of 0.9 g. of IV and 0.2 g. of a 10% palladium-on-charcoal catalyst in 50 ml. of methanol reacted for 24 hr. under 100 atm. of hydrogen pressure at room temperature. The catalyst was removed by filtration and the solvent was evaporated to yield 0.7 g. (77%) of the saturated diol V, m.p. 87–88°. Mixture melting point (86–87°) and comparison of the infrared and n.m.r. spectra established identity with an authentic sample and with the product, derived from catalytic reduction of the polyperoxide.

Preparation of *cis*-2,5-Dimethyl-3-hexene-2,5-diol.—A mixture of 29 g. (0.2 mole) of 2,5-dimethyl-3-hexyne-2,5-diol and 0.5 g. of a 10% palladium-on-charcoal catalyst in 100 ml. of ethanol reacted for 3 min. under 85 atm. of hydrogen pressure at room temperature. The catalyst was removed by filtration, and the solvent was evaporated to yield 28.8 g. (95%) of the crude reduction product that was recrystallized from ether, m.p. 65–68° (*cf.* 69° in the literature[23]). N.m.r. analysis showed that besides the expected *cis*-2,5-dimethyl-3-hexene-2,5-diol, 6% of the *trans*-diol IV, and 5–6% of the saturated diol V were present in the reaction product.

Attempts at Isomerizing *cis*-2,5-Dimethyl-3-hexene-2,5-diol.—A mixture of 5 g. of the diol and 2.7 g. of sodium methoxide in 47 g. of 4-nonylthiophenol was heated to 140°. To assure that the diol had appropriate contact time, the reaction mixture was kept at 50 mm. pressure for 15 min. and it was vigorously stirred. Then the vacuum was increased and 4.5 g. (90%) of the diol was recovered. N.m.r. analysis showed that the configuration of the diol had not changed.

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