

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; neut. equiv., 218. Found: C, 71.45; H, 6.56; neut. equiv., 215.

Elution of the column with 10 l. of pure ether followed by 1:4 acetone-ether removed 4-hydroxy-7-oxo-7-phenylheptanoic acid γ -lactone (V) which crystallized from ethanol as massive orthorhombic prisms, m.p. 76–77° (2.2 g., 4.5%),

b.p. approx. 165–170° (0.04 mm.), $\lambda_{\text{max}}^{\text{EtOH}}$ 243 m μ (ϵ 12,700) and 278 m μ (ϵ 1,050), $\lambda_{\text{max}}^{\text{EtOH}}$ 5.61 and 5.91 μ .

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47; sapon. equiv., 218. Found: C, 71.57; H, 6.43; sapon. equiv., 213.

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Polymeric Peroxide of 1,3-Butadiene

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Controlled peroxidation of butadiene solutions has been found to produce, in high yield, polymer of molecular weight 700–850 comprising vinylthylenedioxy and 2-butenylenedioxy units (equation 1). This polymer is formed by both 1,2- and 1,4-addition of oxygen to butadiene, with 1,4-addition predominating. Structural confirmation was obtained by reduction to the corresponding butenediols and butanediols.

Although the formation of polymeric peroxides from several related dienes has been reported,^{1–4} no detailed study of the peroxidation of 1,3-butadiene appears to have been made. A published reference to a peroxide of this diene describes only an extremely explosive product.⁵ It has now been found that a relatively stable polymeric peroxide can be prepared in high yield by the controlled oxidation of butadiene in solution. This paper describes this synthesis and the characterization of the peroxide.

When the reaction of butadiene and oxygen was carried out in the presence of a suitable solvent at 85–95° and was stopped before more than about 50% of the butadiene had reacted, a liquid peroxide was obtained. The reaction temperature appeared quite critical; reaction below 75° was impractically slow, whereas above 95° secondary reactions took place yielding benzene-insoluble products. The peroxidation followed a typical autocatalytic curve and exhibited a pronounced induction period which could be minimized by the addition of a source of free radicals. The rate of oxidation showed dependence on the concentration of butadiene, but not on oxygen pressure.

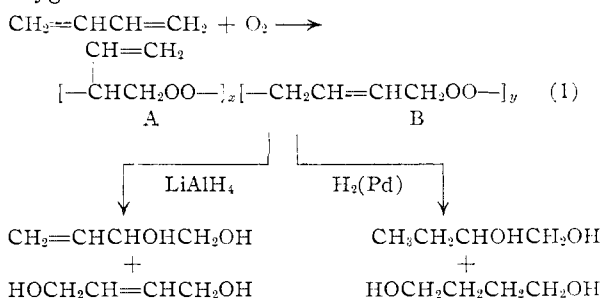
Benzene was the best of the solvents tested; dioxane and 1,1,1-trichloroethane also were satisfactory. Acidic media inhibited the peroxidation, and bases caused destruction of peroxide.

The stability of the peroxide of butadiene is much greater than was expected. Benzene solutions have been stored at 25° for several weeks without significant decomposition. At 100° the solutions had a half-life of about 13 hr. However, in concentrated form the peroxide can be detonated by ignition or severe shock and appropriate precautions must be observed in its handling. A satisfactory method for decomposition of peroxidic residues involves treatment with strong aqueous caustic.

The peroxide obtained by careful evaporation of solvent under reduced pressures was a pale yellow,

slightly viscous oil (n_D^{25} 1.5052). It was readily soluble in acetone, dioxane and chloroform, sparingly soluble in methanol and ether, and insoluble in water. Analyses established an approximate empirical formula $C_4H_6O_2$ and a polymeric structure having 8–10 units. Since iodometry⁶ established that all of the oxygen was present as peroxide, this product must then be an alternating copolymer of butadiene and oxygen.

The points of attachment of the peroxy links were fixed by reduction experiments. Treatment with lithium aluminum hydride gave *trans*-2-butene-1,4-diol and 3-butene-1,2-diol as the only isolable products; catalytic hydrogenation gave the corresponding butanediols. The 1,4-diols predominated, in contrast with work⁴ on peroxides of 2,3-dimethyl-1,3-butadiene in which no 1,4-diols were isolated. Thus, both 1,2- and 1,4-addition of oxygen to butadiene must have occurred.



The infrared absorption pattern for butadiene peroxide is in agreement with this assignment. Other reactions obtained with the peroxide can be explained on the basis of this copolymer structure. Thus thermal decomposition of unit structure A should involve C–C scission with formation of acrolein and formaldehyde, and these compounds have been isolated among the products of pyrolysis of butadiene peroxide to an extent equivalent to

(6) In common with peroxides of other conjugated dienes the peroxide of butadiene does not respond satisfactorily to conventional iodometric procedures. The procedure adopted, involving a digestion with an acetic acid solution of hydroiodic acid at 60°, gave reproducible results with both butadiene peroxide and *t*-butyl peroxide.

(7) C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

(1) K. Bodendorf, *Arch. Pharm.*, **271**, 1 (1933).

(2) E. H. Farmer, *Trans. Faraday Soc.*, **42**, 228 (1946).

(3) (a) W. Kern, H. Jockusch and A. Wolfram, *Makromol. Chem.*, **3**, 223 (1949); (b) W. Kern and J. Stallmann, *ibid.*, **7**, 199 (1951).

(4) F. K. Kawahara, *THIS JOURNAL*, **79**, 1447 (1957).

(5) D. A. Scott, *Chem. Eng. News*, **18**, 404 (1940).

20% of the peroxide. Evidence for structure B was obtained by reaction of the peroxide with phenylhydrazine to produce the bis-(phenylhydrazone) of fumaraldehyde (or malealdehyde), the product Kharasch had obtained from 1,4-bis-(*t*-butyldioxy)-2-butene.⁸

Although the evidence points to a predominance of the 1,4-structure (B) in the polymer chain, the reduction experiments were insufficiently quantitative to establish the precise ratio. Invariably, there were peroxidic materials remaining after catalytic hydrogenation, and small amounts of decomposition products of the peroxides were isolated on distillation. In addition to non-distillable tars, 2-hydroxybutanal and succinaldehyde were obtained in low yields. No evidence was obtained for 8-carbon diols or 4-carbon monohydric alcohols in the reduction products.

Experimental Details

The peroxidation experiments were carried out in pressure equipment in a barricaded area. All exploratory runs were conducted for eight hours, and the progress of the reaction was followed by measurements of changes in pressure. Experiments establishing the effect of concentration, temperature and pressure are summarized below:

PEROXIDATION OF BUTADIENE IN BENZENE

Moles butadiene/ liter benzene	Temp., °C.	Total press., atm.	Conversion to titratable, benzene- soluble peroxide in 8 hr., %
0.5	85	6.8	4
.5	90	6.8	14
.5	95	6.8	24
.5	100	6.8	32 ^a
.5	105	6.8	42 ^a
.5	110	6.8	26 ^a
2.0	85	6.8	18
4.0	85	6.8	40
4.0	90	6.8	51 ^a
4.0	85	34	43
5.0	85	6.8	52
6.0	85	6.8	35

^a A dark, benzene-insoluble oil also formed.

The following is illustrative of the general procedure for peroxidation. Two moles (108 g.) of butadiene, freed from water and acidic components by passing over caustic pellets, in 400 ml. of thiophene-free benzene was placed in a 1-liter, stainless steel rocker bomb. The free space was flushed with oxygen, and the bomb was pressured with oxygen to 3.4 atm. and warmed to 85°. Oxygen was introduced from a calibrated reservoir to bring the pressure to 10.5 atm. and agitation was started. Following a 15-minute induction period, absorption of oxygen commenced and periodic repressuring was required to maintain the pressure. After eight hours, a total of 1.18 moles of oxygen had been absorbed and the reaction was terminated by cooling.

A 1-ml. aliquot from the peroxidized product was added to 25 ml. of glacial acetic acid. The solution and the container were freed from air by sweeping with nitrogen; 5 ml. of 58% HI, decolorized by shaking with mercury, was added and the solution was warmed on a water-bath heated to 60° for 30 minutes. The resulting solution was cooled, diluted with 50 ml. of deaerated water and titrated with 0.1 *N* sodium thiosulfate. The indicated peroxide equivalent of the product of oxidation was 1.04 moles. Evaporation under high vacuum of a larger aliquot of the solution indicated the non-volatile product was equivalent to 1.05 moles of C₄H₆O₂.

Anal. Calcd. for C₄H₆O₂: C, 55.80; H, 6.98; O, 37.2. Found: C, 55.60; H, 7.16; O, 36.6 (as peroxide); mol. wt., (cryoscopically in camphor), 750.

(8) M. S. Kharasch, P. I. Pauson and W. Nudenberg, *J. Org. Chem.*, **18**, 322 (1953).

Thermal Degradation.—An 8.8-g. (0.102 peroxide equivalent) sample was added dropwise over 5.5 hr. to a flask heated to 150°, through which a slow stream of nitrogen passed. The peroxide decomposed violently upon each addition. The emergent gas stream was cooled in ice to strip liquid products and was then scrubbed with water to collect formaldehyde. The residue in the flask was 5.0 g. of a red-amber gum containing 0.017 equivalent of peroxide. Treatment of the aqueous scrub liquors with hydrogen peroxide and titration of the resulting formic acid with standard base indicated 0.022 mole of formaldehyde. The entrained liquid (0.93 g.) had an acrolein odor and reacted with 2,4-dinitrophenylhydrazine to form a solid melting at 163–165°. The literature value for the 2,4-dinitrophenylhydrazone of acrolein is 165°. Attempted purification of the solid by extraction with hot ethyl acetate resulted in conversion to a solid melting at 240°.

Anal. Calcd. for C₉H₈N₄O₄: C, 45.80; H, 3.39; N, 23.70. Found: C, 45.71; H, 3.74; N, 23.40.

These two solids were not characterized further. However, by analogy to work¹⁰ on the reaction of phenylhydrazine with acrolein, they may represent the 2,4-dinitrophenylhydrazone of acrolein and isomeric 2,4-dinitrophenylpyrazoline.

Catalytic Hydrogenation.—A solution of 35.5 g. (0.41 peroxide equivalent) of peroxidized butadiene in 100 ml. of dioxane was introduced into a silver-lined pressure tube with 1 g. of 5% palladium-on-carbon catalyst and was pressured cautiously to 27 atm. with hydrogen. The initial reaction was strongly exothermic and cooling was required. As the reaction moderated, the pressure was increased to 68 atm. and the temperature was held at 50°. Approximately 0.5 mole of hydrogen was adsorbed during four hours. The solution was filtered from the catalyst and was found to contain 0.096 equivalent of peroxide. It was recharged to the tube with 1 g. of ruthenium oxide catalyst and was pressured to 102 atm. with hydrogen at 95°. Additional hydrogen absorption equivalent to about 0.2 mole took place during two hours. The residual solution, which contained 0.043 equivalent of titratable peroxide, was filtered to separate the catalyst and was distilled at 15 mm. pressure. Three fractions were collected: (a) b.p. 79° (15 mm.), *n*_D²⁵ 1.4428, 3.54 g.; (b) b.p. 100° (15 mm.), *n*_D²⁵ 1.4410, 6.34 g.; (c) b.p. 133° (15 mm.), *n*_D²⁵ 1.4491, 7.11 g. The residue (4 g.) was a non-viscous oil.

Fractions a, b and c were identified as 2-hydroxybutanal, 1,2-butanediol and 1,4-butanediol, respectively. The conversions based on initial peroxide were 10, 17 and 19%.

2-Hydroxybutanal.—The infrared absorption pattern for fraction a contained strong hydroxyl and aldehydic carbonyl bands. This fraction gave positive periodic acid, ceric nitrate and Tollens tests.

Anal. Calcd. for C₄H₈O₂: C, 55.80; H, 9.31. Found: C, 55.50; H, 9.37.

The osazone prepared with 2,4-dinitrophenylhydrazine was scarlet colored, m.p. 238–239°.

Anal. Calcd. for C₁₆H₁₄N₈O₈: C, 43.03; H, 3.14; N, 25.12. Found: C, 42.95; H, 3.06; N, 24.58.

1,2-Butanediol.—On redistillation, fraction b gave b.p. 65° (5 mm.), *n*_D²⁵ 1.4358. A sample of 1,2-butanediol prepared from 1,2-dibromobutane *via* the diacetate showed *n*_D²⁵ 1.4367. Both samples gave positive periodic acid tests that distinguish them from 1,4-butanediol.

1,4-Butanediol.—Redistillation of fraction c gave a product, b.p. 100° (5 mm.), *n*_D²⁵ 1.4462, which was converted to an α -naphthylurethan, m.p. 197°.

Anal. Calcd. for C₂₆H₂₄N₂O₂: C, 72.65; H, 6.04; N, 6.51. Found: C, 72.75; H, 5.80; N, 6.45.

A mixed melting point with the bis-(α -naphthylurethan) of a known sample of 1,4-butanediol showed no depression.

Succinaldehyde was found in trace amounts in the lower boiling fraction of a similar hydrogenation. Identification was made by conversion to the bis-(*p*-nitrophenylhydrazone) whose melting point was 183–185° (literature¹¹ value 185°). The bis-(2,4-dinitrophenylhydrazone) melted at 273°.

Anal. Calcd. for C₁₆H₁₄N₈O₈: N, 25.12. Found: N, 24.81.

(9) C. F. H. Allen, *This Journal*, **52**, 2955 (1930).

(10) K. Auwers and A. Kreuder, *Ber.*, **58**, 1974 (1925).

(11) C. Harries and H. Krützfeld, *ibid.*, **39**, 3673 (1906).

Reduction with Lithium Aluminum Hydride.—Dropwise addition of 160 ml. of a benzene solution containing 0.29 equivalent of peroxidized butadiene to 25 g. (0.66 moles) of lithium aluminum hydride in 600 ml. of ether produced a mildly exothermic reaction. After four hours at reflux, the excess hydride was destroyed by the slow addition of 98 ml. of ethyl acetate followed by 10 ml. of water. The aluminum complex was destroyed by addition of 200 ml. of 30% sodium hydroxide and the resulting emulsion was extracted thoroughly with ether. Distillation of the ether extracts separated 9.9 g. (43%) boiling in the range 91–132° (14 mm.). This comprised two products: **3-Butene-1,2-diol**, b.p. 94.5–96° (14 mm.), n_D^{25} 1.4598. *Anal.* Calcd. for $C_4H_8O_2$: C, 55.80; H, 9.31. Found: C, 56.00; H, 9.37.

trans-2-Butene-1,4-diol, b.p. 132° (14 mm.), n_D^{25} 1.4750. *Anal.* Found: C, 55.32; H, 9.38.

The bis-(α -naphthylurethan) of the *trans*-2-butene-1,4-diol, recrystallized from 1-butanol, melted at 220°. *Anal.* Calcd. for $C_{28}H_{22}N_2O_2$: N, 6.57. Found: N, 6.37. Infra-red spectra were consistent with the above assignments.

An alternate procedure giving higher yields involved treatment of the reduction mixture with acetic anhydride according to the method of Lardon and Reichstein.¹² A solution of 8.2 g. (0.095 equivalent) of butadiene peroxide in 30 ml. of dioxane was added dropwise to a stirred solution of 12.5 g. (0.33 mole) of lithium aluminum hydride in 300 ml. of dry ether. Reflux was maintained for 3 hours after addition was complete, and the resulting solution allowed to stand overnight; 70 ml. of acetic anhydride was added cautiously, followed by a more rapid addition of a mixture of 50

ml. of acetic anhydride and 30 ml. of pyridine. The solvent was removed by warming until the solution temperature reached 70°. The residue was saturated with sodium potassium tartrate and extracted with chloroform. The extracts were concentrated and distilled. Two fractions were separated: (a) b.p. 100–124° (20 mm.), 2.93 g., and (b) b.p. 124–134° (20 mm.), 5.47 g. Upon redistillation, fraction a gave b.p. 111° (20 mm.), n_D^{25} 1.4295, and fraction b gave b.p. 133° (20 mm.), n_D^{25} 1.4406, sapon. equiv. 86.0 (calcd. for $C_8H_{12}O_4$, 86.0). No higher boiling esters were found. These products correspond to known diacetates of 3-butene-1,2-diol and *trans*-2-butene-1,4-diol, respectively.^{13,14}

Reaction with Phenylhydrazine.—When a mixture of 1 g. of butadiene peroxide and 5 ml. of phenylhydrazine was warmed cautiously on a steam-bath, a vigorous reaction occurred, and water was evolved. After four hours, a mixture of 5 ml. of acetic acid and 15 ml. of ethyl alcohol was added. The hot solution was diluted with water until permanent turbidity resulted, treated with charcoal, filtered and cooled. The resulting brown crystals, 0.25 g., were recrystallized from alcohol and from benzene to produce brilliant yellow platelets melting with decomposition at 173–175°. This corresponds to the bis-(phenylhydrazone) obtained by Kharasch⁸ from 1,4-bis-(*t*-butyldioxy)-2-butene and to the known bis-(phenylhydrazone) prepared from fumaraldehyde.¹⁵

(13) A. N. Pudovic, *J. Gen. Chem. (USSR)*, **19**, 1179 (1949); *C. A.*, **44**, 1005 (1950).

(14) C. Prévost, *Compt. rend.*, **183**, 1292 (1926).

(15) D. L. Hufford, D. S. Tarbell and T. R. Koszalka, *THIS JOURNAL*, **74**, 3014 (1952).

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(12) A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **32**, 2003 (1949).

[CONTRIBUTION OF THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

Studies of the Peroxybenzoic Acid Oxidation of *p*-Methoxyl Substituted Stilbenes

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The mechanism of the anomalous oxidation of *p*-methoxyl substituted stilbenes by peroxybenzoic acid to give glycol monobenzoate esters has been investigated. The kinetics of the peroxybenzoic acid oxidation of *trans*-stilbene, *trans-p*-methylstilbene, *cis-p*-methoxystilbene and *trans-p,p'*-dimethoxystilbene have been studied by following both the disappearance of the peroxybenzoic acid and the formation of benzoic acid. The results of the kinetic studies support the proposed formation of an epoxide intermediate by a second-order reaction which is not acid catalyzed, followed by a slower opening of the epoxide by benzoic acid present in the system. Studies of the reaction of the epoxide of *trans-p*-methoxystilbene with benzoic acid have given results which agree with those obtained by the kinetic studies of the oxidation. The products obtained include glycol monobenzoate esters and ketones. The ketones obtained demonstrate an interesting tendency for epoxide rearrangement which suggests a correlation with the over-all retention of configuration of the esters.

It has been widely accepted that the formation of glycols or glycol esters from olefins by peroxyacid oxidation results in over-all inversion of configuration.² Recently,^{3,4} however, it has been shown that peroxyacid oxidation of certain olefins yields glycols and glycol esters with over-all retention of configuration. Therefore, it has been suggested³ that the use of peroxyacids for purposes of configuration assignment on olefins should be avoided until the reaction is better understood.

While it is commonly assumed⁵ that the formation of glycols or glycol esters is through an epoxide

(1) National Science Foundation Predoctoral Fellow, 1956–1957, 1957–1958.

(2) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, R. C. Elderfield, editor, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 27.

(3) D. Y. Curtin, A. Bradley and Y. G. Hendrickson, *THIS JOURNAL*, **78**, 4064 (1956).

(4) J. H. Brewster, *ibid.*, **78**, 4061 (1956).

(5) (a) D. Swern, *Chem. Revs.*, **45**, 30 (1949); (b) D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, Chapter 7.

intermediate, there has been no evidence to justify such an assumption in all cases of peroxyacid oxidation of olefins. The most convincing evidence presented has been the demonstration that epoxides often yield the corresponding glycols and glycol esters and that epoxides are formed from peroxyacid oxidation of olefins after shorter periods of oxidation and under milder conditions than those employed for obtaining glycols or esters. There has not been unanimous agreement on the role of the epoxide, however. Levy and Abragam⁶ have postulated that esters are formed by the addition of the elements of peroxyacids to olefins and are intermediates in the formation of epoxides, while Muskat and Herrman⁷ have shown the formation of epoxides from certain glycol esters.

Thus it was felt that in the case of the anomalous formation of glycol monobenzoate esters with re-

(6) J. Levy and D. Abragam, *Bull. soc. chim. France*, [4] **45**, 378 (1929).

(7) I. E. Muskat and M. Herrman, *THIS JOURNAL*, **54**, 2001 (1932).