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The Oxidation of Methyl Sorbate with Monoperphthalic Acid

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The products obtained by treating methyl sorbate with monoperphthalic acid under various conditions were studied by chemical and spectroscopic procedures. From the results of chemical tests and spectroscopic observations in the infrared and ultraviolet regions, it was inferred that the product in all cases is methyl *trans*-4, 5-epoxy-*trans*-2-hexenoate. This inference was confirmed by NMR spectroscopy.

Epoxy compounds are, in general, prepared from non-conjugated fatty acids or their derivatives by treatment with organic peracids. However, some epoxy compounds can be prepared from conjugated unsaturated hydrocarbons by treatment with peracetic acid.1) On the other hand, our previous study2) has shown that the substances obtained by treating β-eleostearic acid (*trans*-9-*trans*-11-*trans*-13-octadecatrienoic acid) and its methyl ester with peracetic, perbenzoic, and monoperphthalic acids are not epoxy compounds but hydroxy-acyloxy compounds. Therefore, an investigation has been made to see whether methyl sorbate (*trans*-2-*trans*-4-hexadienoate) can be epoxidized by the action of an organic peracid. The results of this investigation will be described in this paper.

In the present study, methyl sorbate was treated with monoperphthalic acid under the conditions indicated in Table I.

The saponification values and the oxirane oxygen contents of the products were 396.8—401.7 and 10.3—11.0% respectively; these values agree with the theoretical values of methyl monoepoxyhexenoate (saponification value, 394.7; oxirane oxygen content, 11.3%). Although all the products had small peroxide values (10.3—13.3 meq./kg.), such values may be due to the presence of traces of monoperphthalic acid.

However, the oxidation products cannot be identified with methyl monoepoxyhexenoate on the basis of the above data alone. According to Bauer and Bähr,3) an oxo compound (hexaoxostearic acid) is formed when a conjugated unsaturated fatty acid (eleostearic acid) is treated with perbenzoic acid. Hence, the products obtained in the present study may contain oxo groups.

The carbonyl values of the oxidation products were, therefore, determined by using hydroxylamine hydrochloride. The values obtained were 162.8—179.2. Also, the carbonyl values of methyl sorbate and crotonate, determined for purposes of comparison by the same method, were 175.6 and 101.0 respectively. On the other hand, in the test by Legal reaction with sodium nitroprusside, the oxidation products, methyl sorbate and crotonate, all gave negative results. From these observations it may be considered that the oxidation products do not contain oxo groups and that, in the determination of carbonyl values, hydroxylamine may have interacted with the carbon-carbon double bond presumed to exist in the products.

The fact that hydroxylamine interacts with the carbon-carbon double bond in an α-monoenoic fatty acid has already been reported.4) This fact supports the above inference; it also suggests that the carbon-carbon double bond in the product of the oxidation of methyl sorbate exists in the position α to the carbonyl group.

This predicted position of the double bond was confirmed by ultraviolet spectroscopic studies. The molar absorbance of the product in a heptane solution at λ_{max} 217.7 mμ was 13700. The intense absorption at this wavelength arises from the conjugation of a double bond with a carbonyl group in hydrocarbon chains.5)

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1) V. I. Pansevich-Kolyada, T. S. Strigalova and Z. B. Idel'chik, *Sbornik Stateĭ Obshcheĭ Khim.*, **2**, 1418 (1953); *Chem. Abstr.*, **49**, 4615 (1955). V. I. Pansevich-Kolyada, *Zhur. Obshcheĭ Khim.*, **26**, 2161 (1956); *J. Gen. Chem. U. S. S. R.*, **26**, 2413 (1956). A. V. Pudovik and B. E. Ivanov, *Zhur. Obshcheĭ Khim.*, **26**, 2771 (1956); *J. Gen. Chem. U. S. S. R.*, **26**, 3087 (1956).

2) Y. Suhara and M. Nyui, *J. Japan Oil Chemists' Soc. (Yukagaku)*, **13**, 590 (1964).

3) K. H. Bäuer and O. Bähr, *J. prakt. Chem.*, **122**, 201 (1929).

4) N. E. Kologrivova and V. N. Belov, *Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Sintet. i Natural. Dushistykh Veshchestv*, **1958**, No. 4, 70; *Chem. Abstr.*, **53**, 14929 (1959).

5) C. F. Allen and J. Cason, *J. Biol. Chem.*, **220**, 407 (1956).

TABLE I. REACTION OF METHYL SORBATE WITH MONOPERPHTHALIC ACID

Monoperphthalic acid 0.30 mol.
Ether as solvent 280 ml.

Condition				Result		
Exp. No.	Methyl sorbate g.	Temp. °C	Time hr.	Peracid consumption %	Yield of product	
					Crude g.	Purified g.
1	37.8	20—22	17	81.9	35.2	10.4
2	37.8	20—28 30 37	13 4 2	94.6	35.8	10.8
3	37.8	Room temp. 15 days		92.5	36.1	11.3
4	18.9	30—31 37	21 13	82.0	18.2	10.6

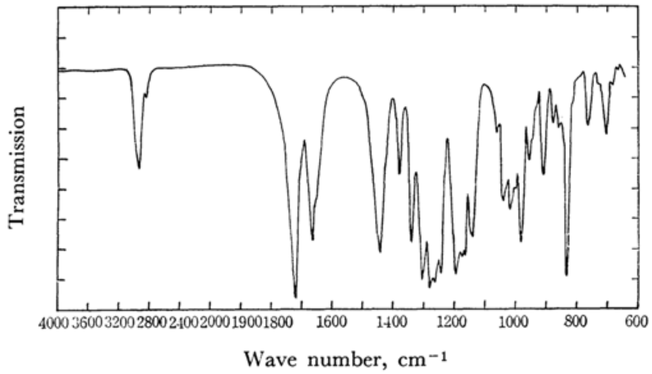
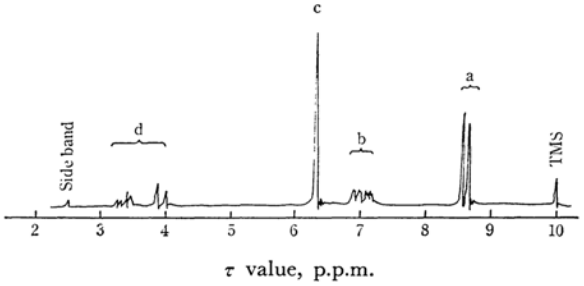


Fig. 1. Infrared absorption spectrum of the oxidation product.



Sweep rate, 3.96 c.p.s./sec.; 100 Mc.; H_1, −70 db

Fig. 2. NMR spectrum of the oxidation product (0.1 g.) in carbon tetrachloride (1 ml.).

The structural characteristics of the oxidation products were further studied by infrared spectroscopy. In this case, the infrared spectra of methyl sorbate, crotonate and levulinate were also determined for purposes of comparison. The infrared spectra of the oxidation products were nearly all the same; one of them is presented in Fig. 1. The band at 980 cm^{-1} is due to the trans double bond existing in the position α to the carbonyl group in unsaturated fatty acids.[6] The absorption band exhibited by the oxidation products at 834 cm^{-}, may correspond to the band at 837 cm^{-1} in the spectrum of methyl crotonate.

The two bands at 1280 and 877 cm^{-1} in the spectrum of the product suggest the presence of *trans*-epoxy groups, because the literature[7] shows that many of the *trans*-epoxy compounds hitherto studied absorb near 1250 and 890 cm^{-1}. This spectroscopic information is in harmony with the results of the oxirane oxygen determination. The slight displacement of the observed bands

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[6] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London (1958), p. 45.

[7] L. J. Bellamy, ibid., p. 115.

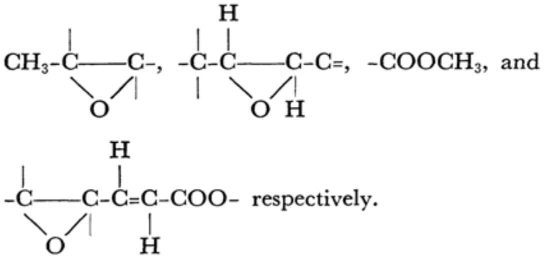
from the normal band positions may be due to the presence of a double bond near the epoxy group in the oxidation product.

The type of epoxy group suggested by the spectrum can be supported theoretically. From the stereochemical point of view, it is evident that the epoxy groups resulting from the reaction of methyl sorbate with paracids must exist in the trans-form, for methyl sorbate contains two trans-double bonds and, according to Lynch and Pausacker,[8] epoxidation with organic peracids always results in cis-addition.

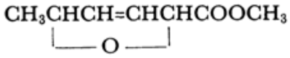
Moreover, no absorption bands due to the conjugated double bond (1614 and 997 cm^{-1} [9]), the γ-keto carbonyl group (1736 cm^{-1} in the spectrum of methyl levulinate) and the hydroxyl group (near 3500 cm^{-1} [10]) appear in the spectrum of the oxidation products.

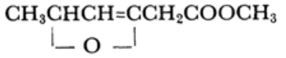
From the results of chemical tests and spectroscopic observations, it follows that the oxidation product obtained in each experiment contains neither a hydroxyl nor a keto carbonyl group, but an epoxy group and a double bond. As the ultraviolet and infrared spectra show, the double bond is in the position α to the ester carbonyl group; hence, the epoxy group is an α-epoxy group.

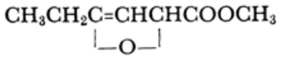
This conclusion was confirmed by NMR spectroscopy. The spectrum is presented in Fig. 2. As might be expected from the molecular structure suggested above, there appear four signals (mostly multiplets), which are marked a, b, c, and d in the figure. The chemical shift and signal intensity (peak area) measurements indicate that the signals, a, b, c, and d, are due to the groups



In a study similar to the present one, Smit[11] has stated that the product obtained by treating 9, 11-octadecadienoic acid with perbenzoic acid is a γ- or β-epoxide. Should the reaction of methyl sorbate with monoperphthalic acid proceed in nearly the same manner as the reaction of 9, 11-octadecadienoic acid with perbenzoic acid, one of the three epoxides represented below by formulas I, II, and III would be formed:


$$CH_3\underbrace{CHCH{=}CHCH}_{O}COOCH_3$$
(I)

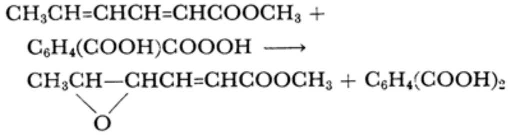

$$CH_3\underbrace{CHCH{=}C}_{O}CH_2COOCH_3$$
(II)


$$CH_3CH_2\underbrace{C{=}CHCH}_{O}COOCH_3$$
(III)

Whichever the product may be, the ultraviolet spectrum will show an absorption peak near 183 mμ (due to the isolated double bond[12]) and the infrared spectrum will show an absorption band in the 1070—1140 cm^{-1} range (associated with the larger ring of the cyclic ether group[7]). Moreover, if the product is epoxide II or III, the NMR spectrum will show five signals.

However, none of these characteristics have been observed in the present study. Hence, there is no possibility of the formation of γ- and β-epoxides under the conditions employed.

On the basis of the information obtained, it can be concluded that the product obtained in each of the present experiments is methyl *trans*-4, 5-epoxy-*trans*-2-hexenoate, and that the reaction of methyl sorbate with monoperphthalic acid proceeds as follows:


$$CH_3CH{=}CHCH{=}CHCOOCH_3 + C_6H_4(COOH)COOOH \longrightarrow \underbrace{CH_3CH{-}CH}_{O}CH{=}CHCOOCH_3 + C_6H_4(COOH)_2$$

Even when the mole ratio of monoperphthalic acid to methyl sorbate is 2 to 1 (Exp. No. 4), the reaction does not give the diepoxide at all. (In this case, the yield of the monoepoxide is about twice the yield obtained when the mole ratio is 1 to 1.) This fact indicates that the double bond in the α position is resistant to the action of monoperphthalic acid.

Experimental*

Materials Used.—Monoperphthalic acid was prepared from phthalic anhydride by treatment with hydrogen peroxide in an ether solution according to the procedure of Goryaev et al.[13] Methyl sorbate, crotonate, and levulinate were prepared from the corresponding fatty acids by esterification with methanol in the presence of sulfuric acid as a catalyst.

Methyl sorbate: Purity: 98.2%. n_D^{25}: 1.5001. Acid value: 2.0.

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[8] B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, **1955**, 1525.

[9] L. J. Allan, G. D. Meakins and M. C. Whiting, ibid., **1955**, 1874.

[10] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen & Co. Ltd., London (1958), p. 96.

[11] M. W. C. Smit, *Rec. trav. chim.*, **49**, 675 (1930).

[12] G. A. J. Pitt and R. A. Morton, "The Chemistry of Fats and Other Lipids," Vol. 4, Pergamon Press, London (1957), p. 229.

* All melting and boiling points are uncorrected.

[13] M. I. Goryaev, G. A. Tolstikov and L. A. El'chibekova, *Zhur. Priklad. Khim.*, **34**, 946 (1961); *J. Appl. Chem. U. S. S. R.*, **34**, 912 (1961).

Saponification value: Found, 447.3; Calcd., 444.8. UV ε: 23500 at λ_{max} 253.5 mμ in a heptane solution.

Analysis.—The consumption of monoperphthalic acid was determined by the method of Wheeler.[14]

The oxirane oxygen content was determined with a hydrogen bromide-glacial acetic acid solution by the method described in our previous paper.[15] The carbonyl values were determined by the method of Milewsky and Wentzel.[16]

The purity of the methyl esters noted above, and of the reaction products, was determined by gas-liquid chromatography. The instrument used was a Hitachi Gas-Liquid Chromatograph KGL-2 with a polyester column.

Spectroscopic Observation.—The ultraviolet absorption was measured in a heptane or ethanol solution with a Hitachi ESP-2U spectrophotometer.

The infrared absorption was measured in liquid films with a Shimadzu IR-27 infrared spectrophotometer, using sodium chloride cells.

The nuclear magnetic resonance spectrum was determined with a Varian HR-100 NMR spectrometer.

The Reaction of Methyl Sorbate with Monoperphthalic Acid.—Methyl sorbate (0.15 or 0.30 mol.) was added to a solution of monoperphthalic acid (0.30 mol.) in ether (280 ml.), and the mixture was stirred under the conditions indicated in Table I. After a specified period of time, the reaction mixture containing the precipitate formed by the reaction was filtered, and the ether in the filtrate was distilled off in vacuo. Chloroform was then added to the distillation residue. At this moment, a precipitate was again formed. The chloroform solution containing the precipitate was filtered; and the filtrate was washed with water and dried over anhydrous sodium sulfate. The chloroform was then distilled off in vacuo; the residue was subjected to vacuum distillation to yield a pure oxidation product of methyl sorbate.

Anal. (Purified Product in Table I, Exp. No. 2).—Found: C, 58.91; H, 7.12; O, 33.87. Calcd. for $C_7H_{10}O_3$: C, 59.14; H, 7.09; O, 33.77%; mol. wt., 142.16. Purity: 98.0%. n_D^{25}: 1.4619. B. p. 81—83°C/8 mmHg.

The precipitate separated from the reaction mixture and that separated from the chloroform solution were combined, and the whole was recrystallized from water. The recrystallization gave monoclinic crystals melting at 208—210°C. A mixture of the crystals with *o*-phthalic acid (m. p. 210—211.5°C) melted at 199.5—202°C. The analytical characteristics of the crystallized precipitate are as follows: Acid value: found, 681.6; calcd. for *o*-phthalic acid, 675.4. Saponification value (found): 678.4. UV ε: 1260 at λ_{max} 274 mμ in an ethanol solution. (The λ_{max} in a methanol solution[17] is 272 mμ.) Therefore, the precipitate is *o*-phthalic acid.

We are grateful to Dr. Osamu Yamamoto for determining the NMR spectrum, to Mr. Katsuhiko Higuchi for performing the gas-liquid chromatographic analysis, and to Mr. Heisuke Sugita for performing the elementary analysis.

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[14] D. H. Wheeler, *Oil and Soap*, **9**, 89 (1932).

[15] Y. Suhara, *J. Japan Oil Chemists' Soc. (Yukagaku)*, **13**, 378 (1964).

[16] R. Milewsky and H. Wentzel, *Fette, Seifen, Anstrichmittel*, **57**, 702 (1955).

[17] Sadtler, 6272U (1960), Samuel P. Sadtler & Son, Inc., Philadelphia.