Notes A department for short papers of immediate interest.

Isolation of Methyl Monohydroperoxido-9-octadecynoate from the Autoxidized Methyl 9-Octadecynoate[1]

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Apart from the synthetic preparation of hydroperoxides of acetylenic hydrocarbons,[2] there has not been any record describing the isolation of hydroperoxides from the autoxidized acetylenic compounds. However, it is known that autoxidation of acetylenic compounds does form peroxides[3] whose structures have never been established.

We wish now to report the isolation of methyl hydroperoxide-9-octadecynoate as the sole product from autoxidized methyl stearolate (9-octadecynoate). The peroxide concentrate representing all autoxidized substances were proved to be methyl hydroperoxide-9-octadecynoate through peroxide values, formation of proper hydroxyl derivatives of methyl stearolate and stearate, and finally through polarographic and infrared analyses. The polarographic studies indicated that the peroxide concentrate consists of over 98% hydroperoxide. Fig. 1 shows the results from infrared analyses on the original methyl stearolate, the isolated peroxide concentrate, and the product from $SnCl_2$ reduction, for a range of more lengths: 2.0–6.0 μ. The hydroperoxide bond appeared at 2.95 μ, the hydroxyl band at 2.89 μ, and the band for triple bond at 4.42 μ. The increment in the absorption by the triple bond in the new products may be attributed to the dissymmetry[4] introduced by the hydroperoxide or by the hydroxyl group. Hence, the peroxide concentrate and its reduced product consist of a pure hydroperoxide and a hydroxy compound respectively.

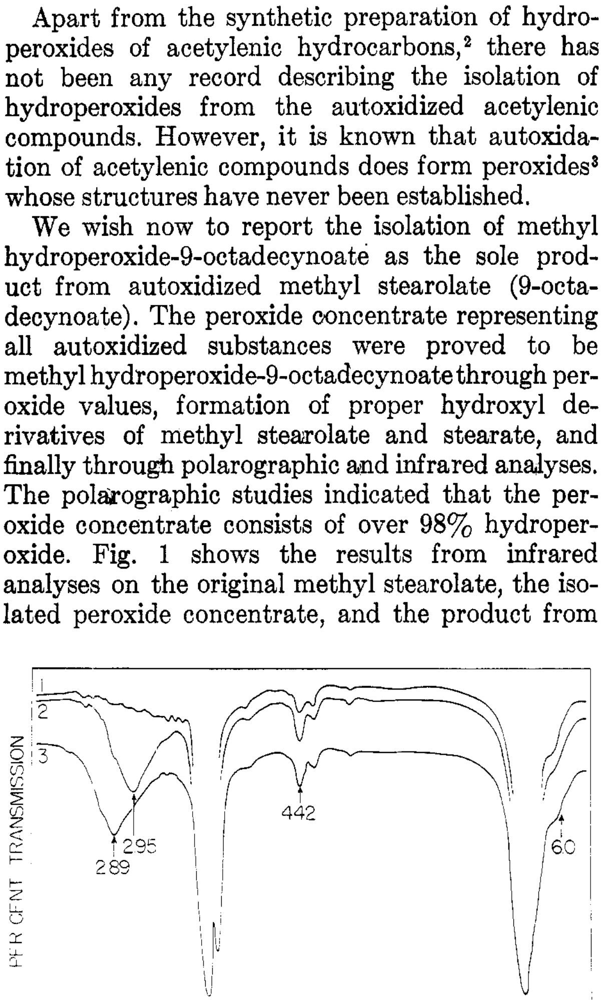

Fig. 1. Infrared absorption spectra: 1. methyl stearolate, 2. peroxide concentrate, 3. reduced peroxide concentrate

The physical and chemical properties of the reduced peroxide concentrate left no doubt as to its identity as methyl monohydroxy-9-octadecynoate.

From these evidences, it may be concluded that methyl stearolate reacts with oxygen and yields monohydroperoxide with the triple bond intact during the initial stages of autoxidation.

EXPERIMENTAL

Autoxidation of methyl 9-octadecynoate. Methyl stearolate (hydrogen absorption value, 1.98 moles/mole) prepared by the method of Khan, *et al.*[5] was autoxidized to 10% peroxide content by bubbling oxygen through a 30% *n*-heptane solution while irradiated by visible light from a 100-watt bulb. The reaction vessel (a three-necked flask fitted with a gas dispersion tube, stirrer, and an outlet connecting a guard tube of anhydrous calcium chloride), was maintained at a constant temperature of 16–17°. *n*-Heptane was freed from the unsaturated substances by the method of Cooper and Melville.[6]

Isolation of methyl monohydroperoxido-9-octadecynoate. The peroxides were quantitatively concentrated by countercurrent extraction,[7] using two immiscible solvents, 87% alcohol and *n*-heptane (each saturated by the other). The peroxide concentrate gave the peroxide value of 6030 m.e./kg. (theoretical value for methyl monohydroperoxido-9-octadecynoate, 6125 milliequivalents/kilogram) and added 2.94 moles H_2 to yield on saponification and subsequent hydrolysis, monohydroxystearic acids (m.p. 75–77.5°;[8] hydroxyl, 1.06 moles/mole). The polarographic studies were conducted by the method of Lewis, *et al.*[9] The infrared spectra were determined in carbon tetrachloride (10% solution), using a Perkin Elmer Model 21 instrument.

Preparation of methyl monohydroxy-9-octadecynoate. The peroxide concentrate was then reduced in alcohol solution (1.0 gm./100 ml.) by agitation with stannous chloride (5 moles $SnCl_2$/mole of peroxide) for 3 hr. with oxygen-free nitrogen. The resulting mixture was diluted with distilled water and then extracted with the peroxide-free ether; the

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(1) Some of the special experiments have been performed in the United States through the courtesy of different laboratories.

(2) N. A. Miles and O. L. Mageli, *J. Am. Chem. Soc.*, **74**, 1471 (1952).

(3) J. A. Nieuwland and R. P. Vogt, *The Chemistry of Acetylene*, Reinhold Publishing Corporation, New York, 1945, pp. 111, 164–5.

(4) N. A. Khan, *J. Am. Oil Chemists' Soc.*, **30**, 355 (1953).

(5) N. A. Khan, F. E. Deatherage, and J. B. Brown, *J. Am. Oil Chemists' Soc.*, **28**, 27 (1951).

(6) H. R. Cooper and H. W. Melville, *J. Chem. Soc.*, 1988 (1951).

(7) N. A. Khan, *Pakistan J. Sci. Ind. Research*, **1**, 12 (1957).

(8) S. Bergstrom, *Nature*, **156**, 717 (1945).

(9) W. R. Lewis, F. W. Quackenbush, and T. De Vries, *Anal. Chem.*, **21**, 762 (1949).

ether extract was washed twice with 3% HCl solution, then with distilled water until free of acid, and finally dried over anhydrous sodium sulfate. Evaporation of the solvent yielded the reduced peroxide concentrate consisting of methyl monohydroxy-9-octadecynoate: hydrogen absorption value, 1.96 moles/mole; hydroxyl, 1.02 moles/mole.

Anal. Calcd. for $C_{19}H_{34}O_3$: C, 73.51; H, 10.97. Found: C, 73.42; H, 10.88.

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Reaction of 1,5-Dinitropentane with Methyl Vinyl Ketone

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Michael-type condensations of aliphatic mononitro and *gem*-dinitro compounds with compounds having an activated double bond have been studied by many investigators.[2-4] However, the literature is void of this reaction with α,ω-dinitro compounds.

This communication deals with the reaction of 1,5-dinitropentane and methyl vinyl ketone, in the presence of a sodium hydroxide catalyst. The reaction was carried out in different solvents and under a variety of conditions. In all runs, besides intractable oils, a solid was obtained which analyzed correctly for a di-addition product. The maximum refined yield of 25% resulted when the reaction was carried out in 90% ethanol at 50° for 20 hr.

Two di-addition products might arise from this reaction, the symmetrical adduct I and the unsymmetrical one (Ia).

$$O_2NCH_2(CH_2)_3CH_2NO_2 \xrightarrow[OH^-]{H_2C{=}CHCOCH_3}$$

$$\underset{\text{I}}{H_3CCO(CH_2)_2CH(NO_2)(CH_2)_3CH(NO_2)(CH_2)_2COCH_3}$$

or

$$\underset{\text{Ia}}{[H_3CCO(CH_2)_2]_2CNO_2(CH_2)_3CH_2NO_2}$$

Proof that 5,9-dinitro-2,12-tridecanedione (I) had formed was obtained by (1) the Nef[5] reaction, (2) the red-white-and-blue test,[6] (3) infrared spectra, and (4) the bromination product.

The Nef reaction of the disodium salt of I gave in 28% yield a white nitrogen-free solid II, which was unstable to light and air at room temperature. The infrared spectrum of II showed a strong absorption peak at 5.93 μ, characteristic of the carbonyl group and no maxima for nitro groups. Since tertiary nitro groups are not affected in the Nef reaction, structure Ia is eliminated.

$$\text{I} \xrightarrow[2.\ H_2SO_4]{1.\ NaOH} \underset{\text{II}}{CH_3CO(CH_2)_2CO(CH_2)_3CO(CH_2)_2COCH_3}$$

When II was reacted with semicarbazide a new compound was obtained, the nitrogen analysis of which gave a low value for the expected tetrasemicarbazone and a high value for a disemicarbazone. It is possible that not all of the carbonyl groups in II had reacted, and it is believed that the product obtained constituted a mixture of semicarbazones. Attempts to form an oxime of II yielded only gummy materials. Treatment of II with 2,4-dinitrophenylhydrazine in sulfuric acid yielded the 2,4-dinitrophenylhydrazone of acetone (III) and some unreacted II. It is believed that III arose from the oxidation of II to acetoacetic acid, followed by decarboxylation.

The presence of secondary nitro groups in the addition product I was further confirmed by the blue color which resulted from the red-white-and-blue reaction. The presence of a primary nitro group would have been indicated by a red color, and a tertiary nitro group is not affected by this test.

The infrared spectrum of the di-addition product exhibited absorption maxima for the carbonyl group at 5.88 μ and the nitro group at 6.50 μ (asym. stretching) and 7.39 μ (sym stretching). These findings are also in agreement with structure I, because according to the studies of Brown,[7] a structure such as Ia should show splitting of the nitro bond in the asymmetric stretching vibration.

Additional evidence for I resulted from its bromination in the presence of two or less-than-two equivalents of base. A dibromo compound was obtained in 61% yield, the analysis and infrared spectrum of which agreed with the expected 5,9-dibromo-5,9-dinitro-2,12-tridecanedione (IV). As expected, IV was insoluble in base and gave a negative red-white-and-blue test.[8] Its infrared spectrum showed a maximum at 5.84 μ for the car-

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[1] From the M.S. Dissertation of Clayton N. Aguilar, Purdue University, May 1956.

[2] L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951).

[3] H. Shechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1276 (1951). Previous pertinent publications are cited in this paper.

[4] E. D. Bergman and R. Corett, *J. Org. Chem.*, **21**, 107 (1956).

[5] J. U. Nef, *Ann.*, **280**, 263 (1894).

[6] H. B. Hass and E. F. Riley, *Chem. Revs.*, **32**, 399, (1948).

[7] J. F. Brown, *J. Am. Chem. Soc.*, **77**, 6341 (1955).

[8] A referee has suggested that besides structures I and Ia, the compounds $CH_3CO(CH_2)_3CO(CH_2)_2CH(NO_2)(CH_2)_3$-$CH_2NO_2$ (V) and $CH_3COCH(CH_2CH_2COCH_3)CH_2CH$-$(NO_2)(CH_2)_3CH_2NO_2$ (VI), derived from an abnormal Michael addition, should be considered. Although in addition reactions of nitro paraffins to methyl vinyl ketone such self-condensations of the ketone have never been reported in the literature, this possibility cannot be ruled out *a priori*. However, the insolubility of the dibromo derivative IV in base, together with the negative color test, is evidence that IV is not a derivative of V or VI.