62. *The Course of Autoxidation Reactions in Polyisoprenes and Allied Compounds. Part VIII. The Photo-oxidation of Methyl Elaidate.*

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Methyl elaidate readily absorbs oxygen at 35° when irradiated by ultra-violet light to form a hydroperoxide-ester as the primary product. The oxidation follows the same course as in the case of methyl oleate, the product yielding on catalytic hydrogenation and saponification a mixture of hydroxystearic acids, of which one was isolated in apparently homogeneous condition. Peroxidation is accompanied by some degree of secondary reaction, which leads, as might be expected, towards scission of the chain.

A SHORT investigation into the photo-oxidation of methyl elaidate was undertaken in order to ascertain whether the course of reaction was essentially the same as that already reported for methyl oleate (Farmer and Sutton, J., 1943, 119). In view of the results recorded in the latter publication, the following experimental method was adopted. Methyl elaidate was shaken in an atmosphere of oxygen at 35° in the light of a mercury-vapour lamp until about 0·2 mol. of oxygen per mol. of ester had been absorbed. The peroxidic oxygen content of the total product was found to be substantially the same as the whole of the oxygen absorbed (maximum peroxide determination error ±5%; maximum gas measurement error ±5%), which indicated that 90% or more of the oxygen taken up still survived as peroxide groups. The whole of the oxidation mixture was then hydrogenated in the presence of Adams's catalyst, in the expectation that the peroxidised material would yield hydroxystearic ester, and the non-oxidised material stearic ester. By saponification with alcoholic alkali, the total hydrogenation product was converted into a mixture of the corresponding acids, the major portion of which was insoluble in cold aqueous alcohol.

From this major portion an attempt has been made to separate the admixed stearic and hydroxystearic acids (proportion *ca.* 4 : 1), which have very similar solubilities in organic solvents, by conversion of the hydroxy-acid into its acetoxy-derivative, followed by fractional crystallisation. The laborious fractional crystallisation was partly successful, serving to isolate about 1·5 g. of crude acetoxy-acid (from 27 g. of original mixed stearic and hydroxystearic acids), which on saponification yielded a mixture of free hydroxystearic acids. Only one of the acids contained in this mixture has been separated in (apparently) homogeneous condition (m. p. 79°). If the mechanism of oxidation of methyl elaidate is that which has been discussed in connection with the linolenic system (Farmer, Koch, and Sutton, J., 1943, 541), the attack by oxygen is likely to have taken place at any or all of the carbon atoms C_8, C_9, C_{10}, and C_{11}, and indeed, Skellon (*J. Soc. Chem. Ind.*, 1931, **50**, 332) obtained a substance which was possibly 10-hydroxystearic acid by the oxidation of oleic acid in presence of added peroxidic catalyst. It was not possible to determine the position of the hydroxyl group in the acid of m. p. 79° owing to the lack of reference compounds and the known difficulty of separating mixtures of isomeric monohydroxystearic acids (Tomecko and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 524).

Accompanying the reduced acids was a small quantity of acid material (soluble in cold aqueous alcohol) of higher oxgen content than monohydroxystearic acid. This was not positively identified, but in view of its properties it must be regarded as an oxygenated scission product (? impure ketononoic acid). There is little doubt that this highly oxygenated material was also present in the crude hydroxystearic ester obtained by catalytic hydrogenation of fairly pure methyl oleate peroxide, and this would explain the fact, already reported that the hydroxy-ester contained a higher percentage of oxygen than the theoretical, whereas the aqueous alcohol-insoluble acid derived from the ester had the correct oxygen content (Farmer and Sutton, *loc. cit.*).

EXPERIMENTAL.

Oxidation of Methyl Elaidate.—Methyl elaidate (35·7 g.) (Found : C, 77·1; H, 12·2. Calc. for $C_{19}H_{36}O_2$: C, 77·0; H, 12·2%) was oxidised during 7 hours in exactly the way described for methyl oleate (Farmer and Sutton, *loc. cit.*). The uptake of oxygen was 2·2% by weight, and the percentage of peroxidic oxygen 2·3 (method of Bolland *et al.*, *Trans. Inst. Rubber Ind.*, 1941, **17**, 29).

Hydrogenation of the total product. The product, dissolved in ethanol (75 c.c.), was hydrogenated in the presence of Adams's catalyst. Absorption was rapid, and ultimately 3090 c.c. of hydrogen (760 mm., 17°) were taken up. The theoretical absorption, assuming both the complete utilisation of the oxygen absorbed for hydroperoxide formation and the survival up to the time of hydrogenation of all the original unsaturation, was 3400 c.c.

Saponification of the mixed esters. The ethanol was removed from the hydrogenation product by evaporation in nitrogen on a steam-bath, the residue taken up in benzene (100 c.c.), and the catalyst removed by centrifuging. The benzene was completely removed at reduced pressure, and the residue taken up in rectified spirit (75 c.c.) containing potassium hydroxide (10 g.) and refluxed for 3 hours. The resulting solution was poured into water, cooled, and acidified with 2N-sulphuric acid.

Examination of the mixed acids. The precipitated acid was filtered off, washed with water, and dried (yield 32·8 g.). The aqueous-alcoholic solution was continuously ether-extracted during 3 days, the extract being evaporated to yield 1·0 g. of a low-melting hygroscopic solid (Found : C, 59·6, 59·3; H, 9·5, 9·2; equiv., 171. Calc. for $C_9H_{18}O_3$: C, 62·0; H, 10·4%; equiv., 174·3. Calc. for $C_9H_{16}O_3$: C, 62·7; H, 9·4%; equiv., 172·3). 27 G. of the precipitated acid, which contained much stearic acid (Found : C, 74·9, 74·75; H, 12·5, 12·4; equiv., 283), were boiled with a large excess of acetic anhydride for 4 hours. The bulk of the acetic anhydride was removed by distillation, and the residue of acid anhydrides boiled with water to re-form the corresponding acids. The mixture of the latter was fractionally crystallised three times from acetone, the most soluble portion, chiefly acetoxy-acids, being kept at each operation. In this way 1·5 g. of soluble acids were segregated, but the separation of acetoxy-acids thus achieved was far from complete. The crude mixture of acetoxystearic acids was saponified with alcoholic potash to regenerate the corresponding hydroxy-acids, which were further crystallised from acetone to remove the residue of the stearic acid. The hydroxy-acids (total 1 g.) were again fractionally crystallised from acetone containing a little water to yield a least-soluble portion (colourless prisms, m. p. 79°; 0·3 g.), which consisted of an apparently homogeneous monohydroxystearic acid [Found : C, 71·85; H, 11·95; OH, 11·5; equiv., 300·2. Calc. for $C_{18}H_{36}O_3$ (2 active H atoms); C, 71·9; H, 12·1; OH, 11·3%; equiv., 300·5]. The mother-liquors yielded on further partial evaporation a hydroxy-acid (0·6 g.) of unsharp m. p. 30—50°.

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