Rearrangement of an Unsaturated Epoxy-ester to a Cyclopropane Compound

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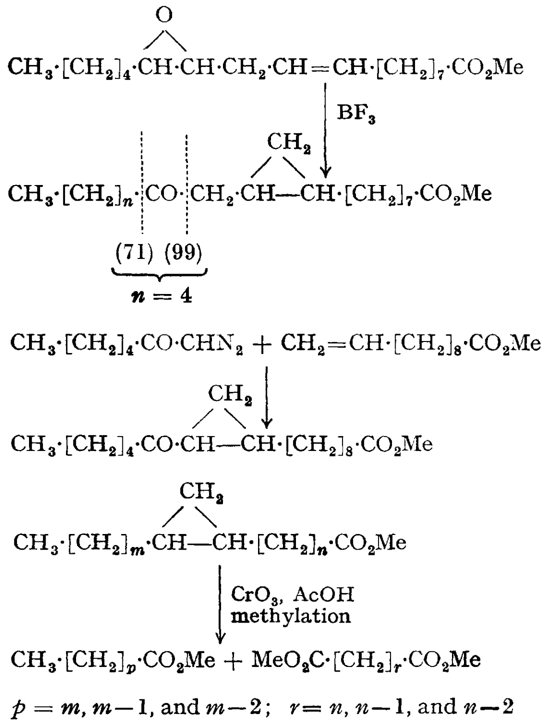
FOLLOWING the suggestion [1] that epoxy-acids may be important intermediates in the biosynthesis of polyunsaturated acids, we are studing the acid- and base-catalysed rearrangement of methyl vernolate (I). We report here an unusual rearrangement of this ester to one containing a keto-group and a cyclopropane ring.

Treated with boron trifluoride etherate in cold or boiling dioxan solution,[2] methyl vernolate gave a number of products including two (8% yield) which had a similar polarity to methyl oxo-oleate (the major product of this reaction) on thin layers of silica, but were separated from this ester by gas–liquid chromatography. When the reaction was effected in cold benzene solution, the same two products were obtained in higher yield (35%). These two compounds have not been isolated separately from each other but they were freed from other reaction products by preparative t.l.c., first on silica and then either with silica–silver nitrate or with silica after treatment with mercuric acetate which reacts with all unsaturated esters.[3] We believe these two compounds to be the *cis*- and *trans*-isomers of the oxo-cyclopropane ester (IIa). The mechanism of this cyclisation presents many interesting points which will be discussed in a fuller publication. Here we deal with evidence for this structure.

The *cis* (19·2 and 25·6) and *trans* (18·8 and 24·8) compounds (IIa) have the carbon numbers indicated on Apiezon L (5%, 210°) and diethylene-glycol succinate (D.E.G.S.) columns (20%, 190°), respectively. They showed no change on catalytic hydrogenation for 2 hr. with 10% palladium–charcoal in methanol but were reduced by sodium borohydride to compounds behaving like hydroxy-esters. Their saturated nature is confirmed by the n.m.r. spectrum which indicated complete absence of olefinic protons. This spectrum also provided evidence for a cyclopropane system with peaks in the τ 9·5—10·3 region.[4] The infrared spectrum showed ester carbonyl (1730 cm.$^{-1}$) and ketone



$$CH_3{\cdot}[CH_2]_4{\cdot}\overset{O}{CH{\cdot}CH}{\cdot}CH_2{\cdot}CH{=}CH{\cdot}[CH_2]_7{\cdot}CO_2Me \qquad (I)$$

$$\downarrow BF_3$$

$$\underbrace{CH_3{\cdot}[CH_2]_n{\cdot}\overset{(71)}{}\,CO{\cdot}\overset{(99)}{}}_{n\,=\,4}CH_2{\cdot}\overset{CH_2}{CH{-}CH}{\cdot}[CH_2]_7{\cdot}CO_2Me \qquad \text{(IIa) } (n = 4) \quad \text{(IIb) } (n = 5)$$

$$CH_3{\cdot}[CH_2]_4{\cdot}CO{\cdot}CHN_2 + CH_2{=}CH{\cdot}[CH_2]_8{\cdot}CO_2Me$$

$$\downarrow$$

$$CH_3{\cdot}[CH_2]_4{\cdot}CO{\cdot}\overset{CH_2}{CH{-}CH}{\cdot}[CH_2]_8{\cdot}CO_2Me \qquad (III)$$

$$CH_3{\cdot}[CH_2]_m{\cdot}\overset{CH_2}{CH{-}CH}{\cdot}[CH_2]_n{\cdot}CO_2Me \qquad (IV)\ (m + n = 14)$$

$$\downarrow \text{CrO}_3\text{, AcOH methylation}$$

$$CH_3{\cdot}[CH_2]_p{\cdot}CO_2Me + MeO_2C{\cdot}[CH_2]_r{\cdot}CO_2Me$$

$p = m, m-1$, and $m-2$; $r = n, n-1$, and $n-2$

carbonyl (1705—1710 cm.^{-1}) absorption along with bands at 3050 and 1020 cm.^{-1}, reported to be characteristic of cyclopropanes.[5] Mass spectra of the two components, after separation by gas–liquid chromatography, were identical, showing molecular-ion peaks at 310 and strong bands at *m/e* 99 and 71. This fixes the oxo-group on C-13 of the C_{18} chain.[6] Removal of the oxo-group by reduction of its toluene-*p*-sulphonhydrazone[7] gave a deoxo-product with infrared spectrum identical with that of methyl 9,10-methyleneoctadecanoate and carbon numbers (17·4 and 17·8 on Ap. L and 18·0 and 18·6 on D.E.G.S.) to be expected of methyl *trans*- and *cis*-methyleneheptadecanoates.[8]

In the belief that our product had the structure (III) we synthesised this from methyl undecenoate and the appropriate C_7-diazo-ketone[9] but it differed from our reaction product in its n.m.r.and i.r. spectroscopic properties. Other evidence then led us to prepare a mixture of the *cis*- and *trans*-isomers of (IIb) [a homologue of (IIa)] from methyl ricinoleate by stereomutation to a mixture of *cis*- and *trans*-isomers, oxidation, and reaction with di-iodomethane and zinc–copper couple.[8] This had n.m.r. and i.r. spectroscopic properties identical with our reaction product and carbon numbers expected of its homologue (19·8 and 20·2 on Ap. L and 25·8 and 26·6 on D.E.G.S.).

We proved the position of the cyclopropane ring by oxidation with chromic acid[10] showing first that four different methyl methyleneoctadecanoates (IV, $n = 6, 7, 8,$ and 9) each gave three monobasic and three dibasic acids which sufficed to characterise the cyclopropane esters. Our oxo-product (IIa) gave the expected dibasic acids (C_7, C_8, and C_9) along with hexanoic acid (any pentanoic acid also formed would not have been detected) and its deoxo-derivative gave the expected dibasic (C_7, C_8, and C_9) and monobasic acids (C_6, C_7, C_8).

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[1] F. D. Gunstone, *Chem. and Ind.*, 1966, 1551.

[2] H. A. Walens, R. P. Koob, W. C. Ault, and G. Maerker, *J. Amer. Oil Chemists' Soc.*, 1965, **42**, 126.

[3] W. Cocker, T. Dahl, and T. B. H. McMurry, *J. Chem. Soc.*, 1963, 1654.

[4] D. E. Minnikin, *Chem. and Ind.*, 1966, 2167; D. T. Longone and A. H. Miller, *Chem. Comm.*, 1967, 447.

[5] R. Wood and R. Reiser, *J. Amer. Oil Chemists' Soc.*, 1965, **42**, 315.

[6] R. Ryhage and E. Stenhagen, *Arkiv Kemi*, 1960, **15**, 545.

[7] L. Cagliotti and P. Grasselli, *Chem. and Ind.*, 1964, 153.

[8] W. W. Christie and R. T. Holman, *Lipids*, 1966, **1**, 176.

[9] D. Lefort, J. Sorba, and A. Pourchez, *Bull. Soc. chim. France*, 1966, 2223.

[10] C. R. Smith, T. L. Wilson, R. B. Bates, and C. R. Scholfield, *J. Org. Chem.*, 1962, **27**, 3112.