# Organic Reactions in Strong Alkalis. Part V.[1] Alkali Fusion of Epoxides and Ethers

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The results obtained from the alkali fusion of long-chain epoxy-acids indicate the occurrence of at least four different reaction pathways, one of which, a β-elimination reaction, appears to be novel for unactivated epoxides. This particular reaction is also shown to occur with simple acylic ethers, as exemplified by 11-alkoxyundecanoic acids.

THE behaviour of a functional group in concentrated alkali metal hydroxides is conveniently studied when such a group is part of a long-chain fatty acid. These compounds are readily soluble in, and retained by, the reaction medium, and the products of the reaction are such that they are conveniently analysed by g.l.c. The behaviour of unsaturated fatty acids,[2] keto- and hydroxy-acids,[3] and acids with vicinal oxygen functions,[1] has been examined previously (for a survey of alkali fusion and some related processes see ref. 4). The present paper reports a study on the alkali fusion of epoxy- and alkoxy-acids.[5]

Although the alkali fusion of epoxides and ethers has previously received little attention, the susceptibility of these compounds to nucleophilic attack [6] suggested that the following reactions might be encountered: hydrolytic fission to the corresponding glycol; hydride ion reduction to a monohydroxy-compound (the transfer of hydride ions is believed to be involved in the conversion of alcohols into carbonyl compounds by alkali fusion); [4] α-elimination as reported [7a] to occur with norbornene oxide as illustrated in Scheme 1a (*cf.* the base-catalysed reaction of cyclodecene oxide [7b]); β-elimination [8] as

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[1] Part IV, R. A. Dytham and B. C. L. Weedon, *Tetrahedron*, 1960, **9**, 246.

[2] (*a*) R. G. Ackman, Sir Patrick Linstead, B. J. Wakefield, and B. C. L. Weedon, *Tetrahedron*, 1960, **8**, 221; (*b*) R. G. Ackman, R. A. Dytham, B. J. Wakefield, and B. C. L. Weedon, *ibid.*, p. 239.

[3] R. A. Dytham and B. C. L. Weedon, *Tetrahedron*, 1960, **8**, 242.

[4] B. C. L. Weedon, ' Techniques of Organic Chemistry,' vol. XI, ed. A. Weissberger, Interscience, New York, 1963.

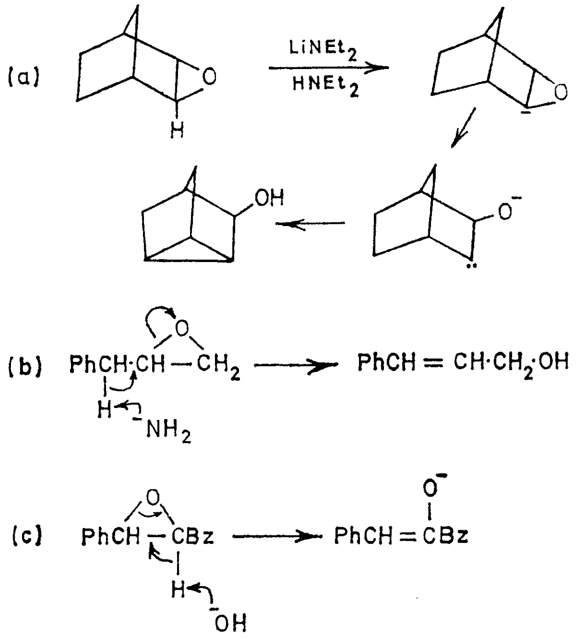
[5] Preliminary communication, M. F. Ansell, A. N. Radziwill, D. J. Redshaw, I. S. Shepherd, D. Wallace, and B. C. L. Weedon, *Agric. and Food Chem.*, 1965, **13**, 399.

[6] (*a*) E. Stande and F. Patat, ' Cleavage of the C–O–C Bond ' in ' Chemistry of the Ether Linkage,' ed. S. Patai, Interscience, New York, 1967; (*b*) R. J. Gritter, ' Reactions of Cyclic Ethers,' *ibid.*, p. 372; (*c*) R. L. Burwell, *Chem. Rev.*, 1954, **54**, 615.

[7] (*a*) J. K. Crandall, *J. Org. Chem.*, 1964, **29**, 2830; (*b*) A. C. Cope, G. A. Berchtold, P. E. Peterson, and S. H. Sharman, *J. Amer. Chem. Soc.*, 1960, **82**, 6370.

[8] S. Winstein and R. B. Henderson in ' Heterocyclic Compounds,' ed. R. C. Elderfield, Wiley, New York, 1950.

illustrated in Scheme 1b; and rearrangement[8] (Scheme 1c). The last two reactions have hitherto only been reported as occurring with specially activated compounds.



SCHEME 1

The main products from the alkali fusion of 9,10-epoxyoctadecanoic acid are octanoic, nonanoic, and nonanedioic acids in roughly equimolar amounts, as with the corresponding dihydroxyoctadecanoic acids (see Table 1). This suggests that nucleophilic attack on the epoxide by hydroxide ion to give the dihydroxy-acid (Scheme 2a) is the main initial reaction. The formation of methylpentadecanoic and methylheptadecenoic acids as by-products (see Table 1) is consistent with this view. The detection of small amounts of decanoic and decanedioic acids, not observed in the reactions of the 9,10-dihydroxyoctadecanoic acids, suggests that reductive ring opening (Scheme 2b) or base-catalysed rearrangement of the epoxide (Scheme 2c) is also occurring. These acids do not arise from the presence of positional isomers in the epoxide, since hydrolysis of the epoxide followed by alkali fusion of the resulting unpurified glycol gave only the products expected from the 9,10-dihydroxyoctadecanoic acids.

TABLE 1

Alkali fusion of *cis*- and *trans*-9,10-epoxyoctadecanoic acids and *threo*- and *erythro*-9,10-dihydroxyoctadecanoic acids at 300° for 1 h

| Acidic products | Product composition[a] *cis*-Epoxide[b] | *trans*-Epoxide[b] | *erythro*-Glycol | *threo*-Glycol[c] |
|---|---|---|---|---|
| Monocarboxylic acids | | | | |
| Heptanoic | Trace | Trace | 3 | 3 |
| Octanoic | 22 | 22 | 21 | 24 |
| Nonanoic | 22 | 14 | 34 | 29 |
| Decanoic | 3 | <1 | | |
| Tetradecanoic | 3 | 9 | | |
| 'Me–C$_{15}$'[d] | <1 | 1 | 5 | 4 |
| Hexadecanoic | 10 | 14 | | |
| 'Me–C$_{17}$'[d] | <1 | <1 | 3 | 4 |
| Dicarboxylic acids | | | | |
| Heptanedioic | 1 | <1 | 2 | 1 |
| Octanedioic | 9 | 19 | | |
| Nonanedioic | 26 | 19 | 33 | 34 |
| Decanedioic | 3 | <1 | | |
| Yield factor[a] | 0·69 | 0·58 | 0·97 | 0·93 |

[a] The yields for each reaction have been normalised to 100% for ease of comparison. The actual yield of a component (in mole %) is obtained by multiplying the normalised yield by the yield factor. [b] Average of three experiments having similar results. [c] Average of four experiments having similar results. [d] Me-C$_{15}$ and Me-C$_{17}$ are branched-chain acids; see refs. 1 and 3.

TABLE 2

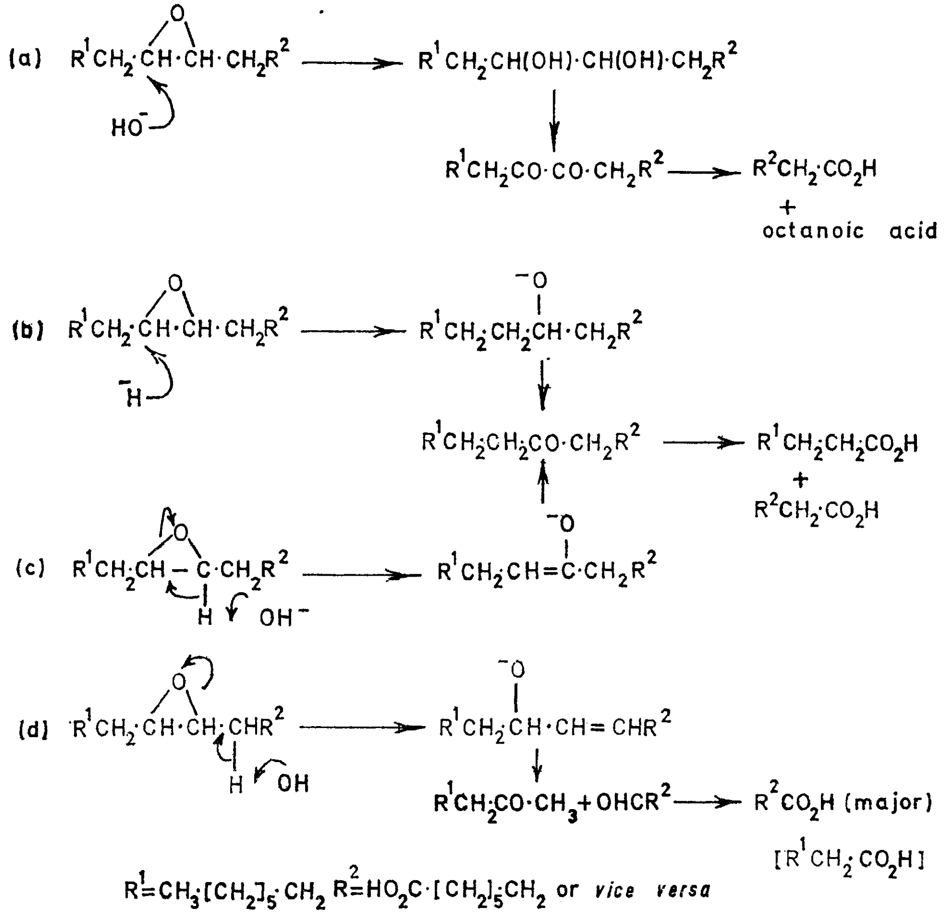
Alkali fusion of 10,11-epoxyundecanoic acid and 10,11-dihydroxyundecanoic acid (1 h at specified temperature)

| Acidic products | Product composition[a] 10,11-Epoxide 200° | 300°[b] | 10,11-Dihydroxy[c] |
|---|---|---|---|
| Monocarboxylic acids | | | |
| Heptanoic | 1 | 1 | |
| Nonanoic | 4 | 7 | 5 |
| Undecanoic | 1 | 1 | |
| Dicarboxylic acids | | | |
| Octanedioic | 0 | 1 | Trace |
| Nonanedioic | 3 | 5 | |
| Decanedioic | 28 | 72 | 95 |
| Undecanedioic | 40 | 12 | |
| Yield factor[a] | 0·25 | 0·74 | 1·0 |

[a] See footnote (*a*) Table 1. [b] From ref. 1. [c] Based on two experiments with similar results.

The formation of hexadecanoic acid may be attributed to loss of oxygen followed by the normal Varrentrapp reaction. However, of greater significance is the formation of octanedioic acid and the slightly greater yield of octanoic acid as compared to nonanoic acid. Since the presence of functional isomers in the starting material has been eliminated it is concluded that the β-elimination mechanism (Scheme 2d) competes to some extent with hydrolysis. The key products from the alkali fusion of 9,10-epoxyoctadecanoic acid were isolated by preparative scale g.l.c. and their identities were confirmed.

The results of the alkali fusion of 10,11-epoxyundecanoic acid (Table 2) are in agreement with the reaction pathways already described for the 9,10-epoxy acids. The formation of decanedioic acid as the main product (at 300°) together with small amounts of octanedioic and nonanoic acids is consistent with an initial hydrolysis to 10,11-dihydroxyundecanoic acid. The formation of undecanedioic acid may arise by reductive ring opening, although nucleophilic attack on the epoxide ring would be expected to occur preferentially at C-11 and thus favour nonanedioic acid. However, a base-catalysed rearrangement, with initial attack at C-11 would lead to 10-formyldecanoic acid, which would be readily converted into undecanedioic acid under the reaction conditions. In the low temperature alkali fusion of 10,11-epoxyundecanoic acid (see Table 2) the yield of undecanedioic acid, relative to decanedioic acid, increases markedly. The formation of nonanedioic acid presumably occurs *via* the β-elimination mechanism and that of nonanoic acid *via* an initial loss of oxygen followed by fission of the resulting undecenoic acid.



SCHEME 2

Recorded in Table 3 are the results of the alkali fusion of *cis*-9,10-*cis*-12,13-diepoxyoctadecanoic acid, which are contrasted with those of the fusion of the corresponding *threo*-9,10-*threo*-12,13-tetrahydroxy-acid. The diepoxy-acid gives hexanoic and nonanedioic acids, the expected products from hydrolytic ring opening of both epoxide groups, but in addition both heptanoic and decanedioic acid are important products. The formation of these acids can be interpreted by invoking intramolecular hydride attacks at C-13 and C-9. Thus if in a β-elimination reaction the departing hydride ion from a position adjacent to one epoxide group is accepted by

TABLE 3

Alkali fusion of *cis*-9,10-*cis*-12,13-diepoxyoctadecanoic acid and related acids at 300° for 1 h

| | Product composition [a] | | | |
|---|---|---|---|---|
| Acidic products | 9,10; 12,13-Diepoxy-acid [c] | 9,10,12,13-Tetrahydroxy-octadecanoic acid [b] | 9,12-Dioxo-octadec-10-enoic acid | 10,11-Epoxy-12-oxo-octadecanoic acid [b] |
| Monocarboxylic acids | | | | |
| Hexanoic | 30 | 43 | 5 | |
| Heptanoic | 14 | 4 | 43 | 50 |
| Octanoic | 4 | 5 | 2 | 5 |
| Nonanoic | 3 | | <1 | 2 |
| Decanoic | 1 | | | |
| Dicarboxylic acids | | | | |
| Heptanedioic | | | 13 | |
| Octanedioic | 3 | 4 | 2 | |
| Nonanedioic | 29 | 43 | 30 | 2 |
| Decanedioic | 13 | 1 | | 10 |
| Undecanedioic | | | | 20 |
| Yield factor [a] | 0·70 | 0·56 | 0·40 | 0·40 |

[a] See footnote (*a*) Table 1. [b] Based on two reactions with similar results. Containing *ca.* 3% unidentified material.

TABLE 4

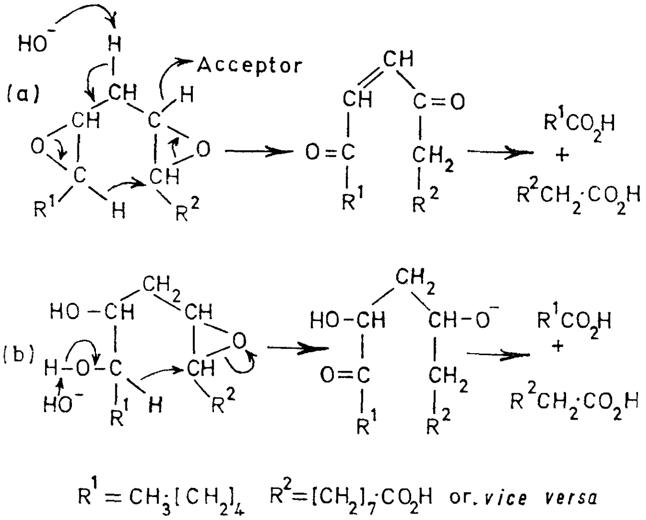
Alkali fusion of 11-alkoxyundecanoic acids $RO\cdot[CH_2]_{10}\cdot CO_2H$ (for 1 h at specified temperature)

| | Product composition [a] | | | | | | |
|---|---|---|---|---|---|---|---|
| Acidic products R: | Me [b] | Et | Pr$^n$ | Pr$^i$ | Bu$^n$ | Bu$^i$ | n-$C_5H_{11}$ |
| Nonanoic | 93 | | 25 | 3 | 44 | 84 | 44 |
| Undecanoic | | | | | | | |
| Nonanedioic | | | 8 | 2 | 6 | 3 | |
| Undecanedioic | 2 | 100 | 63 | 94 | 50 | 12 | 56 |
| Unchanged ether acid | | | 1 | | | | |
| Yield factor [a] | 0·70 | 0·88 | 0·40 | 0·84 | 0·73 | 0·62 | 0·57 |
| Fusion temp. | 360° | 360° | 340° | 330° | 340° | 350° | 345° |

[a] See footnote (*a*) Table 1. [b] 4% Heptanoic acid, a secondary reaction product from nonanoic acid, was also observed.

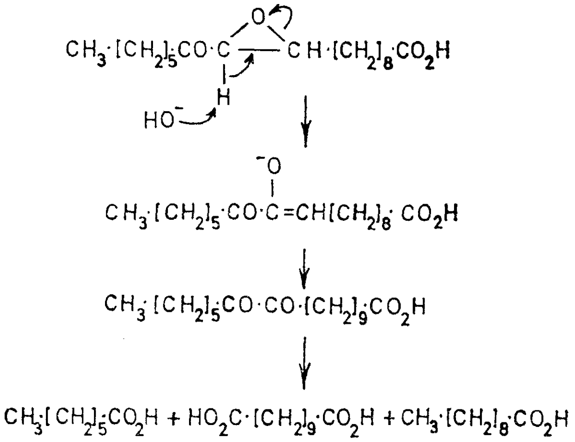
the other epoxide group (Scheme 3a), unsaturated diketones would be obtained which in the presence of alkali would be degraded to hexanoic, heptanoic, nonanedioic, and decanedioic acids, thus explaining the observed results. Alkali fusion of one of the two postulated intermediates (Scheme 3a), 9,12-dioxo-octadeca-*trans*-10-enoic acid, gave rise (see Table 3) to the expected products, heptanoic and nonanedioic acids. By analogy the other expected intermediate would give hexanoic and decanedioic acids.

Alternatively, intramolecular hydride ion attack on one epoxide group may occur after the other group has undergone hydrolytic ring opening (Scheme 3b). The breakdown of the proposed intermediate in Scheme 3b is in accord with the observation [1] that alkali fusion of 9,10,12-trihydroxyoctadecanoic acid yields nonanedioic and heptanoic acid as the main products.



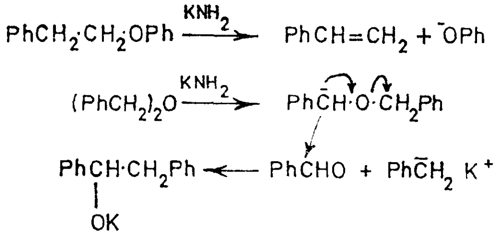
SCHEME 3

Alkali fusion of 10,11-epoxy-12-oxo-octadecanoic acid gave a low yield of identifiable products (Table 3). However the formation of the products could be interpreted in terms of the previously postulated modes of reactions of epoxides. Hydrolytic ring opening of the epoxide group with subsequent fission would account for the formation of decanedioic acid and the β-elimination route for the formation of nonanedioic acid (*cf.* Scheme 2d), in each case the other product being heptanoic acid. The predominant mode of reaction is apparently the base-catalysed rearrangement of the epoxy-ketone (facilitated by the carbonyl group, *cf.* Winstein and Henderson [8]) to the 11,12-diketone, which then reacts as has been shown previously for such compounds to give, among other products, undecanedioic acid and decanoic acid (see Scheme 4).



SCHEME 4

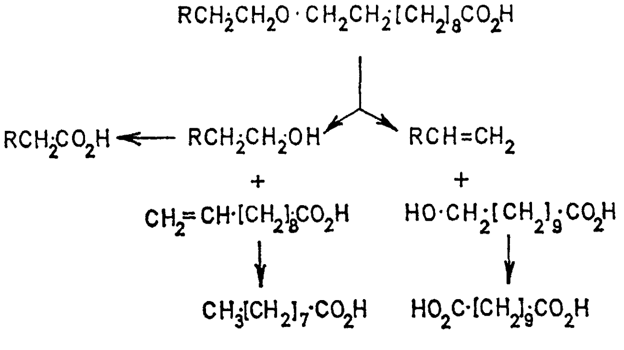
Alkyl ethers have been regarded [6a] as 'stable to alkaline hydrolysis' although ethers containing suitably placed phenyl groups are cleaved by alkali (Scheme 5). In order to determine whether the reactions already described for epoxides occur with simple ethers, a series of 11-alkoxyundecanoic acids was submitted to alkali fusion. Consideration of these results (Table 4) indicated that β-elimination occurs almost exclusively,



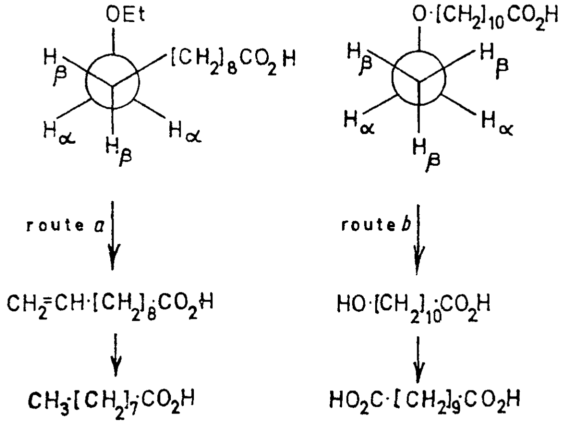
SCHEME 5

leading initially to undec-10-enoic acid and 11-hydroxyundecanoic acid, which, under the reaction conditions, are converted into nonanoic acid and undecanedioic acid (Scheme 6). By carrying out the reaction of 11-ethoxyundecanoic acid at a lower temperature (200°), it was possible to isolate (by preparative scale g.l.c.) the intermediate 11-hydroxyundecanoic acid.

With the exception of 11-methoxyundecanoic acid, which yields nonanoic acid, elimination can occur from either side of the ether function. However fusion of 11-ethoxyundecanoic acid at 360° results exclusively in the formation of undecanedioic acid. This result is consistent with the reaction proceeding by a concerted *E*2 *trans*-elimination. Examination of the Newman projections (Scheme 7) for the two alternative elimination reactions shows that for route *b* the molecule takes up one of the three equally favourable conformations in which the carboxy-containing group is *trans* to a β-proton, whereas for route *a* the molecule must take up a more sterically hindered conformation for a *trans*-elimination to occur. Replacement of a β-proton of the ethyl group of 11-ethoxyundecanoic, giving n-propoxyundecanoic acid, makes route *b* (Scheme 7) less favourable, and the yield of undecanedioic acid obtained on fusion of this acid decreases in favour of nonanoic acid. However replacement of an α-proton by a methyl group, giving 11-isopropoxyundecanoic acid, does not make route *b* (see Scheme 7) significantly less favourable sterically and also favours route *b* statistically as it doubles the number of β-protons available in the alkyl group; as expected undecanedioic acid is the predominant product. Alkali fusion of both n-butoxy- and n-pentoxy-undecanoic acids yields similar amounts of the two major fusion products, route *b* being slightly preferred, the β-proton of the alkyl group being slightly less sterically hindered. [A rough estimate of steric hindrance is taken as a count of the groups 1 : 6 with respect to the point of attack (Newman's rule of six)]. With isobutoxyundecanoic acid, the presence of only one β-proton in the alkyl group favours the operation of route *a* as indicated by the high yield of nonanoic acid.



SCHEME 6



SCHEME 7

Thus the reactions of the alkoxy-acids exhibit normal stereoelectronic features despite the vigorous conditions employed.

## EXPERIMENTAL

*Preparation of Materials.*—*cis*-9,10-Epoxyoctadecanoic acid and *trans*-9,10-epoxyoctadecanoic acid were prepared [9] by the action of peracetic acid on oleic and elaidic acid, respectively. The *trans*-epoxide was also prepared from *threo*-9,10-dihydroxyoctadecanoic acid.[10] 10,11-Epoxyundecanoic acid was prepared from undec-10-enoic acid.[9,11] *cis,cis*-9,10,12,13-Diepoxyoctadecanoic acid was prepared [12] from linoleic acid, and *trans*-10,11-epoxy-12-oxo-octadecanoic acid [13] from 12-oxo-octadec-*trans*-10-enoic acid.[13,14] The method given in ref. 14 was found to give the purer product. Oleic acid was converted into *threo*-9,10-dihydroxyoctadecanoic acid [15] *via* the epoxide and into *erythro*-9,10-dihydroxyoctadecanoic acid [10] by permanganate oxidation. 9,10,12,13-Tetrahydroxyoctadecanoic acid was prepared from linoleic acid by the method of Gunstone and Morris.[16] 9,12-Dioxo-octadec-*trans*-10-enoic acid [13] was obtained by oxidation of 12-oxo-octadec-*trans*-9-enoic acid.

*General Method for Preparation of* 11-*Alkoxyundecanoic Acids.*—A solution of 11-bromoundecanoic acid [17] (A g) in the appropriate alkanol (B ml) was added slowly to a refluxing solution of the sodium alkoxide [from sodium (C g) and alkanol (D ml)]. The solution was boiled for 15 h, the solvent was then distilled off, and the residue was dissolved in water. The aqueous solution was acidified with dilute hydrochloric acid and extracted with ether. Evaporation of the dried ($MgSO_4$) extract gave a crude solid which was recrystallised from acetone at −20° to give the 11-alkoxyundecanoic acid. (For the quantities A, B, C, and D and the physical constants of the acids see Table 5.)

*General Alkali-fusion Procedure.*—All the alkali fusions were carried out in a cylindrical nickel pot (internal dimensions 5·7 × 3·4 cm) having a lid (Syndanio lined with nickel) fitted with nitrogen inlet and outlet ports, a nickel stirrer, and thermometer well. Heat-resistant washers around the stirrer and the lid of the pot rendered the vessel

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[9] T. W. Findley, D. Swern, and J. T. Scanlan, *J. Amer. Chem. Soc.*, 1945, **67**, 412.

[10] W. A. Cramp, F. J. Julietti, J. F. McGhie, B. L. Rao, and W. A. Ross, *J. Chem. Soc.*, 1960, 4257, 4514.

[11] L. J. Morris and R. T. Holman, *J. Lipid Res.*, 1961, **2**, 68.

[12] D. Swern and G. B. Dickel, *J. Amer. Chem. Soc.*, 1954, **76**, 1957.

[13] J. Nichols and E. Schipper, *J. Amer. Chem. Soc.*, 1958, **80**, 5705.

[14] G. King, *J. Chem. Soc.*, 1951, 1980.

[15] D. Swern, J. T. Scanlan, and G. B. Dickel, *Org. Synth.*, Coll. Vol. IV, 1963, p. 317.

[16] F. D. Gunstone and L. J. Morris, *J. Chem. Soc.*, 1957, 487.

[17] R. Ashton and J. C. Smith, *J. Chem. Soc.*, 1934, 435.

TABLE 5

Data concerning the preparation of 11-alkoxyundecanoic acids

| Alkyl group | A | B | C | D | Yield [a] (%) | M.p. $T/°C$ | Formula | | C (%) | H (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Me [b] | 10·6 | 30 | 2 | 32 | 45 | 30—31·5 [c] | $C_{12}H_{24}O_3$ | Calc.: | 66·6 | 11·2 |
| | | | | | | | | Found: | 66·95 | 11·1 |
| Et | 10·6 | 30 | 2 | 32 | 20 | 44·8—45·2 | $C_{13}H_{26}O_3$ | Reqd.: | 67·8 | 11·4 |
| | | | | | | | | Found: | 67·9 | 11·3 |
| $Pr^n$ | 8·0 | 100 | 2 | 60 | 18 | 30·5—31 | $C_{14}H_{28}O_3$ | Reqd.: | 68·8 | 11·55 |
| | | | | | | | | Found: | 68·7 | 11·5 |
| $Pr^i$ | 8·0 | 100 | 2 | 60 | 21 | 29·3—29·8 | $C_{14}H_{28}O_3$ | Reqd.: | 68·8 | 11·55 |
| | | | | | | | | Found: | 69·0 | 11·3 |
| $Bu^n$ | 8·0 | 100 | 2 | 60 | 17 | 30·5—31 | $C_{15}H_{30}O_3$ | Reqd.: | 69·7 | 11·7 |
| | | | | | | | | Found: | 69·95 | 11·6 |
| $Bu^i$ | 8·0 | 100 | 2 | 60 | 14 | 42·6—43·2 | $C_{15}H_{30}O_3$ | Reqd.: | 69·7 | 11·7 |
| | | | | | | | | Found: | 69·95 | 11·5 |
| n-$C_5H_{11}$ | 10·0 | 50 | 2 | 100 | 7 | 32·5—33 | $C_{16}H_{32}O_3$ | Reqd.: | 70·5 | 11·8 |
| | | | | | | | | Found: | 70·6 | 12·0 |

[a] For recrystallised material. [b] Recrystallised from petroleum (b.p. <40°). [c] Recorded m.p.s 32·7° (ref. 18), 32·33° (ref. 19), and 34·5—35° (ref. 20). [d] Potassium used instead of sodium.

reasonably airtight. The starting material (*ca.* 1·0 g) and potassium hydroxide pellets (three times the weight of the fatty acid) were placed in the pot, and the apparatus was assembled. A vigorous stream of dry, oxygen-free nitrogen was passed through the reaction vessel for 5 min, and the gas flow was then reduced to a few ml per min. The stirrer was started and a heated Woods metal bath (heated to 50° above the desired reaction temperature) was applied to the reaction vessel. The reaction temperature was maintained as required, and the reaction then stopped by switching off the stirrer and immersing the reaction vessel in ice–water.

The contents of the pot were dissolved in water (*ca.* 100 ml), the aqueous solution was acidified with dilute hydrochloric acid, and the products were extracted with ether (60, 40, and 40 ml). The residue obtained on evaporation of the dried ($MgSO_4$) extract was methylated [overnight in refluxing methanol–sulphuric acid (1 part residue, 10 parts methanol, 0·1 part conc. $H_2SO_4$; all quantities under 2 g were treated as 2 g)]. Water (100 ml) was then added and the solution was extracted with ether (60, 40, and 40 ml). The extract was shaken with saturated sodium hydrogen carbonate solution (30 ml), dried ($MgSO_4$), and then evaporated. To avoid loss of low b.p. esters, the last traces of ether were not removed.

*G.l.c. Separations.*—A Pye Argon Chromatograph was used. The analytical columns (5 mm) and preparative scale columns (20 mm) used had a polyethylene glycol adipate stationary phase on a Celite support.

An accurately weighed amount (*ca.* 0·09 g) of methylated products was added to an accurately weighed amount of a standard methyl ester (see later). Homogeneity was ensured by adding a little ether and waiting *ca.* 30 min before running the chromatogram. The peak areas of the particular component and added standard were measured (by triangulation) and the yield of component was arrived at by use of the formula derived as follows:

Let $W$ = weight (g) of the starting material (acid)
$P$ = weight (g) of the methylated fusion product
$p$ = weight of methylated fusion product used in quantitative chromatogram
$S$ = weight of standard ester added
$A_s$ = corrected peak area of standard ester

Let $A_c$ = corrected peak area of particular component
$M$ = g mol. wt. of starting material
$E$ = g mol. wt. of standard ester

The number of moles of standard in $(S + p) = S/E = kA_s$ where k = constant for this particular chromatogram.

The number of moles of a particular component in $(S + p) = kA_c$.

The number of moles of a particular component in $P = kA_cP/p$; then substituting for k this becomes $SA_cP/EA_sp$.

Hence the number of mol of a particular component from 1 mol of starting material $= SA_cPM/EA_spW$.

In all cases the molar yield of a particular component was determined from two different chromatograms, one with dimethyl heptanedioate and one with dimethyl octanedioate as standard. When the molar yield of one component had been determined the yields of other components were calculated from the relative peak areas (corrected) of components to that on the same chromatogram of the component whose molar yield had been first calculated.

*Correction factor for gas chromatographic estimation.* For any particular component the molar correction factor is defined by the ratio of the peak area of methyl nonanoate (correction factor defined as zero) to that of the particular component from a chromatogram of a mixture containing equimolar amount of the two esters. Typical correction factors are:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Monocarboxylic acid | $C_6$ | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | $C_{12}$ | $C_{14}$ |
| | 5·56 | 2·10 | 1·23 | 0·00 | 0·87 | 0·74 | 0·70 |
| Dicarboxylic acid | $C_7$ | $C_8$ | $C_9$ | $C_{10}$ | | | |
| | 1·27 | 1·17 | 1·05 | 0·99 | | | |

*Isolation of Products from Alkali Fusion of* cis-9,10-*Epoxyoctadecanoic Acid.*—A sample (200 mg) of the methyl esters from the foregoing reaction were separated by preparative scale g.l.c. into (*a*) methyl nonanoate (54 mg.),

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[18] H. Hunsdiecker, *Ber.*, 1942, **75**, 1190.

[19] G. I. Samokhvalov, V. E. Sibirtseva, E. I. Genkin, and N. A. Preobrazhenskii, *Doklady Akad. Nauk. S.S.S.R.*, 1952, **84**, 729, (*Chem. Abs.*, 1953, **47**, 3230).

[20] R. E. Bowman and R. G. Mason, *J. Chem. Soc.*, 1952, 4151.

derived hydrazide m.p. and mixed m.p. 93—94° (lit.,[21] 94·5—95·5°); (*b*) methyl octanedioate (25 mg), derived acid m.p. and mixed m.p. 138—139° (lit.,[22] 140°); (*c*) methyl nonanedioate (120 mg), derived acid m.p. and mixed m.p. 102—104° (lit.,[22] 106°); (*d*) methyl decanedioate and methyl hexadecanoate (19 mg); the derived acids from (*d*) were separated with petroleum (b.p. 40—60) to give (insoluble) decanedioic acid, m.p. and mixed m.p. 129—131° (lit.,[22] 133°), and (soluble) hexadecanoic acid, m.p. and mixed m.p. 60—61° (lit.,[22] 64°).

*Isolation of Products from Low Temperature Fusion of* 11-*Ethoxyundecanoic Acid*.—The acid (3·0 g) was subjected to alkali fusion under the standard conditions, except that the reaction conditions were 200° for 1 h. G.l.c. analysis of the derived methyl esters showed the presence of methyl nonanoate (trace), methyl 11-ethoxyundecanoate (0·12 mole %), dimethyl undecanedioate (0·57 mole %), and methyl 11-hydroxyundecanoate (0·26 mole %). The last was isolated by preparative scale g.l.c. and the derived acid had m.p. and mixed m.p. 64° (lit.,[23] 66°).

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