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SOME REARRANGEMENTS OF SUBSTITUTED ETHYLENE OXIDES

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Abstract—Thermal rearrangement of butane-2,3-diol cyclic sulphites and BF_3-catalysed rearrangements of *cis*- and *trans*-butene epoxides are described. With BF_3 1,2-di-t-butyl ethylene oxides undergo fragmentation to give pivalaldehyde.

During studies[1] of the rearrangements of some 2,3-oxygenated pinane derivatives it was noted that while Lewis acid catalysed rearrangement of 2,3α-epoxy-10β-pinane (1) gave[2] essentially pure aldehyde (2), pyrolysis of the cyclic sulphite (3) of 10β-pinane-2,3α-diol gave a mixture (98 :2) of pinocamphone (4) and aldehyde (2). This marked difference in product compositions for the two reactions, both of which involve cleavage of the $C^{2\alpha}$—O bond, was ascribed[1] to the differing conformational constraints imposed on the reacting molecules.

At this point it seemed desirable to compare the results of cyclic sulphite pyrolysis and epoxide—Lewis acid reactions for acyclic systems. Accordingly we examined the pyrolysis of the cyclic sulphites (5 and 6) derived[3] from *meso*- and D,L-butane-2,3-diol respectively. Pyrolysis of the *meso*-cyclic sulphite (5) gave an essentially quantitative yield of butan-2-one containing only a trace (<1%) of isobutyraldehyde. Similar treatment of the D,L-cyclic sulphite (6) gave a mixture (9 : 1) of butan-2-one and isobutyraldehyde in addition to some unreacted cyclic sulphite (6; 5%).

Reaction of *cis*- and *trans*-2,3-epoxybutanes (7 and 8) with magnesium bromide gave[4] only butan-2-one (yields 75 and 62% respectively). These reactions were rationalised in terms of the intermediacy of bromomagnesium salts. In contrast while reaction of the *cis*-epoxide (7) with BF_3-etherate in ether solution gave[4] butan-2-one (13% yield) similar treatment of the *trans*-epoxide (8) gave a mixture (10 : 1·8; total yield 12%) of butan-2-one and isobutyraldehyde. These yields were based on the estimated compositions of 2,4-dinitrophenyl-hydrazone mixtures formed from crude reaction products.

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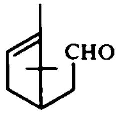

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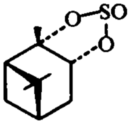

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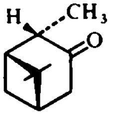

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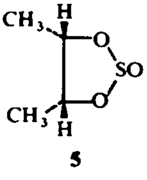

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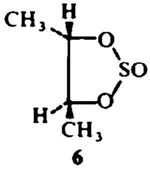

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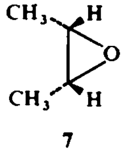

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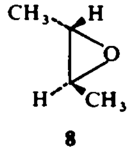

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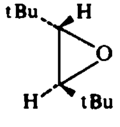
Reaction of the 2,3-epoxybutanes (7 and 8) with BF_3-etherate in ether gave crude products, the composition of which were determined by GLC. While the total yields of butan-2-one and isobutyraldehyde obtained from the *cis*- (7) and *trans*- (8) isomers were similar (60%), the *cis*-compound gave only butan-2-one and the *trans*-isomer a mixture (ca. 3 : 1) of butan-2-one and isobutyraldehyde. Similar product ratios have been reported[5] for the rearrangement of 2,3-epoxybutanes and butane-2,3-diols with aqueous phosphoric acid (70%). The *trans*-epoxide (8) and *meso*-butane-2,3-diol gave mixtures (ca. 3 : 1) of butan-2-one and isobutyraldehyde, while the *cis*-epoxide (7) and D,L-butane-2,3-diol gave essentially pure butan-2-one contaminated with traces (1–6%) of isobutyraldehyde.

In an attempt to assess the effect of the size of the alkyl substituents on the course of the BF_3-catalysed rearrangement of disubstituted ethylene oxides, the rearrangements of *trans*- and *cis*-di-t-butylethylene oxides (9 and 10) were examined. When *trans*-epoxide (9) was treated with BF_3–CCl_4 the NMR spectrum* (δ 1·30 ppm ($W_{h/2}$ 1·6 c/s), 9·38 ppm ($W_{h/2}$ 1·2 c/s); 9H : 1H) of the crude product was markedly similar to that of pivalaldehyde (11) in CCl_4–BF_3; this identification was confirmed by GLC comparison with an authentic sample. GLC examination of the crude product revealed the presence of a compound, tentatively assigned the 2-methyl-but-2-ene structure, which was eluted before diethyl ether. No trace was detected of either the C_{10}-aldehyde (12), δ1·09 ppm (singlet; 18H), 1·70 ppm (1H; $J = 6$ c/s), 9·70 ppm (1H; $J = 6$ c/s), or the C_{10}-ketone (13), δ1·01 ppm (singlet; 9H), 1·08 ppm (singlet; 9H), 2·30 ppm (singlet; 2H).

Similar reaction of the *cis*-epoxide (10) with BF_3–CCl_4 gave a crude product, the NMR spectrum of which was similar to that for the *trans*-epoxide (9) reaction product. The presence of pivalaldehyde (11) as a major product was again demonstrated by GLC.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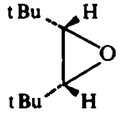
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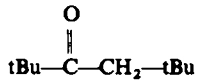
$(CH_3)_3C\cdot CHO$

11

$(tBu)_2CH\cdot CHO$

12


$tBu-\overset{\overset{\Large O}{\|}}{C}-CH_2-tBu$

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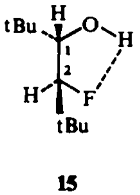
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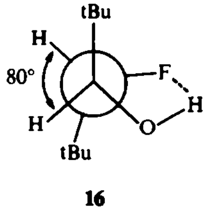

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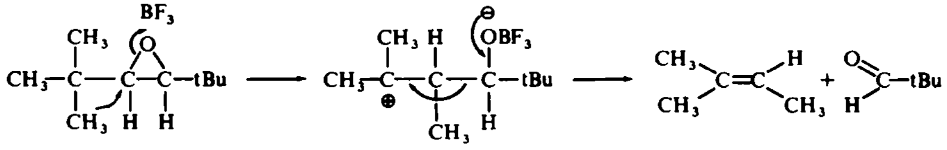
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FIG. 1.

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* Determined at 60 Mc.

The reaction of both *trans*- and *cis*-epoxides (**9** and **10**) with BF_3 is considered to proceed *via* epoxide ring opening accompanied by Me migration to give the intermediate (**14**). Fragmentation of intermediate (**14**), by the retro-Prins reaction path, gives rise to pivalaldehyde (**11**) and 2-methyl-but-2-ene, the latter being readily lost from the reaction system.

Treatment of the *trans*-epoxide (**9**) with BF_3-etherate in ether solution gave only unchanged epoxide. In contrast similar treatment of the *cis*-epoxide (**10**) gave a high yield (80%) of the fluorohydrin (**15**), the structure of which followed from a consideration of its NMR spectrum (Table 1). The signal at 1·80 ppm was removed by D_2O.

TABLE 1. NMR SPECTRUM OF FLUOROHYDRIN (**15**) IN CCl_4 at 60 MC

Assignment	Signal (ppm)	Apparent coupling constants (c/s)
C_1-tBu	0·90 (or 0·98)	$J_{F,tBu} = 1{\cdot}2$ (or $J_{F,tBu} = 1{\cdot}5$)
C_2-tBu	0·98 (or 0·90)	$J_{F,tBu} = 1{\cdot}5$ (or $J_{F,tBu} = 1{\cdot}2$)
—OH	1·80	$J_{H^1,OH} = 10$; $J_{F,OH} = 9$
C_1—H	3·20	$J_{H^1,F} = 19$; $J_{H^1,OH} = 10$
C_2—H	4·15	$J_{H^2,F} = 46$

Additionally the quartet (centre 3·20 ppm) simplified to a doublet, 3·20 ppm ($J_{H^1,F} = 19$), each component of the doublet being broadened ($W_{h/2} = 3{\cdot}5$ c/s). The apparent lack of coupling between C_1—H and C_2—H is interpreted in terms of a fixed (by H-bonding —OH...F) conformation (**16**) in which the H—C_1—C_2—H dihedral angle is close to 80°, when minimal coupling of the protons might be expected.[6]

EXPERIMENTAL

IR spectra (CCl_4 solns unless otherwise stated on a Perkin–Elmer 337 spectrometer); NMR spectra (determined on a Varian A-60 in CCl_4 or $CDCl_3$ with $CHCl_3$ and TMS as internal standards); Analytical GLC (Perkin–Elmer F11 using columns of either 10% Carbowax 20M or a mixture of 4% di-isodecylphthalate and 1% Carbowax 4000 on Chromosorb G (60–80 mesh); Preparative GLC (Aerograph Autoprep 705, using columns of 25% Carbowax 20M on celite (30–80)); $BF_3 \cdot Et_2O$ was distilled several times immediately before use.

BF_3-*Catalysed rearrangement of* cis- *and* trans-*epoxybutanes* (7 and 8)

$BF_3 \cdot Et_2O$ (0·4 ml) was added to a soln of the epoxide (10 μl) in ether (5 ml) containing benzene (2 μl) and the soln kept at 20° for 10 min. The yields of products were calculated by measurement of GLC trace (di-isodecylphthalate–carbowax column) peak areas.

Pyrolysis of cyclic sulphites (5 *and* 6) *from* meso- *and* D,L-*butane-2,3-diols*

The cyclic sulphite was injected (3 ml/hr) into a heated (400°) glass tube (50 × 2·5 mm) packed with glass helices with a N_2 gas flow of 150 ml/min. The products were condensed in a liquid air cooled trap (near quantitative recovery) and the isobutyraldehyde: butan-2-one ratio determined by GLC (20% Carbowax 20M on Chromosorb P 45/60).

trans-1,2-*Di-t-butylethylene oxide* (9)

trans-1,2-Di-t-butylethylene (2 g) was added to an etherial soln of monoperoxyphthalic acid (155 ml; 0·41M) and the soln kept at 5° for 7 days. Isolation by means of Et_2O gave pure (GLC) trans-*epoxide* (9; 1·8 g), M^+ 156·1531 (calc. 156·1514), NMR (CCl_4), δ 0·88 ppm (18H), 2·40 ppm (2H).

cis-1,2-*Di*-t-*butylethylene oxide* (**10**)

cis-1,2-Di-t-butyl ethylene (**10**; 2 g), treated as above, gave the pure (GLC) cis-*epoxide* (**10**; 1·75 g), M^+ 156·1524 (calc. 156·1514), NMR (CCl_4) δ 1·05 ppm (18H), 2·50 ppm (2H).

Rearrangement of epoxides (**9** *and* **10**) *with* BF_3 *gas*—CCl_4

BF_3-gas (60 ml) was bubbled through a soln of the epoxide (50 μl) in CCl_4 (0·5 ml) at 25°. After 15 min the NMR spectrum of the soln from each epoxide reaction revealed two sharp singlets (δ1·30 and 9·38 ppm) in the ratio 9 : 1. This NMR spectrum was duplicated by that for a CCl_4 soln of **11** through which BF_3-gas had been passed.

GLC examination (on di-iso decylphthalate-Carbowax 4000) of the crude product revealed in order of elution: a trace of a low b.p. compound, believed to be 2-methylbut-2-ene; pivalaldehyde. Comparison of retention times with those for a pivalaldehyde–Et_2O soln confirmed the pivalaldehyde identification, and showed the 2-methylbut-2-ene to be eluted before Et_2O.

Reaction of epoxides (**9** *and* **10**) *with* BF_3—Et_2O *in* Et_2O *solution*

(a) trans-*Epoxide* (**9**). $BF_3 \cdot Et_2O$ (0·4 ml) was added to a soln of the epoxide (20 μl) in Et_2O (5 ml). After storage at 20° for 14 days, only epoxide was detected by GLC.

(b) cis-*Epoxide* (**10**). BF_3–Et_2O (3·6 ml) was added to a soln of the epoxide (0·5 ml) in Et_2O (160 ml) and the soln stored at 20° for 3 days. The crude product, isolated by means of Et_2O, was purified by preparative GLC to give the *fluorohydrin* (**15**; 0·4 g), m.p. 50–51°, ν_{max} 3612 cm^{-1}. (Found: F, 10·58. $C_{10}H_{21}FO$ requires: F, 10·80%).

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