Tetrahedron. Vol. 26, pp. 1311 to 1313. Pergamon Press 1970 Printed in Great Britain

THE MECHANISM OF 1,3-DIOXOLANE FORMATION FROM THE BF_3-CATALYSED REACTION OF EPOXIDES WITH CARBONYL COMPOUNDS

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(*Received in the UK* 14 *October* 1969; *Accepted for publication* 6 *November* 1969)

Abstract—*cis*- and *trans*-But-2-ene epoxides react with acetone in the presence of BF_3-etherate to give *trans*- and *cis*-2,2,4,5-tetramethyl-1,3-dioxolanes respectively. Use of O^{18}-labelled acetone allowed the reaction mechanism to be defined.

RECENTLY Yandovoskii and Temnikova[1] have suggested a mechanism for the formation of 1,3-dioxolanes from epoxides and carbonyl compounds under Lewis acid catalysed conditions. We now present evidence in support of this mechanism (Fig. 1) for the reaction of the but-2-ene epoxides with acetone in the presence of BF_3-etherate. In addition we now exclude two further mechanisms 2 and 3 (Figs 2 and 3). One of these (Fig. 2) allowed for the possibility of the presence of a sufficient

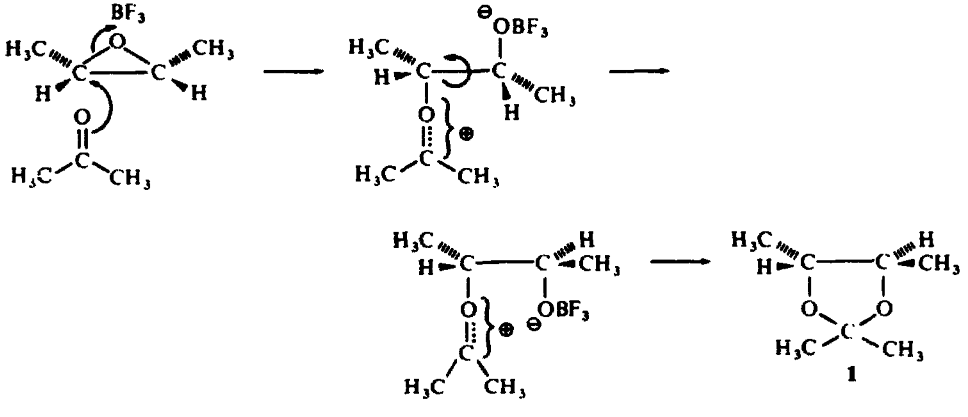

FIG. 1.

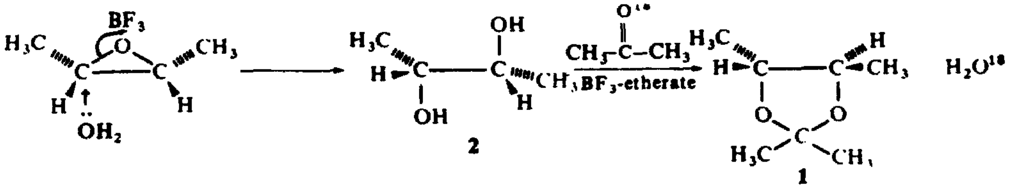

FIG. 2.

concentration of water impurity in the system to produce a diol (eg. 2) as an intermediate which could subsequently react with the carbonyl compound.

Reaction of either *cis*-but-2-ene epoxide or *d,l*-butane-2,3-diol with acetone in the presence of BF_3-etherate gave the *trans*-dioxolane (**1**). Similar treatment of either *trans*-but-2-ene epoxide or *meso*-butane-2,3-diol gave the *cis*-dioxolane (**3**). The stereochemistry of the dioxolane produced from each butane-2,3-diol was the expected[2] one, but the correct interpretation of the stereochemical inversion accompanying dioxolane formation from the but-2-ene epoxides was not clear. However, mechanism 3 may be excluded since that reaction path would lead *either* to retention of configuration (by some form of ion-pair interaction) *or* more probably to mixtures of *cis*- and *trans*-dioxolanes from each epoxide.

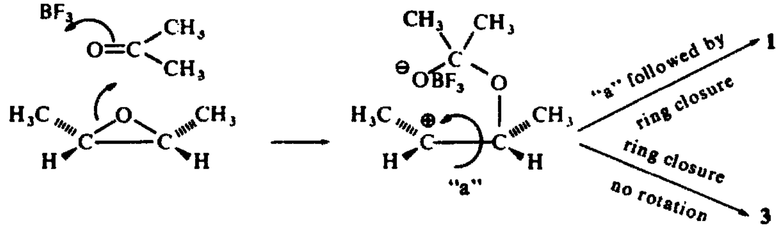

FIG. 3.

In an attempt to decide which of the mechanisms (1 and 2) was operating the diol and epoxide reactions were repeated using O^{18}-labelled acetone (8·9% enriched). Mass spectra for the products and the O^{18}-enriched acetone were recorded at 17eV on an MS902 instrument at a resolving power of 1000 without changing either source or detector settings. No O^{18}-incorporation in the dioxolanes was detected for the diol reactions (as expected), but nearly quantitative incorporation was found for the epoxide reactions (Table 1). While this result at first sight appears to exclude mechanism 2, the free water postulated in the system would be recycled and itself become O^{18}-labelled; the O^{18} content of the dioxolane product would be reduced for low water concentrations (up to ~ 0·3 mole) by at least the ratio moles H_2O/moles epoxide. In order to completely exclude this possibility the epoxide-O^{18}-labelled acetone reactions were repeated in the presence of deliberately added water (0·2 moles). Were mechanism 2 operating the maximum O^{18}-content which could be found for the dioxolane product would be 80% of that found earlier. Since the O^{18}-incorporation was unchanged by the addition of water (0·2 moles) mechanism 2 may be excluded. Mechanism 1 remains for the BF_3-catalysed formation of dioxolanes from the but-2-ene epoxides and acetone.

TABLE 1. PERCENTAGE OF POSSIBLE THEORETICAL O^{18}-INCORPORATION (±3%) IN 2,2,4,5-TETRAMETHYL-1,3-DIOXOLANES ON REACTION OF O^{18}-ACETONE (8·9% moles) WITH SUBSTRATE (1 mole) IN THE PRESENCE OF BF_3-ETHERATE.

	No H_2O added	0·2 moles H_2O added
cis-But-2-ene epoxide	99·4	96·8
trans-But-2-ene epoxide	97·8	102
d,l-Butane-2,3-diol	0	—
meso-Butane-2,3-diol	0	—

EXPERIMENTAL

IR spectra were for liquid films on a Perkin–Elmer 337 spectrometer; NMR spectra were determined on a Varian A60 for 10% w/v $CDCl_3$ solns with $CHCl_3$ and TMS as internal standards; Analytical GLC using Varian Aerograph 1200 using columns of 20% Carbowax 20M on Chromosorb P and 3% Carbowax 20M on Chromosorb G; BF_3-etherate was BDH freshly redistilled.

cis-2,2,4,5-*Tetramethyl*-1,3-*dioxolane* (3)

To a soln of *meso*-butane-2,3-diol (6·8 g) in acetone (2·9 g) was added H_2SO_4 (50%; 0·2 ml) and the soln heated under reflux for 3 hr on a steam bath. The cooled reaction mixture was poured into K_2CO_3 aq and the product isolated by means of ether. Distillation gave the *cis-dioxolane* (3; 2·2 g), b.p. 111–114°, n_D^{25} 1·4000, ν_{max} 1250, 1220, 1104, 1085, 850 cm^{-1}, NMR δ 3·98 ppm ($W_{h/2}$ = 15 cs; C^4-H, C^5-H); 1·32, 1·22 ppm ($C^2(CH_3)_2$); 1·05, 1·03 ppm (J = 6 cs; C^4-CH_3, C^5-CH_3). (Found: C, 64·8; H, 10·7. $C_7H_{14}O_2$ requires: C, 64·6; H, 10·8%).

trans-2,2,4,5-*Tetramethyl*-1,3-*dioxolane*[3] (1)

The dioxolane (1) prepared from *d*, *l*-butane-2,3-diol had b.p. 109–112°, n_D^{25} 1·3953, ν_{max} 1243, 1214, 1080, 841 cm^{-1}, NMR δ 3·43 ppm ($W_{h/2}$ = 11·5 cs; C^4-H, C^5-H); 1·27 ppm ($C^2(CH_3)_2$); 1·15, 1·13 ppm (J = 6 cs; C^4-CH_3, C^5-CH_3).

BF_3-*Catalysed reaction of but-2-ene epoxides with* O^{18}-*labelled acetone*

(a) cis-*Epoxide* (dry). To a soln of *cis*-epoxide (0·05 ml) in acetone (8·9% O^{18}; 0·25 ml) was added BF_3-etherate (0·01 ml) and the mixture kept at 0° for 10 min. The mixture was diluted with ether (25 ml) and washed with water (10 × 5 ml). Ether was removed from the dried soln by distillation to give the *trans*-dioxolane (1), identified by GLC and NMR.

(b) cis-*Epoxide* (wet). Conditions were as for (a) except that water (2·5 ml) was added prior to the BF_3-etherate, and yielded the *trans*-dioxolane (1).

(c) trans-*Epoxide* (dry). Reaction conditions, as for (a), converted the *trans*-epoxide into the *cis*-dioxolane (3), identified by GLC and NMR.

(d) trans-*Epoxide* (wet). Conditions were as for (b); *trans*-epoxide was converted into the *cis*-dioxolane (3).

The percentage of possible theoretical O^{18}-incorporation for the dioxolane products for reactions (a)–(d) is given in Table 1.

BF_3-*Catalysed reaction of butane-2,3-diols with* O^{18}-*labelled acetone*

(a) meso-*Diol*. To a soln of *meso*-butane-2,3-diol (0·05 ml) in acetone (8·9% O^{18}; 0·25 ml) was added BF_3-etherate (0·01 ml) and the reaction kept at 0° for 10 min. Isolation of the product, as for the epoxide reactions, gave the *cis*-dioxolane (3) identified by GLC and NMR.

(b) d,l-*Diol*. Reaction as for (a) using *d,l*-butane-2,3-diol gave the *trans*-dioxolane (1) identified by GLC and NMR.

No O^{18}-incorporation from the acetone into the dioxolanes could be detected (Table 1).

Acknowledgements—The authors acknowledge grants and a Research Fellowship to one of us (GRL) from the Research Committee of the New Zealand Universities Grants Committee, and a grant from the Golden Kiwi Lottery Funds Scientific Research Distributions Committee.

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