Further Rearrangements of Cyclopropyl Epoxides. Formation of Cyclobutanes and Cyclobutenes

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Cyclopropyl epoxides having aryl substituents in the 1-position of the cyclopropane ring underwent acid-catalysed rearrangement to 1- and 2- arylcyclobutenes; in methanol they formed stereoisomeric 1-aryl-1-methoxycyclobutanes. A cyclopropyl epoxide substituted in the 2-position of the cyclopropane ring by geminal methyl groups rearranged to a hexa-2,5-dien-1-ol rather than a 3,6-dihydro-2*H*-pyran. Except in the formation of stereoisomeric pent-2-en-1-ols, cyclopropyl epoxides unsubstituted in the alicyclic ring underwent typical epoxide reactions.

THE rearrangement of oxirans having a contiguous cyclopropane ring has been the subject of recent studies. Prinzbach and Fischer [1] proposed that the rearrangement of an oxabicyclobutane intermediate (II) best accounts for the products obtained in the reaction of a cyclopropene (I) with peracetic acid. This proposal is supported by later work.[2] The oxaspiropentane system has been the subject of a detailed study.[3] Its characteristic rearrangement is to form a cyclobutanone, as exemplified [4] by the parent compound (III). The earliest report of this rearrangement is possibly that involved in the controversy concerning the structure of a terpene (IV) isolated [5] from the oil of *Zieria smithii* and later,[6] but mistakenly,[7] thought to be chrysanthenone (V), to which it readily rearranges.

[1] H. Prinzbach and U. Fischer, *Helv. Chim. Acta*, 1967, **50**, 1669.

[2] (*a*) J. Ciabattoni and P. J. Kocienski, *J. Amer. Chem. Soc.*, 1969, **91**, 6534; 1971, **93**, 4902; *J. Org. Chem.*, 1974, **39**, 388; (*b*) L. E. Friedrich and R. A. Cormier, *ibid.*, 1970, **35**, 450; *Tetrahedron Letters*, 1971, 4761.

[3] J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, 1968, **33**, 991, 3291; *Tetrahedron Letters*, 1969, 2751; *J. Org. Chem.*, 1971, **36**, 1184.

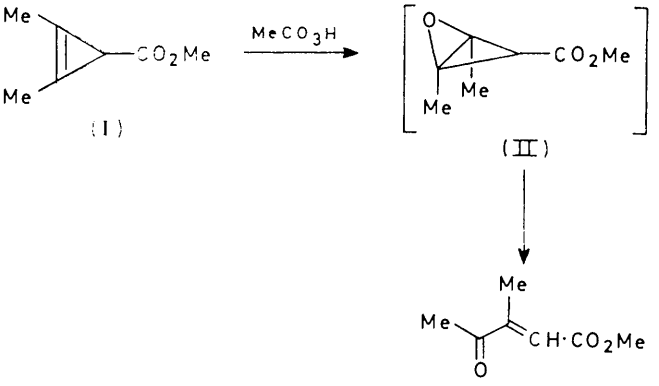
[4] J. R. Salaün and J. M. Conia, *Chem. Comm.*, 1971, 1579; see also B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, 1972, **94**, 4777; 1973, **95**, 289, 2038; J. R. Wiseman and H. Chan, *ibid.*, 1970, **92**, 4749; C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *ibid.*, 1971, **93**, 3771; E. V. Dehmlow, *Z. Naturforsch.*, 1969, **24b**, 1197; B. M. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Letters*, 1970, 3449; D. H. Aue, M. J. Meshishnek, and D. F. Shellhamer, *ibid.*, 1973, 4799; J. M. Denis and J. M. Conia, *ibid.*, 1972, 4593; M. J. Bogdanowicz and B. M. Trost, *ibid.*, 1972, 887; M. J. Bogdanowicz, T. Ambelang, and B. M. Trost, *ibid.*, 1973, 923; J. M. Conia and J. R. Sallaün, *Accounts Chem. Res.*, 1972, **5**, 33; R. E. Erickson and G. D. Mercer, A.C.S. Advances in Chemistry Series, 1972, p. 112.

[5] A. R. Penfold, G. R. Ramage, and J. L. Simonsen, *J. Chem. Soc.*, 1939, 1496.

[6] E. P. Blanchard, *Chem. and Ind.*, 1958, 293.

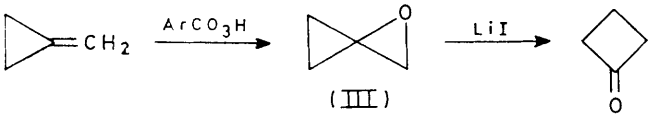
[7] P. Desikan, *Indian J. Chem.*, 1963, **1**, 186.

More recently, a study has been made by us[8] of epoxides connected to a cyclopropane ring by a single bond.[9] For ease in discussion this cyclopropyl epoxide system is numbered as shown in (VI). These compounds



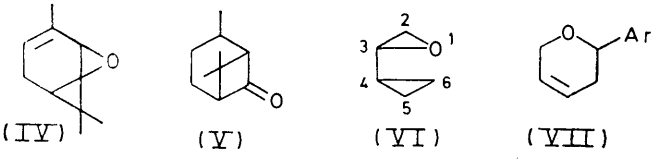
(I) (II)

are readily available from αβ-unsaturated ketones since the development[10] of the ylides dimethyloxosulphonium



(III)

methylide and dimethylsulphonium methylide. They were found[8] to be very reactive when bearing an aromatic substituent in the 6-position and, so substituted,



(IV) (V) (VI) (VII)

their typical rarrangement product is a 2-aryl-3,6-dihydro-2*H*-pyran (VII).

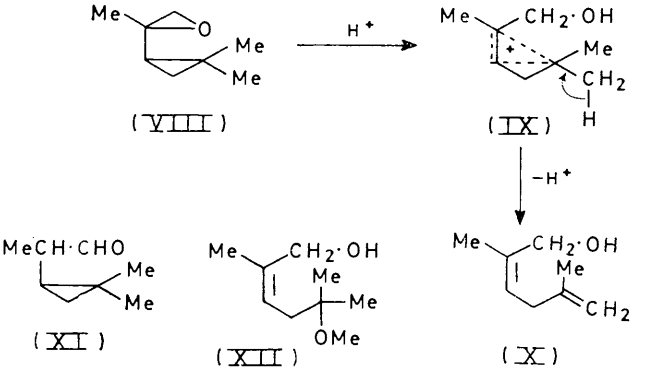
† In this paper, intermediate cyclopropyl cations [*e.g.* (IX)] are represented as bicyclobutanium ions though the nature of these intermediates varies[11] with differing substituents.

[8] (*a*) J. A. Donnelly, P. Bennett, S. O'Brien, and J. O'Grady, *Chem. and Ind.*, 1972, 500; (*b*) J. A. Donnelly, J. G. Hoey, S. O'Brien and J. O'Grady, *J.C.S. Perkin I*, 1973, 2030; (*c*) J. A. Donnelly, S. O'Brien, and J. O'Grady, *ibid.*, 1974, 1674.

[9] See also H. Prinzbach and D. Stusche, *Angew. Chem. Internat. Edn.*, 1970, **9**, 799; P. C. Petrellis, G. W. Griffin, M. E. Hendrick, and M. Jones, *J.C.S. Chem. Comm.*, 1972, 1002; M. Bertrand, P. Archier, and C. Santelli-Rouvier, *Bull. Soc. chim. France*, 1972, 2775; B. A. Arbuzov, Z. G. Isaeva, N. D. Ibragimova, S. G. Vul'fson, and A. N. Vereshchagin, *Doklady Akad. Nauk S.S.S.R.*, 1972, **203**, 581 (*Chem. Abs.*, 1972, **77**, 75344); E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, 1963, **85**, 1782; G. Just, C. Simonovitch, F. H. Lincoln, W. P. Schneider. U. Axen, G. B. Spero, and J. E. Pike, *ibid.*, 1969, **91**, 5364; C. Djerassi, R. Riniker, and B. Riniker, *ibid.*, 1956, **78**, 6377; D. L, Dalrymple and S. P. B. Taylor, *ibid.*, 1971, **93**, 7098; A. Padwa and W. Koehn, *J. Org. Chem.*, 1973, **38**, 4007; H. Newman, *ibid.*, 1971, **36**, 2375; D. C. Kleinfelter, R. A. Aaron, T. J. Gerteiersen, J. M. Miller, and T. B. Bennett, *ibid.*, 1967, **32**, 3521; T. Sasaki, S. Eguchi, and M. Ohno, *ibid.*, 1968, **33**, 676; P. C. Traas, L. M. van der Linde, and H. J. Takken, *Rec. Trav. chim.*, 1974, **93**, 264; C. W. Alexander and J. Grimshaw, *J.C.S. Perkin I*, 1972, 1374; R. Huisgen and G. Juppe, *Tetrahedron*, 1961, **15**, 7; M. Walkowicz, H. Kuczynski, and C. Walkowicz, *Roczniki Chem.*, 1967. **41**, 927; S. Kagabu and H. Prinzbach, *Tetrahedron Letters*, 1975, 29.

In attempting to extend this reaction to the synthesis of 2-alkyl-3,6-dihydro-2*H*-pyrans it has now been found that 3,6,6-trimethylcyclopropyl epoxide (VIII) undergoes a different type of rearrangement,† forming 2,5-dimethylhexa-2,5-dien-1-ol (X) when warmed in benzene with a trace of acid. Such a dienol was obtained[12] when car-2-ene was treated with peracetic acid. The reaction of the trimethyl-substituted cyclopropyl epoxide (VIII) with silica gel gave the 2-cyclopropylpropanal (XI) as well as the 2,5-dien-1-ol (X); with acid in the presence of methanol, 5-methoxy-2,5-dimethylhex-2-en-1-ol (XII) was obtained.

It appears then that geminal methyl substituents at position 6 cannot sufficiently localise charge there to



(VIII) (IX) (XI) (XII) (X)

allow six-membered heterocycle formation by intramolecular oxygen attack to compete with the faster reactions of proton elimination or nucleophilic solvent attack. It has been shown recently,[13] however, that an alkoxy-substituent at position 6 effects the formation of 3,6-dihydro-2*H*-pyrans. The cyclopropyl epoxide-to-dihydropyran rearrangement was invoked[13] in the formation of the major product (XIV) from the reaction of enol ethers (XIII) of 1,3-diketones with dimethylsulphonium methylide.

The well known dependence[11] of cyclopropyl cation reactions on substitution patterns suggested that the course of these cyclopropyl epoxide rearrangements might be altered by suitably substituting the 4- and/or 3-positions. When the 4-(4-methoxyphenyl)cyclopropyl epoxide (XVa) was warmed in benzene with a trace of acid it rearranged, giving the cyclobutenylmethanol (XVIa) as the major product together with the 1,2-diarylcyclobutene (XIXa); the former was reduced to the corresponding cyclobutane for characterisation. Similarly, 3,4-diphenyl cyclopropyl epoxide (XVb) formed 1,2-diphenylcyclobut-2-enylmethanol (XVIb) and 1,2-diphenylcyclobutene (XIXb). A weak signal in the

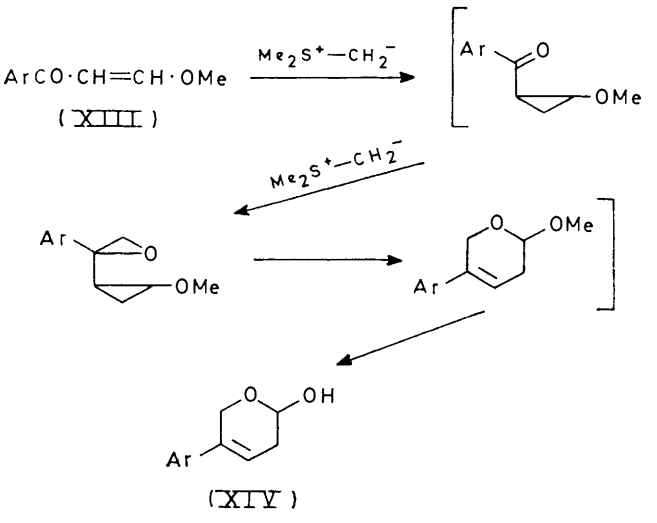
[10] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, 1965, **87**, 1353.

[11] H. G. Richey in ' Carbonium Ions,' ed. G. A. Olah and P. von R. Schleyer, Wiley–Interscience, New York, 1972, **3**, 1201; K. B. Wiberg, B. A. Hess, and A. J. Ashe, *ibid.*, p. 1295.

[12] K. Gollnick and G. Schade, *Tetrahedron Letters*, 1966, 2335; G. Ohloff and W. Giersch, *Helv. Chim. Acta*, 1968, **51**, 1328.

[13] C. M. Harris, J. J. Cleary, and T. M. Harris, *J. Org. Chem.*, 1974, **39**, 72.

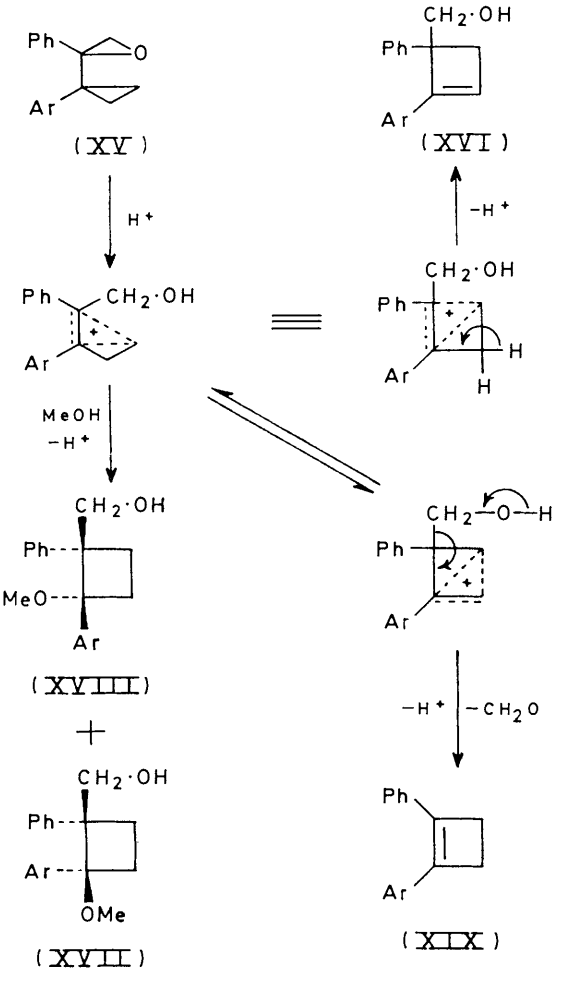
aldehyde region of the ^1H n.m.r. spectrum of the crude product suggested the presence also of some 2-phenyl-2-(1-phenylcyclopropyl)acetaldehyde but this compound was not otherwise observed. 4-(4-Methoxyphenyl)-3-phenylcyclopropyl epoxide (XVa) was converted by acid in methanol into the *cis*- (XVIIa) and *trans*- (XVIIIa) isomers of 1-hydroxymethyl-2-methoxy-2-(4-methoxyphenyl)-1-phenylcyclobutane; some 2-methoxy-2-[1-(4-methoxyphenyl)cyclopropyl]-2-phenylethanol (XX) was also formed. A suggested mechanism



for the formation of the cyclobutane compounds is given in Scheme 1.

Reactions have been reported [14-16] recently of some cyclopropyl epoxides having substituents likely to favour localisation of charge at the 3-position of acid-catalysed reaction intermediates. The parent compound (XXI; R = H) has been found [15] to rearrange to 2-cyclopropylacetaldehyde (XXII; R = H). We have reported [8b] that 3-phenylcyclopropyl epoxide (XXIII) thermally rearranges to 2-cyclopropyl-2-phenylacetaldehyde (XXV). It has now been found that 3-methyl cyclopropyl epoxide (XXI; R = Me) rearranges similarly when treated with acid in benzene and forms 2-cyclopropylpropanal (XXII; R = Me). This epoxide has been reported [16] to react with hydrogen halides to form 5-halogeno-2-methylpent-2-en-1-ols.

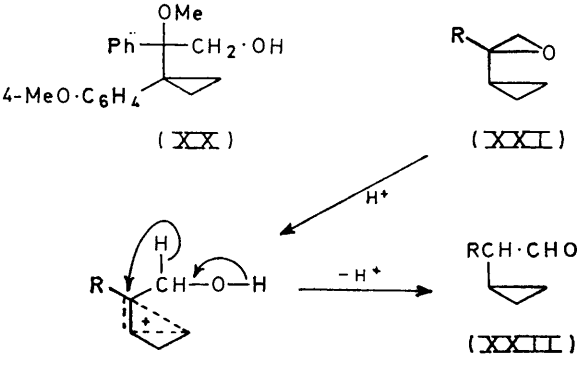
In a more detailed study(Scheme 2) of 3-phenylcyclopropyl epoxide (XXIII), it was found to react with silica gel to form 1-cyclopropyl-1-phenylethane-1,2-diol (XXVIII), as well as 2-cyclopropyl-2-phenylacetaldehyde (XXV). The diol (XXVIII) presumably arises from hydration of the intermediate cyclopropyl cation (XXIV); it can be converted into the aldehyde (XXV) by acid-catalysed dehydration in benzene. With acid in methanol, the epoxide (XXIII) formed 2-cyclopropyl-2-methoxy-2-phenylethanol (XXVII; R = Me) and the



a; Ar = C_6H_4·OMe-4
b; Ar = Ph

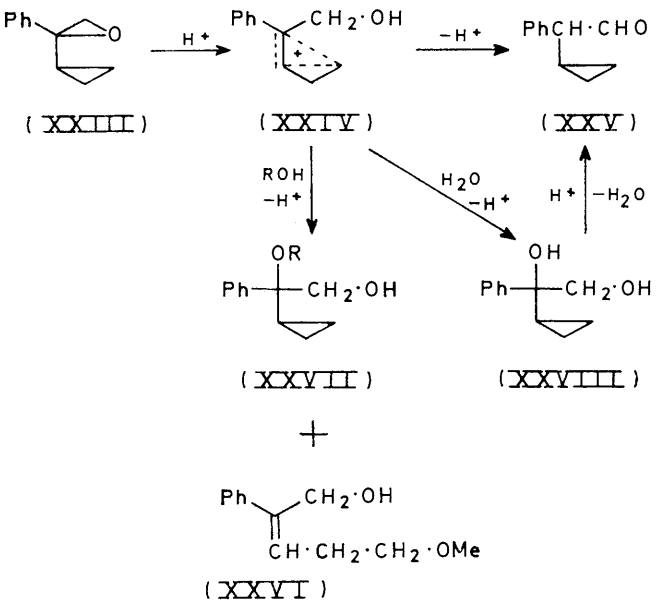
SCHEME 1

stereoisomers of 5-methoxy-2-phenylpent-2-en-1-ol (XXVI); in ethanol only cyclopropyl compounds were



[14] T. Shono, I. Nishiguchi, and R. Oda, *Nippon Kagaku Zasshi*, 1969, **90**, 907; T. Shono, I. Nishiguchi, A. Oku, and R. Oda, *Tetrahedron Letters*, 1967, 517.
[15] M. Kapps and W. Kirmse, *Angew. Chem. Internat. Edn.*, 1969, **8**, 75; W. Kirmse and B. Kornrumpf, *ibid.*, p. 75.
[16] H. Nakamura, H. Yamamoto, and H. Nozaki, *Tetrahedron Letters*, 1973, 111.

isolated: 2-cyclopropyl-2-ethoxy-2-phenylethanol (XXVII; R = Et) and a small quantity of 1-cyclopropyl-1-phenylethane-1,2-diol (XXVIII). Shono and his co-workers [14] have found that the formolysis of



SCHEME 2

3-phenylcyclopropyl epoxide (XXIII) gives a mixture of the formate esters of 2-phenylpent-2-ene-1,5-diol, the cyclopropylaldehyde (XXV), and the dimer of the latter.

EXPERIMENTAL

The ^{1}H n.m.r. spectra were measured with a Perkin-Elmer R12 spectrometer at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal reference.

The successive addition of bromobenzene (4.15 g) in diethyl ether (10 ml) and 1-(4-methoxyphenyl)cyclopropyl cyanide [17] (3.1 g) in diethyl ether (10 ml) to magnesium (0.6 g) in diethyl ether (50 ml), followed by the usual Grignard reaction work-up and by column chromatography on silica gel, gave 1-*benzoyl*-1-(4-*methoxyphenyl*)*cyclopropane* (3.79 g), m.p. 46—47° (Found: C, 80.6; H, 6.7. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%), δ 1.17—1.75 (m, cyclopropyl), 3.73 (s, OMe), and 6.73—7.90 (m, aromatic). The cyclopropyl ketone (4.7 g) was also prepared by the addition of 4-methoxydeoxybenzoin, over 5 min, to sodium (8 g) in liquid ammonia (500 ml), followed, slowly, by 1,2-dibromoethane (50 g). After 6 h, an excess of ammonium chloride was added and the residue left after the ammonia had evaporated was extracted with diethyl ether. The extract was washed, dried, and evaporated to dryness. The residual oil was purified by column chromatography on silica gel.

The epoxides were prepared by the reactions of the corresponding cyclopropyl ketones with dimethylsulphonium methylide.[10] The ^{1}H n.m.r. spectra of the crude products showed no contamination and, with one exception, the epoxides were too reactive [8] to be further purified.

[17] D. D. Roberts, *J. Org. Chem.*, 1968, **33**, 2712.

[18] R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 1967, **89**, 1404.

1-Acetyl-2,2-dimethylcyclopropane [18] (1 g) gave 2-*methyl*-2-(2,2-*dimethylcyclopropyl*)*oxiran* (VIII) as an oil (0.64 g), δ 0.15—1.90 (m, cyclopropyl), 1.10 (s), 1.20 (s), and 1.44 (s) (Me × 3), and 2.50 (s, CH_2O). 1-Benzoyl-1-(4-methoxyphenyl)cyclopropane (2 g) gave 2-[1-(4-*methoxyphenyl*)*cyclopropyl*]-2-*phenyloxiran* (XVa) as an oil (1.90 g), δ 0.80—1.90 (m, cyclopropyl), 2.94 (d) and 3.10 (d) (CH_2O, *J* 5 Hz), 3.75 (s, OMe), and 6.72—7.25 (m, aromatic). 1-Benzoyl-1-phenylcyclopropane [19] (1 g) gave 2-*phenyl*-2-(1-*phenylcyclopropyl*)*oxiran* (XVb) as an oil (0.98 g), δ 0.70—2.00 (m, cyclopropyl), 2.96 (d) and 3.09 (d) (CH_2O, *J* 5 Hz), and 7.22 (s, aromatic) (Found: C, 86.4; H, 6.9. $C_{17}H_{16}O$ requires C, 86.4; H, 6.8%).

A solution of 2-methyl-2-(2,2-dimethylcyclopropyl)oxiran (0.64 g) and toluene-4-sulphonic acid (trace) in dry benzene was refluxed for 12 h, washed with water, and dried. The residue left after removal of the solvent was purified by p.l.c. on silica gel and gave 2,5-*dimethylhexa*-2,5-*dien*-1-*ol* (X) as an oil (0.33 g) (Found: C, 76.3; H, 11.1. $C_8H_{14}O$ requires C, 76.1; H, 11.2%), δ 1.72 (s, Me × 2), 2.00 (s, OH), 2.76 (d, 4-H_2, *J* 7.5 Hz), 4.07 (s, CH_2O), 4.76 (s, 6-H_2), and 5.55 (t, 3-H, *J* 7.5 Hz).

The above reaction of the oxiran (0.75 g), carried out in methanol solution (25 ml) for 4 h, gave 5-*methoxy*-2,5-*dimethylhex*-2-*en*-1-*ol* (XII) as an oil (0.39 g) (Found: C, 68.8; H, 11.6. $C_9H_{18}O_2$ requires C, 68.3; H, 11.5%), δ 1.15 (s, 5-Me × 2), 1.70 (s, 2-Me), 2.26 (d, 4-H_2, *J* 8 Hz), 2.50 (s, OH), 3·22 (s, OMe), 4.1br (s, 1-H_2), and 5.55 (t, 3-H, *J* 8 Hz).

2-Methyl-2-(2,2-dimethylcyclopropyl)oxiran (1.26 g), when chromatographed on silica gel, gave 2,5-dimethylhexa-2,5-dien-1-ol (0.33 g) and 2-(2,2-*dimethylcyclopropyl*)-*propanal* (XI) as an oil (0.20 g), δ 0.5—2.0 (m, cyclopropyl), 1.12 (s, Me × 2), 1.29 (d, 3-Me, *J* 7 Hz), and 9.80 (d, CHO, *J* 1.5 Hz); 2,4-*dinitrophenylhydrazone*, m.p. 108—109° (from ethanol–water) (Found: C, 54.4; H, 5.8; N, 17.7. $C_{14}H_{18}N_4O_4$ requires C, 54.9; H, 5.9; N, 18.3%).

2-[1-(4-Methoxyphenyl)cyclopropyl]-2-phenyloxiran (1.60 g) and toluene-4-sulphonic acid (trace), in dry benzene (50 ml), were refluxed for 2 h, washed with water, and dried. Removal of the solvent and p.l.c. on silica gel gave 2-(4-*methoxyphenyl*)-1-*phenylcyclobut*-2-*enylmethanol* (XVIa) as an oil (1.26 g), δ 1.8br (s, OH), 2.46 (q) and 2.82 (q) (4-CH_2, *J* 14 and 1 Hz), 3.79 (s, OMe), 4.28 (s, CH_2O), 6.52br (s, 3-H), and 6.8—7.5 (m, aromatic). Also obtained was 1-(4-*methoxyphenyl*)-3-*phenylcyclobutene* (XIXa) as an oil (0.13 g), δ 2.80 (s, CH_2·CH_2), 3.85 (s, OMe), and 6.85—7.70 (m, aromatic). Both cyclobutenes partially decomposed when chromatographed. The former (0.45 g) was hydrogenated in ethanol (10 ml) over palladized charcoal and gave 2-(4-*methoxyphenyl*)-1-*phenylcyclobutylmethanol* (0.27 g) as an oil (Found: C, 80.1; H, 7.3. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%), δ 1.2br (s, OH), 2.1—2.8 (m, CH_2·CH_2), 3.70 (CH_2O), 3.80 (s, 2-H), 3.8 (s, OMe), and 6.65—7.50 (m, aromatic).

2-[1-(4-Methoxyphenyl)cyclopropyl]-2-phenyloxiran (0.96 g) and toluene-4-sulphonic acid (trace) were dissolved in methanol (30 ml) and the solution was refluxed for 30 min. The solvent was then removed under reduced pressure and the residue was fractionated by p.l.c. on silica gel giving c-2-*methoxy*-2-(4-*methoxyphenyl*)-1-*phenylcyclobutan*-r-1-*ylmethanol* (XVIIa) (0.43 g), m.p. 88—89° (from ethanol) (Found: C, 76.9; H, 7.5. $C_{19}H_{22}O_3$ requires C, 76.5; H,

[19] S. C. Bunce and J. B. Cloke, *J. Amer. Chem. Soc.*, 1954, **76**, 2244.

7.4%), δ 1.0br (s, OH), 2.1—2.9 (m, CH_2·CH_2), 2.89 (s, 2-OMe), 3.4br (s, CH_2O), 3.85 (s, MeOAr), and 6.9—7.6 (m, aromatic); and the trans-*isomer* (XVIIIa) (0.30 g), m.p. 84° (from ethanol–water) (Found: C, 76.3; H, 7.8. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.4%), δ 2.1—3.0 (m, CH_2·CH_2), 3.18 (s, 2-OMe), 3.75 (s, MeOAr), 3.91 (d) and 4.30 (d) (CH_2O, *J* 12.5 Hz), and 6.65—7.35 (m, aromatic). 2-*Methoxy*-2-[1-(4-*methoxyphenyl*)*cyclopropyl*]-2-*phenylethanol* (XX) (0.15 g), m.p. 73—75° (from ethanol–water) was also obtained (Found: C, 76.6; H, 7.7. $C_{19}H_{22}O_3$ requires C, 76.5; H, 7.4%), δ 0.3—1.6 (m, cyclopropyl), 2.15br (s, OH), 3.25 (s, 2-OMe), 3.85 (s, MeOAr), 3.93 (d) and 4.27 (d) (CH_2O, *J* 12.5 Hz), and 6.55—7.5 (m, aromatic).

A solution (40 ml) in benzene of 2-phenyl-2-(1-phenylcyclopropyl)oxiran (0.67 g) and toluene-4-sulphonic acid (trace) was refluxed for 1 h and worked-up as above. It gave 1,2-diphenylcyclobutene (XIXb) (0.18 g), m.p. 50—52° (lit.,[20] 50—52°), δ 2.82 (s, CH_2·CH_2) and 7.3—7.8 (m, aromatic); and 1,2-diphenylcyclobut-2-enylmethanol (XVIb) as an unstable oil (0.16 g), δ 2.3br (s, OH), 2.39 (q) and 2.77 (q) (4-H_2, *J* 15 and <1 Hz), 4.30 (s, CH_2O), 6.65br (s, 3-H), and 7.2—7.6 (m, aromatic). Substrate (0.22 g) was recovered.

The reaction of 2-cyclopropyl-2-methyloxiran [16] (0.20 g) with toluene-4-sulphonic acid in benzene (25 ml), as above, gave 2-cyclopropylpropanal [21] (XXII; R = Me) as an oil (0.18 g); 2,4-*dinitrophenylhydrazone*, m.p. 126—127° (Found: C, 52.0; H, 5.0; N, 19.8. $C_{12}H_{14}N_4O_4$ requires C, 51.8; H, 5.1; N, 20.1%).

2-Cyclopropyl-2-phenyloxiran (0.73 g) was converted by p.l.c. on silica gel into 2-cyclopropyl-2-phenylacetaldehyde [8b] (XXV) (0.45 g) and 1-*cyclopropyl*-1-*phenylethane*-1,2-*diol* (XXVIII) (0.20 g), m.p. 51—52° [from benzene–light petroleum (b.p. 40—60°)] (Found: C, 64.3; H, 8.1. $C_{11}H_{14}O_2$ requires C, 74.1; H, 7.9%), δ 0.10—1.37 (m, cyclopropyl), 3.35br (s, OH × 2), 3.78 (d) and 3.94 (d) (CH_2O, *J* 11 Hz), and 7.32—7.65 (m, aromatic). This diol (0.13 g) reacted with toluene-4-sulphonic acid (trace) in refluxing benzene solution (25 ml) for 12 h to give 2-cyclopropyl-2-phenylacetaldehyde [8b] (XXV) as an oil (0.10 g). Similar treatment of 2-cyclopropyl-2-phenyloxiran (0.75 g) in benzene (50 ml) also gave 2-cyclopropyl-2-phenylacetaldehyde (0.68 g).

A solution of 2-cyclopropyl-2-phenyloxiran (0.72 g) and toluene-4-sulphonic acid (trace) in methanol (30 ml) was refluxed for 1 h. The solvent was removed under reduced pressure and the residue was fractionated by p.l.c. on silica gel. It gave 2-*cyclopropyl*-2-*methoxy*-2-*phenylethanol* (XXVII; R = Me) as an oil (0.61 g) (Found: C, 74.9; H, 8.2. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%); and a mixture (0.07 g) of the stereoisomers of 5-*methoxy*-2-*phenylpent*-2-*en*-1-*ol* (XXVI) (Found: C, 74.9; H, 8.4. $C_{12}H_{16}O_2$ requires C, 75.0; H, 8.4%), δ 2.1—2.8 (m, 4-H), 2.45br (s, OH), 3.32 (s) and 3.40 (s) (OMe), 3.44 (t) and 3.55 (t) (5-H_2, *J* 6.5 Hz), 4.35 (s) and 4.50 (s) (1-H_2), 5.98 (t, 3-H, *J* 8 Hz), and 7.28—7.60 (m, aromatic).

Similar treatment of 2-cyclopropyl-2-phenyloxiran (0.57 g) with toluene-4-sulphonic acid in ethanol (20 ml) at room temperature gave 1-cyclopropyl-1-phenylethane-1,2-diol (XXVIII) (0.07 g) and 2-*cyclopropyl*-2-*ethoxy*-2-*phenylethanol* (XXVII; R = Et) as an oil (0.47 g) (Found: C, 75.7; H, 9.0. $C_{13}H_{18}O_2$ requires C, 75.7; H, 8.8%), δ 0.30—0.75 (m, cyclopropyl), 1.23 (t) and 3.58 (q) (OEt, *J* 7 Hz), 2.1br (s, OH), 3.59 (d) and 3.95 (d) (1-H_2, *J* 10 Hz), and 7.3—7.6 (m, aromatic).

[5/736 *Received*, 18*th April*, 1975]

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