1,2-Epoxycyclo-octanes: Effect of Unsaturation on the Course of Ring Opening and Rearrangement with Acids

By **N. Heap,** Chemistry Department, The University, Birmingham 15
G. E. Green and **G. H. Whitham,*** The Dyson Perrins Laboratory, South Parks Road, Oxford

The products from the reactions of 1,2-epoxycyclo-octane (I), 3,4-epoxycyclo-octene (II), and 5,6-epoxycyclo-octa-1,3-diene (III) with a number of acids in ethereal solution have been studied. It is found that the ratio of intramolecular-isomerisation reactions to ring-opening processes involving incorporation of external nucleophile, increases with increasing degree of unsaturation in the substrate. Particular attention is paid to the reaction of (III), and it is suggested that the isomerisation to cyclo-octa-2,4-dienone may involve the first example of a 1,6-sigmatropic shift in a pentadienyl cation.

RING-opening and rearrangement reactions of epoxides promoted by acids have been extensively studied and adequately reviewed.[1] In medium rings, although the reaction of 1,2-epoxycyclo-octane (I) with a variety of carboxylic acids has been carefully scrutinised by Cope, Grisar, and Peterson [2] to determine the extent of transannular reaction, little work has been done on reactions of unsaturated relatives of this system with acids. In contrast, the base-catalysed rearrangements of unsaturated medium-ring epoxides have received more attention.[3]

We were interested in finding out how the progressive introduction of double bonds along the series 1,2-epoxycyclo-octane (I) 3,4-epoxycyclo-octene (II), and 5,6-epoxycyclo-octa-1,3-diene (III) would influence their reaction with acids. In particular, we wished to investigate such reactions in relatively nonpolar, poorly ionising media so as to enhance the possibility of intramolecular rearrangements, since the hydroxycyclo-octadienyl cation derivable from (III) might conceivably undergo interesting sigmatropic rearrangements.

1,2-Epoxycyclo-octane (I) [4] and 3,4-epoxycyclo-octene (II)[5] were prepared by literature procedures. 5,6-Epoxycyclo-octa-1,3-diene (III) has been briefly mentioned by Sanne and Schlichting,[6] but no details of its preparation have been given. We have found that epoxidation of cyclo-octa-1,3,5-triene (prepared by a modification of the method of Cope, Stevens and Hochstein [7]) using peracetic acid in dichloromethane buffered with sodium carbonate [8] gives predominantly the desired epoxide (III) together with a small amount (5%) of the isomeric 3,4-epoxycyclo-octa-1,5-diene (IV). The high position-specificity for attack on a terminal double-bond in the triene is rather surprising since epoxidation rates are usually accelerated additively by conjugating substituents at both ends of the double bond.[9] One contributing factor may be the nonplanar nature of the triene which

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[1] (*a*) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, **59**, 737; (*b*) A. Rosowsky in 'Heterocyclic Compounds with Three- and Four-membered Rings,' ed. A. Weissberger, Interscience, 1964, part I, p. 1.

[2] A. C. Cope, J. M. Grisar, and P. E. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 1640.

[3] (*a*) J. K. Crandall and L. H. Chang, *J. Org. Chem.*, 1967, **32**, 532; (*b*) A. C. Cope and B. D. Tiffany, *J. Amer. Chem. Soc.*, 1951, **73**, 4158.

[4] A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Amer. Chem. Soc.*, 1952, **74**, 5884.

[5] (*a*) A. C. Cope and P. E. Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 1643; (*b*) N. Heap and G. H. Whitham, *J. Chem. Soc.* (*B*), 1966, 164.

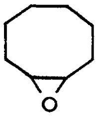
[6] W. Sanne and O. Schlichting, *Angew. Chem.*, 1963, **75**, 156.

[7] A. C. Cope, C. L. Stevens, and F. A. Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2510.

[8] M. Korach, D. R. Nielsen, and W. H. Rideout, *Org. Synth.*, **42**, 50.

[9] *Cf.* B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1955, 1525.

would detract from a stabilisation which involves allylic cation-character in the transition state.



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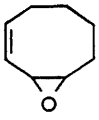

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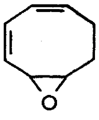

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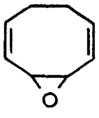

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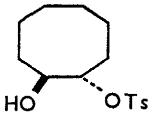
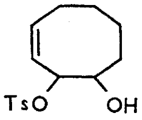


(V)

1,2-Epoxycyclo-octane (I) underwent ring-opening on being heated with anhydrous toluene-*p*-sulphonic acid in ether (3 hr. reflux) to give the mono-toluene-*p*-sulphonate of *trans*-cyclo-octane-1,2-diol (V). The structure of the latter was assigned on the basis of its reaction with ethanolic potassium hydroxide to regenerate the parent epoxide (I). The straight-forward nature of the reaction contrasts with the extensive transannular-rearrangements observed by Cope [2] in solvolyses of the epoxide (I) in carboxylic acids. Presumably, in the poorly ionising solvent ether, an ion-pair comprising protonated epoxide and toluene-*p*-sulphonate ion is formed which collapses essentially by a 'borderline' S_N2 process. Analogous *trans*-opening of normal ring epoxides with sulphonic acids in ether has been observed by other workers.[10] The epoxide (I) was recovered unchanged after being heated for a prolonged period with trichloracetic acid in ether.

3,4-Epoxycyclo-octene (II) reacted rapidly with toluene-*p*-sulphonic acid in ether at 0° to give a hydroxy-toluene-*p*-sulphonate. When less than one equivalent of toluene-*p*-sulphonic acid was used, reaction proceeded until all the acid was consumed and then stopped; the i.r. spectrum of the crude product showed bands due to the hydroxy-toluene-*p*-sulphonate and unchanged epoxide. The hydroxy-toluene-*p*-sulphonate is considered to be (VI), stereochemistry unspecified, partly by analogy with the reaction of (II) with trichloracetic acid described below. Reduction of (VI) with lithium aluminium hydride gave a mixture of cyclo-oct-2-enol and cyclo-oct-3-enol. Treatment of (VI) with ethanolic potassium hydroxide gave a mixture of unsaturated glycols which was not investigated in detail. Although these reactions are consistent with structure (VI) for the hydroxy-toluene-*p*-sulphonate neither can be used to give unequivocal evidence on its structure and stereochemistry since alkyl–oxygen cleavage of the allylic toluene-*p*-sulphonate is presumably involved.

With trichloracetic acid in ether, 3,4-epoxycyclo-octene (II) gave a mixture of hydroxy-trichloracetates assigned structures (VII; X = $COCCl_3$) and (VIII; X = $COCCl_3$) the former predominating, on the evidence given below combined with the expectation of allylic C–O bond cleavage. Alkaline hydrolysis of the trichloracetate mixture gave *trans*-cyclo-oct-3-ene-1,2-diol (VII; X = H) as a major product (*ca.* 80%) together with a diol mixture which was considered to be largely the *cis*-diol (VIII; X = H) on the basis of its n.m.r. spectrum which showed: τ at 60 MHz, 4·1—4·8 (2H, m, vinyl protons), 5·4—6·1 (1H, m, C_2-*H*), 6·3—7·0 (1H, m, C_1-H), and 7·5—9·0 (8H, methylene protons). The lack of complete *trans*-stereospecificity in the ring-opening is ascribed to increased S_{N1} character of the reaction, *i.e.* contribution of the allylic carbonium-ion (IX) to the transition state.



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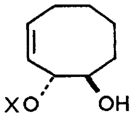

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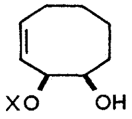
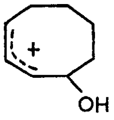
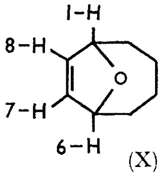


(VIII)



(IX)

In contrast to the above reactions, 3,4-epoxycyclo-octene underwent acid-catalysed rearrangement to 9-oxabicyclo[4,2,1]non-7-ene (X) on treatment with less than an equimolar quantity of perchloric acid in ether. A small amount of a diol mixture with chromatographic behaviour similar to the diols [(VII) and (VIII, X = H] was also formed and was considered to have been produced by hydrolysis of the hydroxy-perchlorate during work up. The n.m.r. spectrum of the bicyclic ether (X) was somewhat unusual since the vinyl protons gave rise to a signal at τ 4·2 which was apparently a singlet. However this behaviour is compatible with 7-H and 8-H being the A part of an AA′XX′ system for which $J_{7,1}$ and $J_{8,1}$ are approximately equal in magnitude, of opposite sign, and small compared with $J_{7,8}$.[11] These conditions are reasonable when considered in the light of the values of allylic and vicinal coupling-constants derived for the related compound (XI),[12] $J_{7,8}$ 6·0 Hz, $J_{7,6}$ 1·8 Hz, and $J_{8,6}$ −1·3 Hz.



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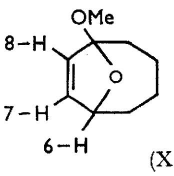

(XI)

We regard the bicyclic ether (X) as being derived by intramolecular transannular attack of OH at C-4 of the hydroxy-carbonium ion (IX). However a suprafacial 1,3-sigmatropic shift [13] involving oxygen as the migrating group cannot be excluded. Apparently the lower nucleophilicity of perchlorate ion allows rearrangement to compete favourably with attack of the acid anion.

In the reaction of 3,4-epoxycyclo-octene (II) with a Lewis acid, magnesium iodide, the familiar type of hydride-shift rearrangement to a ketone [14] occurred with formation in high yield of cyclo-oct-3-enone. With other Lewis acids the isomerisation proceeded less cleanly. Clearly the direction of rearrangement is governed by cleavage of the allylic C–O bond.

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[10] L. N. Owen and G. S. Saharia, *J. Chem. Soc.*, 1953, 2582; L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 1952, 4026; M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 1949, 315; R. Criegee and H. Stanger, *Ber.*, 1936, **69**, 2753.

[11] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, 1965, vol. 1, p. 396.

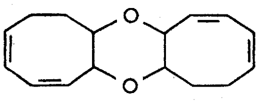
[12] N. Heap, unpublished work.

[13] J. A. Berson, *Accounts of Chemical Research*, 1968, **1**, 152.

[14] Ref. (1*b*), p. 230.

The reaction of 5,6-epoxycyclo-octa-1,3-diene (III) with either toluene-*p*-sulphonic acid or perchloric acid in ether followed a similar course. Since the products were somewhat cleaner from perchloric-acid catalysis, the results are described for this case. Besides hydroxylic material, presumably obtained by hydrolysis of hydroxyperchlorate, three products were isolated. Two of these were shown to be isomers of starting epoxide (III) produced in roughly 30 and 13% yields, and the third was a dimer obtained in 3% yield.

The dimer was tentatively assigned the structure 2,11-dioxatricyclo[10,6,0,^{3,10}]octadeca-4,6,13,15-tetraene (XII) on the basis of spectral data summarised in the Experimental section. The less-abundant, more-polar isomer of (III) was readily shown to be cyclo-octa-2,4-dienone (XIII) by consideration of spectral data followed by comparison with an authentic sample. The more abundant less-polar isomer was shown to be 9-oxabicyclo]4,2,1]nona-2,4-diene (XIV): its u.v. spectrum, $\lambda_{max.}$ (in EtOH) 254 mμ (ε 4670) was that expected for a conjugated diene constrained in such a bicyclic environment (*cf.* the bicyclic compound (XV) has $\lambda_{max.}$ (in MeCN) 255 mμ (ε 4500)] [15] and the n.m.r spectrum was consistent with this structure. Confirmation was provided by hydrogenation to a compound which was inseparable from 9-oxabicyclo[4,2,1]nonane [16] on g.l.c.



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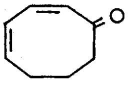

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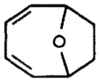
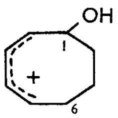


(XIV)

(XV)



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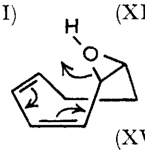
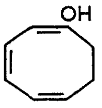


(XVII)

Appropriate control experiments showed that the isomers (XIII) and (XIV) were kinetic products and that neither was converted into the other under the conditions of the reaction. The bicyclic ether (XIV) is probably produced by transannular attack of —OH at C-6 in the hydroxy-cyclo-octadienyl cation (XVI), although an alternative hypothesis envisages a symmetry-allowed suprafacial 1,5-sigmatropic shift [17] involving the protonated epoxide, *cf.* (XVII). We believe, however, that the more interesting product in terms of reaction mechanism is the cyclo-octa-2,4-dienone.

Three mechanistic possibilities can be envisaged for this transformation. The most obvious, (A), involves an opening of the protonated epoxide to the hydroxydienyl cation (XVI) followed by proton loss to the conjugated trienol (XVIII) and subsequent protonation and protropic rearrangement. Our experience with the protonation of conjugated medium-ring dienols [5b] suggests that (XVIII) would protonate preferentially to the unconjugated dienone (XIX) and only on repeated formation and reprotonation of the trienol (XVIII) would conversion to the conjugated ketone (XIII) occur. Mechanism (A) is excluded by the observation that unconjugated ketone (XIX) is not converted into cyclo-octa-2,4-dienone under the conditions of the isomerisation. This evidence equally excludes mechanism (B) which is a variant of (A) in which transannular bond-formation occurs by proton loss to a bicyclic diene, (XX) ⟶ (XXI), followed by valency-bond tautomerism to the monocyclic trienol (XVIII) of mechanism (A).



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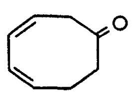

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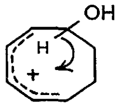

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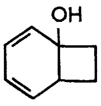

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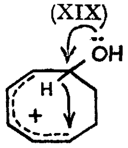

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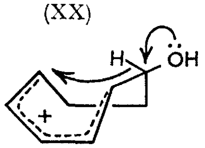

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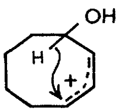

(XXIV)

We are left therefore with the third possibility, mechanism (C), in which cyclo-octa-2,4-dienone is formed directly from the hydroxycyclo-octadienyl cation by transannular hydride-migration (XXII). It is attractive to speculate that this transannular reaction is a *bona-fide* example of a 1,6-sigmatropic hydride-shift in a pentadienyl cation, *cf.* (XXIII), a process which was predicted by Woodward and Hoffmann [17] on orbital symmetry grounds but which has apparently not been previously observed. Some support for this view is provided by the observation already made that 1,2-epoxycyclo-oct-3-ene (II) underwent acid-catalysed rearrangement to the bicyclic ether (X) and *not* to cyclo-oct-2-enone. In the hydroxycyclo-octenyl cation derivable from (II) the steric relationship between C_1–H and electron deficient C-4 is closely analogous, see (XXIV), to that of C_1–H and C-6 in (XXII). However the suprafacial 1,3-sigmatropic hydride-shift would be symmetry-forbidden in this case.[17]

EXPERIMENTAL

*5,6-Epoxycyclo-octa-*1,3-*diene.*—Cyclo-octa-1,5-diene (100 g.) was brominated with *N*-bromosuccinimide (150 g.) by the method of Cope *et al.*[7] to give a mixture of monobromo-compounds (69·4 g., 44% based on *N*-bromosuccinimide.), b.p. 80—84°/2·6 mm.

The monobromo-compounds (66 g., 0·353 mole) were added to a solution of potassium-t-butoxide [57·4 g., 0·513 mole, from potassium (20 g.) in dry t-butyl alcohol (350 ml.)]. The mixture was stirred at 36° for 40 hr. under nitrogen and was then poured into water (approx. 500 ml.); the hydrocarbon layer was separated, washed with water (twice), and dried ($CaCl_2$). Distillation under nitrogen gave cyclo-octa-1,3,5-triene (20·1 g., 54%) b.p. 38—40°/14 mm. G.l.c. (polyethylene glycol column at 50°) showed it to be more than 95% pure (containing less than 5% of cyclo-octa-1,5-diene and bicyclo[4,2,0]octa-2,4-diene [18] com-

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[15] A. G. Anastassiou, *J. Amer. Chem. Soc.*, 1965, **87**, 5512.

[16] F. G. Bordwell and M. L. Douglass, *J. Amer. Chem. Soc.*, 1966, **88**, 993.

[17] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 2511.

[18] A. C. Cope, A. L. Haven, F. L. Ramp, and E. R. Trumbull, *J. Amer. Chem. Soc.*, 1952, **74**, 4867.

bined.) Its i.r. spectrum was identical with that of a sample purified by its silver nitrate adduct.[19]

Cyclo-octa-1,3,5-triene (20·1 g., 0·19 mole) in dichloromethane (150 ml.) containing anhydrous sodium carbonate (30 g.) was stirred during the addition of peracetic acid (23%; 56 g., 0·17 mole) which had been previously shaken with anhydrous sodium acetate (2 g.). The temperature was maintained at 15—20° during the addition. After 20 hr. at room temperature, water was added to the mixture and the organic layer was separated, washed with water, and dried ($MgSO_4$). The dichloromethane was removed under reduced pressure, and the residue was distilled to give the product (8·4 g.) b.p. 58—74°/14 mm., which was purified by distillation through a spinning-band column (to remove unchanged triene) to give an epoxide mixture (5·65 g.) b.p. 68—69°/13 mm. (Found: C, 78·4; H, 8·2. $C_8H_{10}O$ requires C, 78·7; H, 8·2%). The mass spectrum showed a molecular ion of mass 122. The mixture was shown to contain approximately 95% 5,6-*epoxycyclo-octa-*1,3-*diene* and 5% 3,4-epoxycyclo-octa-1,5-diene by the reduction described below.

Reduction of the Epoxide Mixture.—The epoxide mixture (70 mg.) was reduced upon being heated under reflux in ether for 11 hr. with lithium aluminium hydride. The product, after isolation was shown by g.l.c. (polyethylene glycol adipate column at 125°) to contain 95% cyclo-octa-3,5-dienol and 5% cyclo-octa-2,6-dienol, by comparison with authentic specimens of the latter alcohols.

Reaction of 1,2-*Epoxycyclo-octane with Acids.*—(i) *Toluene-*p-*sulphonic acid.* 1,2-Epoxycyclo-octane (1 g., 0·008 mole)[4] in ether (60 ml.) was added to toluene-*p*-sulphonic acid (1·5 g., 0·009 mole) and the mixture was heated under reflux for 3 hr. After the mixture had been washed with aqueous sodium carbonate, the product was isolated (1·3 g.). Its i.r. spectrum showed bands at 1170—1185 (sulphonate group), and at 3400—3500 cm.$^{-1}$ (OH) which indicated the formation of hydroxy-toluene-*p*-sulphonate. Potassium hydroxide (0·3 g., 0·005 mole) was added to the above product (1·3 g., 0·003 mole) in ethanol and the mixture was heated under reflux for 1 hr. The ethanol was removed under reduced pressure, and water was added. The product was isolated with ether. Its i.r. spectrum was identical with that of *cis*-1,2-epoxycyclo-octane.

(ii) *With trichloracetic acid.*—Trichloracetic acid (1·3 g., 0·008 mole) was added to the epoxide (0·95 g., 0·008 mole. in ether (20 ml.) and the mixture was heated under reflux for 48 hr. After the mixture had been washed with aqueous sodium carbonate the product was isolated (0·85 g.); its i.r. spectrum was identical with that of starting material.

Reaction of 3,4-*Epoxycyclo-octene with Acids.*—(i) *Toluene-*p-*sulphonic acid.* Toluene-*p*-sulphonic acid (4·5 g., 0·026 mole) was added to the epoxide (2·9 g., 0·0234 mole) in ether (40 ml.) at 0°, and the mixture was set aside for 30 min. at 0° (after being shaken to dissolve most of the acid). After the mixture had been washed with aquous sodium carbonate the product was isolated (5 g.), its i.r. spectrum showed bands at 1180 and 1360 cm.$^{-1}$ (sulphonate group) and 3400—3500 cm.$^{-1}$ (OH) which indicated the formation of hydroxy-toluene-*p*-sulphonate. The product was identical (i.r. spectrum) with that obtained when the reaction mixture had been left at room temperature for 24 hr. (For reaction with less than equimolar amounts of acid see the Discussion.)

Lithium aluminium hydride (0·5 g. 0·013 mole) was added to the above hydroxy-toluene-*p*-sulphonate (3·33 g., 0·011 mole) in ether and the mixture was heated under reflux for 1 hr. Moist ether and then water were added, and the ether layer was separated, washed with dilute sodium carbonate solution and water, and dried. The ether was removed to give the crude product (1·66 g.). The major components were separated by preparative t.l.c. (Kieselgel H F, the eluant was a mixture of equal volumes of ether–light petroleum; yield 0·65 g.) and shown by g.l.c. (polyethylene glycol adipate column at 125°) to be cyclo-oct-2-enol and cyclo-oct-3-enol (in approximately equal amounts), by comparison with authentic samples of the alcohols.[5b]

(ii) *Trichloracetic acid.* The epoxide (3 g., 0·0242 mole) in ether (60 ml.) was added to trichloracetic acid (4·5 g., 0·0274 mole) and the mixture was heated under reflux for 6 hr. After the mixture had been washed with aqueous sodium carbonate the product was isolated (5·58 g.); its i.r. spectrum showed bands at 1248 and 1755 (Cl_3CCO_2), and 3450 cm.$^{-1}$ (OH) which indicated that a hydroxy-trichloracetate had been formed. T.l.c. indicated that two products and unchanged epoxide were present. Potassium hydroxide (1·2 g., 0·02 mole) was added to the product (5·56 g., 0·02 mole) in ethanol, and the mixture heated under reflux for 20 min. The ethanol was distilled off under reduced pressure, and water was added. The product (1·7 g., 61%), isolated with ether, was dissolved in hot light petroleum (b.p. 40—60°) and cooled to give trans-*cyclo-oct-*3-*en-*1,2-*diol* (0·52 g.) m.p. 84—85° (from light petroleum) (Found: C, 67·4; H, 9·95. $C_8H_{14}O_2$ requires C, 67·55; H, 9·9%); τ ($CDCl_3$ at 60 Mc./sec.) 4·4 (2, m, vinyl protons) 5·6 (1, quadruplet, C_2-H), 6·5 (1, m, C_1-H), 6·9 (2H, s, hydroxy-protons), 7·6—8·9 (8H, overlapping multiplets, methylene protons). The filtrate which contained 0·8 g. of product was chromatographed on silica gel (20 g.) and elution with graded ether–light petroleum (b.p. 40—60°) mixtures gave the following fractions: (a) unchanged epoxide (0·06 g.; identified by its i.r. spectrum), (b) a mixture of glycols (0·22 g.) (see Discussion for further details), and (c) *trans*-cyclo-oct-3-en-1,2-diol (0·20 g.)

The crystalline cyclo-oct-3-en-1,2-diol was shown to be the *trans*-isomer by hydrogenation of 100 mg. in ethyl acetate over 10% palladium on charcoal (the i.r. spectrum of the product was identical with that of *trans*-1,2-cyclo-octanediol). The bisphenylurethane of the product was prepared; it crystallised from ethanol as white needles, m.p. 170—171°; mixed m.p. with an authentic sample of *trans*-1,2-cyclo-octanediol bisphenylurethane[4] was 169·5—170·5°. (The mixed m.p. of *cis*- and *trans*-1,2-cyclo-octanediol bisphenylurethanes is approx. 20° below that of the pure derivatives and extends over a 9° range). *cis*- and *trans*-1,2-Cyclo-octanediols were inseparable by g.l.c. (polyethylene glycol adiptate column at 175°) or t.l.c.

(iii) *Perchloric acid.* Perchloric acid [86 mg., 0·0009 mole; prepared by the addition of 60% perchloric acid to ether and drying the solution ($MgClO_4$). The concentration of acid was determined by titration with sodium hydroxide] in ether (12 ml.) was added to the epoxide (0·873 g., 0·007 mole) in ether (2 ml.) at 0°, and the mixture left for 30 min. After the mixture had been washed with aqueous sodium carbonate the product was isolated (0·69 g.). It was dissolved in ether–light petroleum (b.p. 40—60°) mixture (1 : 1) and filtered through alumina (25 g. neutral, activity III) to separate highly polar materials (0·19 g. not further

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[19] A. C. Cope and F. A. Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2515; K. Alder and H. A. Dortmann, *Chem. Ber.*, 1954, **87**, 1492.

characterised) from the volatile products (0·44 g.). The latter, after distillation was shown by g.l.c. (polyethylene glycol column at 100°) to comprise unchanged epoxide (10%) and 9-*oxabicyclo*[4,2,1]*non*-7-*ene* (90%) (Found: C, 77·6; H, 9·85. $C_8H_{12}O$ requires C, 77·4; H, 9·7%). The i.r. spectrum showed a strong band at 1090 cm.$^{-1}$ (C–O stretch) and no bands attributable to epoxide hydroxy or carbonyl were present, τ at 100 Mc./sec.: 4·2 (2H, s, vinyl protons), 5·03 (2H, d, *J* 6·7 c./sec., bridgehead protons) and 7·7—8·8 (8, m, methylene protons).

(iv) *Magnesium iodide*. Magnesium iodide in ether was prepared by heating a mixture of magnesium (0·1 g., 0·004 mole; finely divided turnings) and iodine (1 g., 0·004 mole) under reflux in ether until the solution was pale yellow. This was filtered and added to the epoxide (0·47 g., 0·004 mole) in ether. The mixture was left at room temperature for 20 hr. Water was then added and the ether layer was separated, washed with dilute sodium thiosulphate solution, water, and saturated brine, and dried. Removal of the ether under reduced pressure gave the product (0·38 g., 81%) which had an i.r. spectrum identical with that of cyclo-oct-3-enone. G.l.c. (polyethylene glycol adipate column at 125°) showed it to be 95% ketone, 4% of a compound considered to be cyclo-octa-2,4-dienol, and 1% of an unknown compound.

Reaction of 5,6-*Epoxycyclo-octa*-1,3-*diene with Perchloric Acid*.—Perchloric acid (315 mg., 0·003 mole prepared as above) in ether (60 ml.) was added to the epoxide (3·87 g., 0·032 mole) in ether (5 ml.) at 0°, and the mixture was stirred for 5 min. The product was isolated (3·77 g.). This was dissolved in a mixture of ether–light petroleum (87 : 13) and filtered through a short column of alumina (neutral, activity I) to give 1·6 g. of non-hydroxylic material. The latter was shown by g.l.c. (polyethylene glycol column at 100°) to contain cyclo-octa-2,4-dienone (28%, comparison with an authentic sample of the ketone prepared as below) and a compound which was assigned the structure 9-oxabicyclo[4,2,1,]nona-2,4-diene (72%).

The non-hydroxylic material was chromatographed on alumina (80 g. neutral, activity I) using graded ether–light petroleum (b.p. 40—60°) mixtures to give: (a) a crystalline compound (102 mg.) which on recrystallisation from aqueous ethanol had m.p. 135—138°. This was tentatively assigned the structure 2,11-dioxatricyclo[10,6,0^{3,10}]octadeca-4,6,13,15-tetraene (XII). The mass spectrum showed a molecular ion of mass 244 followed by peaks of mass 123, 122 and 121 suggesting a dimer; $\lambda_{max.}^{EtOH}$ at 233 mμ (ε 11,570), $\nu_{max.}$ among others, 1090 (C–O stretch), 1630 and 1645 (C=C) 3000 and 3030 cm.$^{-1}$ (vinyl C–H) and no bands due to hydroxy or carbonyl functions; τ in $CDCl_3$ at 100 Mc./sec. 3·8—4·7 (8H, m, vinyl protons), 5·67 (2H, t, 3-H and 12-H, *J* 8·6 Hz), 6·6 (2H 2t, 1-H and 10-H, J 4 Hz), 7·2—8·6 (8H overlapping multiplets, methylene protons); (b) 9-oxabicyclo[4,2,1]nona-2,4-diene (380 mg.), $\nu_{max.}$ (liq. film) notably 3020, 2940, 1070, 1000, 920, 870, and 700 cm.$^{-1}$, $\lambda_{max.}^{EtOH}$ 254 mμ (ε 4670); τ (CCl_4) at 60 Mc./sec.: 3·7—4·5 (4H, vinyl protons), 5·3—5·6 (4H, bridgehead protons), and 7·5—8·1 (4H, methylene protons); (c) cyclo-octa-2,4-dienone (550 mg.) identified by comparison (i.r., n.m.r., and g.l.c.) with an authentic sample (see below) and by preparation of the 2,4-dinitrophenylhydrazone, red needles from ethanol m.p. and mixed m.p. 175·5—180° (Found: C, 55·65; H, 4·95. Calc. for $C_{14}H_{14}N_4O_4$: C, 55·65; H, 4·65%).

The highly polar material from the reaction was eluted from the short alumina-column with ether to give 1·9 g. which had $\lambda_{max.}^{EtOH}$ 231 mμ (ε 4250 based on *M* 140) indicative of a cyclo-octa-1,3-diene, $\nu_{max.}$ 3450 and 1090 cm.$^{-1}$ intense absorption due to C–OH.

Hydrogenation of 9-*Oxabicyclo*[4,2,1]*nona*-2,4-*diene*.—A small sample of the bicyclic ether (30 mg.), which had somewhat deteriorated on standing) was hydrogenated in ethyl acetate over Adams platinum until absorption of hydrogen ceased. Evaporation gave a product comprising *ca.* 90% of one volatile component on g.l.c. This material was inseparable from an authentic specimen of 9-oxabicyclo-[4,2,1]nonane [16] on both polyethylene glycol and polyethylene glycol adipate columns.

Behaviour of 9-*Oxabicyclo*[4,2,1]*nona*-2,4-*diene with Perchloric Acid*.—Perchloric acid (3·3 mg., 0·00003 mole; prepared as above) in ether (0·5 ml.) was added to the bicyclic ether (32 mg., 0·0003 mole) in ether (0·5 ml.) at 0° and the mixture was left for 5 min. The product was isolated (20 mg.) and shown by g.l.c. (polyethylene glycol column at 100°) to be starting material.

Cyclo-octa-2,4-*dienone*.—Cyclo-octa-1,3-diene (47 g., 0·435 mole) was brominated with *N*-bromosuccinimide (50 g., 0·284 mole) by the same procedure used for cyclo-octa-1,5-diene (see above) to give a mixture of monobromo-compounds (26·21 g., 50% based on *N*-bromosuccinimide) b.p. 46—50°/0·12 mm. Water (30 ml.) was added and the mixture was made homogeneous with acetone. Sodium hydrogen carbonate (100 g., 1·17 mole) was added and the mixture was stirred for 1 hr. at 50°. After the suspension had been cooled it was filtered and most of the acetone was removed under reduced pressure. The product was isolated with ether to give an alcohol mixture (15·1 g., 87%). The latter (undistilled to prevent formation of cyclo-oct-3-enone from cyclo-octa-2,4-dienol by rearrangement),[3a] in acetone, was stirred at 0° during the addition of 6N-chromic acid (43 ml., 0·129 mole.) After the addition the mixture was left at room temperature for 15 min. Water was then added and the product was isolated with ether; distillation gave 8·18 g. (54%) of material. Redistillation through a spinning band column gave *cyclo-octa*-2,4-*dienone* (6 g.) b.p. 45·5—48·5°/0·12 mm. followed by a mixture of cyclo-octa-2,4- and 2,7-dienones. The i.r. spectra of the later fractions showed bands at 1155, 1230, 1290, 1410 and 1640 cm.$^{-1}$ (C=O) which were presumed to be due to the 2,7-dienone. The earlier fractions, which did not show these bands and were homogeneous to t.l.c., were considered to be pure cyclo-octa-2,4-dienone (Found: C, 78·45; H, 8·6. $C_8H_{10}O$ requires C, 78·7; H, 8·2%) $\lambda_{max.}^{EtOH}$ 278 mμ (ε 5770); τ in $CDCl_3$ at 100 mc./sec. 3·5—3·9 (3H, m, vinyl protons at C-3, C-4 and C-5), 4·2 (1H, d, *J* 12·9 Hz, 2-H split by 3-H), 7·45 (2H, t, *J* 6-Hz, 8-Hz split by 7-H2, 7·6—8·2 (4H, m, methylene protons at C-7 and C-6). The 2,4-dinitrophenylhydrazone was obtained as red needles (from EtOH), m.p. 177·5—180°.

Behaviour of Cyclo-octa-2,4-*dienone with Perchloric Acid*.—Perchloric acid (11 mg., 0·0001 mole) in ether (2 ml.) was added to cyclo-octa-2,4-dienone (103 mg., 0·0008 mole) in ether (0·5 ml.) at 0° and the mixture was left for 5 min. The i.r. spectrum of the product (63 mg.) was identical with that of starting material.

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