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# THE REARRANGEMENT OF VINYL EPOXIDES DERIVED FROM BICYCLO[4.2.0]OCTA-2,4,7-TRIENES

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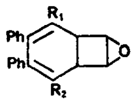
As part of our interest[1,2] in the preparation of the 8-oxatricyclo[4.3.0.0$^{7,9}$]nona-2,4-diene ring system (1), we investigated the epoxidation of bicyclo[4.2.0]octa-2,4,7-trienes (biCOTs) (2). While several examples of epoxidation of cyclobutene π-systems have been reported[3], and even the preferential epoxidation of a ring-strained π-bond in the presence of a 1,3-diene system elsewhere in the molecule[4], the reaction of biCOTs (2) with m-chloroperbenzoic acid (m-CPBA) was not successful as a route to the required ring-system (1). In the event a new type of end-product was obtained which has not previously been observed in m-CPBA reactions, and this is the subject of the present report.



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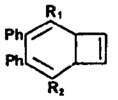

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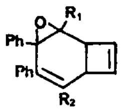

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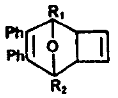

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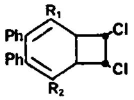

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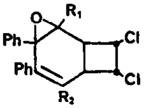

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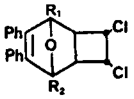

(7)

(a) R$_1$= Me,R$_2$= Ph (b) R$_1$=R$_2$= Ph (c) R$_1$=R$_2$=Me (d) R$_1$=Ph,R$_2$= Me.

Initially the biCOT (2a)[6] was treated with m-CPBA in chloroform solution (3 days, r.t.) and a single product obtained. Purification by p.l.c. (silica $CH_2Cl_2$/petrol) and crystallisation ($CHCl_3$/EtOH) yielded a product, m.p. 139°C, *m/e* 362. The p.m.r. spectrum (Fig. 1) showed that epoxidation had not occurred at the cyclobutene π-bond. The u.v. spectrum [$\lambda_{max}$ 223, 275 nm in EtOH] indicated that the original diene chromophore [$\lambda_{max}$ 248, 311 nm in hexane for (2a)] had been modified, but a decision between the 1,2-epoxides (3a or 3d), and the 1,4-oxide (4a) was more difficult.

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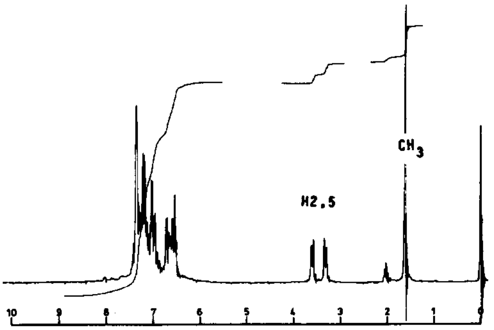


-*FIG. 1*-
*100 MHz p.m.r. spectrum of compound (4a) in acetone-$d_6$.*

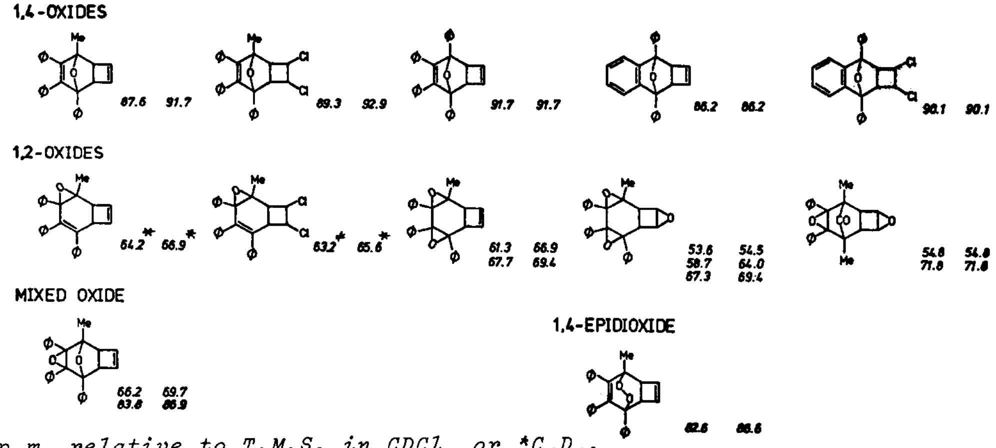
A definitive judgement in favour of the 1,4-oxide was forthcoming from the $^{13}$C-n.m.r. spectral data. Thus the C-resonances at 91.7, 87.6 p.p.m. were assigned to the 1,4-oxygen bridged carbon atoms, since such resonances fall within the range 80-95 p.p.m. whereas those associated with 1,2-epoxides fall in the range 40-75 p.p.m.[7] The constancy of these assignments is supported by literature values as well as a large amount of our own data, a selection of which is summarised in Fig. 2.

The formation of 1,4-oxides was quite general with similarly substituted compounds, and the related tetraphenylbiCOT (2b) yielded a 1,4-product, m.p. 173°C. In this case the symmetry of the $^1$H- and $^{13}$C-n.m.r. spectra added support to the 1,4-oxide formulation. The reaction also occurred with the 7,8-dichlorobicyclo[4.2.0]octa-2,4-diene (5a) which yielded (chloroform solution)[9] a mixture of *endo*- and *exo*-1,4-oxides (7a), m.p. 181°C, 195°C, resp., together with the benzocyclobutene (8), m.p. 144°C.

There are numerous examples of 1,4-oxides being formed from ene epoxides under thermal[11], photochemical[12], or metal carbonyl promoted rearrangement[13], but to our knowledge no reports of acid-catalysed transformation have appeared. Indeed ene epoxides are usually transformed into ketone, ene-diol or related derivatives upon treatment with acid.[14] In fact the biological formation of ene diols from enzymatically produced ene epoxides has recently gained importance in the metabolism of carcinogenic hydrocarbons.[15]

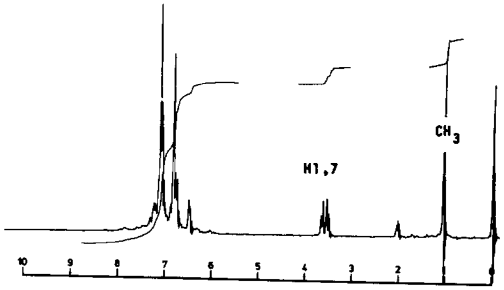
In the conversion of (2) to (4) there seemed good precedent to suspect the intermediacy of ene epoxides, and this premise was borne out by carrying out the m-CPBA reaction in a basic, two phase medium ($CH_2Cl_2$/0.5M aq. $NaHCO_3$). In the case of biCOT (2a) the crystalline epoxide (3a), m.p. 142°C, was the exclusive product. The $^1$H-n.m.r. spectrum of this compound (Fig. 3) showed a strong spectral similarity with the 1,4-oxide (4a), but the $^{13}$C-n.m.r. clearly indicated the presence of the epoxide ring with resonances at 66.9, 64.2 p.m.r. Dissolution of (3a) in $CDCl_3$ (but not in acetone or benzene)[9] at ambient temperature, caused rapid rearrangement to the 1,4-oxide, the traces of acid impurities present in commercial $CDCl_3$ being sufficient to catalyse the reaction. A mechanism involving the stabilised carbocation (9) is proposed to account for the ene epoxide to dihydrofuran rearrangement. An intermediate such as (9) also accounts for the formation of the methylene alcohol (10) when 2,5-dimethyl-3,4-diphenylbiCOT (2c) is treated with m-CPBA in $CHCl_3$.[16]

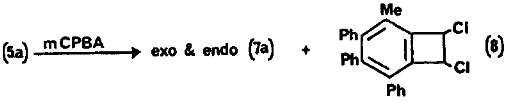
-FIG. 2-Selected $^{13}$C-n.m.r. data of 1,2- and 1,4-oxides

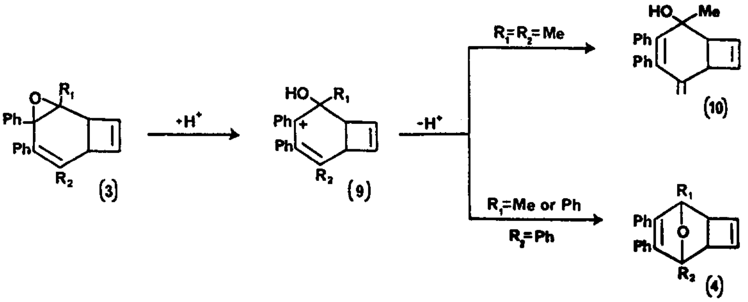


δ p.p.m. relative to T.M.S. in $CDCl_3$ or $^*C_6D_6$.

-FIG. 3-
100 MHz p.m.r. spectrum of the 1,2-epoxide(3a) in acetone-$d_6$.







Treatment of a chloroform solution of the biCOT (2a) with molecular oxygen (in the dark) at 0°C, resulted in the slow formation of the 1,4-oxide (4a). When the reaction was carried out in the absence of acid the epoxide (3a) could be detected, but under these reaction conditions (benzene r.t.) a significant amount of the related cyclooctatetraene was also observed. This latter compound results from a disrotatory ring-opening of the biCOT, a reaction known to occur under thermal conditions.

A precedent exists for the formation of 1,2-epoxides from conjugated polyenes on treatment with molecular oxygen[17], and the 1,4-oxide is presumed to again arise from the acid catalysed pathway.

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## REFERENCES AND FOOTNOTES

1. R.N. Warrener, R.A. Russell and R.Y.S. Tan, *accompanying communication.*
2. M.G. Hyman, M.N. Paddon-Row and R.N. Warrener, *Synthetic Commun.*, 1975, 5, 107.
3. a) L.A. Paquette and M.J. Carmody, *J. Amer. Chem. Soc.*, 1976, 98, 8175. b) W. Henne, G. Plinke and G. Schröder, *Chem. Ber.*, 1975, 108, 3753. c) H.H. Westberg and R.N. Warrener, *Synthetic Commun.*, 1972, 2, 43.
4. Reaction of tricyclo[4.4.1.1.$^{2,5}$]dodeca-3,7,9-trien-11-one with m-CPBA yields the $\Delta^{3,4}$ epoxide.[5] Another example, although less selective, is reported in ref. 3b.
5. J. Haywood-Farmer, B.T. Friedlander and L.M. Hammond, *J. Org. Chem.*, 1973, 38, 3145.
6. R.Y.S. Tan, *unpublished results.*
7. A single report[8] of 80 p.p.m. has been made for an epoxide carbon, but this seems anomalous.
8. W. Hertz, P.S. Kalyanaraman and G. Ramakrishnan, *J. Org. Chem.*, 1977, 42, 2264.
9. Isomeric *exo*- and *endo*-1,2-epoxides (6a) were obtained upon treatment with m-CPBA in the two phase medium. Dissolution of these isomers in $CDCl_3$ caused rearrangement to a pair of isomeric 1,4-oxides (7).
10. The structure of (8) was confirmed by separate synthesis from (5a) by treatment with DDQ.
11. a) W. Eberbach and J.C. Carré, *Tetrahedron Lett.*, 1976, 3299. b) J.-C.-Paladini and J. Chuche, *Bull. Soc. Chim. France*, 1974, 197. c) W. Eberbach and B. Burchardt, *Tetrahedron Lett.*, 1976, 3887. d) H. Hasegawa, H. Saito and K. Tsuchitani, *Chem. Lett.*, 1977, 797.
12. a) W. Eberbach and U. Trostmann, *Tetrahedron Lett.*, 1977, 3569. b) H. Hart, C. Peng and E. Shih, *J. Org. Chem.*, 1977, 42, 3635.
13. R. Aumann and H. Averbeck, *J. Organomet. Chem.*, 1975, 85, C4.
14. a) R.E. Parker and N.S. Isaacs, *Chem. Rev.*, 1957, 59, 737. b) G. Berti, "Topics in Stereochemistry", Vol 7, p. 97. Wiley-Interscience, 1973. c) H. Hart and A.J. Waring, *J. Amer. Chem. Soc.*, 1964, 86, 1454.
15. B. Witkop, *Agnew. Chem. Int. Ed.*, 1977, 16, 559.
16. Spectral evidence for the 1,2-epoxide could be obtained, but the methylene compound was formed upon work up, even under basic conditions.
17. H. Hart and P.B. Lavrik, *J. Org. Chem.*, 1974, 39, 1793.