Acid-catalysed Isomerisations of 5,6,7,8-Tetrachloro-3,4-dihydro-1,4-dimethyl-1,4-ethenonaphthalen-2(1*H*)-one (1,4-Dimethyltetrachlorobenzobarrelenone)

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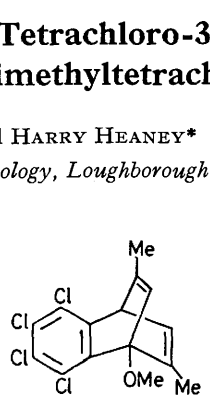
Summary The rearrangement of the title compound (**2**) in fluorosulphonic acid or sulphuric acid (98%) affords the ketone (**6**) in good yield whereas the ketones (**2**) and (**6**) both give rise to mixtures of the isomers (**5**) and (**9**) in sulphuric acid (90%).

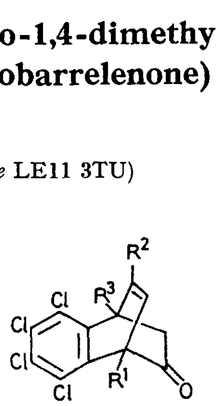
Continuing interest in acid-catalysed rearrangement reactions of $\beta\gamma$-unsaturated ketones,[1] and in particular octamethylbicyclo[2,2,2]octa-2,5-dien-7-one[2] and a related hexamethyl-analogue[3] prompts us to report some of our results. Our earlier studies have established certain features involved in the rearrangements of 1-methoxybenzobarrelenes.[4] Octamethylbenzobarrelenone gives rise to an equilibrium mixture of bicyclic- and tricyclic-ketones in trifluoroacetic acid.[5]

We now report that 1,4-dimethyltetrachlorobenzobarrelenone (**2**) undergoes further rearrangements in the presence of strong acids to afford structural types which have not been observed in previous investigations. Compound (**1**), in trifluoroacetic acid, affords the expected[4] mixture of the isomeric ketones (**2**) and (**3**) in a combined yield† of 21% together with compounds (**4**) and (**5**) in 52 and 24% yield respectively.

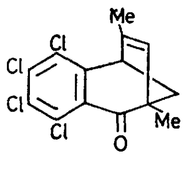
In the presence of sulphuric acid (98%) or fluorosulphonic acid the ketone (**2**) was converted into the isomer (**6**) in 70 and 34% yield respectively. Although the structure of compound (**6**) was not immediately obvious its constitution was established from spectral data and further chemical interconversions. Thus the ^{1}H n.m.r. spectrum



(1)



(2; R^1 = R^3 = Me; R^2 = H)
(3; R^1 = R^2 = Me; R^3 = H)



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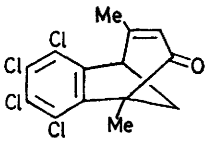
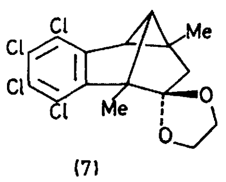


(5)



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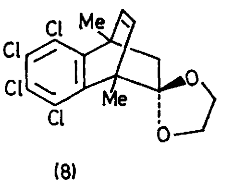

(8)

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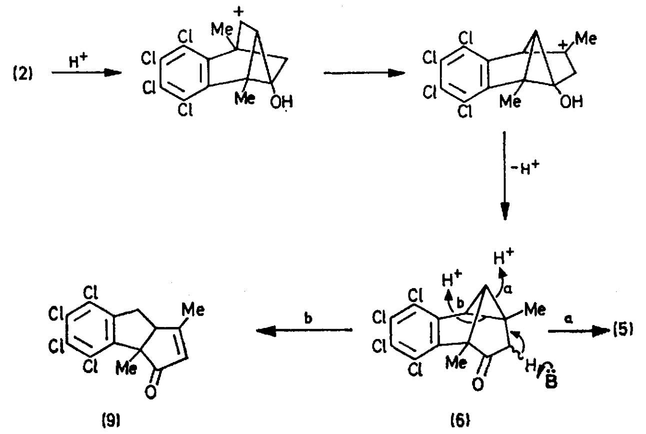
† The precise ratio of the compounds (**2**) and (**3**) was found to depend on the amount of water present in the trifluoroacetic acid.

showed doublets ($|J|$ 6 Hz) from the cyclopropane hydrogens at τ 7·15 and 7·46,[6] a multiplet for the methylene group at τ 7·61, and the two methyl resonances at τ 8·31 and 8·55. The assignments are supported by studies using a europium shift reagent and by ^{13}C n.m.r. spectroscopy.



SCHEME

The ethylene acetal (7) of the ketone was identical with a sample prepared by the photoisomerisation of the acetal (8). The di-π-methane rearrangement is known to be directed by *endo*-hetero-substituents.[7]

In the presence of aqueous sulphuric acid (90%) the ketone (2) was converted into the isomer (9) in 72% yield while in aqueous sulphuric acid (95%) the ketone (6) gave rise to a mixture of the isomers (5) and (9) in 5·5 and 43% yield respectively. The structures of compounds (5) and (9) followed from their spectroscopic properties and those of their dihydro-derivatives. For example the i.r. C=O stretching frequency in the compound (9) was observed at 1710 cm^{-1} and in its dihydro-derivatives at 1750 cm^{-1}.

The results obtained may be rationalised in accord with the Scheme.

Compound (1) is also a suitable starting material for the preparation of compounds (6) and (9). Thus in fluorosulphonic acid compound (1) gave the ketone (6) in 40% yield while in sulphuric acid (95%) the ketones (6) and (9) were obtained in 17 and 15% yield respectively. These results are in accord with other results[4] which indicate that the initial protonation of double bonds in 1-methoxybenzobarrelenes favour the production of a cation at C-3 as the acid strength is increased and which would result in an increase in the proportion of intermediates such as the compounds (2) and (3).

Evidently the precise location of methyl groups affects the eventual outcome of these multi-step rearrangement reactions in ways which are not thoroughly understood. Nevertheless these reactions do allow the synthesis of structural types which are otherwise inaccessible.

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[1] R. L. Cargill, T. E. Jackson, N. P. Peet, and D. M. Pond, *Accounts Chem. Res.*, 1974, **7**, 106.

[2] H. Hart and G. M. Love, *J. Amer. Chem. Soc.*, 1971, **93**, 6264.

[3] H. Hart and I. C. Huang, *Tetrahedron Letters*, 1974, 3245; and references cited therein.

[4] H. Heaney, and S. V. Ley, *Chem. Comm.*, 1971, 224, 1342; N. J. Hales, H. Heaney, and S. V. Ley, *J.C.S. Perkin* 1, 1974, 2702.

[5] H. Hart and G. M. Love, *Tetrahedron Letters*, 1971, 2267.

[6] See for example J. P. N. Brewer, I. F. Eckhard, H. Heaney, M. G. Johnson, B. A. Marples, and T. J. Ward, *J. Chem. Soc* (*C*), 1970, 2569; H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *J. Amer. Chem. Soc.*, 1968, **90**, 6096.

[7] S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, 1973, **73**, 531.