Acid-catalysed Rearrangements of 3,5-Dimethyl-1-methoxy-tetrafluorobenzobarrelene (5,6,7,8-Tetrafluoro-1,4-dihydro-3,10-dimethyl-1-methoxy-1,4-ethenonaphthalene)

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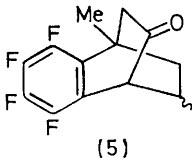
Summary The title compound undergoes rearrangement in trifluoroacetic acid to afford almost exclusively the benzobarrelenone (2) whereas in concentrated sulphuric acid the lactone (3) is obtained in quantitative yield.

WE,[1] and others,[2] have recently reported acid-catalysed rearrangement reactions of certain 1-methoxybenzobarrelene derivatives. One can, in certain instances, obtain an entry into these rearrangements from other compounds.[3] The mechanisms of these rearrangements are complex.[4]

We now report that the course of the rearrangement reactions of the title compound (1)† is apparently controlled by the methyl groups and not by the methoxy-group, and further, that the rearrangements can proceed beyond the benzobarrelenone (2) to the lactone (3). When the compound (1) in *O*-deuteriotrifluoroacetic acid was heated under reflux, we obtained the ketone (2) in which one deuterium atom was incorporated into the methylene group. The compound (1) was rearranged rapidly in concentrated sulphuric acid at room temperature to afford the lactone (3) quantitatively after the addition of the reaction mixture to water. Using deuteriosulphuric acid and deuterium oxide the lactone (3) contained three deuterium atoms. Similarly the undeuteriated ketone (2) gave the lactone (3) containing two deuterium atoms. When the rearrangement was carried out in a mixture of concentrated sulphuric acid and water (7 : 3 v/v) at 0° we obtained the compounds (2) and (3) in 14% and 39% yield, respectively, together with the naphthalene derivative (4) in 40% yield. The



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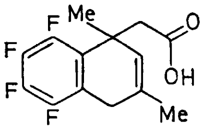

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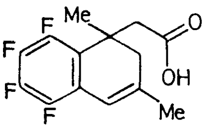

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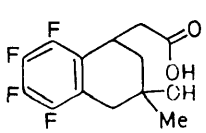

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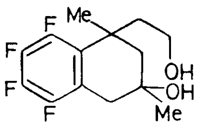

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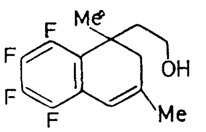

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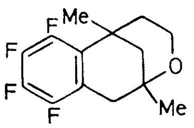

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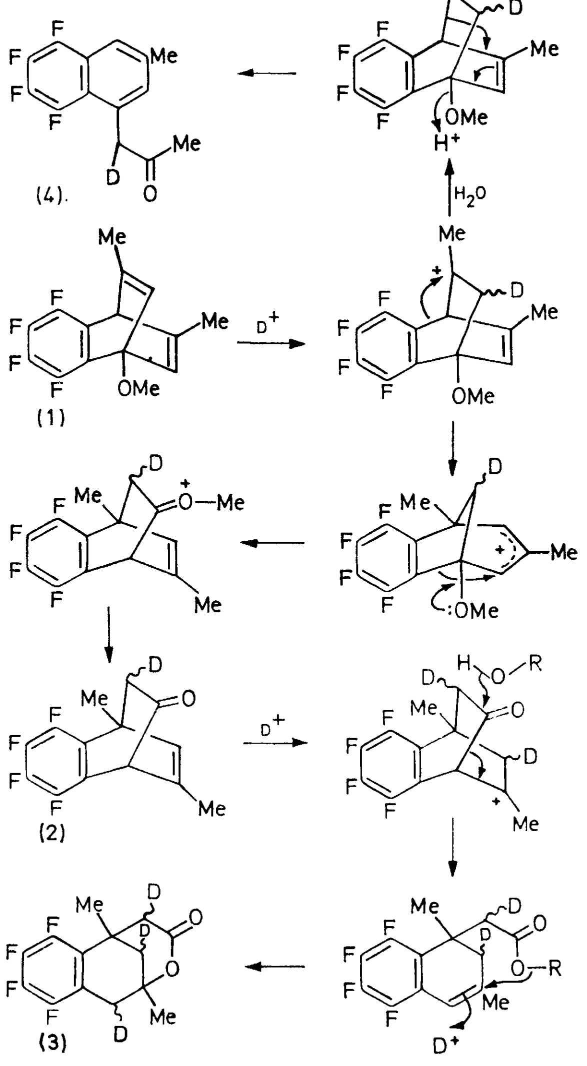

SCHEME

R = H or SO_3H

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† Satisfactory analytical and spectroscopic data are available for all of the compounds described.

compound (4) is not produced from the ketone (2). Further, the benzobarralanones (5) are unaffected by concentrated sulphuric acid. A mechanism which accounts for these data is shown in the Scheme.‡

The compounds (6), (7), and (8) all readily gave the lactone (3). Similarly the diol (9) and the hydroxy-olefin (10) both gave the cyclic ether (11), and the diol (9) gave the lactone (3) when oxidised with Jones' reagent.

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‡ For brevity certain of the steps are shown as being concerted, but may not necessarily be so. The number and positions of the deuterium atoms were determined by a combination of ^{1}H n.m.r. spectroscopy and mass spectrometry.

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[4] H. Hart and G. M. Love, personal communication; H. Heaney and S. V. Ley, unpublished observations.