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THE PHOTOISOMERISATION OF 5,6,7,8-TETRAFLUORO-1,4-DIHYDRO-1,4-ETHANONAPHTHALENE

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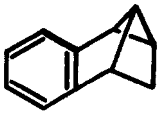
We have previously reported photoisomerisation reactions of tetrafluorobenzobarrelene both in the presence, and in the absence of triplet sensitisers.[1] The photoisomerisations of barrelene,[2] substituted barrelenes,[3] and benzobarrelene[4] and derivatives[5] have also been studied. The major pathway in the unsensitised isomerisations of benzobarrelene[4] apparently involves four centre vinyl-benzo cycloaddition to give quadricyclane -like intermediates. This is analogous to the suggested route involved in the photoisomerisation of 1,4-dihydro-1,4-epoxynaphthalene.[6] The photoisomerisation of 1,4-dihydro-1,4-methanonaphthalene[7] yields (1), and 3,7-methano-benzo-cyclohepta-1,4-diene rearranges to (2) both in the presence and in the absence of sensitisers.[8]

In view of these studies we now report the results of the photoisomerisation of the title compound (tetrafluorodihydrobenzobarrelene) (3). Irradiation of a 0.3% solution of (3) in diethyl ether using a medium pressure mercury source gave, after four hours, a 56% conversion to a major product, which has been shown to have the structure (4).



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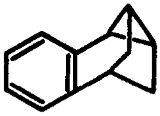

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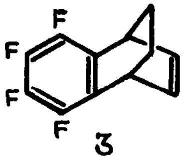

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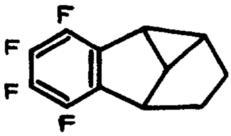

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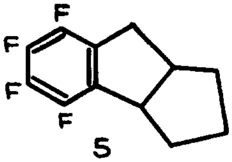

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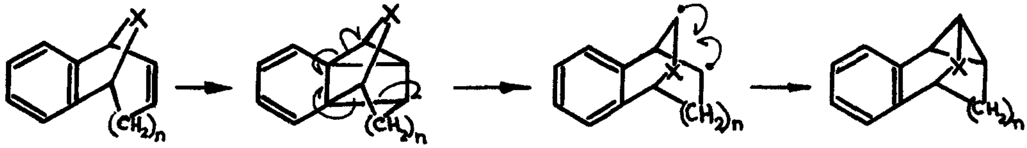
The same major product was also isolated in the presence of triplet sensitisers. The product (4) was shown to be isomeric with starting material by analysis and mass spectrometry. Important peaks were observed in the mass spectrum at m/e 228, 213, 200, and 187. The ultraviolet spectrum showed λ_{max}^{hexane} 210 (6100) and 262 (300) nm. The ^{1}H n.m.r. spectrum which cannot be analysed by first-order methods, showed multiplets at: τ 6.24 (1H), 7.14 (1H), 7.49 (1H), 8.05 (4H), and 8.78 (1H).

The compound (4) is identical with the reduction product obtained from controlled hydrogenation of tetrafluorobenzosemibullvalene.[1] Further reduction gives a product which from its ^{1}H n.m.r. spectrum probably has structure (5). Resonances were observed at τ 6.2 (1H), 6.6 (1H), 7.1 (2H), and at 7.75 - 8.85 (6H).

The rearrangements to (1), (2), and (4), can be rationalised (scheme) like the other examples quoted, in terms of four centre vinyl-benzo cycloaddition to give quadricyclane-like intermediates, and is further evidence in support of the generality of this mechanism.



X = CH$_2$ or (CH$_2$)$_2$; n = 0 or 1

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