

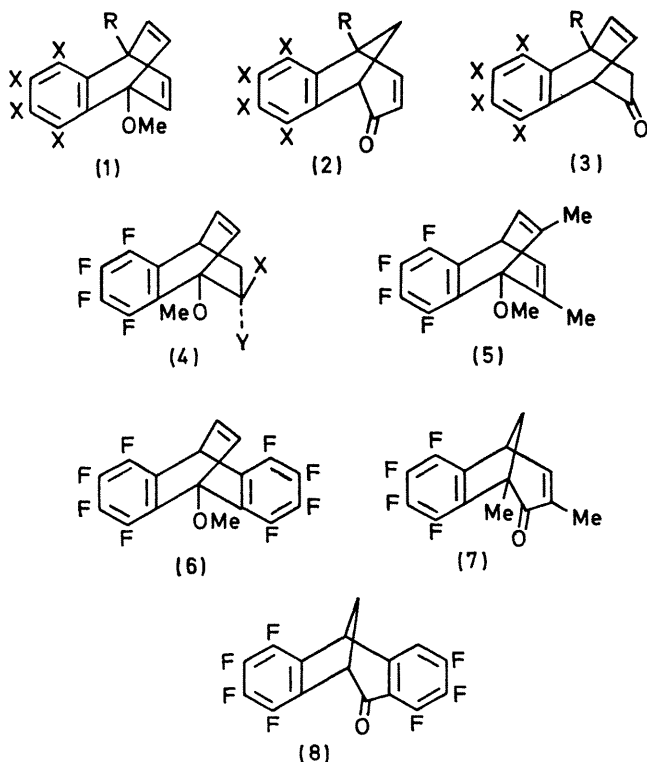
Multiple Rearrangement Reactions of 1-Methoxybenzobarrelene (1,4-Dihydro-1-methoxy-1,4-ethenonaphthalene) Derivatives

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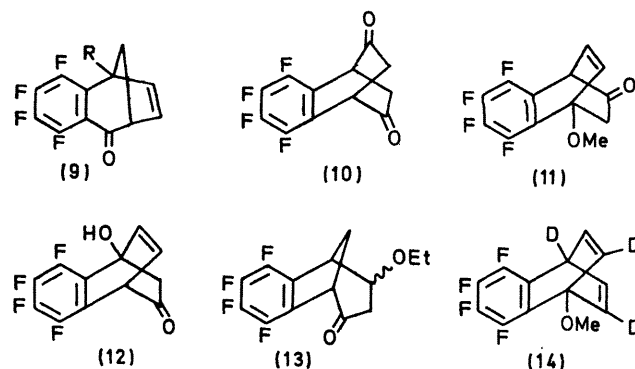
Summary The title compounds are rearranged to afford mixtures of carbonyl compounds in sulphuric acid; evidence in favour of the course of the multiple rearrangement reactions involved is indicated by deuteration and other studies.

CONSIDERABLE interest has been shown in the rearrangement reactions of benzobarrelene derivatives,¹ and in benzo-bicyclo-systems in general.² We have reported rearrangement reactions of 1-*NN*-dimethylaminobenzo-barrelene derivatives in protic media.³ We now report that the title compounds, although stable in dilute aqueous acidic media, undergo multiple rearrangement reactions in sulphuric acid.

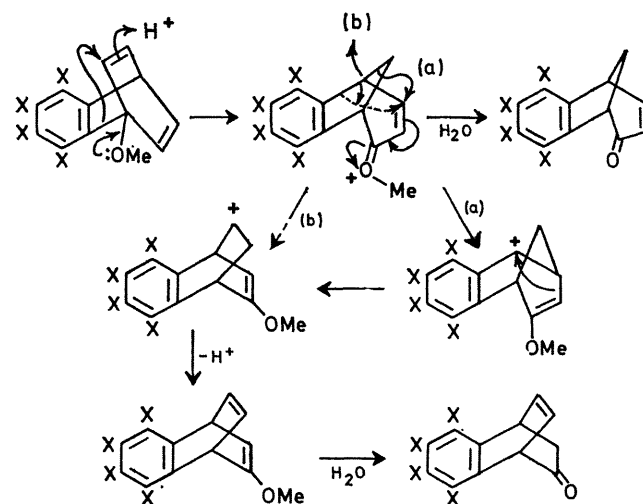


We prepared 1-methoxybenzobarrelene† (1; X = H, R = H) by the decomposition of benzenediazonium-2-carboxylate⁴ in anisole. Compound (1; X = H, R = H) rearranged very rapidly in a mixture of concentrated sulphuric acid and water (3:1 v/v) to afford a mixture of (2; X = H, R = H) (4%) and (3; X = H, R = H)⁵† (17%) together with more polar compounds. The more readily available⁶ compound (1; X = F, R = H) when dissolved

in concentrated sulphuric acid at room temperature and then immediately poured into an excess of water gave the compounds (2; X = F, R = H) and (3; X = F, R = H) in 6% and 65% yield, respectively. The ratio of the two latter products was found to depend upon the reaction conditions used and was 1:3 when the dissolution was carried out at 0°. Compound (2; X = F, R = H) was also prepared in 37% yield by rearrangement of the *exo*-toluene-*p*-sulphonate (4; X = O-SO₃-C₆H₄Me-*p*, Y = H) in aqueous sulphuric acid.



A mechanism which accounts for these products is shown in the Scheme. Compound (1; X = F, R = Me) gave, in agreement with this mechanism, the compounds (2; X = F, R = Me) and (3; X = F, R = Me) in 6% and 53% yield, respectively. The product expected by the mechanism involving path (b) was not detected. Similarly the compounds (5) and (6) gave (7) and (8), respectively.



SCHEME

† Satisfactory analytical and spectroscopic data were obtained for all of the new compounds described.

‡ We thank Prof. H. E. Zimmerman for copies of the i.r. and ¹H n.m.r. spectra of this compound.

Competing vinyl group migration,⁷ as in the ready rearrangement of the *endo*-toluene-*p*-sulphonate (**4**; X = H, Y = O·SO₃·C₆H₄Me-*p*) to (**9**; R = H), under mild conditions, also occurs in the rearrangement of compound (**1**; X = F, R = OMe). Two carbonyl compounds (**9**; R = OMe) and (**10**) were isolated in this latter reaction in 18 and 20% yield, respectively.

Compound (**10**) was not detected when compound (**11**) was allowed to rearrange, which further suggests that demethylation steps only occur on addition of the reaction mixture to water. Compound (**12**) was obtained, presumably by aryl migration to the carbonyl group.

Rearrangement of compound (**1**; X = F, R = H) in deuteriosulphuric acid and deuterium oxide (3 : 1 v/v) gave the expected incorporation of deuterium into (**2**; X = F, R = H) [in the methylene group and α to the carbonyl group in the vinyl residue] and in (**3**; X = F, R = H) as shown by mass spectral and ¹H n.m.r. data. The reversible

Michael addition of deuteriosulphuric acid which presumably results in the incorporation of deuterium α to the carbonyl group in the vinyl-residue in (**2**; X = F, R = H) finds analogy in the addition of ethanol which occurred when the compound (**4**; X = O·SO₃·C₆H₄Me-*p*, Y = H) was rearranged by means of hydrochloric acid in ethanolic solution. This resulted in the formation of the compounds (**13**). Finally an experiment in which the trideuterio-compound (**14**) was used gave mass spectral and ¹H n.m.r. data which showed that both paths (a) and (b) in the Scheme are involved in the rearrangement of (**1**; X = F, R = H) to (**3**; X = F, R = H).

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