On the Stereoselectivity of the Electrocyclic Process, Benzocyclobutene to o-Quinone Dimethide

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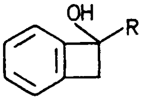
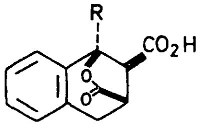
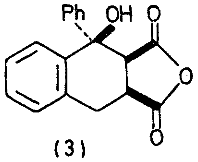
Summary Benzocyclobutene derivatives bearing an oxygen substituent at position 1 undergo conrotatory thermal ring opening to yield reactive diene species in which the oxygen substituent preferentially adopts the (*E*)-configuration.



(1) R = Ph
(6) R = $CH=CH_2$



(2) R = Ph
(8) R = Me



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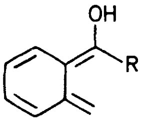
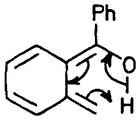


(4) R = Ph
(9) R = Me



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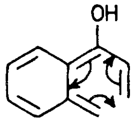

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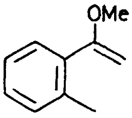

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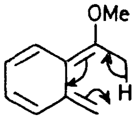

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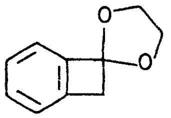

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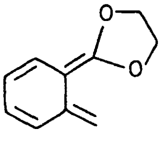

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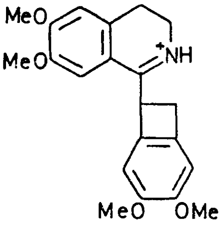
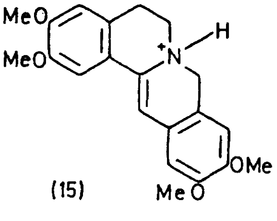
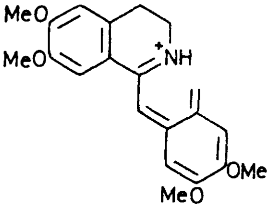


(14)



(15)



(16)

THE effect of electronic as well as steric perturbations on electrocyclic processes is attracting increased attention.[1] In pursuit of studies on the thermal reactions of benzocyclobutenols[2] several 1-substituted benzocyclobuten-1-ols and related derivatives have been prepared and the direction of their thermal, conrotatory ring opening has been investigated. In the presence of one equivalent of maleic anhydride at 110°, (**1**)[3] readily formed the adduct (**2**) in 75% yield. This adduct was formerly prepared by heating the initial photochemical adduct (**3**) of 2-methylbenzophenone and maleic anhydride.[4] The adduct (**3**) is derived from the (*E*)-dienol (**4**)[5] and hence it appeared that the benzocyclobutenol (**1**) had ring opened to yield this species in preference to the (*Z*)-dienol (**5**). The latter would be expected to collapse rapidly to 2-methylbenzophenone by an intramolecular 1,5-hydrogen shift and indeed very little of the ketone could be detected in the reaction mixture. Heating (**1**) alone at 110°, however, caused its quantitative conversion into 2-methylbenzophenone, presumably by external protonation of the dienol (**4**).

The stereoselective nature of the above conrotatory process was also exhibited by 1-vinylcyclobuten-1-ol† (**6**). This proved to be a very unstable compound and on heating at 110° for 30 min it gave a quantitative yield of α-tetralone. This reaction can again be visualised as proceeding *via* the (*E*)-dienol (**7**), followed by the thermal, disrotatory cyclisation indicated. No 2-methylacrylophenone, which would arise from intramolecular ketonisation of any (*Z*)-dienol, could be detected in the reaction mixture; authentic 2-methylacrylophenone was stable to the reaction conditions. That the ring opening of the vinyl derivative (**6**) was easier than for the parent benzocyclobutenol parallels the behaviour of the 1-phenyl derivative (**1**), indicating that such vinyl groups aid the electrocyclic process of ring opening.

1-Methylbenzocyclobuten-1-ol reacts very slowly at 110° with maleic anhydride to yield the adduct (**8**), m.p. 183–184° (70%), which is again derived from the (*E*)-dienol (**9**) and 1-methoxy-1-methylbenzocyclobutene has been shown to rearrange thermally to give the styrene derivative (**10**) *via* intramolecular hydrogen transfer within the dienoid species (**11**). In contrast, the acetal (**12**) did not react with maleic anhydride, even after prolonged heating at 110° or higher temperatures. In this case one of the oxygen atoms would have to move into a cisoidal orientation in transposing into a diene, *viz.* (**13**). Despite the fact that the intermediate (**13**) appears to be a reasonable structure, the fact that it was not trapped with maleic anhydride implies that the process leading to it is highly unfavourable.

Since the size of a hydroxy-group is smaller than that of a methyl group[6] electronic effects of substituents, such as the

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† All new compounds gave satisfactory microanalytical and spectral data.

presence or absence of unshared electrons, must be important in the above transformations. Such effects could be operating in the experiments recently described by Kametani *et al.*[7] in which the salt (**14**) rapidly gave the ammonium salt (**15**) on heating, presumably *via* the (*Z*)-diene (**16**). In contrast, the free base did not give an analogous product, possibly because the (*E*)-diene is then favoured.

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[1] *Cf.* T. Miyashi, M. Nitta, and T. Mukai, *J. Amer. Chem. Soc.*, 1971, **93**, 3441; J. E. Baldwin and M. S. Kaplan, *ibid.*, p. 3969 J. E. Baldwin and M. S. Kaplan, *ibid.*, 1972, **94**, 668; U. Svanholm and V. D. Parker, *J.C.S. Chem. Comm.*, 1972, 646.

[2] B. J. Arnold and P. G. Sammes, *J.C.S. Chem. Comm.*, 1972, 30.

[3] L. Horner, P. V. Subramanian, and K. Eiben, *Annalen*, 1968, **714**, 91.

[4] F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398.

[5] *Cf.* S. M. Mellows and P. G. Sammes, *Chem. Comm.*, 1971, 21.

[6] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, 3rd edn., New York, 1960, p. 260.

[7] T. Kametani, K. Ogasawara, and T. Takahashi, *J.C.S. Chem. Comm.*, 1972, 675.