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THERMAL REARRANGEMENTS OF VINYLBENZOCYCLOBUTENES[1]

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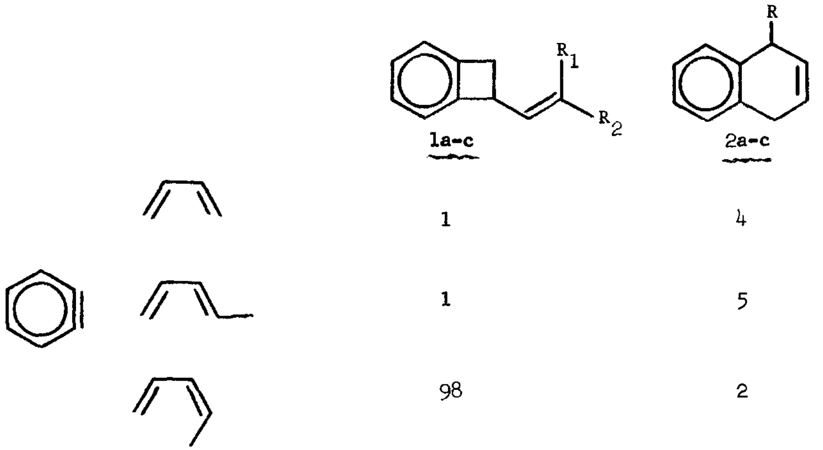
Current interest in the reactivity and electronic structure of o-xylylene[4] prompts us to report the transient formation of vinyl substituted homologues by pyrolysis of vinylbenzocyclobutenes. Since Wittig and Dürr's report of the first vinylcyclobutene,[5] only a few more elaborate examples of such species have appeared.[6] In addition, a number of benzocyclobutenes have also been reported in which the vinyl group is replaced by a carbonyl.[7] In some of these cases thermal rearrangements have been described and unanimously rationalized in terms of intermediate o-xylylenes.[6,7]

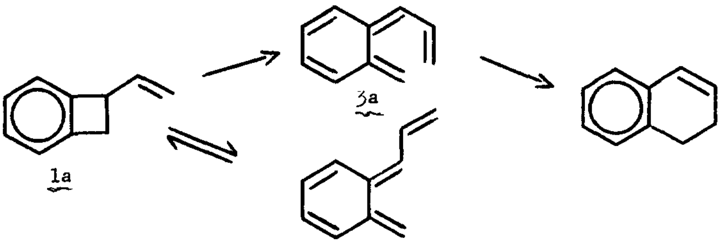
We describe here the formation and rearrangement of simple methyl substituted vinylbenzocyclobutenes and the pathways available to the intermediate o-xylylenes. The dependence of the rearrangement path on stereochemistry is particularly clear in these simple examples.

Expanding upon our earlier report[8] and that of Wittig and Dürr,[5] we find that cycloaddition of benzyne and butadienes provides a convenient source of several vinylbenzocyclobutenes. Benzyne generated photochemically from phthaloyl peroxide reacts with butadiene to afford ca. 5% of the parent hydrocarbon **1a** in addition to the Diels-Alder adduct. Similarly trans- and cis-piperylene yielded the methyl substituted vinylbenzocyclobutenes **1b** and **1c**. Rather striking is the absence of the Diels-Alder adduct in the case of the cis diene. This phenomenon, also noted by Waali,[9] is attributed to the reluctance of the dienic substrate to adopt the requisite s-cis conformation. The yields of benzyne cycloadducts range from 20 to 30%.[10]



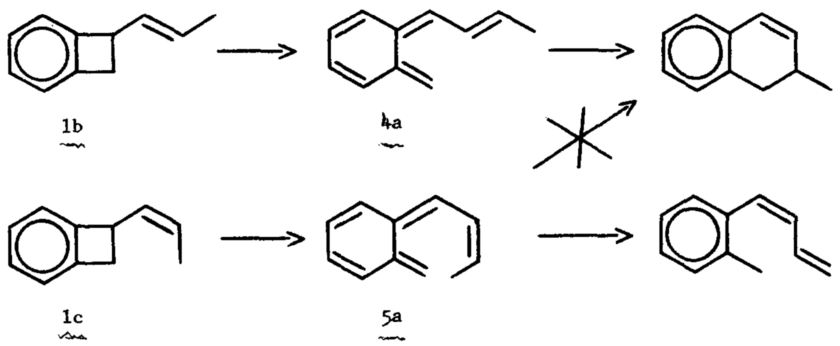
1a, $R_1 = R_2 = H$; 1b, $R_1 = H$, $R_2 = CH_3$; 1c, $R_1 = CH_3$, $R_2 = H$
2a, R = H; 2b, 2c, $R = CH_3$

Complete thermal rearrangement of compounds 1a-1c was effected by glc using an injector port heated to 250-300°. Compound 1c was extensively rearranged at 190° and the products characterized by pmr spectroscopy. 1-Vinylbenzocyclobutene, 1a, rearranged cleanly to 1,2-dihydronaphthalene. Although a [1,3] carbon shift cannot be ruled out, a likely pathway for this process is disruption of the benzocyclobutene by conrotatory ring opening to o-xylylene 3a followed by electrocyclic ring closure. Note that of the two conrotatory modes available to 1a, only the less favored can lead to product.

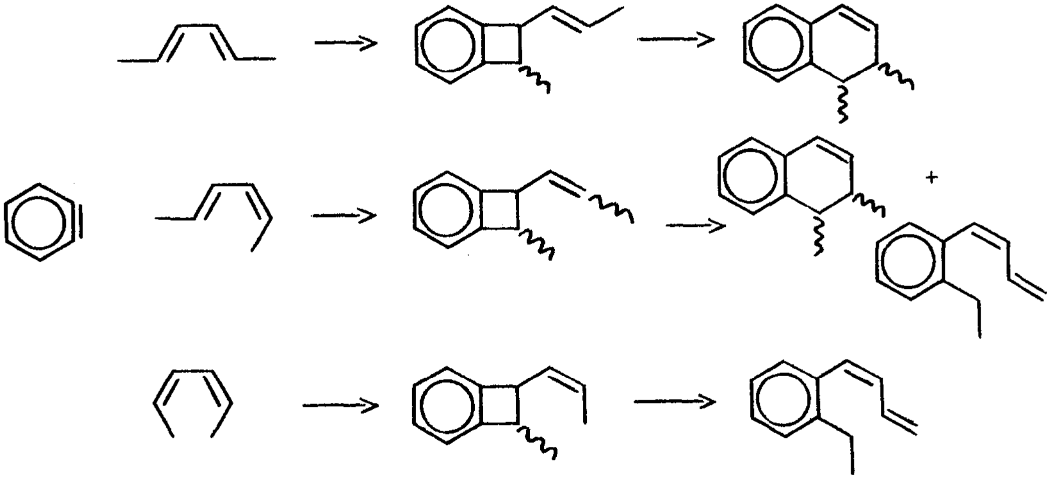


Thermolysis of the methyl labeled vinylbenzocyclobutenes 1b and 1c provides unambiguous evidence of an o-xylylene intermediate and also illustrates the mechanistic alternatives available to such a species. Compound 1b is converted thermally to 2-methyl-1,2-dihydronaphthalene by a process assumed to be analogous to that for the unsubstituted compound. In contrast, vinylbenzocyclobutene 1c rearranged upon pyrolysis to 1-(o-tolyl)-butadiene. The postulated intermediate 4a is presumably sufficiently twisted to facilitate an antarafacial

[1,7] hydrogen shift to the exclusion of ring closure. Since o-xylylenes 4a and 5a provide mutually exclusive products, stereochemistry at the vinyl group must control the reaction pathway.



In addition to 2 + 4 cycloadducts and ene products, the reaction of benzyne with the various hexa-2,4-dienes also provides vinylbenzocyclobutenes in moderate to pitiful yields. The reactions are far more complex than those preceding and we have been unable to separate and characterize some of the minor products. The vinylbenzocyclobutenes are labile even under very mild glc conditions, but their gross structures have been deduced by examination of their rearrangement products. As before, the intermediate o-xylylenes partition themselves between ring closure and [1,7] hydrogen shifts. Some of these o-xylylenes are identical to those postulated by Seeley,[11] and our observed products are consistent with those assumed by Seeley to be formed from further thermal reactions of the o-xylylenes.



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