Reaction of Benzyne with Butadiene

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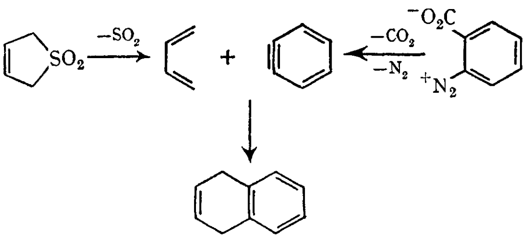
BENZYNE has been shown to act as a dienophile with cyclic dienes, but apparently not with acyclic dienes. The reason has been given that benzyne does not survive long enough to permit the open-chain diene to assume the requisite *cis*-like arrangement that the cyclic dienes possess.[1] We have now been able to effect this type of reaction.

Benzyne and buta-1,3-diene, generated by the concurrent thermal decomposition of benzenediazonium-2-carboxylate[2] and 3-sulpholene (2,5-dihydrothiophen 1,1-dioxide) respectively, react in pentan-2-one at 100° to give a 9% yield of 1,4-dihydronaphthalene. A temperature of 100° is necessary to provide a reasonable, continuous concentration of butadiene from the 3-sulpholene; the method of Friedman and Logullo[3] was therefore useful for the preparation and decomposition *in situ* of benzenediazonium-2-carboxylate.



It is suggested that the nascent butadiene from the decomposition of 3-sulpholene would be in the preferred *cis*-conformation, thus enabling reaction to take place.

That 3-sulpholene acts simply as a source of butadiene, and that the SO_2 entity is not involved in a transition state is shown by kinetic data[4] obtained from the thermal decomposition of 3-sulpholene in the presence and absence of maleic anhydride as the dienophile. The reactions are first order with $k = 2{\cdot}4 \times 10^{-3}$ (min.$^{-1}$). At temperatures below the decomposition temperature of 3-sulpholene, no addition product is formed with benzyne.

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