

The Reaction Between Isosafrole and
Diazotised Anthranilic Acid Under Different Conditions.

S. F. Dyke, A. J. Floyd and S. Ward.

School of Chemistry and Chemical Engineering,
Bath University of Technology, Bath, Somerset, England.

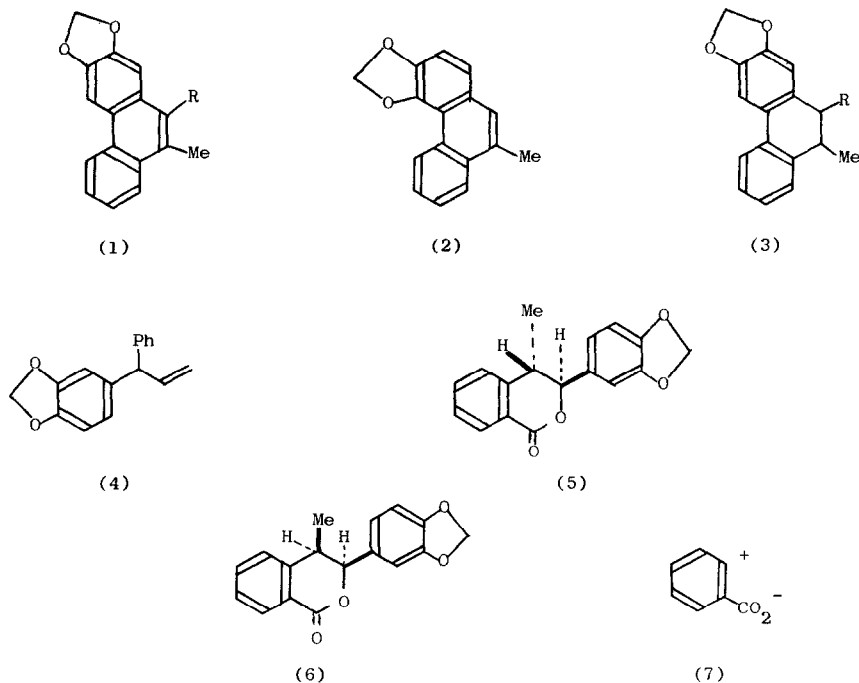
(Received in UK 28 May 1969; accepted for publication 15 June 1969)

It has been reported recently¹ that benzyne generated from a variety of precursors, under widely differing sets of conditions, exhibit essentially similar properties when trapped with 1,4-dimethoxyanthranene. Our experiences, in which benzyne was generated from anthranilic acid under three sets of conditions, and reacted with isosafrole, may be of some general interest.

We had previously reported² that when benzyne was formed by the aprotic diazotisation of anthranilic acid in the presence of a refluxing solution of isosafrole in acetonitrile, the isomeric phenanthrenes (1, R=H) and (2) were isolated in 22% and 4% yields respectively, allowing for recovered isosafrole. In a closer chromatographic examination of the non-nitrogenous fraction of the reaction mixture, the yield of (2) has been found to be 8%, and compounds (3, R=Ph) (1,2%) and (4) (3%) have also been isolated and identified⁴. When benzene diazonium-2-carboxylate was prepared³ and decomposed in a solution of isosafrole in acetonitrile at room temperature, the same four products were formed in the same ratio, but yields were substantially reduced. This is almost certainly a simple temperature effect.

However, when benzene diazonium-2-carboxylate hydrochloride⁶, was prepared separately and added to a refluxing solution of isosafrole in acetonitrile, a dramatic change in products was observed. Thus, the yields of (1, R=H), (2) and (3, R=Ph) dropped to 1.2, 0.8 and 1.1% respectively and small amounts (0.4 and 1.8% respectively) of (1, R=Ph) and (3, R=H) were also isolated. The major product (9.5%) was shown to be the trans-dihydroisocoumarin (5), and it was accompanied by 0.7% yield of the cis-isomer (6).

Clearly, whilst under the first two sets of conditions elimination of nitrogen and carbon dioxide occurs in a concerted manner from the diazotised anthranilic acid, giving benzyne, in the last reaction nitrogen is eliminated first to form⁷ (7) and a dipolar addition of this to the olefinic double bond of isosafrole occurs more rapidly than the further decomposition of (7) to form benzyne.



References

1. B. H. Klanderma and T. R. Criswell, *J.Amer.Chem.Soc.*, **91**, 510 (1969).
2. S. F. Dyke, A. R. Marshall and J. P. Watson, *Tetrahedron*, **22**, 2515 (1966).
3. L. Friedman and F. M. Logullo, *J.Amer.Chem.Soc.*, **85**, 1549 (1963).
4. Satisfactory analytical and spectral data have been obtained for all compounds described.
5. M. Stiles, R. G. Miller and U. Burckhardt, *J.Amer.Chem.Soc.*, **85**, 1792 (1963).
6. L. Friedman, private communication; F. M. Logullo, Ph.D. thesis; Case Institute of Technology, 1965.
7. S. Yaroslavsky, *Chem.Ind.*, 765 (1965).