The Reaction of Benzenediazonium-2-carboxylate with Acrylonitrile and Ethyl Acrylate

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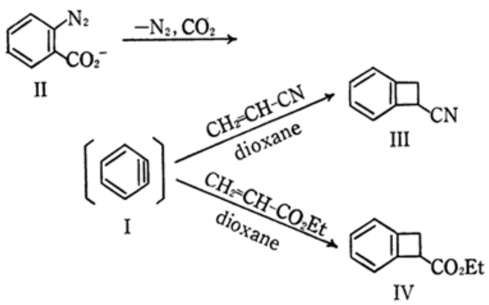
(Received October 23, 1965)

Stiles et al.[1] have reported a new route for obtaining the benzyne intermediate (I) by the thermal decomposition of benzenediazonium-2-carboxylate (II); they confirmed its formation by studying a Diels-Alder reaction with furan and anthracene. This procedure to obtain I has several advantages over the method usually adopted, in which aryl halides are reacted with strong bases, alkali metals or organometallic compounds in the presence of appropriate substrates. First, I can be allowed to react in situ with the compounds which have functional groups that are sensitive to strong bases or organometallic reagents. Second, the reaction may be carried out in various solvent.

In the course of our study of the chemical behavior of I in this route, we found that 1, 2-cycloaddition of I, with acrylonitrile and ethyl acrylate, proceeded to give benzocyclobutene derivatives under some conditions.

Stiles et al. carried out their experiment on I in non-polar solvents, such as benzene or furan. However, the reaction of II with either acrylonitrile or ethyl acrylate at 50—60°C for 6 hr. resulted in excessive polymerization, and no other isolable product was obtained. In view of the salt-like nature of II, we felt that the use of some polar solvent in place of a non-polar solvent would give rise to a better result. Although dimethylformamide and II, when treated at 55—60°C for 6 hr., afforded salicylaldehyde in a 18% yield[2] (as identified by a study of its infrared spectrum and that of its semicarbazone), dioxane was found to be a favorable solvent. Thus, the reaction of II and furan in dioxane at 50—55°C for 13 hr. gave a 65% yield of 1, 4-dihydronaphthalene-1, 4-endoxide, m. p. 55.5—56.1°C (lit.[1] 55.2—56.2°C). A comparable yield was, therefore, attained in a much shorter reaction time than that reported by Stiles et al. The following experiments were, then, all carried out in dioxane.

A suspension of 10.9 g. of freshly-prepared II in a mixture of 5.74 g. of acrylonitrile and 150 ml. of dioxane was stirred under nitrogen at 50—55°C for 6 hr. After the dioxane and acrylonitrile had been distilled off under a vacuum, the flash distillation of the residue gave a yellow liquid, b. p. 48—86°C/0.6 mmHg; 1.92 g. (20%). The redistilled product, b. p. 54—55°C/0.3 mmHg; n_D^{26} 1.5442, which was found to be pure by gas chromatographic analysis, showed a C≡N stretching band at 2250 cm^{-1}, and both its ultraviolet absorption and its NMR spectrum [(p. p. m. from TMS and relative areas), 7.14 (4.3), 4.09 (1.0): quartet, and 3.45 (1.9): triplet], were found to be consistent with the structure of 1-cyano benzocyclobutene (III). Further proof of the structure was obtained by the hydrolysis of the nitrile to the carboxyamide, m. p. 155.1—155.6°C (lit.[3] 155—156°C) and to the carboxylic acid, m. p. 74.8—75.4°C (lit.[3] 74.0—75.5°C).



In nearly the same procedure, the reaction of II, 2.09 g., and freshly-distilled ethyl acrylate, 2.0 g., in 50 ml. of dioxane at 50—55°C for 6 hr. gave a raw product, b. p. 82—108°C/3.5 mmHg; 0.25 g. (8%), and a considerable amount of a residue. The separation of the main constituent (90%) of the product by the gas chromatographic method gave nearly pure ethyl benzocyclobutene-1-carboxylate (IV); its identity was confirmed by a comparison of its infrared specturm with that of the authentic ester, prepared by the esterification of benzocyclobutene-1-carboxylic acid.

The reaction of II with maleic anhydride in dioxane was examined, but phenol was the only product identified.

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[1] M. Stiles and R. G. Miller, *J. Am. Chem. Soc.*, **82**, 3802 (1960); M. Stiles, R. G. Miller and U. Burckhardt, ibid., **85**, 1792 (1963).

[2] S. Yaroslavsky (*Tetrahedron Letters*, **1965**, 1503) has recently reported the formation of salicylaldehyde in a 32% yield.

[3] J. F. Bunnett and J. A. Skorcz, *J. Org. Chem.*, **27**, 3836 (1962).