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THE FRAGMENTATION OF A 1,2,5-THIADIAZOLE

C. W. BIRD and C. K. WONG

Department of Chemistry, Queen Elizabeth College, London, W8 7AH

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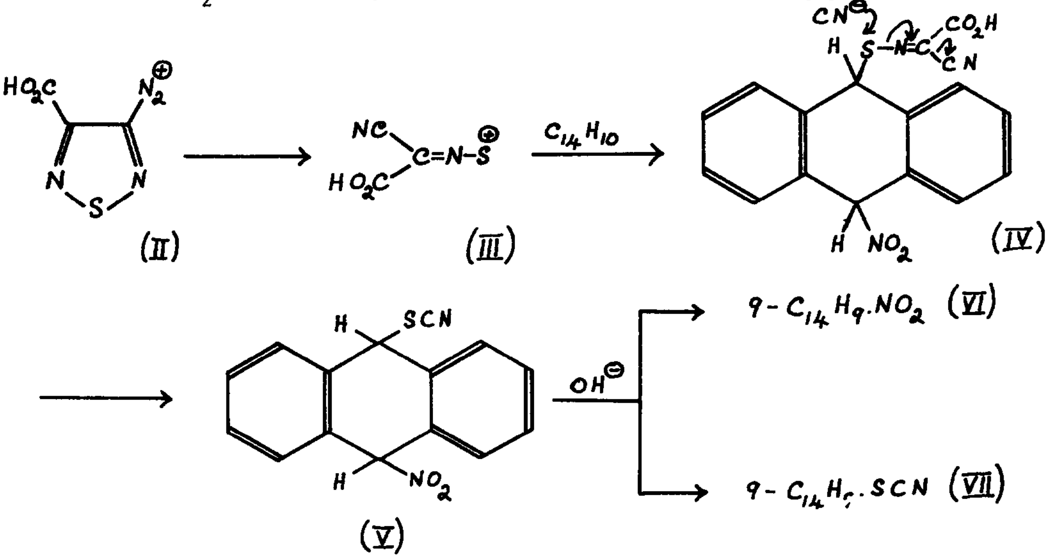
In the course of attempts to generate 1,2,5-thiadiazolyne we have encountered an unexpected fragmentation of a 1,2,5-thiadiazole. Diazotisation[1] of 3-amino-1,2,5-thiadiazole-4-carboxylic acid (I) in the presence of an excess of anthracene yielded none of the anticipated thiazolyne adduct. Instead we obtained a difficultly separable mixture comprising 9-nitroanthracene (VI) and small amounts of 9-thiocyanoanthracene (VII). These two compounds were not obtained when acid (I), pK_a 3.22, was replaced by terephthalic acid, pK_a 3.51, hence both (VI) and (VII) presumably result from a common process.

An attractive mechanistic pathway is shown below. The key step entails the collapse of the diazonium cation (II) to the electrophilic sulphur cation (III). Attack of this species on anthracene and subsequent addition of nitrite ion yields (IV). Displacement of the organic residue attached to sulphur by cyanide ion forms (V) and liberates two cyanide anions after decomposition of $HO_2C.CN$. Finally base treatment as used in the work up procedure leads to



rearomatisation with formation of (VI) and (VII). The preponderance of 9-nitroanthracene is attributable to the greater acidity of the proton geminal to the nitro group in (V).

REFERENCE

1. L. F. Fieser, "Organic Experiments", Heath, Boston, 1964, p.315