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BASE CATALYSED REACTION OF ARYLIDINEMALONONITRILES WITH BENZOFUROXANES

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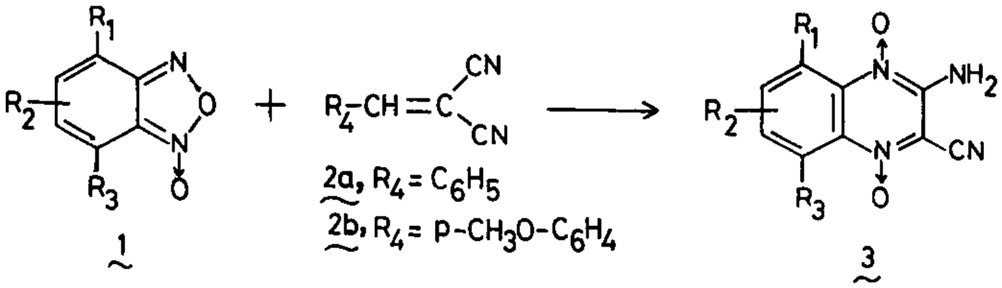
Abstract - Arylidinemalononitriles (2) react with benzofuroxanes (1) to afford quinoxaline N,N'-dioxides (3) in good yields.

Syntheses using benzofuroxanes (BFOS) have attracted considerable attention in the quinoxaline chemistry. The reactions of BFOS with a variety of nucleophiles, enamines and enolates have afforded interesting range of products[1]. The electron deficient double bond in the systems such as α,β-unsaturated aldehydes and ketones also participates in the above reactions, when catalysed with organic bases, to give quinoxaline oxides[2]. Imines conjugating with the electron deficient double bond react with BFOS to afford a novel class of quinoxaline N,N'-dioxide imines without using any external base[3]. This reaction appears to be self catalysed, since the imines as such are sufficiently basic in character. However, these reactions have uncovered diverse type of organic N-oxides of preparative as well as mechanistic interest. We report here the reaction of arylidinemalononitriles with BFOS, catalysed with triethylamine.

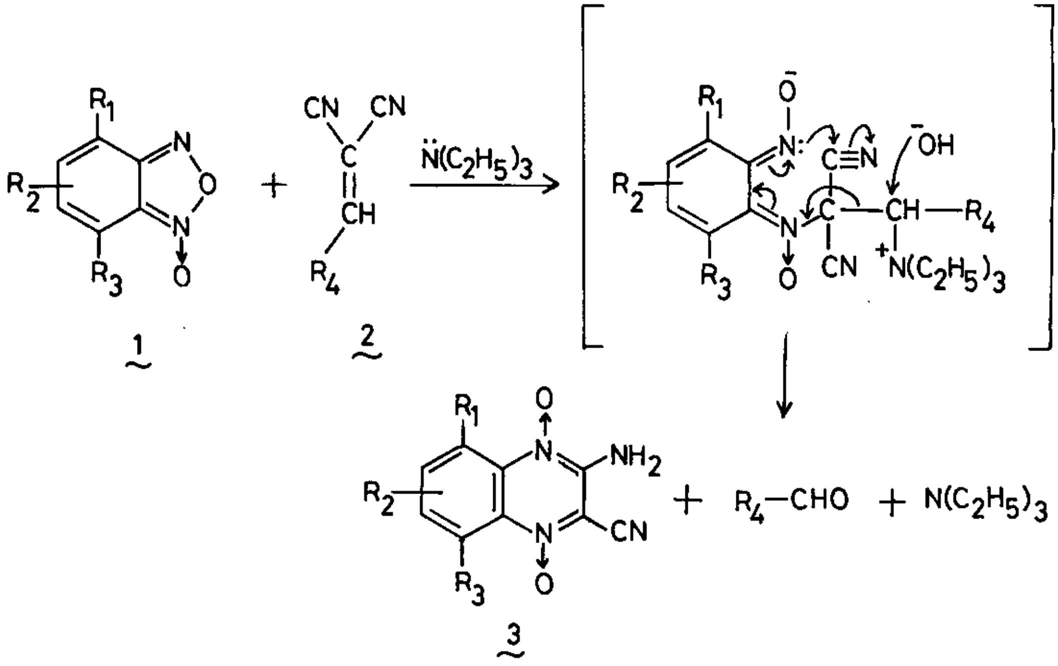
The reaction of benzofuroxane (1a) and arylidinemalononitrile (2a) in ethanol at room temperature in the presence of catalytic amount of triethylamine afforded the red crystalline compound (3a) in 80% yield, m.p. 230-232°C (dec.) from acetone. The structure of 3a is fully corroborated by its elemental as well as spectral analyses : m/z 202 (M^+), ν max (KBr) 2225 (-CN), 3250, 3350 ($-NH_2$) cm^{-1}, and ^1H NMR ($CDCl_3$) δ 7.67 (m, 1H), 7.96 (m, 1H), 8.08 (bs, 2H), 8.28 (d, 1H), 8.31 (d, 1H) ppm. Similarly, the reactions of 1b and 1c with 2a provided 3b and 3c in 86% and 83% yields, respectively : 3b, m/z 237 (M^+) ν max (KBr) 2220 (-CN), 3225, 3310 ($-NH_2$) cm^{-1},



	R_1	R_2	R_3
a	H	H	H
b	H	Cl	H
c	H	CH_3	H.

and ^{1}H NMR ($CDCl_3$) δ 7.70 (m, 1H), 8.10 (bs, 2H), 8.27 (m, 1H), 8.30 (m, 1H) ppm ; 3c, m/z 216 (M^+), ν max (KBr) 2230 (-CN), 3225, 3320 ($-NH_2$) cm^{-1}, and ^{1}H NMR ($CDCl_3$) δ 2.57 (s, 3H), 7.93 (m, 1H), 8.13 (bs, 2H), 8.27 (m, 1H), 8.32 (m, 1H) ppm.

Concerning the mechanism of this reaction, the corresponding arylaldehydes have been identified through GLC. This fact provides some clue to a plausible mechanism outlined below.



When the substituted BFOS (1b,c) were employed, the corresponding products (3b,c) were obtained, which lent a support to the above proposed mechanism. In most of the reactions of BFOS with activated alkenes, 1,4-cycloaddition of the Diels-Alder type is always ruled out. The reaction of 1 with tetracyanoethylene in the presence of triethylamine produced 3 but in poor yields. When all these electron deficient alkenes were used in the absence of the catalyst, no reaction took place even under reflux.

General Procedure

To a mixture of benzofuroxane 1a (1.36 g, 10 mmol) and arylidinemalononitrile 2a (1.54 g, 10 mmol) in ethanol (50 ml) was added catalytic amount of triethylamine. The reaction mixture was stirred at room temperature for 4 hours, wherein the solution turned to a red colour and red crystals precipitated. The crystals were separated out, and they were recrystallised from acetone (1.61 g, 80%). The reaction of 1a (1.36 g, 10 mmol) with 2b (1.84 g, 10 mmol) and triethylamine in ethanol (50 ml) also gave 3a (1.65 g, 82%).

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