Synthesis of a Novel Class of Pyrazolobenzofurazan *N*-Oxides: Reaction of Nitrobenzofurazan *N*-Oxides with Diazoacetates

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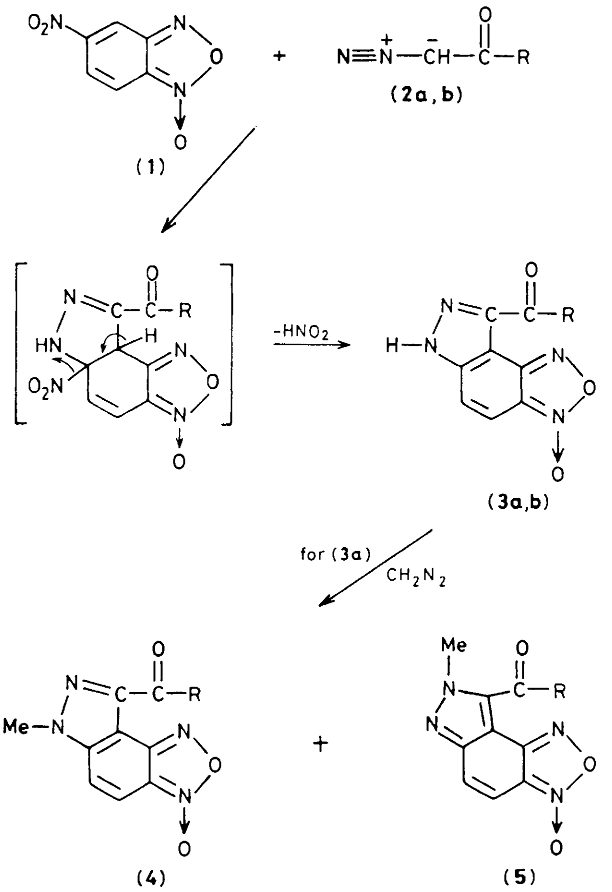
The diazoacetates (**2a,b**) and nitrobenzofurazan *N*-oxides (**1**) react to give the pyrazolobenzofurazan *N*-oxides (**3a,b**) in good yields.

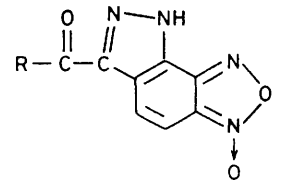
Benzofurazan *N*-oxides are very useful synthons in the synthesis of biologically active organic *N*-oxides.[1-3] Most of these reactions involve the heterocyclic ring but only in a few does the homocyclic ring participate.[4,5] We report an interesting reaction of 4-nitro- and 5-nitro-benzofurazans with diazoacetates wherein the furazan moiety remains intact and the benzene ring is attacked to give novel pyrazolobenzofurazan *N*-oxides.

When an equimolar mixture of 5-nitrobenzofurazan (**1a**) and ethyl diazoacetate (**2a**) was heated on a water bath for 3 h, addition of dry diethyl ether gave a white solid (**3a**) which was recrystallised from dimethyl sulphoxide [m.p. 185—186 °C,



Scheme 1. **a**, R = OEt; **b**, R = OMe.

85% yield; ^1H n.m.r. (100 MHz, $CDCl_3$), δ 1.32 (3 H, t), 4.36 (2 H, q), 7.21 (1 H, d, *J* 9.0 Hz), 7.56 (1 H, d, *J* 9.0 Hz); *m/z* 248 (100%), 232 (84.37), 220 (59.00); i.r. (KBr) 1725, 1610, 1375, and 3250 cm^{-1}].† The product (**3a**) was readily methylated with an ethereal solution of diazomethane to give the expected isomeric methylated pyrazoles (**4**) and (**5**) which were separated by t.l.c. (Scheme 1). The compound (**4a**) was recrystallised from chloroform, m.p. 197—199 °C in 70% yield and the minor product (**5a**), m.p. 179—180 °C was isolated in 15.4% yield. The N-Me group of the major product (**4a**) appeared at δ 4.25 (s) and that of the minor product (**5a**) was observed at δ 4.23 (s) in their respective ^1H n.m.r. spectra.



(**6**) a; R = OEt
b; R = OMe

The reaction between (**1**) and (**2a**) is assumed to proceed *via* 1,3-dipolar cycloaddition of the diazoacetate to the benzofurazan followed by elimination of nitrous acid. Similarly, when methyl diazoacetate (**2b**) reacted with (**1**), (**3b**) was obtained in 82% yield [m.p. 240—242 °C; ^1H n.m.r. (100 MHz, $CDCl_3$), δ 3.93 (3 H, s), 7.22 (1 H, d, *J* 9.1 Hz), 7.52 (1 H, d, *J* 9.0 Hz); *m/z* 234 (100%), 218 (72.15), 202 (60.25); i.r. (KBr), 1725, 1610, 1375, and 3250 cm^{-1}].

4-Nitrobenzofurazan also reacted smoothly with (**2a**) and (**2b**) and the pyrazoles (**6a**) and (**6b**) were obtained in good yields.[6] [(**6a**), ^1H n.m.r. (100 MHz, $CDCl_3$) δ 1.36 (3 H, t), 4.36 (2 H, q), 7.16 (1 H, d, *J* 9.0 Hz), 7.76 (1 H, d, *J* 9.0 Hz); *m/z* 248 (100%), 232 (82.32), 220 (58.8); i.r. (KBr), 1685, 1605, 1362, and 3225 cm^{-1}. (**6b**), ^1H n.m.r. (100 MHz, $CDCl_3$) δ 3.97 (3 H, s), 7.19 (1 H, d, *J* 9.2 Hz), 7.75 (1 H, d, *J* 9.2 Hz); *m/z* 234 (100%), 218 (72.5), 202 (60.05), 186 (83.25); i.r. (KBr), 1687, 1605, 1362, and 3225 cm^{-1}.]†

When unsubstituted benzofurazan was used instead of (**1**) in Scheme 1 no characterisable product was obtained. It is of interest that we did not observe any other products under the conditions we used which might have arisen from the rupture of the furazan part of (**1**).[6]

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† The structural assignments of the products (**3**) and (**6**) are based mainly on the well established regiochemical control in 1,3-dipolar cycloadditions as the available spectral data could not resolve ambiguities in structures. The pyrazoles (**6**) gave correct elemental analyses and spectral data in accord with their assigned structures.

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