Nitrobenzofurazans and Nitro-2,1,3-benzothiadiazoles: Unexpected Reactivity towards Nucleophilic Attack

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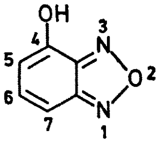
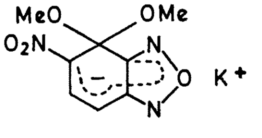
Summary The reactivity of 4-chlorobenzofurazan towards methoxide ion is about the same as that of *o*-nitrochlorobenzene, but the reactivity of 4-chloro-5-nitrobenzofurazan towards the same reagent exceeds that of picryl chloride: other examples of unexpectedly high reactivity of related compounds towards nucleophilic reagents are given.

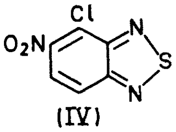
4-HYDROXYBENZOFURAZAN (I) has a pK_a of 6·83, suggesting that the annellated furazan ring is slightly more electron-withdrawing than an *o*-nitro-group.[1] (pK_a of *o*-nitrophenol = 7·21.[2]) In accord with this expectation, the rate of reaction of 4-chlorobenzofurazan with methoxide ion in methanol ("methoxydechlorination" in Bunnett's nomenclature[3])is very similar to that of *o*-nitrochlorobenzene.[4] It is therefore not unreasonable to suppose that the reactivity of 4-substituted 5-nitrobenzofurazans might be similar to, that of the corresponding 1-substituted 2,6-dinitrobenzenes.



(I)



(III)

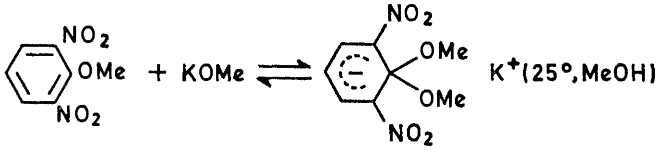


(IV)

We were therefore surprised to find that the rate constant for methoxydechlorination (0°, methanol) of 4-chloro-5-nitrobenzofurazan was 2·75 l mole^{-1} s^{-1}, the rate constant for the corresponding reaction of 2,6-dinitrochlorobenzene[5] being only $5{\cdot}2 \times 10^{-5}$ l mole^{-1} s^{-1}. The reactivity of 4-chloro-5-nitrobenzofurazan in fact exceeds that of 2,4,6-*tri*nitrochlorobenzene (rate constant for methoxydechlorination at 0° in methanol = $6{\cdot}7 \times 10^{-1}$ l mole^{-1} s^{-1})[5].

5-Chloro-4-nitrobenzofurazan was found to be even more reactive towards attack by methoxide in methanol than the 4-chloro-5-nitro-isomer; *k* (0°) being equal to 18·6 l mole^{-1} s^{-1}. Dal Monte and Sandri[4] have found 5-chlorobenzofurazan to be more rapidly methoxydechlorinated (*ca.* 5×) than the 4-chloro-isomer.

Similar high reactivity towards attack by methoxide was shown by 4-methoxy-5-nitrobenzofurazan (II). When a solution of (II) in methanol (λ_{max} 357 nm, ϵ $3{\cdot}3 \times 10^3$) was treated with an excess of KOMe in methanol, a new spectrum appeared with λ_{max} 369 nm, ϵ $1{\cdot}5 \times 10^4$. In order to investigate the nature of the reaction, a solution of (II) in methanol was treated with an equimolar amount of KOMe in methanol, and evaporated to low bulk. Orange crystals were deposited; these were washed with dry ether, and dried *in vacuo*. An n.m.r. spectrum of the product in $(CD_3)_2SO$ showed absorptions at 7·86 (d, 1H) 5·56 (d, 1H), and 3·06 p.p.m. (s, 6H). Elemental analysis was corrcet for $C_8H_8N_3O_5K$. These observations establish the structure of the product as the σ (Meisenheimer) complex (III).



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The equilibrium constant for the reaction:

$$\text{(II)} + \text{KOMe} \rightleftharpoons \text{(III)} \ (25°, \text{MeOH})$$

was found to be $5{\cdot}1 \times 10^3$ l mole^{-1}. Hammett extrapolation of the data of Fendler, Fendler, and Griffin[6] suggest that for the corresponding equilibrium (Scheme) *K* is *ca.* 10^{-5} l mole^{-1}.

The data of Dal Monte and Sandri[1,4] show that an annellated 2,1,3-thiadiazole ring is *less* electron-withdrawing than a nitro-group. In view of the observations reported above, it was of interest to examine the reactivity of 4-chloro-5-nitrobenzothiadiazole (IV) towards methoxide in methanol. The rate constant for methoxydechlorination at 0° was $3{\cdot}1 \times 10^{-3}$ l mole^{-1} s^{-1} (*cf.* value of $5{\cdot}2 \times 10^{-5}$ l mole^{-1} s^{-1} reported for 2,6-dinitrochlorobenzene above). The 5-chloro-4-nitro-isomer showed similar reactivity: k (0°) $2{\cdot}44 \times 10^{-3}$ l mole^{-1} s^{-1}.

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[3] J. F. Bunnett, *Quart. Rev.*, 1958, **12**, 1.
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