

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

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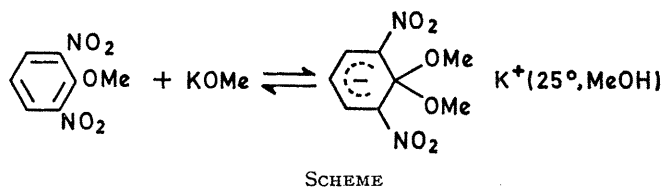
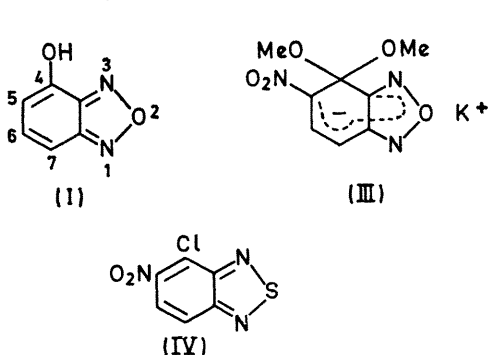
Summary The reactivity of 4-chlorobenzofurazan towards methoxide ion is about the same as that of *o*-nitrochlorobenzene, but the reactivity of 4-chloro-5-nitrobenzofurazan towards the same reagent exceeds that of picryl chloride: other examples of unexpectedly high reactivity of related compounds towards 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 nomenclature³) 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.

4-chloro-5-nitrobenzofurazan in fact exceeds that of 2,4,6-trinitrochlorobenzene (rate constant for methoxydechlorination at 0° in methanol = $6.7 \times 10^{-1} \text{ l mole}^{-1} \text{ s}^{-1}$)⁵.

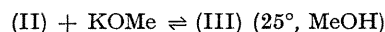
5-Chloro-4-nitrobenzofurazan was found to be even more reactive towards attack by methoxide in methanol than the 4-chloro-5-nitro-isomer; k (0°) being equal to $18.6 \text{ l mole}^{-1} \text{ s}^{-1}$. Dal Monte and Sandri⁴ have found 5-chlorobenzofurazan to be more rapidly methoxydechlorinated (*ca.* $5 \times$) 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 3.3×10^3) was treated with an excess of KOMe in methanol, a new spectrum appeared with λ_{max} 369 nm, ϵ 1.5×10^4 . 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 $(\text{CD}_3)_2\text{SO}$ showed absorptions at 7.86 (d, 1H) 5.56 (d, 1H), and 3.06 p.p.m. (s, 6H). Elemental analysis was correct for $\text{C}_8\text{H}_8\text{N}_3\text{O}_5\text{K}$. These observations establish the structure of the product as the σ (Meisenheimer) complex (III).

The equilibrium constant for the reaction:



was found to be $5.1 \times 10^3 \text{ l mole}^{-1}$. Hammett extrapolation of the data of Fendler, Fendler, and Griffin⁶ suggest that for the corresponding equilibrium (Scheme) K is *ca.* $10^{-5} \text{ l mole}^{-1}$.

We were therefore surprised to find that the rate constant for methoxydechlorination (0°, methanol) of 4-chloro-5-nitrobenzofurazan was $2.75 \text{ l mole}^{-1} \text{ s}^{-1}$, the rate constant for the corresponding reaction of 2,6-dinitrochlorobenzene⁵ being only $5.2 \times 10^{-5} \text{ l mole}^{-1} \text{ s}^{-1}$. The reactivity of

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 $3.1 \times 10^{-3} \text{ l mole}^{-1} \text{ s}^{-1}$ (*cf.* value of $5.2 \times 10^{-5} \text{ l mole}^{-1} \text{ s}^{-1}$ reported for 2,6-dinitrochlorobenzene above). The 5-chloro-4-nitro-isomer showed similar reactivity: k (0°) $2.44 \times 10^{-3} \text{ l mole}^{-1} \text{ s}^{-1}$.

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⁶ J. H. Fendler, E. J. Fendler, and C. E. Griffin, *J. Org. Chem.*, 1969, **34**, 689.