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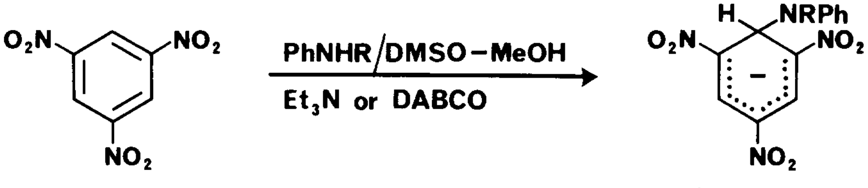
DIRECT (UNCATALYSED) FORMATION OF MEISENHEIMER COMPLEXES FROM PRIMARY, SECONDARY AND TERTIARY ARYLAMINES

Robert J. Spear, William P. Norris[1] and Roger W. Read

Materials Research Laboratories, P.O. Box 50, Ascot Vale, Victoria, 3032, Australia

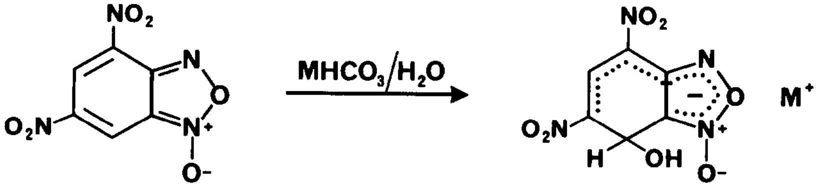
Abstract. Aniline, N-methylaniline and N,N-dimethylaniline react through their para positions with 4,6-dinitrobenzofurazan 1-oxide to form stable Meisenheimer complexes.

Prior to 1972 it was thought that arylamines would not form stable Meisenheimer (or sigma) complexes with electron deficient aromatics but that only weak charge transfer complexes could be obtained.[2,3] However since 1972 Buncel and co-workers have achieved Meisenheimer complex formation between a series of primary[4] and secondary[5] aromatic amines and 1,3,5-trinitrobenzene (TNB) indirectly by displacement of the methoxy group from the TNB-methoxide adduct,[4] and subsequently directly on TNB using base catalysis by tertiary amines.[6] The latter reaction fails in the absence of added base.



(1) R=H,Me

4,6-Dinitrobenzofurazan 1-oxide (DNBF), first prepared by Drost in 1899,[7] is undoubtedly the most powerful of the electron deficient aromatics with respect to formation of stable Meisenheimer complexes.[8] The ability of DNBF to form these complexes can be readily gauged from its reaction with aqueous alkaline bicarbonates: DNBF dissolves with evolution of carbon dioxide to form the hydroxy adducts (2). The potassium, sodium and silver salts of (2) were first isolated by Drost[7] but their structure was not determined until 1965.[9]



DNBF

(2) M=K,Na,Ag,H

An unusual reaction of DNBF reported by Drost[7] was formation of an "anilide" via reaction with an equimolar quantity of aniline in ethanol. Unlike (2), this "anilide" was not decomposed by acid.[7] Upon repetition of this reaction in methanol, we obtained a crystalline product with identical properties to Drost's product. N-Methylaniline and, surprisingly, N,N-dimethylaniline afforded similar products upon reaction with DNBF.

These materials all exhibited an intense u.v.-vis absorption of 472-4 nm, c.f. (2), M = K, 463 nm (Table 1), immediately identifying them as Meisenheimer complexes. The ^{1}H n.m.r. spectra (Table 2) conclusively defined the structures as (3)-(5)[10] where reaction had occurred not through nitrogen, as would be expected from the results for TNB → (1)[4-6] but through the position para to the amino function. There were only four aromatic protons which resonated as an AA'BB' system or singlet, and three exchangeable protons. The chemical shifts of the aromatic protons suggest that the extra exchangeable proton was largely associated with the amino group.[11] The chemical shifts of H4 and H6 were as expected from comparison with (2), M = K (Table 2). The structure readily explains the non-susceptibility of (3) to acid.[7]

Table 1: U.v.-vis absorption spectra (in MeOH) for Meisenheimer complexes formed from DNBF

Complex	λ_{max}(nm) [ε_{max}($M^{-1}cm^{-1}$)]			
(3)	473 [24,400]	364 [6,550]	295 [8,850]	248 [16,700]
(4)	472 [25,500]	364 [6,800]	294 [9,550]	256 [19,000]
(5)	474 [23,100]	364 [6,220]	294 [9,330]	262 [20,100]
(2) M=K[a]	463 [25,500]		302 [8,060]	263 [11,200]

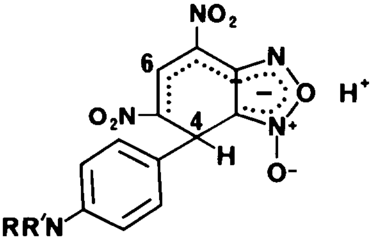
[a] Data from Ref. 9, recorded in H_2O.

Table 2: ^{1}H n.m.r. spectra (in $(CD_3)_2SO$) for Meisenheimer complexes formed from DNBF

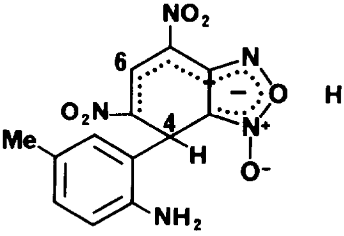
Complex	H4	H6	Data[a] Aromatic Protons	Other Signals
(3)	5.40	8.80	7.35, 7.39 AA'BB' system	9.0 (broad), NH
(4)	5.41	8.78	7.42	8.0 (broad), NH 2.95 NMe
(5)	5.40	8.77	7.45	6.95 (broad), NH 3.15 NMe
(2) M=K[b]	5.84, dd J 8.0, 0.65	8.59, d J 0.65	-	6.21, d, J 8.0, OH
(6)	5.79	8.71	6.8-7.3, m	7.5 (broad), NH 2.15 Me

a All signals are singlets unless otherwise stated.

b Data from Ref. 13.



	R	R'
(3)	H	H
(4)	H	Me
(5)	Me	Me



(6)

(3)-(5) are the first isolable Meisenheimer complexes observed to form between an aromatic amine and an electron deficient aromatic, and the first reported instance where aniline has reacted with aromatic carbon through the para position and not nitrogen. The only comparable reaction which has been observed is that between TNB and potassium phenoxide to form the corresponding Meisenheimer complex.[12] However this latter reaction is rather slow whilst the rate of the reactions observed here is very high: an equimolar quantity of DNBF, when added to a solution of aniline in $(CD_3)_2SO$, produced an immediate deep red colouration while the ^{1}H n.m.r. spectrum of this solution consisted only of signals for (3). If the para position was blocked by a methyl group, i.e. aniline replaced by p-toluidine, reaction with DNBF in $(CD_3)_2SO$ slowed considerably: the ^{1}H n.m.r. spectrum initially consisted only of the π-complex but this was transformed, $t_{\frac{1}{2}}$ about 5 min, into the ortho substituted complex (6). Our attempts to isolate (6) by reaction in methanol have been unsuccessful.

We are currently examining these reactions with respect to further changes in the amine substrates.

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7. P. Drost, Justus Liebigs Ann. Chem., 1899, 307, 49. The correct structure wa not known at the time and Drost named (1) as m-dinitro-o-dinitrosobenzene.
8. The pKa^{H_20} for formation of (2), M = H from DNBF is 3.75.[14] This figure can be compared with TNB where the corresponding figure is 13.43,[14] nearly 10 powers of 10 weaker.
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10. Satisfactory elemental analyses have been obtained for (3)-(5).
11. For example, the chemical shifts for HAr in p-toluidine in $(CD_3)_2SO$ are 6.45 and 6.80 ppm while protonation by addition of a drop of TFA results in near equivalence, 7.25 and 7.3 ppm.
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