Reaction of Nitrosobenzene with 4-Methoxy-*N*-methyleneaniline

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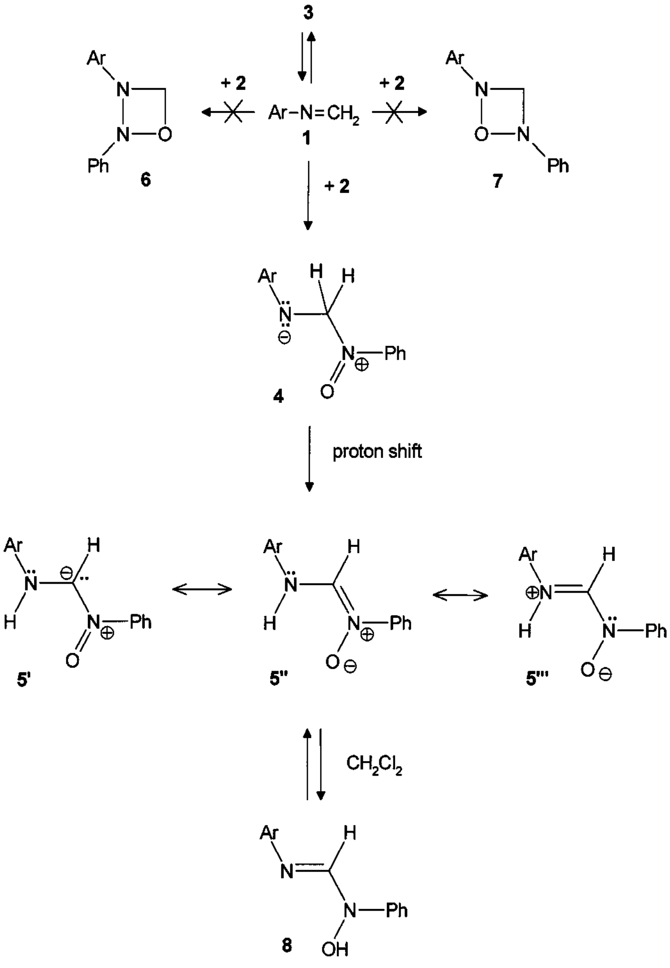
A 1:1 adduct produced in the reaction of nitrosobenzene (**2**) with 1,3,5-tris(4-methoxyphenyl)-1,3,5-triazinane (**3**) has been shown by X-ray diffraction structure analysis to be the *N′*-(4-methoxyphenyl)-*N*-phenyl-*N*-oxyformamidinium species **5**.

Recent studies[1] have given fresh insights into the nature of *N*-methyleneamines **1** and their oligomers, in particular 1,3,5-trisubstituted 1,3,5-triazinanes. These species are stable products, but are also a ready source of reactive **1** in solution. Ingold et al.[2] reported the reactions of a number of derivatives of type **1** with nitrosobenzene (**2**), the products of which were identified as four-membered 1:1 addition compounds of type **7** (Scheme 1).

We have now studied the reaction between 1,3,5-tris(4-methoxyphenyl)-1,3,5-triazinane (**3**)[1a,c] and nitrosobenzene (**2**). Upon mixing these compounds in chloroform, the slow formation of a new product (**5**; resonance structures **5′**, **5′′** and **5′′′**) could be monitored by ^{1}H-NMR spectroscopy. The initial intermediate **4**, arising from attack by the highly electrophilic methylene carbon atom of **1** on the nitrogen atom of the nitroso group of **2**, does not undergo ring closure to either **6** or **7**,[2] but rather a proton shift from the methylene group to the negatively charged adjacent nitrogen center takes place, thereby yielding **5** (Scheme 1). The unusual structure of the product was unambiguously confirmed by X-ray diffraction structure analysis (Figure 1).

The crystallographic data show that all the non-hydrogen atoms making up the framework of **5** are essentially coplanar, so as to maximize the π-delocalization. The bond lengths within the ONCN sequence are highly indicative of substantial contributions of the two zwitterionic structures **5′′** and **5′′′**. One important feature revealed by the X-ray analysis is the extensive array of hydrogen bonding, both intra- and intermolecular, involving the charged oxygen atom.



Scheme 1. Addition of nitrosobenzene to *N*-methylenearylamine; Ar = 4-methoxyphenyl

The ^{1}H-NMR spectrum offered less conclusive evidence for such a structure, exhibiting a sharp singlet at $\delta = 8.36$ and a very broad signal for one proton at $\delta = 9.15$ in thoroughly dried CD_2Cl_2. On the other hand, an NOE differential experiment in CD_2Cl_2 was suggestive of similar interactions between the protons of *both* aromatic systems and the proton at $\delta = 9.15$.[3] This observation can be interpreted in terms of a rapid interconversion between the tautomeric forms **5** and **8** (Scheme 1).

Elemental analysis data, as well as the EI mass spectrum (*m/z*: 242 [M$^+$]) of **5** indicated it to be a 1:1 addition product; water elimination from the parent ion was a notable feature of the mass-spectral pattern. A strong, broad absorption at 3500 cm^{-1} in the infrared spectrum could not be unambiguously assigned, although it was clearly indicative of either an N−H or an O−H bond with hydrogen-bond association to another center.

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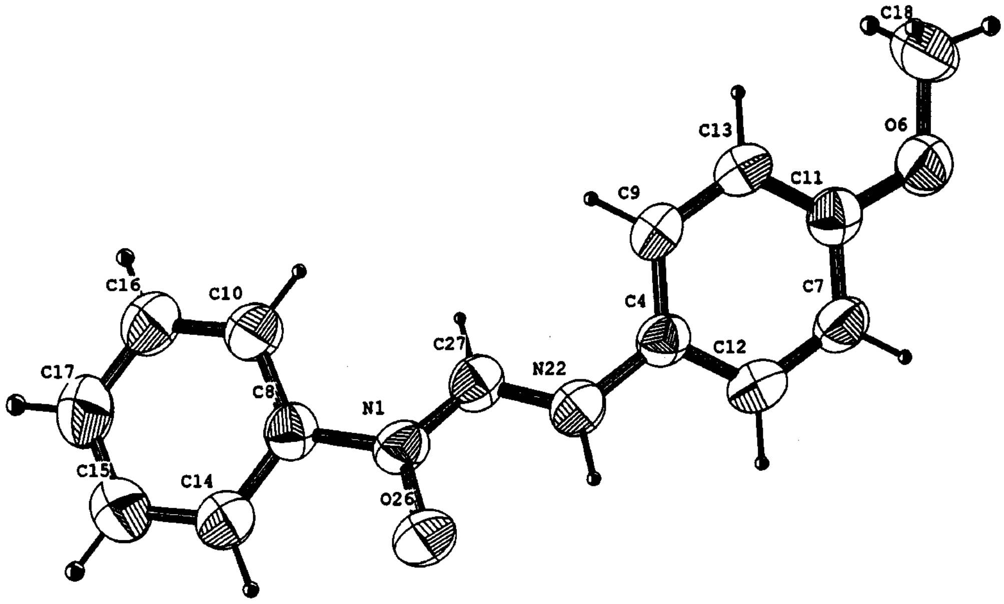

Figure 1. ORTEP view of **5**

Treatment of **5** with Zn and hydrochloric acid resulted in its reduction and cleavage to aniline, 4-methoxyaniline, 4-methoxy-*N*-methylaniline, and *N*-methylaniline as the primary products of reduction to a methanediamine.

Experimental Section

Preparation of 1,3,5-Tris(4-methoxyphenyl)-1,3,5-triazinane (3): 1,3,5-Tris(4-methoxyphenyl]-1,3,5-triazinane (**3**) was prepared by refluxing 4-methoxyaniline with paraformaldehyde (1.3 equiv. CH_2O) in toluene for 30 min, and then distilling off the toluene in order to remove the excess formaldehyde.[1a,c] The solid product was obtained in quantitative yield upon complete evaporation of the solvent at water-pump pressure. Recrystallization from hexane/ethyl acetate yielded a colourless, crystalline product, m.p. 135 °C. After melting, the product solidified upon cooling and retained the same m.p. and spectroscopic properties.

Reaction of 1,3,5-Tris(4-methoxyphenyl)-1,3,5-triazinane (3) with Nitrosobenzene: A mixture of 1,3,5-tris(4-methoxyphenyl)-1,3,5-triazinane (**3**) (1.9 g, 4.7 mmol) and nitrosobenzene (**2**) (1.5 g, 14 mmol) in $CHCl_3$ (50 mL) was left to stand at room temperature in the dark for 10 d. Thereafter, the solvent was removed, and the residue was recrystallized from AcOEt/hexane. The product **5** was obtained in 70% yield (2.4 g) as light-yellow crystals, m.p. 135 °C. − IR (KBr pellet): $\tilde{\nu} = 3500\ cm^{-1}$, 3150, 3085, 1676, 1515, 1255, 1235, 1038, 834, 768. − ^1H NMR (CD_2Cl_2/TMS): $\delta = 3.77$ (s, 3 H, CH_3), 6.85 (d, 2 H, aromatic H, $J = 8.9$ Hz), 7.09 (d, 2 H, aromatic H, $J = 8.9$ Hz), 7.25−7.34 (m, 2 H, aromatic H), 7.36−7.49 (m, 2 H, aromatic H), 7.63−7.7 (m, 1 H, aromatic H), 8.36 (s, 1 H), 9.15 (br. s, 1 H). − ^{13}C NMR (CD_2Cl_2): $\delta = 55.39$, 114.75, 118.70, 119.00, 127.27, 128.96, 132.31, 134.36, 143.43, 156.20. − MS (70 eV); *m/z* (%): 242 (32) [M^+], 227 (11), 226 (56), 225 (15), 224 (16), 209 (16), 150 (11), 135 (12), 134 (100), 123 (54), 109 (37), 108 (51), 107 (24), 104 (11), 93 (63), 92 (25), 77 (37). − $C_{14}H_{14}N_2O_2$ (242.3): calcd. C 69.44, H 5.82, N 11.65; found C 69.82, H 5.96, N 12.02.

Crystallographic Data for 5: X-ray diffraction analysis of the sample was carried out with a Philips PW-1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation ($\lambda = 0.7107$ Å) at 298 K. 2201 unique reflections were obtained up to $2\theta = 50°$ from an orthorhombic crystal ace group *Pbca*, $a = 9.982(3)$, $b = 25.413(11)$, $c = 9.811(4)$ Å, $V = 2488.77$, $Z = 8$, $D = 1.302\ g\ cm^{-3}$] of dimensions 0.35 × 0.43 × 0.61 mm. The structure of $C_{14}H_{14}N_2O_2$ was solved by means of direct methods and refined by full-matrix least-squares methods using the SIR97 package.[4] The non-hydrogen atoms were refined anisotropically by using 1474 reflections with $F_o > 3\sigma(F_o)$; the H atoms were placed in calculated positions. Final $R = 0.055$ and $R_w = 0.073$. X-ray data have been deposited at the Cambridge Crystallographic Data Centre (deposition number CCDC-102848). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ [Fax: (internat.) + 44-1223/336033; E-mail: deposit@ccdc.cam.ac.uk].

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[3] Selective irradiation of the phenyl and methoxyphenyl groups produced NOEs of ca. 40% and 50%, respectively, on the signal at δ = 9.15.

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