Photolysis of some *N*-nitroso- and *N*-nitro-anilines in solution

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The photolyses of three *N*-methyl-*N*-nitrosoanilines and two *N*-methyl-*N*-nitroanilines in organic solvents have been studied in the range of 300–340 nm. The influence of solvent character and the presence or absence of oxygen play important roles in the product composition range. The primary photochemical process involves N–N fission, this being homolytic in aprotic solvents and heterolytic in methanol. Three novel mechanistic conclusions are proposed, namely photosolvolysis of a nitrosamine in methanol, photooxidation of nitrosamines in aprotic solvents and the production of biphenyl derivatives on photolysis of nitro-substituted nitrosamines and nitramines in aromatic solvents.

The reaction of nitrogen dioxide with *N*-methyl-4-nitroaniline produces a variety of products. In the course of a study of these reaction products it became apparent that some of the *N*-nitroso and *N*-nitro compounds produced displayed interesting photochemical reactions. Our earlier studies on the photochemistry of many *C*-nitroso compounds[1] and a couple of *N*-nitroso compounds[2] had demonstrated the importance of solvent character in photolyses where nitric oxide was a primary photochemical product. It was therefore of interest to study the photolyses of aromatic *N*-nitroso compounds paying attention to any differences between protic and aprotic solvents. The compounds chosen in this investigation comprise three nitrosamines and two nitramines.

Experimental

N-Methyl-*N*-nitrosoaniline (**1a**) was prepared by nitrosation of *N*-methylaniline (**1A**) using established procedures.[3]

N-Methyl-4-nitroaniline (**2A**) (commercial) was recrystallised from ethanol and then nitrosated using excess nitrogen dioxide dissolved in methylene chloride after Stoermer's method.[4] The nitrosamine (**2a**) was obtained by solvent evaporation and recrystallised from ethanol and shown to be pure by TLC, mp 101 °C (lit.,[5] 100–101 °C); ν_{max}(KBr)/cm^{-1} 1510, 1460, 1340 and 1080; λ_{max}(cyclohexane)/nm 308 (ε_{max}/dm^3 mol^{-1} cm^{-1} 16 800); δ_H($CDCl_3$, 60 MHz) 3.5 (3 H, s, H_a), 7.82 (2 H, d, *J* 10, $H_{b,e}$) and 8.43 (2 H, d, *J* 10, $H_{d,c}$).

N-Methyl-*N*-nitroaniline (**1b**) was prepared from aniline *via* the potassium antidiazotate,[6] followed by oxidation to *N*-nitroaniline[7] and subsequent methylation.[8] The product was obtained in ethereal solution, which on evaporation left a yellow oil which crystallised in the cold. Subsequent vacuum sublimation yielded the pure solid, mp 39 °C (lit.,[8] 38.5–39.5 °C); ν_{max}(KBr)/cm^{-1} 1590, 1520, 1415, 1280 and 1090; λ_{max}(cyclohexane)/nm 250 (ε_{max}/dm^3 mol^{-1} cm^{-1} 5260).

N-Methyl-*N*,4-dinitroaniline (**2b**) was prepared from 1 g *N*-methyl-4-nitroaniline suspended in 10 cm^3 acetic acid to which was added 1 cm^3 anhydrous nitric acid in 2 cm^3 acetic anhydride. After 1 h, the mixture was poured into water and the colourless solid which separated was filtered and recrystallised from ethanol giving colourless needles, mp 138–139 °C (lit.,[9] 139 °C); ν_{max}(KBr)/cm^{-1} 1520, 1350 and 1300; λ_{max}(cyclohexane)/nm 284 (ε_{max}/dm^3 mol^{-1} cm^{-1} 8600); δ_H($CDCl_3$, 60 MHz) 3.82 (3 H, s, H_a), 7.55 (2 H, d, *J* 10, $H_{e,b}$) and 8.38 (2 H, d, *J* 10, $H_{d,c}$).

N-Methyl-2,4-dinitroaniline (**3A**) was donated by Dr P. N. Preston, mp 178 °C (lit.,[10] 178 °C), ν_{max}(KBr)/cm^{-1} 3360, 1625, 1590 and 1340; δ_H($CDCl_3$, 60 MHz) 3.21 (3 H, d, *J* 5, H_a), 8.5 (1 H, br, H_b), 9.19 (1 H, d, *J* 3, H_c), 8.35 (1 H, dd, *J* 10, 3, H_d) and 6.95 (1 H, d, *J* 10, H_e). The corresponding *N*-methyl-*N*-nitroso-2,4-dinitroaniline (**3a**) was prepared from the above aniline by adapting the method of Bamberger,[11] in which a chloroform solution of the aniline was cooled to 0 °C and saturated with nitrogen dioxide with constant stirring and exclusion of light. Following neutralisation ($NaHCO_3$ solution) the chloroform layer was separated, shaken with activated charcoal, filtered and evaporated to dryness in the dark. **3a** was recrystallised from methylene chloride–light petroleum and stored at −20 °C. The light yellow crystals had mp 83.5–84 °C (lit.,[11] 83–85 °C); ν_{max}(KBr)/cm^{-1} 3095, 1610, 1540, 1470 and 1350; δ_H($CDCl_3$, 60 MHz) 3.5 (3 H, s, H_a), 7.85 (1 H, d, *J* 9, H_d), 8.62 (1 H, dd, *J* 9, 3, H_c) and 8.88 (1 H, d, *J* 3, H_b).

N-Methyl-2-nitro- (*ortho*-**2A**) and *N*-methyl-3-nitro-aniline were prepared by sealed tube methylation of the corresponding nitroanilines using methyl iodide (1 day, 110 °C) followed by neutralisation and extraction with diethyl ether and evaporation to dryness.[12,13] The former compound was separated by vacuum sublimation, mp 36 °C (lit.,[14] 35–37 °C); ν_{max}/cm^{-1}

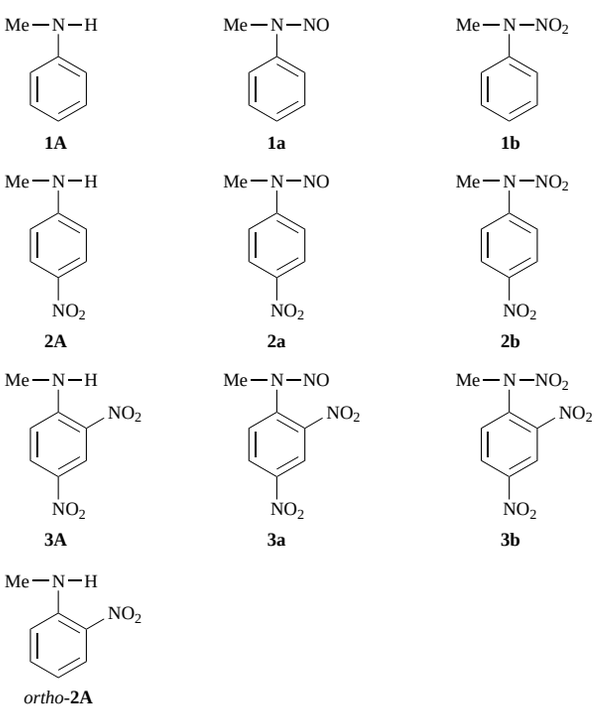

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Table 1 Photolyses of nitrosamine **1a** and nitramine **1b**

Solvent	Concentration/ mmol dm^{-3}	Time/h	%Photolysed	%Yields[a] *ortho*-**2A**	%Yields[a] **2A**	Analytical method
Benzene	5.12[b]	3	38	28	14	HPLC
Benzene–O_2	5.9[b]	1	26	33	22	HPLC
Benzene	4.26[c]	0.75	25	40	18	HPLC

[a] In mol% of photolysed substrate. [b] Concentration of **1a**. [c] Concentration of **1b**.

3400, 1620, 1570 and 1510; δ_H($CDCl_3$, 60 MHz) 3.03 (3 H, d, *J* 5), 6.75 (2 H, m), 7.52 (1 H, m), 7.58–8.5 (1 H, br) (disappears on addition of CF_3COOH) and 8.22 (1 H, dd, *J* 9, 2). The latter compound was recrystallised from ethanol; mp 67 °C (lit.,[15] 68 °C); ν_{max}(KBr)/cm^{-1} 3400, 1625, 1540 and 1340; δ_H($CDCl_3$, 60 MHz) 2.85 (3 H, d, *J* 5), 3.8–4.5 (1 H, br) and 6.7–8 (4 H, m).

4-Nitrobiphenyl was made by direct nitration of biphenyl with conc. nitric acid, separation of the resultant products by column chromatography, followed by recrystallisation from ethanol, mp 114–115 °C (lit.[16] 114–114.5 °C); ν_{max}(KBr)/cm^{-1} 1595, 1510, 1345, 850 and 740; δ_H($CDCl_3$, 60 MHz) 7.4–8.2 (7 H, m) and 8.25–8.7 (2 H, m).

Benzene was shaken repeatedly with conc. sulfuric acid until the acid layer remained colourless, shaken with water, followed by 10% sodium bicarbonate solution and then separated and dried over calcium chloride. Finally it was filtered, distilled and passed through a column of activated alumina. Methanol was dried over sodium and distilled. It was then refluxed over aluminium powder (10 g dm^{-3}) and potassium hydroxide (10 g dm^{-3}), redistilled and passed through an activated alumina column. Tests for the presence of aldehydes (Schiff's reagent) were negative. Cyclohexene was passed through an activated alumina column to remove any peroxides and water before use. Commercial spectroscopic quality cyclohexane was further purified by passing through an activated alumina column. Chlorobenzene was purified in a similar manner to benzene.

Photolyses were carried out using a 125 W water-cooled, pyrex-filtered medium-pressure mercury lamp located within an immersion thimble within the appropriate reaction vessel of capacity 1.1, 0.4 or 0.23 dm^3. The solvents employed were used either under an atmosphere of oxygen, air or thoroughly deoxygenated by degassing under vacuum and maintained under an atmosphere of nitrogen. When the solvent was used under oxygen it was first saturated with oxygen by bubbling a continuous stream of the gas through the solvent.

Mass spectra were recorded on an AEI MS 30 double beam mass spectrometer. ^{1}H NMR spectra were measured using a Perkin-Elmer R.12 spectrometer. Electronic absorption spectra were recorded with a Pye-Unicam SP 1800 spectrophotometer using 1 cm fused silica cells. Solutions of known concentration were prepared with spectroscopic grade solvents using standard procedures. Preparative chromatographic plates were Merck silica gel F_{254} precoated plates. TLC plates were self-made (Merck Kieselgel GF_{254} type 60). Column chromatography was carried out using Merck Kieselgel 60, 0.040–0.063 mm (230–400 mesh ASTM) with benzene as solvent. HPLC was carried out using a Haskell pressure multiplying pump, the eluted fractions being monitored at a wavelength of 380 nm with a Cecil CE 212 variable wavelength UV monitor connected to a Servoscribe 1s chart recorder. The HPLC columns were 5 mm bore, internally polished stainless steel tubes, of lengths 25 and 45 cm. The columns were filled with 5 μ Spherisorb silica gel by slurry packing from a reservoir under a pressure of 3000 psi‡ using methanol. Following this the solvent composition was gradually changed to isooctane–methylene chloride 60:40. Initially (2-nitrophenyl)phenylamine was used as internal standard for the HPLC analyses but this was discontinued following the establishment of the fact that syringe injection was as accurate and reproducible. Prior to HPLC analysis of a photolysis sample, the constituents of the sample were identified, their retention times obtained, and calibration of the HPLC established by injection of the compounds in known concentration using a fixed wavelength (usually 380 nm). Change in solution composition with photolysis time could thereby be obtained. Analysis for methyl nitrite, produced in the photolysis of **2a** in methanol was made by vacuum distillation followed by electronic absorption spectroscopy at 352 nm.[1] Note that with the exception of those in methanol, photolysed solutions regularly contained uncharacterised insoluble materials in the form of tars which were removed by filtration through silica gel prior to analysis.

‡ 1 psi = 6895 Pa.

Results

Typical examples of those for **1a** and **1b** are presented in Table 1 and for **2a** and **2b** in Table 2. The aniline products which feature in these tables are **2A** (*N*-methyl-4-nitroaniline), *ortho*-**2A** (*N*-methyl-2-nitroaniline) and **3A** (*N*-methyl-2,4-dinitroaniline). Product yields are given as mol% of the photolysed nitroso- and nitro-amine. The analytical technique employed for each determination is identified in the appropriate column.

The nitrosamine **3a** was photolysed to completion in benzene solution and the products analysed by preparative TLC to display two products the first of which was shown by IR, NMR and MS to be **3b**. The second low yield product had IR and MS spectra in accord with 2,4-dinitrobiphenyl. Quantitative photolysis in benzene established the yield of **3b** as 81% together with trace quantities of the 2,4-dinitrobiphenyl. When the photolysis was repeated using deoxygenated benzene no products could be detected and the same result was obtained when a 40-fold excess of nitrogen dioxide was present.

The time variation in concentrations of reactant and products for some photolyses of **1a** and **1b** are shown in Figs. 1–3.

Discussion

The photolyses of nitrosamines in neutral media have received much less attention than those in acid media, but there is sufficient evidence to demonstrate that whether in the gas phase[17,18] or in neutral solution[2,19–21] photolysis occurs with initial fission of the N–N bond, the observed low quantum yields being due to the reversibility of this step assisted in solution by the caging effect of the solvent. Further reaction of the initial radical product with the solvent and of nitric oxide with dissolved oxygen[20,21] have also been suggested to account for products observed in such photolyses.

Such reaction possibilities are of obvious significance in the case of our aryl-substituted nitrosamines, but in addition our observed reaction products suggest that the occurrence of rearrangement reactions of the arylamino radicals requires consideration. The products observed on photolysis of **2a** permit the following conclusions. The initial process following absorption of light in the 300–340 nm range is fission of the N–N bond. This process is homolytic in all cases where a non-polar solvent is used, but modified to a heterolytic one in methanol where the polar solvent can stabilise the charge trans-

Table 2 Photolyses of nitrosamine **2a** and nitramine **2b**

Solvent	Concentration/ mmol dm^{-3}	Time/h	%Photolysed	%Yields[a] N[b]	**2A**	**3A**	**2b**	Analytical method
Benzene	3.72[c]	8	49	9	0	1	55	CC
Benzene[d]	1.57[c]	8.5	52	7	0	34	0	PrepTLC
PhCl	3.99[c]	13	58		*e*			CC + MS
c-C_6H_{12}	5.0[c]	10.25	70		*f*	13	61	CC
c-C_6H_{12}	0.6[c]	2.5	72		17	17	44	NMR
c-C_6H_{12}/O_2	1.29[c]	1.5	85		14	22	40	NMR
c-C_6H_{12}[d]	1.23[c]	1	28		67	0	24	NMR
MeOH	5.9[c]	3.5	100		87[g]	0	0	PrepTLC
Benzene[d]	3.9[h]	7	89	8	3	64	(17)[i]	CC
c-C_6H_{12}[d]	1.3[h]	1.25	62		13	20		NMR
c-C_6H_{12}[d]	0.71[h]	2.5	75		21	20		NMR

[a] In mol% of photolysed substrate. [b] N = 4-nitrobiphenyl. [c] Concentration of **2a**. [d] Rigorously degassed solvent. [e] Analysed for substituted biphenyls; two different 2,4-dinitrochlorobiphenyls and two different nitrochlorobiphenyls present in respective yields of 0.6 and 0.8%. [f] Severe tailing on column prevented quantitative analysis. [g] 81% yield of methyl nitrite obtained *via* electronic absorption spectroscopy. [h] Concentration of **2b**. [i] Yield of **2a**.

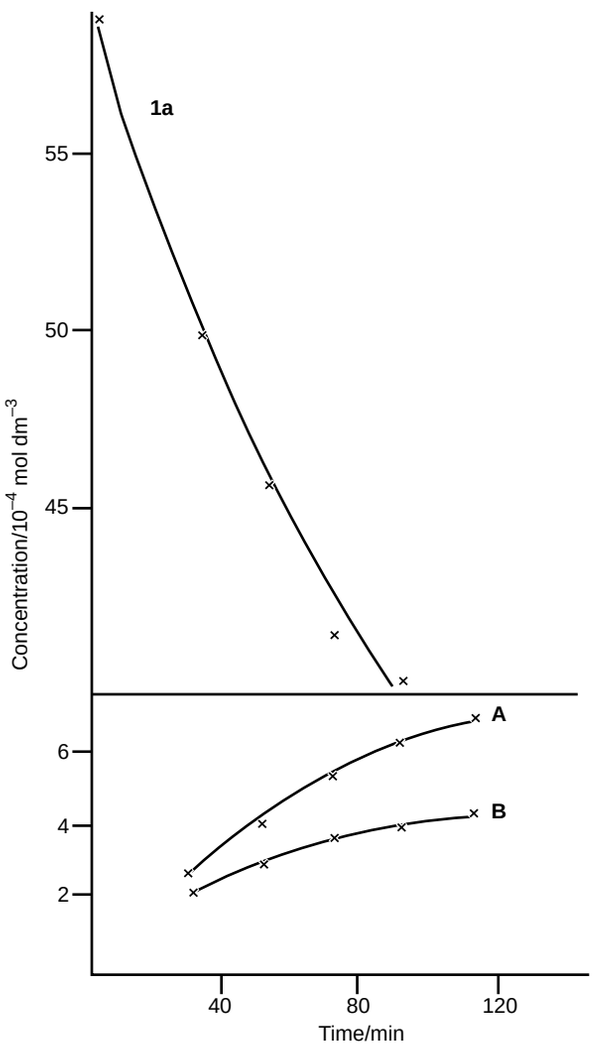


Fig. 1 Concentration–time dependence for nitrosamine **1a** and products for photolysis in benzene saturated with oxygen under an atmosphere of oxygen. Product A = *ortho*-**2A**, product B = **2A**.

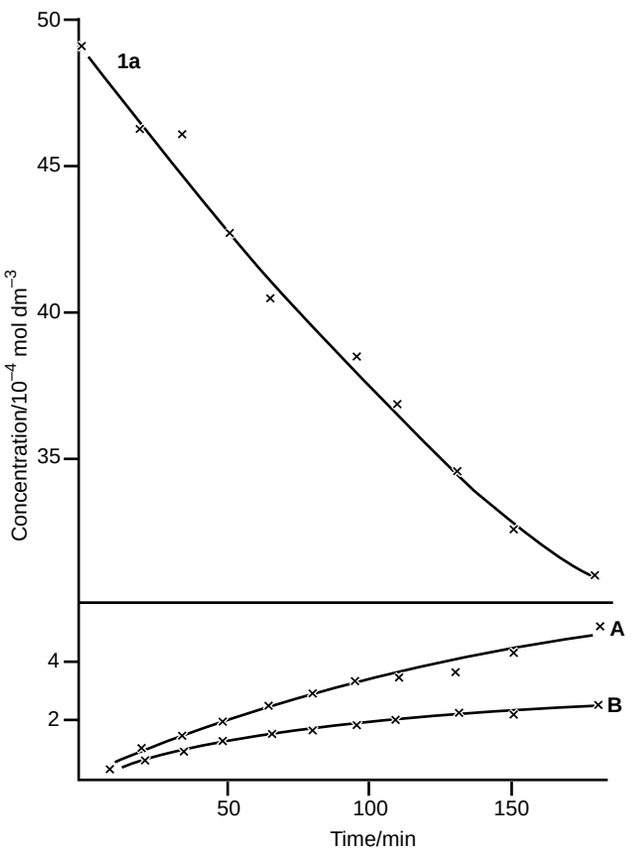


Fig. 2 Concentration–time dependence for nitrosamine **1a** and products for photolysis in degassed benzene. Product A = *ortho*-**2A**, product B = **2A**.

fer excited state. In the initial process the excited state of the nitrosamine will lead to the formation of a singlet or triplet radical pair followed by separation of this pair from the solvent cage. The formation of the various reaction products is clearly dependent upon the presence or absence of oxygen and the ability of the anilino radical to abstract hydrogen from the solvent molecule. For the case of cyclohexane as solvent, whether in equilibrium with air or when oxygen saturated, the products are nitramine **2b** together with the anilines **2A** and **3A**. Removal of oxygen caused a marked change in the product distribution and the rate of production of the photolysis products was halved with a considerable increase in the production of the aniline **2A**, disappearance of aniline **3A** and a large reduction in the nitramine **2b**. The formation of **2A** is due to the hydrogen abstraction reaction (see Scheme 1) and the resultant cyclohexyl radical can then catalyse the disproportionation of nitric oxide to nitrogen and nitrogen dioxide *via* the intermediate formation of nitrosocyclohexane. When the photolysis is carried out in the presence of oxygen, however, the nitric oxide is directly oxidised thereby to nitrogen dioxide which can then combine with the anilino radical to give **2b**. This would thereby diminish the formation of **2A** from the hydrogen abstraction from the solvent. The formation of the aniline **3A** can be ascribed to photolysis of the nitramine **2b**. In a separate study of this nitramine in deoxygenated cyclohexane both of the anilines **2A** and **3A** were

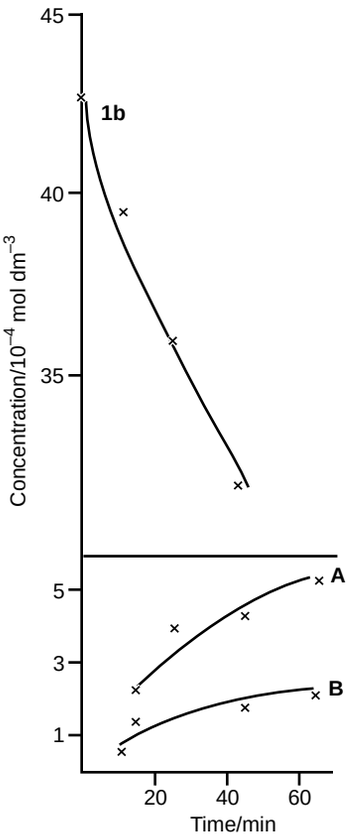
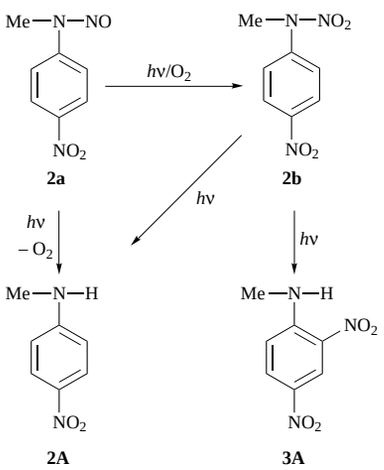


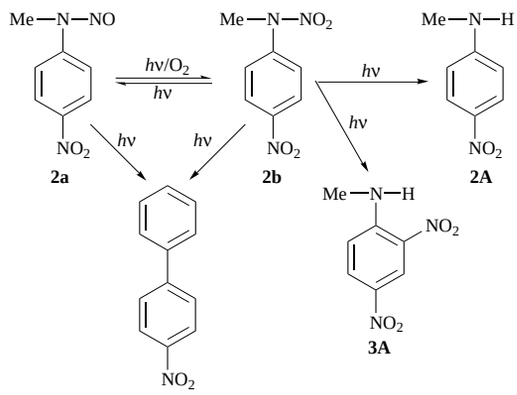
Fig. 3 Concentration–time dependence for nitramine **1b** and products in benzene with oxygen removed by a stream of nitrogen. Product A = *ortho*-**2A**, product B = **2A**.



Scheme 1

produced in approximately equimolar quantities. The absence of **3A** in the photolysis products of **2a** in deoxygenated cyclohexane implies that the production of **2A** cannot be due to secondary photolysis of **2b**. In contrast to this in the photolysis products of **2a** in oxygen-saturated cyclohexane the approximate equivalence of **2A** and **3A** suggests that they are both derived from secondary photolysis of **2b** and that the anilino radicals are unable to undergo hydrogen abstraction with the solvent because they have been scavenged by reaction with oxygen. It is also possible that there is a direct photooxidation of the excited nitrosamine **2a** to **2b** by the dissolved oxygen. Scheme 1 summarises the possible reactions.

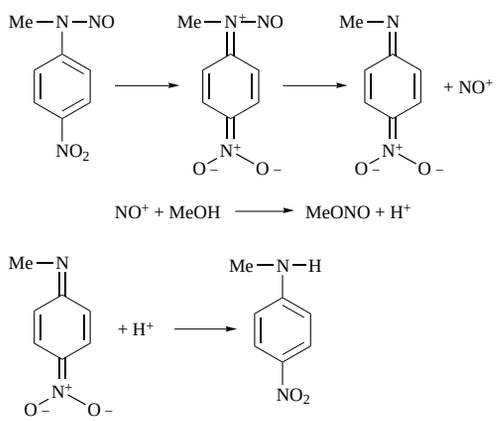
The photolysis of **2a** in benzene shows some differences from that in cyclohexane. It is to be expected that the hydrogen abstraction from the solvent molecules would be much less likely to occur for benzene than for cyclohexane. The unexpected formation of 4-nitrobiphenyl may afford significant clues to reaction pathways particularly as it is formed in similar yields in the presence or absence of oxygen and also results from the photolysis of the nitro compound **2b** in chlorobenzene where the generality of this reaction with the solvent is emphasised by the production of two chloronitrobiphenyls. Addition of either the anilino radical or of the excited substrate to the benzene can be envisaged followed by the removal of methylimino-containing fragments. Scheme 2 illustrates the products



Scheme 2

obtained from **2a** and **2b**. The production of the dinitroaniline **3A** in the photolyses of **2a** and **2b** further illustrates the complexity of the processes that are occurring when photolysis takes place using benzene as the solvent.

The photolysis of **2a** in methanol gives **2A** and methyl nitrite in equivalent high yield. The addition of acid and cyclohexene did not alter the formation of **2A**. The structure of **2a** has a large charge transfer contribution in the ground state and an excited charge transfer state would be stabilised by the polar methanol solvent. Subsequent heterolysis of the N–N bond would lead to the observed products as in Scheme 3. Note that tarry products are absent in this case.



Scheme 3

The photolysis of the nitrosamine **1a** and the nitramine **1b** in benzene appear simpler in relation to the products formed (Table 1) and the ratio of the two nitroanilines produced, *ortho*-**2A** and **2A**, is almost 2:1. The nitrogen dioxide formed from oxidation of nitric oxide in photolysis of **1a** or directly from photolysis of **1b** then undergoes radical addition to the amino radical with the formation of the observed products in the statistical *ortho*:*para* ratio of 2:1.

The photolysis of **3a** to completion in oxygen-containing benzene gave the nitramine **3b** in high yield together with a trace quantity of 2,4-dinitrobiphenyl. In deoxygenated benzene with similar concentration of **3a** no products could be detected after photolysis for three times the previous exposure time. In a further photolysis experiment using a 40-fold excess of nitrogen dioxide in the deoxygenated solvent, no products were observed after an exposure time twice that for the deoxygenated solvent.

It therefore appears that direct oxidation of the nitrosamine by nitrogen dioxide does not occur and that the oxidation is brought about by addition of oxygen to nitric oxide to form nitrogen trioxide; the oxidation pathway is given in reactions (1) and (2).

$$NO + O_2 \longrightarrow NO_3 \quad (1)$$

$$RR'N–NO + NO_3 \longrightarrow RR'N–NO_2 + NO_2 \quad (2)$$

In conclusion we note that three new features have emerged from this study namely the photosolvolysis of nitrosamine **2a** in methanol, the efficient photooxidation of nitrosamines in aprotic solvents and the production of biphenyl derivatives when two nitro-substituted nitrosamines and one nitro-substituted nitramine are photolysed in aromatic solvents.

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References

1 B. G. Gowenlock, G. Kresze and J. Pfab, *Tetrahedron Lett.*, 1972, 593; *Tetrahedron*, 1973, **29**, 3587; *Liebigs Ann. Chem.*, 1975, 1903; D. Forrest, B. G. Gowenlock and J. Pfab, *J. Chem. Soc., Perkin Trans. 2*, 1979, 576.
2 B. G. Gowenlock, J. Pfab and G. C. Williams, *J. Chem. Res.* (*S*), 1978, 362.
3 *Organic Syntheses*, Collective Volume 2, ed. A. H. Blatt, Wiley, New York, 1943, p. 460.
4 R. Stoermer, *Ber. Dtsch. Chem. Ges.*, 1898, **31**, 2523.
5 R. Meldola and E. H. R. Salmon, *J. Chem. Soc.*, 1888, **53**, 776.
6 *Methoden der Organischen Chemie,* (*Houben-Weyl*), ed. E. Müller, Georg Thieme, Stuttgart, 1965, bd. 10/3, p. 557.
7 *Methoden der Organischen Chemie,* (*Houben-Weyl*), ed. E. Müller, Georg Thieme, Stuttgart, 1958, bd. 11/2, p. 125.
8 E. Bamberger, *Ber. Dtsch. Chem. Ges.*, 1894, **27**, 359.
9 E. D. Hughes and G. T. Jones, *J. Chem. Soc.*, 1950, 2678.
10 H. Leymann, *Ber. Dtsch. Chem. Ges.*, 1882, **15**, 1235.
11 E. Bamberger, *Ber. Dtsch. Chem. Ges.*, 1900, **33**, 111.
12 O. Fischer, *Ber. Dtsch. Chem. Ges.*, 1892, **25**, 2841.
13 O. Fischer and M. Busch, *Ber. Dtsch. Chem. Ges.*, 1891, **24**, 2682.
14 J. J. Blanksma, *Recl. Trav. Chim. Pays-Bas*, 1902, **21**, 272.
15 E. Nötling and Th. Stricker, *Ber. Dtsch. Chem. Ges.*, 1886, **19**, 548.
16 F. Bell, J. Kenyon and P. H. Robins, *J. Chem. Soc.*, 1926, 1242.
17 C. H. Bamford, *J. Chem. Soc.*, 1939, 12.
18 G. Geiger and J. R. Huber, *Helv. Chim. Acta*, 1981, **64**, 989.
19 C. J. Micheida and T. Rydstrom, in *N–Nitroso Compounds: Occurrence, Biol. Eff. Relevance Hum. Cancer*, vol. 57, IARC Sci. Publ., Lyon, 1984, pp. 365–369.
20 E. M. Burgess and J. M. Lavanish, *Tetrahedron Lett.*, 1964, 1221.
21 N. Fiz, J. L. Usero and J. Casado, *Int. J. Chem. Kinet.*, 1993, **25**, 341.

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