

1-azirine intermediate in this reaction, using the cyclone 6 in refluxing chloroform or benzene. In fact the reaction path of **13** → **14** + **15** was completely unaltered by addition of 6.

It is noteworthy that the *in situ* generation of the azirines lacking a 2 substituent, from the terminal vinyl azides **5a** and **5b**, produces species with greatly enhanced dienophilic properties when compared to those possessing a 2 substituent.^{2,3} Details of this enhanced property will shortly be revealed.

Experimental Section¹⁰

Reaction of Cyclone 6 and 1-Azido-2-phenylethylene (5a).—The vinyl azide (0.8 g, 5.5 mmol) and the dienone (1.4 g, 5.5 mmol) were heated under reflux in toluene (25 ml) for 2 hr. Removal of the solvent yielded an orange oil, which rapidly solidified (1.30 g, 69%). Recrystallization from ethanol gave colorless needles of **2,5-dimethyl-3,4,7-triphenyl-3H-azepine (7a)**: mp 108°; τ (CDCl₃) 7.91 (s, 3 H), 7.72 (s, 3 H), 4.59 (s, 1 H), 3.87 (s, 1 H), 2.94–2.45 (m, 15 H); mass spectrum *m/e* (rel intensity) 350 (25), 349 (100), 348 (52), 334 (10), 308 (20), 293 (12), 272 (11), 246 (8), 231 (8), 229 (9), 215 (34), 115 (7) 91 (13).

Anal. Calcd for C₂₅H₂₃N: C, 89.4; H, 6.6. Found: C, 89.1; H, 6.8.

Reaction of Cyclone 6 and 1-Azido-2-tert-butylethylene (5b).—The vinyl azide (1.25 g, 10 mmol) and the dienone (2.60 g, 10 mmol) were heated under reflux in toluene (25 ml) for 5 hr. Removal of the solvent afforded an orange oil. Chromatography using dichloromethane-pentane (1:4) eluent afforded a pale yellow oil which solidified (2.35 g, 71%) on trituration. Recrystallization from ethanol afforded large, pale yellow crystals of **7-tert-butyl-2,5-dimethyl-3,4-diphenyl-3H-azepine (7b)**: mp 97°; nmr (CDCl₃) τ 9.14 (s, 9 H), 7.97 (s, 3 H), 7.72 (s, 3 H), 4.74 (s, 1 H), 4.20 (s, 1 H), 2.89 (s, 5 H), 2.65 (s, 5 H); mass spectrum *m/e* (rel intensity) 330 (25), 329 (100), 328 (25), 314 (55), 287 (27), 273 (50), 258 (77), 257 (58), 246 (30), 231 (25), 215 (20), 91 (17).

Anal. Calcd for C₂₄H₂₇N: C, 87.5; H, 8.3. Found: C, 87.8; H, 8.2.

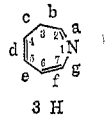
Reaction of Cyclone 6 and 4-Azido-1,2-dihydronaphthalene (9).—The vinyl azide (1.71 g, 10 mmol) and the dienone (2.60 g, 10 mmol) were heated under reflux in toluene (25 ml) for 8 hr. Removal of the solvent and chromatography of the residue (dichloromethane) afforded **2,5-dimethyl-3,4-diphenyl-1,2-dihydronaphtho[3,4-f]-3H-azepine (12)**¹¹ (1.2 g, 32%) as golden plates from ethanol: mp 163°; nmr (CDCl₃) τ 8.04 (s, 3 H), 7.68 (s, 3 H), 8.35–6.55 (m, 4 H), 4.92 (s, 1 H), 3.15–2.56 (m, 14 H); mass spectrum *m/e* (rel intensity) 376 (32), 375 (100), 374 (44), 360 (12), 284 (60), 178 (10), 115 (7), 91 (17).

Anal. Calcd for C₂₈H₂₅N: C, 89.6; H, 6.7. Found: C, 89.8; H, 6.8.

Ethyl acetate-dichloromethane (1:19) eluted unreacted dienone (1.5 g, 58%). Use of a threefold excess of the vinyl azide gave **12** in 45% yield.

(10) All melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 457 spectrophotometer as KBr pellets. Nmr spectra were recorded with a Varian A-60A spectrometer using tetramethylsilane as an internal standard. The elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(11) Since the numbering of the azepine system is not completely systematic,¹² the lettering system adopted in this paper follows the numbers shown.



(12) L. A. Paquette in "Nonbenzenoid Aromatics," Vol. 1, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1969, p 249.

Registry No.—**5a**, 16722-99-9; **5b**, 40168-86-3; **6**, 26307-17-5; **7a**, 40168-88-5; **7b**, 40168-89-6; **9**, 16719-58-7; **12**, 40168-91-0.

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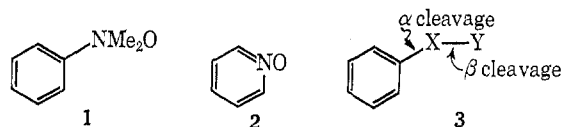
Nitrogen Photochemistry. XIII. The Deoxygenation of Aniline and Naphthylamine *N*-Oxides

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We are studying various aniline and naphthylamine *N*-oxide derivatives as potential sources of atomic oxygen in the liquid phase since these *N*-oxides are expected not to rearrange in contrast to the well-studied *N*-oxides where the nitrogen is part of the aromatic ring. It is important that a distinction be made between the amine oxide photochemistry described in this article, *e.g.*, of **1**, and that of the aromatic *N*-oxides such as **2**. Only the latter has been extensively studied. The former has a benzene chromophore and the latter a pyridine chromophore. *N*-Oxides such as **2** rearrange and undergo α cleavages on irradiation,¹⁻⁵ whereas we now wish to demonstrate that the excited state of **1** leads almost exclusively to β cleavages and, importantly, with little rearrangement. The nomenclature is that defined on structure **3**.⁶ This article contains the descriptive work on aniline and naphthylamine *N*-oxide photochemistry.



Previously Jerina, Boyd, and Daly⁷ irradiated *N,N*-dimethylaniline *N*-oxide to gain deuterium retention data during the photochemical hydroxylation of 4-deuterioanisole and demonstrated that an undefined oxygen species was transferred to anisole forming *p*-hydroxyanisole. No other products were reported.

With *N,N*-dimethylaniline *N*-oxide, there are two chromophores in the near-uv spectrum. Its uv spectrum is recorded in Figure 1 together with those of benzene and aniline for reference purposes. The 260-nm chromophore of *N,N*-dimethylaniline *N*-oxide is essentially the π, π^* transition of benzene with slight modification for the functional group. This is expected because the parent amine *N*-oxide chromophore,

- (1) J. Streith, B. Danner, and C. Sigwalt, *Chem. Commun.*, 979 (1967).
- (2) T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2213 (1970).
- (3) H. Igeta, T. Tsuchiya, M. Yamada, and H. Arai, *Chem. Pharm. Bull.*, **16**, 767 (1968).
- (4) T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2747 (1969).
- (5) M. Ogata and K. Kano, *Chem. Commun.*, 1176 (1967).
- (6) V. I. Stenberg and D. R. Dutton, *Tetrahedron*, **28**, 4635 (1972). This article is regarded as part XII of this series.
- (7) D. M. Jerina, D. R. Boyd, and J. W. Daly, *Tetrahedron Lett.*, 457 (1970).

TABLE I
 PRODUCTS FROM THE IRRADIATION OF AMINE *N*-OXIDES

| Amine oxide | Conditions | Products ^a |
|---|---|---|
| (CH ₃) ₃ NO · 2H ₂ O | Solid, quartz CH ₃ OH, quartz | (CH ₃) ₃ N (9%); (CH ₃) ₂ NH (2%); H ₂ O; ^c (CH ₃) ₂ NCHO (CH ₃) ₃ N (30%); H ₂ O ^c (83%) |
| (C ₂ H ₅) ₃ NO · 2H ₂ O | Solid, quartz | (C ₂ H ₅) ₃ N (major); (C ₂ H ₅) ₂ NH (minor); CH ₃ CHO (trace) |
| C ₆ H ₅ N(CH ₃) ₂ O · H ₂ O | CH ₃ OH, Vycor | C ₆ H ₅ N(CH ₃) ₂ (55%); C ₆ H ₅ NH(CH ₃) ^b (31%); 2-(OH)C ₆ H ₄ N(CH ₃) ₂ (5%); H ₂ O ^c (73%) |
| 2-C ₁₀ H ₇ N(CH ₃) ₂ O | CH ₃ CHOHCH ₃ , Pyrex | <i>N,N</i> -Dimethyl-2-naphthylamine; <i>N</i> -methyl-2-naphthylamine |
| 1-C ₁₀ H ₇ N(CH ₃) ₂ O | CH ₃ CHOHCH ₃ , Pyrex | <i>N,N</i> -Dimethyl-1-naphthylamine (57%); <i>N</i> -methyl-1-naphthylamine ^b (23%); H ₂ O ^c (58%); CH ₃ COCH ₃ (18%) |

^a The percentage yields are based on converted starting material. ^b Both the monomethyl- and dimethylamines are primary products since irradiation of either *N,N*-dimethylaniline or *N,N*-dimethyl-1-naphthylamine under similar conditions does not give the corresponding monomethylamines. ^c Water was measured quantitatively by injecting an aliquot of the reaction solutions directly into the glpc (Porapak Q column).

as illustrated in the uv spectrum of trimethylamine *N*-oxide in Figure 1, is virtually transparent above 250 nm. With a Vycor filter, incident light, which is directed at the S₀ → S₁ transition, causes efficient deoxygenation in methanol, Table I. Demethylation also occurs to a significant extent to give monomethylaniline. Altogether, 86% of deoxygenated products are produced together with 73% water. A small yield of the rearrangement product, 2-hydroxy-*N,N*-dimethylaniline, is observed. In the better hydrogen-donor solvent, 2-propanol,⁸ little change of products is noted other than the formation of acetone.

The *N,N*-dimethylnaphthylamine *N*-oxides have uv spectra similar in most characteristics to naphthalene rather than parent amine spectra, Figure 1. Their relatively long wavelength absorption bands conveniently allow excitation of S₀ → S₁ transition in Pyrex glassware. The extinction coefficient at 300 nm of the α isomer is larger than that of the β which makes it the more desirable. The irradiation of *N,N*-dimethyl-1-naphthylamine *N*-oxide in several solvents provides 80–94% total yields of the two amines *N,N*-dimethyl-1-naphthylamine and *N*-methyl-1-naphthylamine, Table I. Again the expelled oxygen atom could only be found in the form of water.

The irradiation of trialkylamine *N*-oxides shows the consequences of n, σ^* excitation of the amine oxide functional group. Trimethyl- and triethylamine *N*-oxides when irradiated as solids in thin films provide the corresponding parent amines as the major products. Minor amounts of the secondary amines are also formed, and dimethylformamide was identified as a secondary product from the irradiation of solid trimethylamine *N*-oxide dihydrate. In methanol solution, the irradiation of trimethylamine *N*-oxide dihydrate produces trimethylamine, dimethylamine, and water. However, the aliphatic *N*-oxides are undesirable as potential sources of atomic oxygen since they have virtually transparent near-uv absorption spectra, Figure 1, and they are very polar compounds which are nearly insoluble in most organic solvents.

Experimental Section

Reagents.—Trimethylamine *N*-oxide was purchased from Chemical Procedurement Laboratories, College Point, N. Y. Triethylamine *N*-oxide,⁹ *N,N*-dimethylaniline *N*-oxide,¹⁰ and 2-hydroxy-*N,N*-dimethylaniline¹¹ were prepared by known pro-

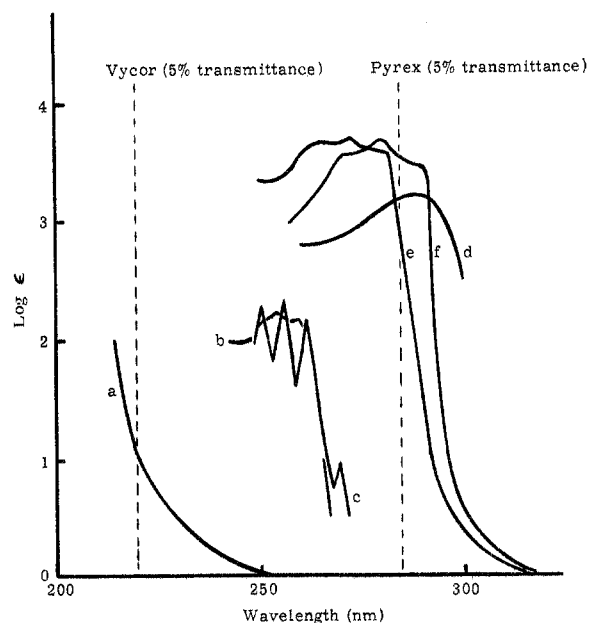


Figure 1.—Ultraviolet spectra of trimethylamine *N*-oxide (a) and *N,N*-dimethylaniline *N*-oxide (b) in 2-propanol; benzene (c) and aniline (d) in isoctane; and *N,N*-dimethyl-2-naphthylamine (e) and *N,N*-dimethyl-1-naphthylamine (f) in 2-propanol.

cedures. The amines were methylated using either dimethyl sulfate¹² or trimethyl phosphate.¹³ Methanol was purified by distillation from magnesium. 2-Propanol was treated similarly and distilled a second time after a 2-hr reflux with NaBH₄.

Irradiation of Aniline and Naphthylamine *N*-Oxides.—The amine oxide was dissolved in alcohol (typically 0.1 g of oxide in 25 ml). The solution was vacuum degassed and irradiated in a Rayonet photochemical reactor. The 253.7-nm lamps were used for the aniline oxides and the 300-nm ones for the naphthylamine oxides. In 3–6 hr, 50–75% of the starting material reacted. Afterward the solvent was removed by distillation, the products were separated from the amine oxide by washing the residue with ether, and the ether extract was analyzed by glpc using a Carbowax 20M column (10 ft × 0.25 in. on Chromosorb W, 150–230°). Water was determined by direct gspe analysis of the irradiation solution before work-up (10 ft × 0.25 in. Porapak Q, 125°).

Besides their glpc retention times, *N,N*-dimethylaniline, *N*-methylaniline, *o*-hydroxy-*N,N*-dimethylaniline, *N,N*-dimethyl-1-naphthylamine, and *N*-methyl-1-naphthylamine were identified by ir and nmr spectroscopy; *N,N*-dimethyl-2-naphthylamine was identified by its nmr spectrum and mp 40–41°, mmp 40.5–42.5° (lit.¹⁴ 46–47°), and *N*-methyl-2-naphthylamine by its nmr spectrum.

General Procedure for the Preparation of *N,N*-Dimethyl-1-naphthylamine *N*-Oxide and *N,N*-Dimethyl-2-naphthylamine

(8) R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3480 (1966).

(9) W. R. Dunstan and E. Goulding, *J. Chem. Soc.*, **75**, 1004 (1899).

(10) N. G. Chernova and A. S. Khokhlov, *Zh. Obshch. Khim.*, **30**, 1281 (1960); *Chem. Abstr.*, **55**, 551e (1961).

(11) E. Boyland, D. Manson, and P. Sims, *J. Chem. Soc.*, 3623 (1953).

(12) H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1500 (1936).

(13) J. H. Billman, A. Radike, and B. W. Mundy, *J. Amer. Chem. Soc.*, **64**, 2977 (1942).

(14) "Dictionary of Organic Compounds," 4th ed, Oxford University Press, London, 1965, p 1185.

Oxide.—The method of Chernova and Khokhlov¹⁰ was not successful for the preparation of these oxides from the amines in our laboratory. Oxidation of the amines was accomplished by peroxybenzoic acid.¹⁵ A stoichiometric quantity of peroxybenzoic acid in CHCl_3 (100 ml of 0.05 *M*) was added dropwise with stirring to a solution of the amine in CHCl_3 (0.86 g in 50 ml) at -35° . After 2 hr the solution was warmed to room temperature. After all the peracid had reacted, the CHCl_3 was removed under vacuum and the residue washed with ether. An equivalent of 6 *M* HCl was then added to give the amine oxide hydrochloride which could be recrystallized from acetone. The hydrochloride of *N,N*-dimethyl-1-naphthylamine *N*-oxide melts at 170° dec and *N,N*-dimethyl-2-naphthylamine *N*-oxide hydrochloride melts at $146\text{--}148^\circ$ dec with nmr signals (acetone- d_6 - D_2O , 5:1), at δ 9.5–7 (m, 7) and 3.76 [s, $\text{NO}(\text{CH}_3)_2$, 6]. The amine oxide was obtained using Ag_2O and recrystallized from acetone. *N,N*-Dimethyl-2-naphthylamine *N*-oxide had mp $152\text{--}155^\circ$ dec and nmr (acetone- d_6 - D_2O , 5:1) δ 9–7 (m, 7) and 3.93 [s, $\text{NO}(\text{CH}_3)_2$, 6]. *N,N*-Dimethyl-1-naphthylamine *N*-oxide rapidly hydrated and gave a variable melting point.

Irradiation of Trimethyl- and Triethylamine *N*-Oxides.—The amine oxide (1 g) was dissolved in methanol and the solvent allowed to evaporate in a rotating, cylindrical vessel leaving a thin film of the oxide. This solid was irradiated in a vacuum with a medium-pressure, mercury-arc lamp in a quartz immersion well until all the amine oxide had disappeared from the surface (1–3 hr). The products, in a cold trap attached the vessel, were analyzed by gpc using a Poropak Q column (10 ft \times 0.25 in., 60–120 $^\circ$).

The irradiation solution of trimethylamine *N*-oxide was degassed and irradiated with the medium-pressure lamp in quartz. The products were separated from unreacted amine oxide by bulb-to-bulb distillation and analyzed by glpc. Besides their glpc retention times, trimethylamine was identified by its nmr spectrum, dimethylamine by mp $167\text{--}169^\circ$, mmp $166\text{--}168^\circ$ (lit.¹⁶ mp 171°) of its hydrochloride salt, water by its melting point and color change with anhydrous copper sulfate, and dimethylformamide by its ir spectrum.

Registry No.—Trimethylamine *N*-oxide, 1184-78-7; triethylamine *N*-oxide, 2687-45-8; *N,N*-dimethylaniline *N*-oxide, 874-52-2; 2-hydroxy-*N,N*-dimethylaniline, 3743-22-4; 1-*N,N*-dimethylnaphthylamine *N*-oxide, 830-70-6; 2-*N,N*-dimethylnaphthylamine *N*-oxide, 34418-90-1; *N,N*-dimethyl-1-naphthylamine *N*-oxide hydrochloride, 39717-26-5; *N,N*-dimethyl-2-naphthylamine *N*-oxide hydrochloride, 39717-27-6; peroxybenzoic acid, 93-59-4.

Acknowledgments.—This investigation was supported by a Public Health Service Research Career Development Award (1-K4-GM 9888: V.I.S.) from the National Institute of General Medical Sciences and a NDEA traineeship (J. E. S.).

(15) J. R. Moyer and N. C. Manley, *J. Org. Chem.*, **29**, 2099 (1964).

(16) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 52nd ed. Chemical Rubber Publishing Co., Cleveland, Ohio, 1971–1972, p C101.

Triangular Kinetic Schemes. An Elaboration

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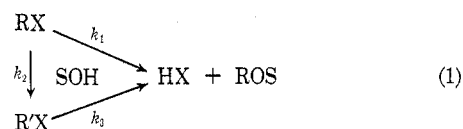
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We recently reported¹ the derivation of the analytical equations governing triangular kinetic schemes of the

(1) (a) R. S. Macomber, *J. Org. Chem.*, **36**, 2182 (1971). (b) For a description of similar schemes, including those with reversible reactions, see R. A. Alberty and W. G. Miller, *J. Chem. Phys.*, **26**, 1231 (1957).

type particularly common to solvolytic processes. Judging by the response to this paper, some amplification of the assertions given there is in order.



The exact solution^{1a} (in closed form) of the differential equations appropriate to eq 1 provides the relationship²

$$[\text{HX}]_t = [\text{RX}]_0 \left[1 + \frac{(k_3 - k_1)e^{-(k_1 + k_2)t} - k_2e^{-k_3t}}{k_1 + k_2 - k_3} \right] \quad (2)$$

The instantaneous "first-order" titrimetric rate constant (k_{inst}) can be obtained as follows.

$$\ln \left(\frac{[\text{HX}]_\infty}{[\text{HX}]_\infty - [\text{HX}]_t} \right) = \ln \left[\frac{k_1 + k_2 - k_3}{k_2e^{-k_3t} + (k_1 - k_3)e^{-(k_1 + k_2)t}} \right] \quad (3)$$

$$k_{\text{inst}} = \frac{d}{dt} \ln \left(\frac{[\text{HX}]_\infty}{[\text{HX}]_\infty - [\text{HX}]_t} \right) \quad (4)$$

$$= \frac{d}{dt} \ln \left[\frac{k_1 + k_2 - k_3}{k_2e^{-k_3t} + (k_1 - k_3)e^{-(k_1 + k_2)t}} \right] \quad (5)$$

Extraction of the derivative, then multiplication by $\exp(k_3t)$, leads to

$$k_{\text{inst}} = \left[\frac{k_2k_3 + (k_1 - k_3)(k_1 + k_2)e^{Kt}}{k_2 + (k_1 - k_3)e^{Kt}} \right] \equiv \frac{N}{D} \quad (6)$$

where $K = k_3 - k_1 - k_2$

The proof that the sense of curvature of "first-order" plots of titrimetric data ($\ln [\text{HX}]_\infty / [\text{HX}]_\infty - [\text{HX}]_t$ vs. time) depends only on the relative magnitudes of k_1 and k_3 can be seen by examining the first derivative of k_{inst}

$$\text{curvature} = \frac{dk_{\text{inst}}}{dt} = \frac{D \frac{dN}{dt} - N \frac{dD}{dt}}{D^2} \quad (7)$$

The sign of curvature is a function of the numerator in eq 7, which expands to

$$\begin{aligned} \text{sign} &= [k_2 + (k_1 - k_3)e^{Kt}] [(k_1 - k_3)(k_1 + k_2)Ke^{Kt}] - \\ &\quad [k_2k_3 + (k_1 - k_3)(k_1 + k_2)e^{Kt}] [(k_1 - k_3)Ke^{Kt}] \\ &= k_2(k_1 + k_2 - k_3)K(k_1 - k_3)e^{Kt} \\ &= (k_3 - k_1)K^2k_2e^{Kt} \end{aligned} \quad (8)$$

Since the last three terms are strictly positive, the nature of curvature is determined by $(k_3 - k_1)$; if $k_3 > k_1$, the plot will be concave upward and k_{inst} will increase with time, while if $k_3 < k_1$, the curve will exhibit negative curvature and k_{inst} will fall off with time. Clearly, the magnitude of curvature (which can be calculated with eq 7) will depend on the relative magnitudes of all three rate constants. If $k_1 = k_3$, the effect of the k_2 pathway will be titrimetrically unobservable.^{1a}

It has on occasion been incorrectly stated that extrapolation of k_{inst} (as defined by eq 4) to $t = 0$ provides a value of $(k_1 + k_2)$, even though Winstein and co-workers have used such graphical extrapolations to ob-

(2) For the relevant equations when $k_3 = k_1 + k_2$, see footnote 9 of ref 1a.