The combined organic layers were washed with water (2 × 50 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The product was recrystallized from 1:1 CH_2Cl_2/hexane to yield 576 mg (95%) of **13** as pale yellow crystals: mp 177–179 °C dec.

Aceanthrylene (3). To a slurry of 1-aceanthrenol (**13**) (380 mg, 1.72 mmol) in 50 mL of dry toluene was added Al_2O_3 (5 g, neutral, dried 8 h at 180 °C/0.1 mm). This solution was refluxed for 10 min, cooled to room temperature, and filtered. The Al_2O_3 was washed in toluene (2 × 20 mL), and the combined organic layers were concentrated to yield 317 mg (93%) of **3** as bright red crystals, mp 103–104 °C (lit.[27] mp 95.0–96.0 °C, lit.[28] mp 103–104 °C, lit.[29] mp 94–95 °C).

NMR parameters of acephenanthrylene (**2**) in THF-d_8. δ ^1H: 8.80 (d, J = 8.0 Hz, 1 H); 8.53 (dd, J_1 = 6.8 Hz, J_2 = 1.9 Hz, 1 H); 8.11 (s, H_4); 8.10 (dd, J_1 = 7.4 Hz, J_2 = 1.5 Hz, 1 H); 7.70 (m, 4 H); 7.28 (d, J = 5.2 Hz, H_2); 7.17 (d, J = 5.2 Hz, H_1). δ ^{13}C: 139.4, 138.0, 134.0, 131.7, 130.8, 130.2, 128.5, 127.9, 127.5, 127.0, 126.2, 125.7, 125.6, 122.8, 121.9, 121.0.

NMR parameters of aceanthrylene (**3**) in THF-d_8. δ ^1H: 8.58 (s, H_{10}); 8.40 (d, J = 8.4, 1 H); 8.20 (d, J = 8.5 Hz, 1 H); 8.08 (d, J = 7.4 Hz, 1 H); 7.88 (d, J = 6.8 Hz, 1 H); 7.72 (d, J = 5.2 Hz, H_2); 7.65 (m, 3 H); 7.54 (dd, J_1 = 8.6 Hz; J_2 = 1.4 Hz, 1 H); 7.19 (d, J = 5.1 Hz, H_1). δ ^{13}C: 139.9, 134.9, 133.8, 129.6, 128.7, 127.3, 127.3, 127.0, 127.0, 126.8, 126.7, 126.1, 126.0, 124.9, 124.0, 123.4.

Acknowledgment. We gratefully acknowledge financial support from the United States National Science Foundation, the National Institutes of Health (L.T.S.), and the U.S. Israel Binational Science Foundation (M.R. and L.T.S.).

Registry No. 2, 201-06-9; 2^{2-}, 109669-63-8; $2^{2-}/2Na^+$, 109669-59-2; $2^{2-}/2Li^+$, 109669-61-6; 3, 202-03-9; 3^{2-}, 109669-62-7; $3^{2-}/2Li^+$, 109686-30-8; $4^{1-}/Li^+$, 109686-31-9.

Supplementary Material Available: A more detailed report that includes spectroscopic data and elemental analyses for the synthetic compounds as well as acquisitions and processing parameters of the 2D NMR experiments and figures of the ^1H NMR 2D COSY spectra of **2** and **3**, the T_1 inversion–recovery spectrum of 2^{2-}, and the ^1H NMR 2D J-resolved spectra of 3^{2-} and 4^- (38 pages). Ordering information is given on any current masthead page.

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Photosubstitution of 1-Methoxy-4-nitronaphthalene with Amine Nucleophiles: Dual Pathways[†]

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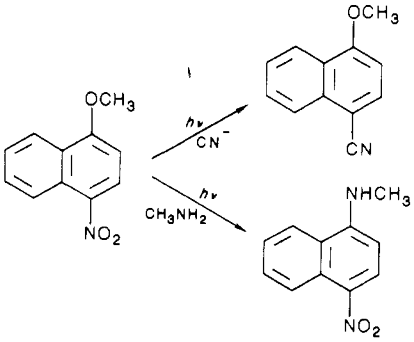
Received March 16, 1987

The photosubstitution of 1-methoxy-4-nitronaphthalene (MNN) with amines has been investigated by a combination of continuous and time-resolved experiments. Primary amines cause replacement of the nitro group, while secondary amines displace the methoxy substituent. Both reactions involve attack of the amine upon the triplet excited state of MNN. Spectroscopic evidence for the radical anion $MNN^{\bullet-}$ has been obtained; the yield of this species depends upon the structure of the amine in the order $RNH_2 < R_2NH < R_3N$. It is concluded that the reaction with secondary amines is an electron-transfer process leading to $MNN^{\bullet-}$, but that the reaction with primary amines is most probably an example of an S_N2 Ar* process. The results for MNN and related compounds are discussed in the context of the orientation rules proposed by Mutai et al.

Nucleophilic photochemical substitutions have been a subject of intense research activity since their first discovery in 1956. The scope of these reactions,[1] empirical rules for product predictions,[2] and possible mechanisms[3] have all been reviewed. Of considerable importance in developing our ideas about the scope and mechanisms of these photosubstitutions have been reactions carried out on methoxy nitro compounds as substrates, notably with 3- and 4-nitroanisoles and 4-nitroveratrole.

The subject of experimentation in the present work is the nucleophilic photosubstitution of 1-methoxy-4-nitronaphthalene (MNN). Letsinger and Hautala[4] found that when MNN was irradiated with aqueous cyanide ion the nitro group was displaced, while Havinga and Cornelisse[1] reported that the corresponding reaction with methylamine led to the replacement of the methoxy substituent (Scheme I). This example was used by Havinga and Cornelisse as the basis of the empirical "merging resonance stabilization" rule for product prediction.[2] Cyanation was interpreted as leading to the replacement of one electron-attracting substituent (NO_2) by another (CN), while the reaction with

Scheme I



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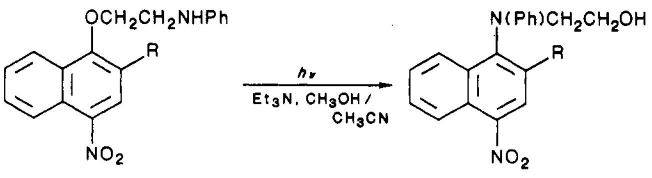
Scheme II



1, R = H or OCH$_3$

methylamine caused the replacement of the electron-donating CH_3O by the similarly behaved CH_3NH group.

Other reported photosubstitutions on MNN include the replacement of the nitro group by hydrogen using sodium borohydride[5] and the replacement of the nitro substituent by methoxide ion,[6] the latter in apparent violation of the merging resonance stabilization rule.

Very recently, Mutai and Nakagaki[7] have studied the intramolecular substitutions of the MNN analogues shown in Scheme II. For R = H or OCH_3, the intramolecular reaction involves replacement of the alkoxy substituent by an amine function and is therefore consistent with the displacement of methoxide by methylamine previously referred to.[2]

Van Riel et al.[8] have pointed out that there are three kinds of pathways leading to nucleophilic photosubstitution. These are a direct displacement (S_N2 Ar*), electron transfer from the "nucleophile" to the aromatic substrate, and electron transfer from the aromatic component to an acceptor, followed by attack of the nucleophile on the aromatic cation radical.

Our purpose in studying the photoreactions of MNN with nucleophiles was to discover the mechanistic basis for the merging resonance stabilization rule. Mutai and his collaborators have recently shown that in several systems[9] the course of nucleophilic photosubstitution may be predicted from an examination of the frontier molecular orbitals of the aromatic substrate. They view S_N2 Ar* reactions as involving principally an interaction between the nucleophile HOMO and the aromatic substrate's HOMO; the nucleophile attacks the position(s) where the MO coefficient of the aromatic substrate's HOMO is high. An alternative interaction is between the LUMO of the aromatic substrate and the HOMO of the nucleophile; if an electron is transferred from the "nucleophile" to the aromatic substrate, the nucleophile radical cation will then attack at the position where the aromatic substrate has the highest LUMO coefficient.

Results and Discussion

Characterization of Triplet 1-Methoxy-4-nitronaphthalene. It will be convenient to discuss first the characterization of the excited state. Aromatic nitro compounds usually undergo intersystem crossing $S_1 \rightarrow T_1$ with high efficiency; consistent with this generalization, MNN shows no fluorescence. Time-resolved nanosecond flash photolysis experiments allowed us to observe a transient species that was identified as the triplet of MNN as follows.

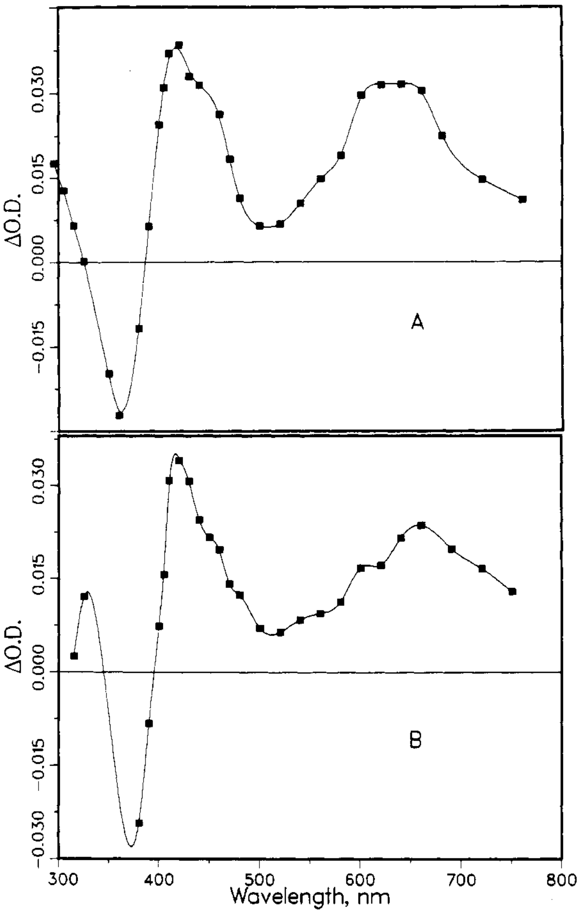


Figure 1. Transient absorption spectrum produced by 337-nm excitation of 0.3 mM MNN in acetonitrile (A) and 3:1 acetonitrile/water (B).

Table I. Quenching of Triplet MNN at 293 K

quencher	solvent	k_q (M^{-1} s^{-1})
diethylamine	CH_3CN	$(1.6 \pm 0.1) \times 10^9$
isobutylamine	CH_3CN	$(8.9 \pm 1.0) \times 10^7$
morpholine	CH_3CN	$(1.3 \pm 0.1) \times 10^9$
DABCO	CH_3CN	$(1.2 \pm 0.2) \times 10^{10}$
diethylamine	3:1 CH_3CN/H_2O	$(2.1 \pm 0.1) \times 10^8$
isobutylamine	3:1 CH_3CN/H_2O	$(5.5 \pm 0.4) \times 10^7$
DABCO	3:1 CH_3CN/H_2O	$(2.5 \pm 0.3) \times 10^9$
triethylamine	3:1 CH_3CN/H_2O	$(7.6 \pm 0.9) \times 10^8$
oxygen	CH_3CN	$\sim 2 \times 10^9$
1,3-cyclohexadiene	CH_3CN	$(4.5 \pm 0.2) \times 10^9$
diisopropylamine	3:1 CH_3CN/H_2O	$(5.2 \pm 0.5) \times 10^7$
triethylamine	1:1 CH_3CN/H_2O	$\sim 4 \times 10^8$
tert-butylamine	CH_3CN	$(4.7 \pm 0.3) \times 10^6$

Excitation of 0.3 mM 1-methoxy-4-nitronaphthalene in acetonitrile produced a transient with λ_{max} at 420 and ~630 nm (Figure 1A). The spectrum in Figure 1A also shows bleaching of the ground-state aromatic substrate between 325 and 390 nm. The transient is completely formed during the time of the laser pulse and has a lifetime of 4–5 μs, although the decays do not follow clean first-order kinetics. Kinetics monitored at either 420 or 630 nm give identical results, suggesting that both bands arise from the same transient species.

The above transient is efficiently quenched by oxygen and 1,3-cyclohexadiene, giving rate constants for quenching (k_q) of $\sim 2.0 \times 10^9$ and $(4.5 \pm 0.2) \times 10^9$ M^{-1} s^{-1} (errors as $\pm 2\sigma$ throughout), respectively, from the slope of a plot of k_{decay} vs. [quencher]. 1,3-Cyclohexadiene has a triplet energy of ca. 52 kcal/mol[10] and is expected to be a good quencher of MNN, which has a triplet energy of 55.3

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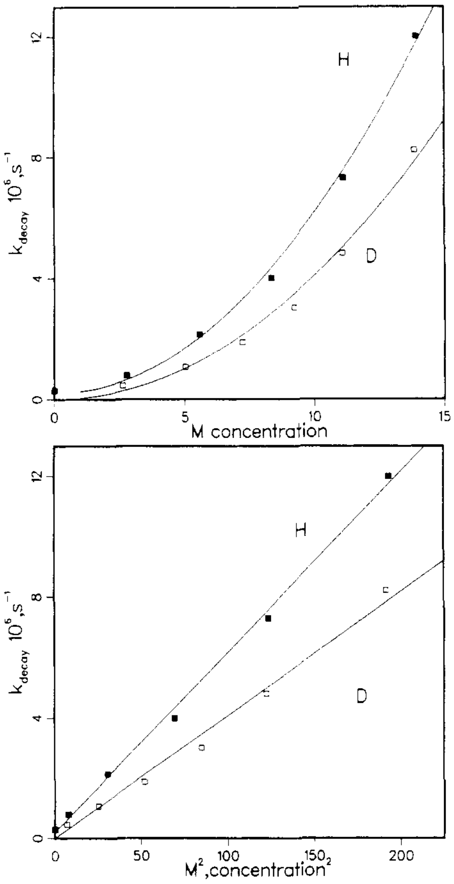


Figure 2. Decay of triplet MNN as a function of [water] (top) and [water]^2 (bottom) for H_2O (H) and D_2O (D).

kcal/mol (phosphorescence). The 420- and 630-nm bands are quenched at the same rate, confirming that a single transient is present (Table I). From the evidence just presented, it is reasonable to assign this transient to the triplet of MNN. Various naphthalene triplets absorb in the 420-nm region[11] and nitro-substituted naphthalenes have also been reported to show a second broad absorption band in the 600-nm region.[12]

Excitation of MNN in 3:1 acetonitrile/water yields a transient (Figure 1B) similar to that observed in neat acetonitrile, but with a much shorter lifetime (85 ns). The lifetime is further shortened to ~25 ns in a 1:1 mixture of the two solvents. Examination of the transient decay in acetonitrile as a function of the water concentration gives the curved plot shown in Figure 2a. Similar results were obtained by using D_2O although higher concentrations were required to obtain a similar decrease in the lifetime. Plots of k_{decay} against [water]^2 were linear for both H_2O and D_2O (Figure 2b). The lines in Figure 2b followed the mathematical relationship 1a and 1b where the values

$$\text{for } H_2O \qquad k_{obsd} = k_0 + k_{H_2O}[H_2O]^2 \qquad (1a)$$

$$\text{for } D_2O \qquad k_{obsd} = k_0 + k_{D_2O}[D_2O]^2 \qquad (1b)$$

of k_{H_2O} and k_{D_2O} are $(6.0 \pm 0.4) \times 10^4$ M^{-2} s^{-1} and $(4.1 \pm 0.4) \times 10^4$ M^{-2} s^{-1}, respectively.

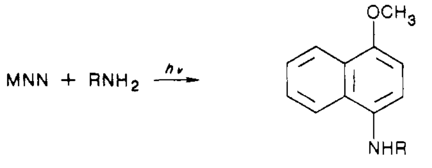
In methanol MNN gave a transient similar to that in acetonitrile with λ_{max} at 430 and ~650 nm and with a 310-ns lifetime. A 3:1 $MeOH/H_2O$ mixture decreased the lifetime to 55 ns. Similarly, in cyclohexane triplet MNN had λ_{max} at 400 and 610 nm and a lifetime of ca. 2.5 μs.

Attempts were made to discover the physical basis of the quenching by water. Because the second-order dependence of quenching of ^{3}MNN upon $[H_2O]$ was reminiscent of the autoprotolysis of water, experiments were carried out at constant $[H_2O]$ with the addition of acetic acid to the solvent. In neat acetonitrile a quenching rate constant of $(1.2 \pm 0.1) \times 10^6$ M^{-1} s^{-1} was obtained. The short triplet lifetime for MNN in 3:1 acetonitrile/water prevented the accurate determination of k_q for acetic acid in this solvent. Thus the quenching mechanism does not involve protonation of the aromatic substrate. Quenching is accompanied by a deuterium isotope effect but the value of k^H/k^D varies with $[H_2O]$ (k_{H_2O}/k_{D_2O} is constant but refers to the third-order rate constant).

Attack of CN^- on 1-Methoxy-4-nitronaphthalene. In confirmation of the results of Letsinger and Hautala,[4] we found that cyanide ion reacts cleanly with MNN in aqueous mixtures, affording 4-methoxy-1-naphthalenecarbonitrile in high yield. The nitro group is displaced as NO_2^-. The reported effect of water on the progress of the reaction, namely, that the chemical yield of nitrile increases at higher water content in the solvent but the quantum yield of MNN reaction drops as the water content is raised, is explicable in terms of the shorter lifetime of ^{3}MNN in the more highly aqueous mixtures. Although we did not reexamine it, we presume that the reported effects of water in the reaction of MNN with $NaBH_4$[5] can be explained similarly.

Addition of CN^- to MNN in 19:1 CH_3CN/H_2O under conditions of flash photolysis led to quenching of ^{3}MNN at $[CN^-]$ up to 0.04 M. The triplet lifetime decreases from 1.3 μs to 0.6 μs upon addition of 0.04 M KCN. At higher $[CN^-]$ no further decrease in the triplet lifetime was observed, a result possibly attributable to ion pairing complexation of free CN^- in the aqueous organic mixture. In methanol ^{3}MNN was quenched by CN^- with a rate constant of $(6.3 \pm 1.2) \times 10^6$ M^{-1} s^{-1}; there was no evidence for leveling off of the triplet lifetime at the highest concentration used (0.45 M).

Reactions of Amines with 1-Methoxy-4-nitronaphthalene. We were unable to reproduce the report[2] that photolysis of methylamine with MNN affords 1-(methylamino)-4-nitronaphthalene. In our hands the reaction led instead to displacement of the nitro group, with the production of 1-methoxy-4-(methylamino)naphthalene (eq 2), whether aqueous or organic solutions of methyl-



(2)

2, R = CH_3, C_3H_7, *iso*-C_4H_9

amine were used. The product, a liquid, was identified by ^{1}H NMR and by mass spectrometry, and the identity was confirmed by conversion to the *p*-nitrobenzamide. The alternative mode of substitution could only be observed when the reaction mixture was left for long periods in the dark; in other words, methoxy displacement appears to be a thermal rather than a photochemical process. Reactions analogous to that just described were also observed with propylamine and isobutylamine, but *tert*-butylamine was unreactive.

The photosubstitution took a different course with secondary amines and led to displacement at the methoxy substituent (eq 3). Control experiments were necessary to show that these were truly photochemical reactions,

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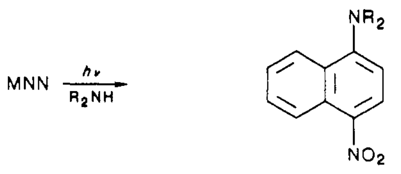

(3)

3, $R_2 = (CH_3)_2, (C_2H_5)_2, (CH_2)_4, (CH_2)_5$

because the same product can be formed thermally. Substitution predominated in 1:1 aqueous acetonitrile but photoreduction, affording 4-methoxy-1-naphthylamine, became more important in less aqueous media and only the naphthylamine was observed in dry acetonitrile. Photoreduction of aromatic nitro compounds by amines is well-known;[13] it involves a sequence of one electron transfers initiated by electron transfer from the amine to the nitro compound. When $CH_3CN–D_2O$ was used as the solvent for the MNN/Et_2NH reaction, no deuterium was incorporated into **3** (R = Et) or into the recovered MNN. The use of Et_2ND in pure acetonitrile did afford deuteriated 4-methoxy-1-naphthylamine, but the location of the deuterium was not determined.

When aniline was irradiated with MNN in either aerated $CH_3CN–H_2O$ or in cyclohexane, the only product that could be isolated was azobenzene, albeit in low yield. It is reasonable to suppose that the oxidation of aniline would be the result of electron transfer from aniline to ^{3}MNN, but the reaction was not studied in detail.

Consistent with the observations already cited showing that ^{3}MNN is formed rapidly after photoexcitation, conventional sensitization and quenching experiments showed that eq 2 (R = isobutyl) and 3 (R = ethyl) are triplet-state processes. In time-resolved experiments, triplet MNN was quenched by a variety of primary, secondary, and tertiary amines in both acetonitrile and 3:1 acetonitrile/water. The results have been included in Table I and indicate that for a given amine the quenching rate is from 2 to ~10 times faster in acetonitrile than in the mixed solvent. Furthermore, the rate constants increase in the order primary < secondary < tertiary. In all cases, identical results could be obtained by monitoring the triplet decay at either 420–430 nm or ~640 nm. However, the latter was more useful in that product fluorescence and interference from other transients in the presence of amines were minimal in this region. Representative plots for diethylamine (A) and isobutylamine (B) in 3:1 acetonitrile/water are shown in Figure 3.

Examination of the transient spectrum from MNN in the presence of amines reveals the growth of a new species with λ_{max} at 390–420 nm, depending on the solvent. Figure 4 shows an early and a late spectrum for MNN in the presence of 0.08 M diethylamine in 3:1 acetonitrile/water. The former is predominantly that of the triplet while the latter shows a single narrow band with λ_{max} at 395 nm. Figure 5 shows a comparison of the triplet decay at 630 nm and the growth of the new transient at 395 nm. The excellent agreement between the two indicates that the triplet is the precursor to the new transient. Similar results were also obtained for isobutylamine and triethylamine.

A possible candidate for the transient observed from solutions of MNN and amines is the radical anion formed by electron transfer from the amine (Am), i.e.

$$MNN + Am \xrightarrow{h\nu} MNN^{\bullet -} + Am^{\bullet +}$$

In order to test for this possibility the spectrum from MNN in the presence of 0.008 M diazabicyclo[2.2.2]octane (DABCO) in 3:1 CH_3CN/H_2O was examined (Figure 6). In addition to the 395-nm transient, there is an additional signal in the 420–520-nm region that is consistent with the known spectrum of the DABCO radical cation.[14]

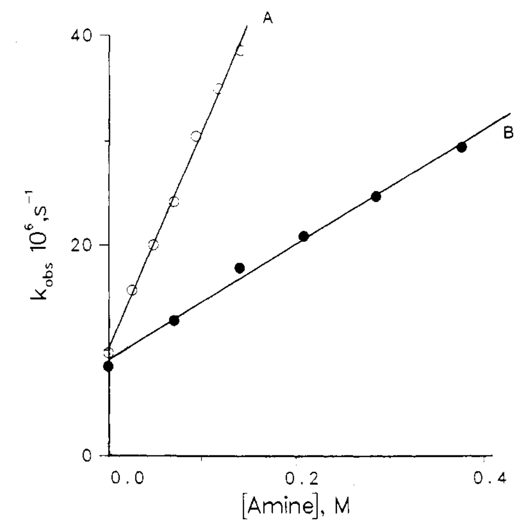

Figure 3. Plot of the rate of decay of triplet MNN as a function of amine concentration for 0.3 mM MNN in 3:1 acetonitrile/water for diethylamine (A) and isobutylamine (B).

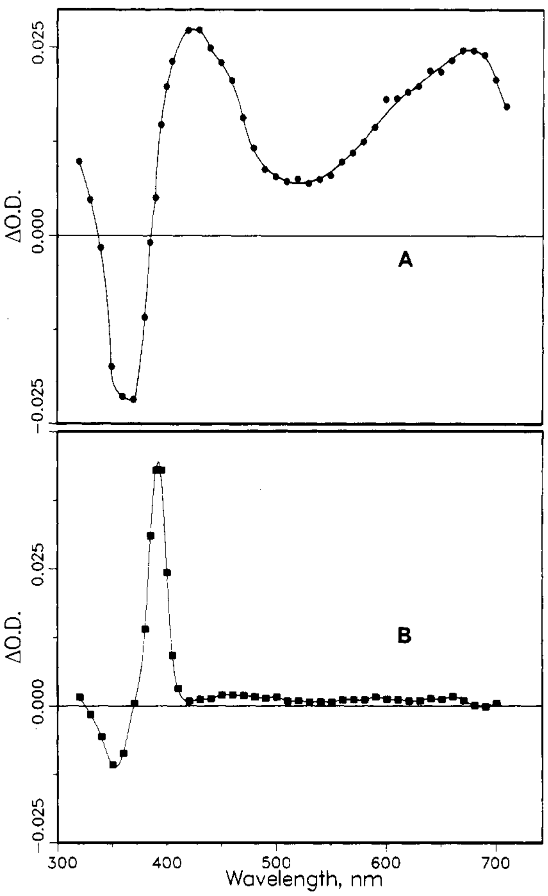

Figure 4. Early (A, 25 ns after laser) and late (B, 350 ns after laser) transient absorption spectra produced by 337-nm excitation of 0.3 mM MNN and 0.08 M diethylamine in 3:1 acetonitrile/water.

The effect of oxygen on the 395-nm transient was examined for a solution containing 0.3 mM MNN and 3 mM DABCO in acetonitrile. Under these conditions the triplet

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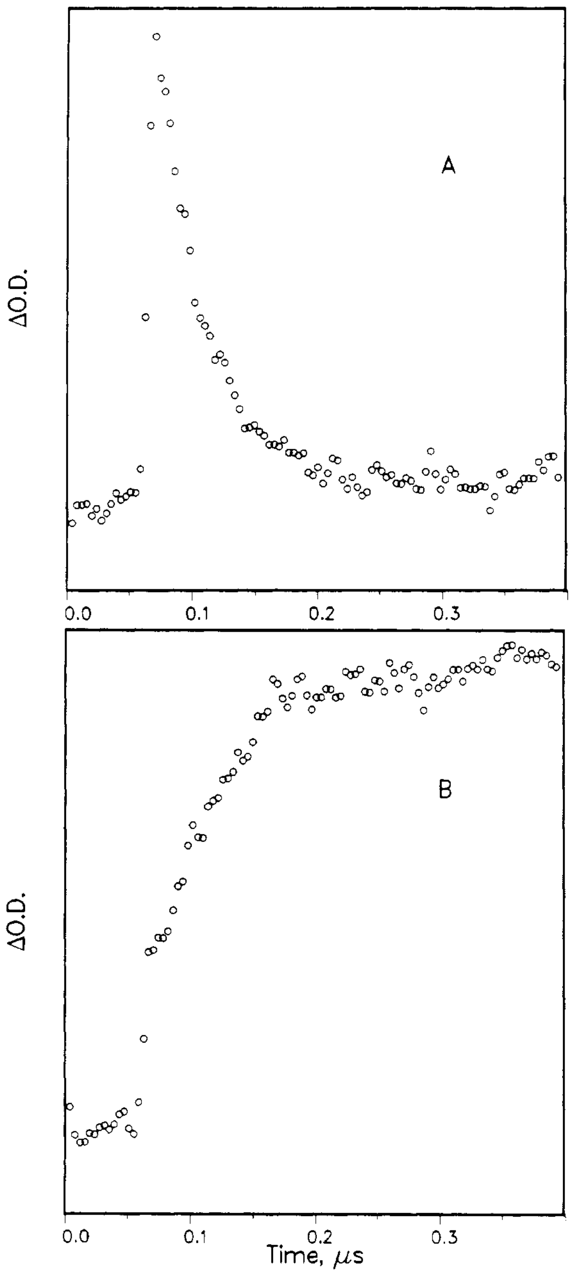

Figure 5. Transient decay traces monitored at 630 nm (A) and 395 nm (B) following 337-nm excitation of 0.3 mM MNN and 0.08 M diethylamine in 3:1 acetonitrile/water.

lifetime of MNN is ~25 ns. A rate constant for oxygen quenching of the radical anion of 2.2 × 10^9 M^{-1} s^{-1} was obtained. However, this number may have considerable error due to problems associated with measuring the decay of the transient assigned to the radical anion in the presence of contributions from the triplet and a long-lived residual absorption that is probably due to DABCO radical cation. It is nevertheless clear that scavenging of $MNN^{\bullet-}$ by oxygen is a very efficient process.

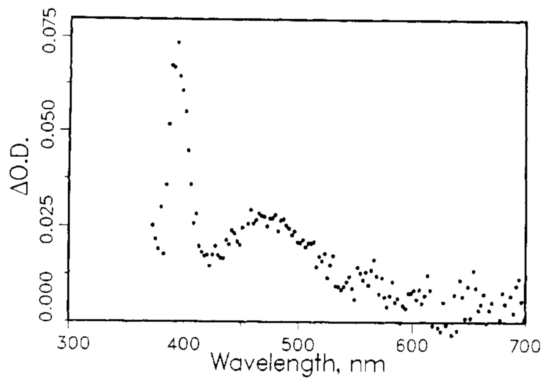

Figure 6. Transient absorption spectrum produced by 337-nm excitation of 0.3 mM MNN and 0.008 M DABCO in 3:1 acetonitrile/water.

The relative yields of the radical anion were determined for isobutylamine, diethylamine, and triethylamine by measuring the OD changes at 395 nm for a series of solutions whose amine concentrations were adjusted such that the decay rates of ^{3}MNN were equal (τ_T ~25 ns). However, this experiment was complicated by the fact that on long timescales the 395-nm transient in the presence of triethylamine showed an additional slow growth (τ_{growth} ~0.5 μs for [MNN] = 5.9 × 10^{-4} M) on top of the fast jump due to the reaction of ^{3}MNN with amine. This slow growth was attributed to formation of the radical anion via reaction of aminoalkyl radicals (from disproportionation of the amine radical cation and a neutral amine molecule[15]) with MNN, i.e.

$$\mathrm{Et_2{}^{+}\dot{N}CH_2CH_3 + Et_2NCH_2CH_3 \rightarrow Et_2N\dot{C}HCH_3 + Et_2\overset{+}{H}NCH_2CH_3}$$

$$\mathrm{Et_2N\dot{C}HCH_3 + MNN \rightarrow MNN^{\bullet-} + Et_2NCH{=}CH_2 + H^+} \quad (4)$$

Similar reactions have been shown to occur for a variety of aminoalkyl radicals with benzil.[16] This explanation is also supported by the fact that the kinetics for the slow growth of the 395-nm transient for constant amine concentration were dependent on the concentration of MNN, giving a rate constant of ~3 × 10^9 M^{-1} s^{-1} for reaction 4. The slow growth made only a small contribution (~5%) to the total 395-nm transient for diethylamine and was negligible for isobutylamine. The relative yields of radical anion were measured from the fast component of the 395-nm transient and were 1.0, 0.75, and 0.40 for triethylamine, diethylamine, and isobutylamine, respectively.

The assignment of the 395-nm transient to the radical anion of MNN was consistent with the results of experiments in which the transient species was quenched by the methyl viologen cation (MV^{2+}). A series of experiments was carried out in 3:1 acetonitrile/water, in the presence of 0.036 M triethylamine. These experiments were also complicated by the excellent electron-donor properties of α-aminoalkyl radicals, since both $MNN^{\bullet-}$ and α-aminoalkyl radicals can react with MV^{2+}, i.e.

$$\mathrm{MNN^{\bullet-} + MV^{2+} \xrightarrow{k_{MV}{}^{1}} MNN + MV^{\bullet+}}$$

$$\mathrm{Et_2N\dot{C}HCH_3 + MV^{2+} \xrightarrow{k_{MV}{}^{2}} Et_2NCH{=}CH_2 + MV^{\bullet+} + H^+}$$

Under our experimental conditions the triplet lifetime was 27 ns, and additions of moderate concentrations of MV^{2+} led to the readily detectable growth of the reduced form, $MV^{\bullet+}$ (λ_{max} 603 nm).[17] Analysis of the data gave a composite rate constant, k_{MV} = 5 × 10^9 M^{-1} s^{-1}; this is ~4 times higher than the value for $k_{MV}{}^2$ (1.3 × 10^9 M^{-1} s^{-1})[15] and suggests that reaction of $MNN^{\bullet-}$ ($k_{MV}{}^1$) is the dominant process contributing to the reduction of methyl viologen.

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Scheme III

$$\mathrm{MNN} \xrightarrow{h\nu,\ \mathrm{ISC}} {}^3\mathrm{MNN}$$

$${}^3\mathrm{MNN} \xrightarrow{k_1} \mathrm{MNN}$$

$${}^3\mathrm{MNN} + \mathrm{Am} \xrightarrow{k_2} (\mathrm{MNN}^{\bullet -} + \mathrm{Am}^{\bullet +}) \quad \text{electron transfer}$$

$$(\mathrm{MNN}^{\bullet -} + \mathrm{Am}^{\bullet +}) \xrightarrow{k_3} \mathrm{MNN} + \mathrm{Am}$$

$$(\mathrm{MNN}^{\bullet -} + \mathrm{Am}^{\bullet +}) \xrightarrow{k_4} \mathbf{3}$$

$${}^3\mathrm{MNN} + \mathrm{Am} \xrightarrow{k_5} \mathrm{X} \quad \mathrm{S_N2\ Ar^*}$$

$$\mathrm{X} \xrightarrow{k_6} \mathrm{MNN} + \mathrm{Am}$$

$$\mathrm{X} \xrightarrow{k_7} \mathbf{2}$$

We can summarize the flash photolysis experiments as follows. Triplet MNN is formed rapidly (<10 ns) after photoexcitation and is quenched by amines. Primary, secondary, and tertiary amines all cause electron transfer, producing the radical anion of MNN, and the yields follow the order tertiary > secondary > primary. Quenching of ^{3}MNN by amines is faster in the order primary < secondary < tertiary, consistent with the ease of oxidation of these amines. The rate constants for quenching are somewhat lower when water is added to the acetonitrile solvent.

We return now to the continuous irradiation experiments. Here a pronounced solvent effect is seen. In cyclohexane, primary amines caused substitution, but secondary amines were unreactive. In acetonitrile, primary amines again caused substitution, but with secondary amines (and triethylamine) photoreduction occurred. Only in aqueous acetonitrile was substitution observed for both primary (NO_2 replacement) and secondary (OCH_3 replacement) amines.

The quantum yields of photosubstitution were studied in some detail in the cases of isobutylamine and diethylamine as nucleophiles. At amine concentrations of 0.3 M, the quantum yields for MNN loss were found to be 0.058 and 0.021, respectively. Quantum yields of product formation were studied at varying amine concentration and in each case linear relationships between ϕ_p^{-1} and $[\text{amine}]^{-1}$ were found. This is consistent with bimolecular attack of the amine on triplet MNN.

We shall interpret our results in terms of the mechanism outlined in Scheme III. Although caged radical ions have been drawn, it is clear that some must escape to be detected by flash photolysis. For the case of diethylamine as nucleophile, the radical anion is observed spectroscopically, but there is no evidence that k_5 is of significant magnitude. Application of the steady-state condition and assuming $k_5 \simeq 0$ (because product **2** is not observed in this system) gives eq 5 as the dependence of the quantum yield of formation of *N*,*N*-diethyl-4-nitro-1-naphthylamine upon the diethylamine concentration.

$$\frac{1}{\phi_p} = \left(1 + \frac{k_3}{k_4}\right)\left(1 + \frac{k_1}{k_2[\mathrm{Et_2NH}]}\right) \qquad (5)$$

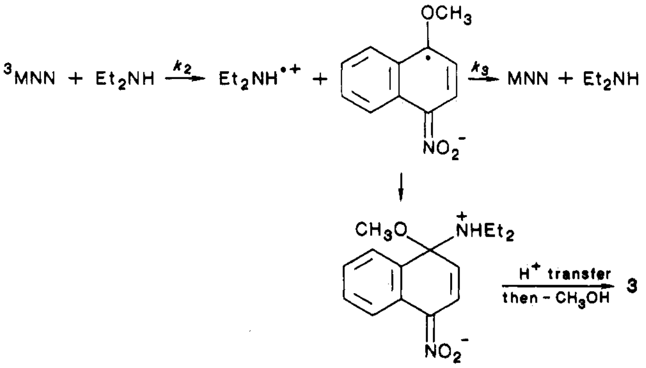
We associate k_1^{-1} with the unquenched lifetime of MNN, and k_2 with k_q, the rate constant for quenching ^{3}MNN by amine. Thus k_2/k_1 is the same as $k_q{}^3\tau$ and should be obtainable also as the parameter intercept/slope from a plot of ϕ_p^{-1} vs. $[\mathrm{Am}]^{-1}$. These quantities are shown in Table II, although we must stress that the solvent compositions are not mutually consistent in each case. This is because the short lifetime in highly aqueous acetonitrile made accurate time-resolved quenching studies impossible.

Table II. Comparison of Flash Photolytic and Steady State Reactions of 1-Methoxy-4-nitronaphthalene with Isobutylamine and Diethylamine

	isobutylamine	diethylamine
	Flash Photolysis	
k_q, M^{-1} s^{-1}	5.5×10^7 (3:1)[a]	2.1×10^8 (3:1)
${}^3\tau$, s	8.5×10^{-8} (3:1)	2.5×10^{-8} (1:1)
$k_q{}^3\tau$, M^{-1}	4.7	5.3
	Continuous	
intercept	14.3 (7:3)	52.5 (1:1)
slope, M	2.1 (7:3)	18.8 (1:1)
intercept/slope, M^{-1}	6.8	2.8

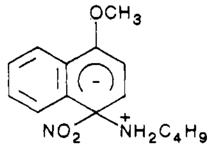
[a] Numbers in parentheses are volume ratios CH_3CN/H_2O in the solvent.

Therefore, the value of $k_q{}^3\tau$ in 1:1 CH_3CN/H_2O will actually be smaller than the 5.3 M^{-1} recorded in Table II, and hence more closely in accord with the continuous irradiation results. We therefore conclude that when diethylamine is the nucleophile, the reaction can be described in a self-consistent manner by postulating electron transfer from diethylamine to MNN, with the resulting radical anion $\mathrm{MNN}^{\bullet -}$ identified as the intermediate en route to 1-(methylamino)-4-nitronaphthalene. The low overall quantum efficiency is due to the factor $(1 + k_3/k_4) = 53$, implying that the majority of radical anion pairs fail to proceed to product. A reasonable, but entirely speculative, route to the product is shown below.



When isobutylamine is the nucleophile, electron transfer still occurs, as evidenced by the flash photolysis results, but the yield of the radical anion is lower. Hence another quenching mechanism must operate in addition. Because the product is completely different, we have postulated that this other mechanism (which does not yield an observable transient) leads to product. Equation 6 gives the new dependence of ϕ_p upon the amine concentration. The parameter intercept/slope is associated with $(k_2 + k_5)/k_1$, where k_1 is once again $1/{}^3\tau$ and $(k_2 + k_5) = k_q$. Again, there is reasonable agreement (factor of 2) between the steady-state and the flash photolysis results, but it is not possible to distinguish kinetically whether the product of the isobutylamine reaction actually proceeds through $\mathrm{MNN}^{\bullet -}$ or not. We speculate that the reaction mechanism is $\mathrm{S_N2\ Ar^*}$ and that structure **4** or a prototropic analogue of it is

$$\frac{1}{\phi_r} = \left(1 + \frac{k_6}{k_7}\right)\left(1 + \frac{k_2}{k_5} + \frac{k_1}{k_5[\mathrm{BuNH_2}]}\right) \qquad (6)$$

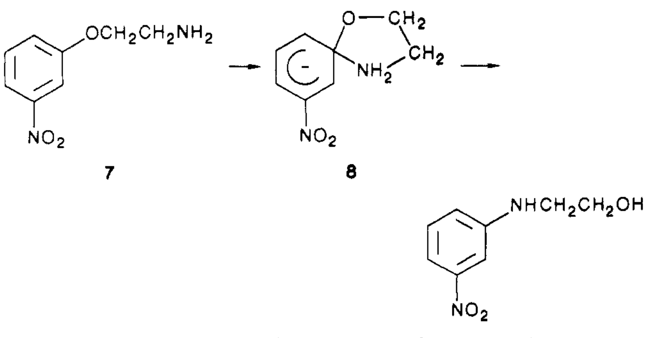


4

involved. According to this interpretation, the course of a nucleophilic photosubstitution upon 1-methoxy-4-nitronaphthalene will be determined by the relative magnitudes of *k*(S_N2 Ar*) and *k*(electron transfer). For aliphatic amines *k*(electron transfer) increases in the order primary < secondary < tertiary amines, in line with their ease of oxidation.

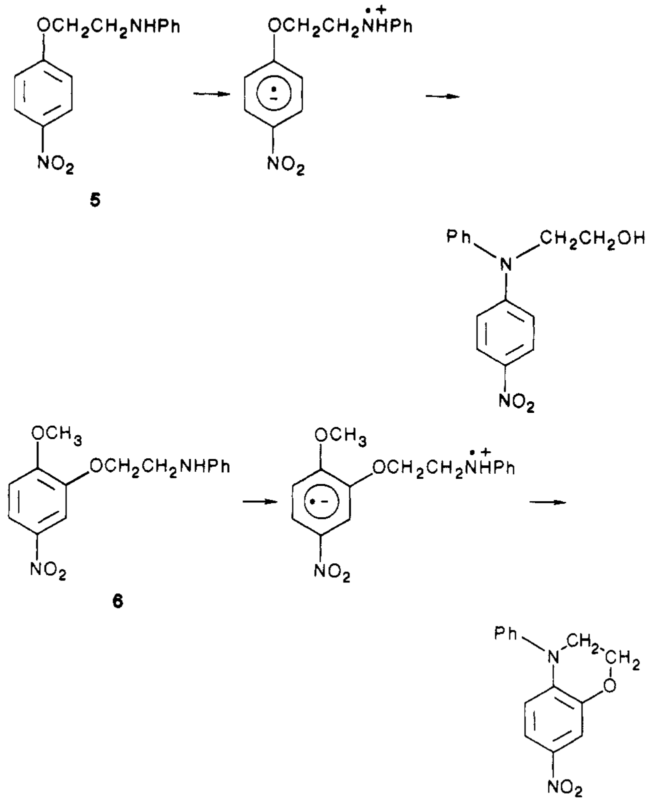
Competition experiments are consistent with the mechanistic outline in which electron transfer leads to methoxy replacement and S_N2 Ar* to nitro replacement. When *tert*-butylamine is added to the MNN/isobutylamine photolysis mixture, the rate of formation of the substitution product is unaffected. This is consistent with the failure of *tert*-butylamine to give substitution and with the low quenching rate constant ($k_q = (4.7 \pm 0.3) \times 10^6$ M^{-1} s^{-1}, Table I) of ^{3}MNN by *tert*-butylamine. A similar experiment with diethylamine/diisopropylamine/MNN led to substitution being retarded compared with diethylamine/MNN alone. Diisopropylamine, being oxidizable comparably easily with diethylamine, does quench ^{3}MNN with the formation of $MNN^{\bullet-}$ ($k_q = (5.2 \pm 0.5) \times 10^7$ M^{-1} s^{-1}, Table I) but does not afford a substitution product, possibly for steric reasons.

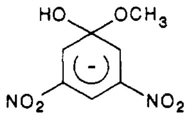
We now compare our results with previous investigations of alkoxy nitro aromatic compounds. The closest of these is the recent study by Mutai and Nakagaki[7] of the intramolecular photosubstitution of 1 (Scheme II). These workers were not able to observe any intermediates by laser flash photolysis in this system, but based on their frontier MO analysis, they concluded that the reaction is an electron-transfer process. This is consistent with our observation that intermolecularly, aniline is photooxidized to azobenzene by MNN. In the benzene series Mutai et al. had been able to obtain strong evidence for the involvement of radical ion pairs in the photorearrangements of 5[18] and 6[19] (Scheme IV). The photolysis of 6 is particularly noteworthy in that the usual photosubstitution of a *m*-alkoxynitrobenzene involves attack meta to nitro (the S_N2 Ar* process). Para attack occurs here because the reaction is electron transfer in nature rather than S_N2 Ar*. In contrast, Wubbels et al.[20] have found that the intramolecular substitution of 7 is an S_N2 Ar* reaction; this is reasonable because the primary amine nucleophile is less easily oxidized than an aromatic amine nucleophile, and this is consistent with our own observations on MNN.



It is clear that the radical ion products resulting from electron transfer may be readily observed by time-resolved spectroscopy. That from compound 6, for example, has λ_{max} near 400 nm. The absorption characteristics of the σ complexes in S_N2 Ar* reactions are less well documented; 8 has been reported[20] to have a broad absorption near 400 nm, while the complex 9 resulting from the attack of OH^- on 3,5-dinitroanisole[21] appears to have λ_{max} near 480 nm. We had hoped that it would be possible to observe both the σ complex (with MNN/RNH_2) and the radical ion (with MNN/R_2NH), but in the event only the latter could be detected in our system.

Scheme IV





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The photochemistry of methoxy nitro aromatic compounds with nucleophiles has received renewed attention recently, and it is now possible to make mechanistic

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[25] No reports on the substitution of *m*-nitroanisole with secondary amines have appeared. In unpublished work we have found that diethylamine does not give substitution with *m*-nitroanisole in CH_3CN–H_2O (S. R. Cater, Ph.D. Thesis, University of Guelph, 1986), although photoreduction occurs with diethylamine in nonpolar media: Barltrop, J. A.; Bunce, N. J. *J. Chem. Soc. C* **1968**, 1467.

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statements that are more definite than was previously possible. As it happens, MNN, *m*-nitroanisole, *p*-nitroanisole, and 4-nitroveratrole and their derivatives appear to be rather similar in their triplet energies and their redox behavior. If we consider intra- and intermolecular reactions together, we find the following relationships.

MNN: S_N2 Ar* with CN^- (ref 4), OCH_3^- (ref 6),
BH_4^- (ref 5), RNH_2 (this work);
electron transfer with R_2NH(this work) and
aniline nucleophiles[7]

m-nitroanisole: S_N2 Ar* with CN^- (ref 22),
RNH_2,[20-23] OH^- (ref 24);
no electron transfer reactions
documented[25]

p-nitroanisole: S_N2 Ar* with CN^-[26] (at C(2)),
RNH_2,[27] OH^- and pyridine[28] (ipso
attack at NO_2);
electron transfer with various aliphatic
amines[29] and aniline nucleophiles[18]

4-nitroveratrole: S_N2 Ar* with CN^-,[30] OH^-,[8] RNH_2;[31]
electron transfer with R_2NH and
aniline nucleophiles[19]

These relationships lead to three generalizations: (1) The S_N2 Ar* reaction is in competition with electron transfer, especially for amine nucleophiles. The S_N2 Ar* chemistry is seen when electron transfer is not energetically favored. (2) The S_N2 Ar* mechanism leads to replacement of a substituent meta to a nitro group, or if that is not possible, to ipso substitution at the nitro group. (3) Electron transfer leads to replacement of substituents para to nitro, the nitro group stabilizing the radical anion, and is in competition with photoreduction.

Experimental Section

1-Methoxy-4-nitronaphthalene was prepared by nitrating 1-methoxynaphthalene after the procedure of Alcorn and Wells.[32] After chromatography over silica gel and recrystallization from methanol the product had mp 83–83.5 °C (lit.[32] mp 85 °C) and melting point and NMR and mass spectra the same as a commercial sample.

1-Fluoro-4-nitronaphthalene was prepared by nitrating 1-fluoronaphthalene by the method of Schiemann et al.[33] The product, recrystallized from ethanol, had mp 72.5–73.0 °C (lit.[33] mp 80 °C) but had an NMR spectrum identical with that previously reported.[34]

1-(Dimethylamino)-4-nitronaphthalene was prepared from 1-fluoro-4-nitronaphthalene and dimethylamine in aqueous EtOH at reflux.[35] The deep yellow product had the following: mp 59–60 °C (lit.[36] mp 58 °C, mp[37] 65 °C); MS, M^+ 216; NMR (60 MHz, $CDCl_3$) δ 3.0 (s, 6 H, NMe_2), 6.85 (d, *J* = 9 Hz, 1 H, H(2)), 7.4–7.7 (m, 2 H, ArH), 8.1–8.3 (m, 1 H, Ar H), 8.25 (d, *J* = 9 Hz, 1 H, H(3)), 8.65–8.85 (m, 1 H, Ar H). Similarly prepared were 1-(diethylamino)-4-nitronaphthalene [oil; MS, M^+ 244; NMR δ 1.1 (t, *J* = 7 Hz, 6 H, CH_3), 3.3 (q, *J* = 7 Hz, 4 H, CH_2), 6.93 (d, *J* = 8 Hz, 1 H, H(2)), 7.3–7.8 (m, 2 H, Ar H), 8.1–8.3 (m, 1 H, Ar H), 8.25 (d, *J* = 8 Hz, 1 H, H(3)), 8.6–8.8 (m, 1 H, Ar H)] and 1-(methylamino)-4-nitronaphthalene [orange needles; mp 184–185 °C (lit.[37] mp 185 °C); NMR δ 3.1 (d, *J* = 3 Hz, collapsed to s in D_2O, 3 H, CH_3), 6.55 (d, *J* = 9 Hz, 1 H, H(2)), 7.5–7.9 (m, 2 H, Ar H), 8.1–8.3 (m, 1 H, Ar H), 8.5 (d, *J* = 9 Hz, 1 H, H(3)), 8.9–9.0 (m, 1 H, Ar H)].

4-Methoxy-1-naphthylamine was prepared by hydrogenation of 1-methoxy-4-nitronaphthalene over Pd/C at 1 atm and 22 °C. The product had the following: NMR ($CDCl_3$) 3.7 (br s, removed in D_2O, 2 H, NH_2), 3.85 (s, 3 H, OCH_3), 6.55 (s, 2 H, Ar H), 7.2–7.8 (m, 3 H, Ar H), 8.1–8.3 (m, 1 H, Ar H). It darkened rapidly in air and was converted to the acetamide derivative, white needles from methanol, mp 184–185 °C (lit.[38] mp 187 °C), M^+ 215.

Semipreparative Irradiations. These were all done under ambient air, using a Pyrex immersion well photoreactor of capacity 310 mL, the contents of which were continuously stirred, and a Hanovia 450-W medium pressure mercury arc.

MNN with CN^-. MNN (0.31 g), KCN (2.44 g), and CH_3CN–H_2O (95:5) were irradiated for 1 h. VPC showed 90% loss of MNN and the formation of two products in a 95:5 ratio. The minor product had the same retention behavior as 4-methoxy-1-naphthylamine, but it was not isolated. The major product, isolated by preparative TLC, was obtained in 0.20-g (73%) yield and had physical properties the same as those of authentic 4-methoxy-1-naphthalenecarbonitrile.

MNN with CH_3NH_2. MNN (0.31 g), 25% aqueous CH_3NH_2 (10 mL), and CH_3CN–H_2O (1:1) were irradiated for 2 h. After concentration, benzene (25 mL) and 4-nitrobenzoyl chloride (0.27 g) were added; the mixture was heated to reflux for 15 min and then washed successively with 2% $NaHCO_3$, 2% HCl, and water. After chromatography over silica gel a yellowish solid (0.18 g) was obtained; two recrystallizations from methanol afforded *N*-methyl-*N*-(4′-methoxy-1′-naphthyl)-4-nitrobenzamide: mp 131.5–132 °C, MS, M^+ 336; NMR ($CDCl_3$) δ 3.50 (s, 3 H, NCH_3), 3.90 (s, 3 H, OCH_3), 6.50 (d, *J* = 8 Hz, 1 H, H(2′)), 6.98 (d, *J* = 8 Hz, 1 H, H(3′)), 7.2–8.4 (m, 8 H, Ar H). Anal. ($C_{19}H_{16}N_2O_4$) Calcd C, 67.85; H, 4.79; N, 8.33. Found: C, 67.42; H, 5.19; N, 8.11.

MNN with Isobutylamine. MNN (0.30 g), isobutylamine (7.4 mL), and CH_3CN–H_2O (1:1) were irradiated for 1 h. VPC showed 90% loss of MNN and a single product. Concentration and extraction gave a brown solid which was converted to the nitrobenzamide by using the same procedure as above. The product (0.30 g) was twice chromatographed over silica gel and then recrystallized several times from methanol affording *N*-isobutyl-*N*-(4′-methoxy-1′-naphthyl)-4-nitrobenzamide as yellow needles: mp 154.5–155 °C; NMR ($CDCl_3$) δ 0.8–1.3 (m, 7 H, $CH(CH_3)_2$), 3.2 (m, 2 H, NCH_2), 3.9 (s, 3 H, OCH_3), 6.4–8.3 (m, 10 H, Ar H); MS, M^+ 378. Anal. ($C_{22}H_{22}N_2O_4$) Calcd C, 69.83; H, 5.86; N, 7.40. Found: C, 69.72; H, 6.22; N, 7.15.

MNN with Propylamine. MNN (0.31 g), propylamine (12.5 mL), and CH_3CN–H_2O (1:1) were irradiated for 1 h, causing 95% loss of MNN. The single product (oil) had NMR consistent with that of 1-(propylamino)-4-methoxynaphthalene (δ 1.03 (t, *J* = 7 Hz, 3 H, CH_3), 1.73 (m, 2 H, CH_2CH_3), 3.13 (t, *J* = 7 Hz, 2 H, NCH_2), 3.87 (s, 3 H, OCH_3), 6.40 (d, *J* = 4 Hz, 1 H, Ar H), 6.67 (d, *J* = 4 Hz, 1 H, Ar H), 7.5–7.9 (m, 3 H, Ar H), 8.3–8.5 (m, 1 H, Ar H)). The benzamide derivative was formed and crystallized with difficulty: mp 123–124 °C; MS, M^+ 319.

MNN with Diethylamine. MNN (0.31 g), diethylamine (7.8 mL), and CH_3CN–H_2O (1:1) were irradiated for 1 h, causing 62% loss of MNN. Concentration followed by extraction of the residual brown liquid with concentrated HCl gave 1-(diethylamino)-4-nitronaphthalene (27%) identical with the synthetic sample. The unextractable portion contained three components by VPC and these decomposed further upon standing. Tentative identifications were made by GC-MS for 1-methoxynaphthalene, 1-amino-4-(diethylamino)naphthalene, and 1-(diethylamino)-naphthalene.

MNN with Aniline. MNN (0.31 g), aniline (6.8 mL), and CH_3CN–H_2O (1:1) were irradiated for 1.5 h, affording a reddish solution. VPC indicated 23% loss of MNN and the formation of a product whose retention time matched that of azobenzene. Concentration, extraction, and preparative TLC on silica gel afforded azobenzene (21 mg), having physical properties the same as an authentic sample.

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Table III. Loss of MNN and Appearance of Substitution Product When 5.0×10^{-3} M MNN and Various Isobutylamine Concentrations Were Irradiated in CH_3CN-H_2O (7:3) for 15 min

[amine], M	loss of MNN, %	yield,[a] %	[amine], M	loss of MNN, %	yield,[a] %
0	0	0	0.25	43	55
0.10	30	34	0.30	51	55
0.15	38	38	0.35	56	58
0.20	40	43	0.40	54	66

[a] Relative to added VPC standard, see text.

Sensitization and Quenching Studies. MNN (5.0×10^{-3} M), 3-methoxyacetophenone, and the amine (0.3 M) were irradiated under air by using a Rayonet RPR photoreactor equipped with 300-nm lamps. When isobutylamine was the amine, the sensitizer concentration was 0.050 M and >90% of the incident radiation was absorbed by the sensitizer. After 15 min of irradiation (solvent was CH_3CN-H_2O (7:3)), 46% of the MNN was consumed, while in control samples from which the sensitizer was omitted 55% consumption of MNN occurred. When diethylamine was the amine the sensitizer concentration was 0.086 M, the solvent was 1:1 CH_3CN-H_2O, and the irradiation time was 30 min. The sensitized solutions showed 52% loss of MNN and 21% yield of substitution product, compared with 30% loss and 9% yield for the control samples. The quenching experiments used the same solvents as those just described, and freshly distilled 0.01 M 1,3-cyclohexadiene (with 0.3 M isobutylamine) or 0.01 M 2,5-dimethyl-2,4-hexadiene (with 0.3 M diethylamine). In the case of MNN (4.7×10^{-3} M, 15 min) and cyclohexadiene, the addition of quencher reduced the yield of substitution product by 35%, while with MNN (4.9×10^{-3} M, 30 min) and 2,5-dimethyl-2,4-hexadiene, the presence of the quencher almost completely suppressed the substitution product.

Quantum Yields (under Air). (i) With ~0.3 M Amine. The method of Bunce et al.[39] involving the use of three solutions, and azoxybenzene as the actinometer, was used. The quantum yields were MNN (4.70×10^{-3} M, isobutylamine 0.30 M, RPR photoreactor, 15 min), $\phi_r = 0.058$, and MNN (4.93×10^{-3} M, Et_2NH 0.34 M, RPR photoreactor, 30 min), $\phi_r = 0.021$, and were calculated by using the relationship given in eq 7, where c_0 and

$$\phi_r = \frac{c_0 \ln (c_0/c_t)}{\text{mol L}^{-1} \text{ photons absorbed}} \qquad (7)$$

c_t are the concentrations of the reactant at the beginning and the end of the photolysis.

Given the short triplet lifetimes in water containing solvents (see Figure 1), air is not expected to have much of an effect on the primary triplet reaction. Since all these experiments had been initially carried out under air, we have checked the importance of oxygen in the reaction with isobutylamine. Thus, matched pairs of samples (2 mL, under air and under nitrogen) containing 4.90 mM MNN and 0.30 M isobutylamine in 7:3 acetonitrile/water were irradiated at ~300 nm. No change in the products was observed, although their yield at low conversion (≤25%) was about 25% higher in the deaerated solution. The difference was smaller at the higher conversions, probably suggesting partial oxygen depletion as the reaction proceeds. Extrapolation of this behavior to the higher conversions and concentrations used in preparative experiments suggests that the effect would be negligible under these conditions.

(ii) Dependence of ϕ_r and ϕ_p upon [Amine]. Several solutions were irradiated simultaneously in the RPR photoreactor. Details of these experiments are given in Tables III and IV. In the case of isobutylamine where the pure substitution product (as opposed to its *p*-nitrobenzamide) was not available, the "relative yields" are VPC area ratios relative to a known amount of fluorenone added as a standard.

GC/MS Results. Solutions of MNN (5×10^{-3} M) and of 0.5 M propylamine, diethylamine, pyrrolidine, or piperidine in 50% aqueous acetonitrile were irradiated for 30 min, except in the case when the amine was piperidine where a 2-h irradiation was used. In all cases a small amount of an unidentified component of short retention time was obtained having *m/e* (relative intensity) 221 (5), 220 (26), 206 (15), 205 (100).

Table IV. Loss of MNN and Appearance of Substitution Product When 4.7×10^{-3} M MNN and Various Diethylamine Concentrations Were Irradiated in CH_3CN-H_2O (1:1) for 30 min

[amine], M	loss of MNN, %	yield, %	[amine], M	loss of MNN, %	yield, %
0	6.1	0	0.30	40.3	15.9
0.01	11.1		0.35		17.0
0.10	37.6	8.0	0.40	45.7	16.5
0.15		11.0	0.50		25.1
0.20	33.3	12.3	0.60		26.7

Propylamine gave 1-(propylamino)-4-methoxynaphthalene: MS, *m/e* (relative intensity) 216 (10), 215 (64, M^+), 201 (15), 200 (100), 186 (22), 170 (11), 158 (49).

Irradiation with isobutylamine gave 1-(isobutylamino)-4-methoxynaphthalene: MS, *m/e* (relative intensity) 230 (13), 229 (83, M^+), 214 (51), 187 (14), 186 (100), 170 (16), 158 (57), 156 (10), 155 (58), 154 (22).

Irradiation with diethylamine gave 1-(diethylamino)-4-nitronaphthalene: MS, *m/e* (relative intensity) 245 (6), 244 (39, M^+), 229 (44), 213 (17), 212 (100), 183 (17), 182 (49), 168 (14), 167 (15) as the major component. There were also produced very small amounts of a compound, tentatively identified as 1-amino-4-(diethylamino)naphthalene [MS, *m/e* 214 (8, M^+), 185 (31), 158 (13), 157 (100), 142 (21), 128 (14), 127 (27), 114 (43)] and possibly an unresolved mixture of this latter compound with 1-(diethylamino)-naphthalene [MS, *m/e* 215 (14), 214 (24), 200 (17), 199 (100), 185 (20), 170 (47), 169 (51), 144 (18), 143 (34), 115 (33)]. Irradiation in 1/1 acetonitrile/D_2O caused no incorporation of deuterium into either the substitution product or the unreacted MNN, and the intensity ratios were exactly the same as for irradiation in water. There was deuterium incorporated into the unidentified material that was present in all irradiations having *m/e* (relative intensity) 221 (14), 220 (26), 206 (54), 205 (100) and into the unresolved mixture assigned as 1-amino-4-(diethylamino)naphthalene and 1-(diethylamino)naphthalene [MS, *m/e* 215 (47), 214 (82), 200 (58), 199 (100), 185 (23), 171 (31), 170 (72), 169 (54), 144 (35), 143 (42), 116 (27), 115 (47)]. No peak attributed to the 1-amino-4-(diethylamino)naphthalene alone was observed.

Pyrrolidine gave the major component as 1-nitro-4-pyrrolidinonaphthalene [MS, *m/e* 243 (15), 242 (100, M^+), 241 (37), 212 (47), 208 (42), 207 (31), 196 (20), 195 (21), 167 (30)] with a trace amount of 1-methoxy-4-pyrrolidinonaphthalene [MS, *m/e* 228 (8), 227 (38, M^+), 213 (14), 212 (100)].

Piperidine gave very small yields of products. The major product was 1-methoxy-4-piperidinonaphthalene [MS, *m/e* 242 (9), 241 (52, M^+), 227 (17.5), 226 (100), 115 (21)]. Small amounts of 1-nitro-4-piperidinonaphthalene [MS, *m/e* 257 (19), 256 (86, M^+), 255 (86), 210 (18), 209 (31), 208 (25), 207 (59), 127 (42)] and possibly 4-piperidino-1-naphthylamine [MS, *m/e* 227 (16), 226 (100, M^+), 225 (62), 169 (33), 115 (27)] were also present.

Laser Flash Photolysis. Solutions of ca. 0.3 mM MNN in the appropriate solvent were degassed by nitrogen purging unless otherwise indicated and were contained in 3×7 mm^2 cells. Most of the quenching runs were done as flow experiments to minimize problems due to sample depletion and build up of fluorescent impurities. The 337-nm pulses from a Molectron UV-29 nitrogen laser (~8 ns pulse, ≤10 mJ/pulse) were used for sample excitation. Some spectra were measured with an EG&G gated intensified optical multichannel analyzer equipped with a 20-ns gate. Further details of the laser flash photolysis system have been described elsewhere.[40,41]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support of part of this work through an operating grant

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to N.J.B. and a postgraduate scholarship to S.R.C.

Registry No. DABCO, 280-57-9; 1-methoxy-4-nitronaphthalene, 4900-63-4; 1-fluoro-4-nitronaphthalene, 341-92-4; dimethylamine, 124-40-3; 1-(dimethylamino)-4-nitronaphthalene, 39139-76-9; 4-methoxy-1-naphthylamine, 16430-99-2; methylamine, 74-89-5; 1-(methylamino)-4-nitronaphthalene, 7000-88-6; 1-(diethylamino)-4-nitronaphthalene, 27210-64-6; diethylamine, 109-89-7; 4-methoxy-1-naphthalenecarbonitrile, 5961-55-7; *N*-methyl-*N*-(4'-methoxy-1'-naphthyl)-4-nitrobenzamide, 109392-85-0; isobutylamine, 78-81-9; propylamine, 107-10-8; aniline, 62-53-3; *N*-isobutyl-*N*-(4'-methoxy-1'-naphthyl)-4-nitrobenzamide, 109392-86-1; 1-(propylamino)-4-methoxynaphthalene, 109392-87-2; 1-nitro-4-pyrrolidinonaphthalene, 109392-88-3; 1-methoxy-4-pyrrolidinonaphthalene, 109432-29-3; 1-methoxy-4-piperidinonaphthalene, 109392-89-4; 1-nitro-4-piperidinonaphthalene, 34599-45-6; 4-piperidino-1-naphthylamine, 109432-30-6; pyrrolidine, 123-75-1; piperidine, 110-89-4; morpholine, 110-91-8; triethylamine, 121-44-8; diisopropylamine, 108-18-9; *tert*-butylamine, 75-64-9; KCN, 151-50-8.

Thermolysis and Photolysis of 3-Chloro-3-benzyldiazirines in Alkenes: Evidence for a Carbene–Alkene Complex

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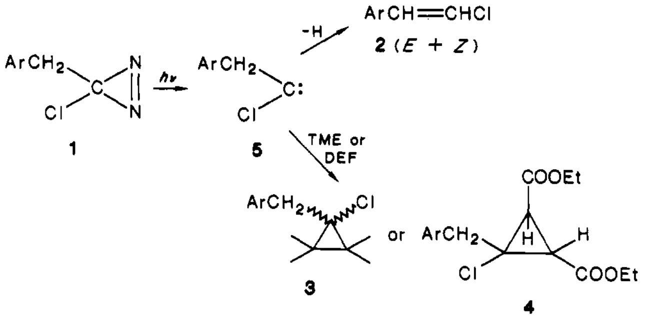
Received February 20, 1987

Photolysis and thermolysis of substituted 3-chloro-3-benzyldiazirines in alkenes yielded cyclopropanes and chlorostyrenes as products. The results suggest that the cyclopropanation of benzylchlorocarbenes is independent of substituents. However, 1,2-hydrogen migration is accelerated by OCH_3 or CH_3 substituents, and is decelerated by a Cl substituent on the phenyl ring. These results support the existence of an energy barrier to 1,2-H migration. Evidence is provided for carbene–alkene complexation.

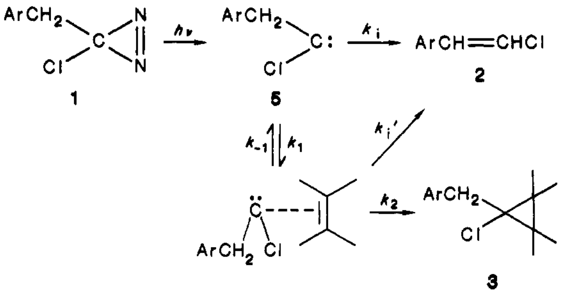
Time-resolved flash spectroscopic investigations[1,2] have shown that the reactions of singlet arylhalocarbenes with alkenes are consistent with the existence of transient carbene/alkene intermediates. Recent investigation on the additions of arylhalocarbenes to alkenes[3] suggest, however, that the observed negative activation energies could be explained in two ways. These results could be analyzed according to the Houk model.[4] Here, the carbene adds to the alkene in a single step, and the activation energy is entropic controlled. On the other hand, Turro and Moss[1,2] proposed a multistep model. In this case, the formation of a carbene–alkene complex could also be used to explain the results.

Our investigation shows that upon photolysis or thermolysis, 3-chloro-3-benzyldiazirine undergoes dinitrogen extrusion, and in the presence of alkene, the cyclopropanation directly competes with the intramolecular 1,2-hydrogen migration. The intervention of a reversibly[5–7] formed intermediate of carbene with alkene has also been advanced to rationalize the complex kinetic data for competitive carbene reactions. Giese and co-workers[8] have also suggested the general existence of intermediates in cyclopropanation reactions of singlet carbenes. The reactions of substituted benzylchlorocarbene with electron-rich (tetramethylethylene) and electron-poor (diethyl fumarate) alkenes were carried out to gain further insight into the 1,2-H migration and the cycloaddition of chlorocarbene. The results of the investigations are reported here.

Scheme I



Scheme II



Results and Discussion

3-Chloro-3-benzyldiazirines were synthesized by Graham's methods.[9] Irradiation of 3-chloro-3-benzyldiazirine at 4 K gives no detectable ESR signal.[6] The addition of benzylchlorocarbenes to alkene is stereospecific[5] which confirms that the carbenes are reacting as ground-state

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