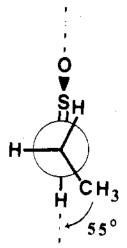

spectra of (*Z*)-propanethial *S*-oxide (**6**) suggest that the preference for the skew conformation is not a very strong one. Unlike the parent sulfine,[2a] sulfines **6** and **9** are stable in the waveguide at 50 mTorr and 25 °C. It has not yet proven possible to observe directly by microwave spectroscopy (or other spectral means) 1-alkenesulfenic acids either in the pyrolysis of **7** or **8** or in the vapors or extract from homogenized onions.

Careful FT NMR analysis of the isolated onion LF as well as the sulfines from pyrolysis of alkenyl sulfoxides **7** and **8** reveals the presence in each case of a minor (<10%) component characterized as the (*E*)-sulfine (e.g., **4** from the onion and from **7**). Details of this work will be presented elsewhere.

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(7) In the literature dealing with the onion LF there is no specific mention of the possibility of geometric isomers for propanethial *S*-oxide despite the extensive research on geometric isomerism in thiocarbonyl *S*-oxides.[8] In some studies propanethial *S*-oxide is depicted with a linear CSO grouping devoid of any stereochemistry,[9,10] while in other papers an *E* stereochemistry is somewhat arbitrarily indicated.[11,12]

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(15) Details of the isolation and an FT NMR study of the onion LF and related alkanethial *S*-oxides will be described elsewhere.

(16) The salient points on which we base our conclusions are the following. (a) The onion enzyme alliinase converts sulfoxide **1c** to *n*-propyl propanethiosulfinate, a process which likely involves the intermediacy of propanesulfenic acid.[14] (b) When the LF is generated in D_2O the M^+ ion in its mass spectrum shifts from 90 to 91 indicating a single exchangeable proton.[6] The monodeuterio LF loses OH rather than OD on electron impact.[6] Since methanesulfenic acid is known to have the exchangeable hydrogen on oxygen,[14] which form should readily lose OH on electron impact, rearrangement of the monodeuterio LF must precede fragmentation. (c) The *direct* formation of the LF **6** from precursor **1a** is postulated to involve a retro-ene reaction.[11] It would be remarkable if the same enzyme alliinase could catalyze both the sulfoxide elimination reaction described in (a) above as well as a retro-ene process with **1**. (d) An alternative mechanism from **1a** to **6** which we cannot exclude at this time would involve elimination from the Schiff base of Scheme I giving the anion of acid **5** which could directly give **6** on protonation of the appropriate resonance form.

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(18) Prepared by oxidation of the corresponding known sulfide or via reaction of the alkenyl Grignard reagent with 2-methyl-2-propanesulfinyl chloride.

(19) All new compounds have been fully characterized by spectral methods.

(20) For examples of addition of α,β-unsaturated (and other) sulfenic acids to alkynes, see Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974,** *96*, 2931–3928, 3929–3944. For an example of an intramolecular addition of an α,β-unsaturated sulfenic acid, see Baxter, A. G. W.; Stoodley, R. J. *J. Chem. Soc., Chem. Commun.* **1976,** 366–367.

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(22) We have also observed that methanesulfenic acid on FVP undergoes dehydration to thioformaldehyde[14] and that methyl vinyl sulfide on FVP (at 770 °C) gives thioketene. These reactions may all involve mechanistic pathways similar to those proposed by Kwart for other gas phase thermolytic β-eliminations.[23]

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Eric Block,* Robert E. Penn,* Larry K. Revelle
Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121

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Photochemical Reaction of Dicyanoanthracene with Acetonitrile in the Presence of an Aliphatic Amine. A Novel Photochemical Amination

Sir:

Photochemical reactions involving electron transfer followed by proton transfer are well examined on arene-amine systems.[1] For instance, irradiation of a solution of anthracene and a secondary amine in acetonitrile yielded both the 1:1 adducts and the reduction products of anthracene.[2] We now report that irradiation of 9,10-dicyanoanthracene (**1**), a more powerful electron acceptor than anthracene itself, in acetonitrile in the presence of a primary, secondary, or tertiary amine did not yield the 1:1 adduct of the amine and **1** but reaction products between **1** and acetonitrile.

Irradiation of a mixture of **1** (70 mg) and butylamine (20 mL) in acetonitrile (300 mL)[3] with a Pyrex-filtered medium-pressure mercury arc (100 W) for 4 h under nitrogen gave 9-amino-10-cyanoanthracene (**2**), mp 259–260 °C (lit.[4] mp 262–263 °C), *m/e* 218 (M^+), in 64% yield. Acetaldehyde and butyraldehyde were also identified in the reaction mixture as the corresponding 2,4-dinitrophenylhydrazones. A similar result was obtained when **1** in the acetonitrile[3] was irradiated in the presence of diethylamine or triethylamine producing **2** in 42 or 34% yield together with acetaldehyde, respectively.

To clarify the origin of the nitrogen in the amino group of **2**, we carried out similar photochemical reactions of **1** in 90% aqueous acetonitrile-^{15}N (96.9 atom %) in the presence of triethylamine. The mass spectra clearly showed that the major product (>95%) was ^{15}N-incorporated **2.** This result explicitly indicates that the nitrogen in the amino group of **2** originates from the acetonitrile. In accord with this result, when methanol or benzene was substituted for acetonitrile, 9-cyanoanthracene

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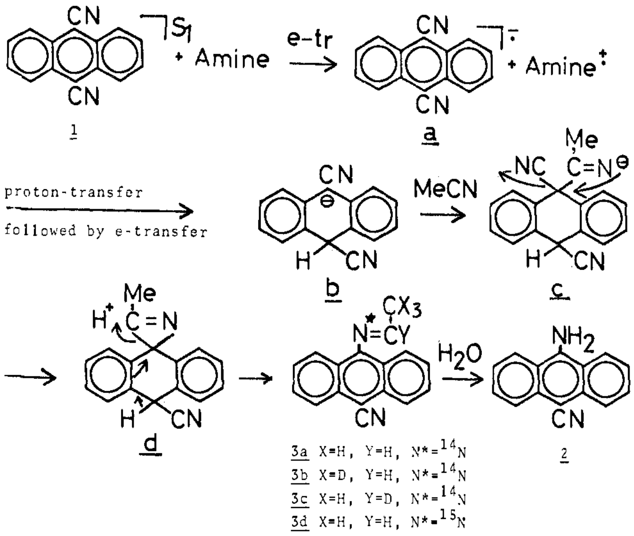
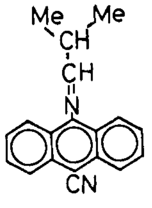
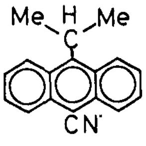
Scheme I





5



6

(**4**) was obtained instead of **2** in a reasonable yield[5] through the photoinduced Birch reduction.[6]

To reveal the reaction sequence, we studied differences resulting from mechanistic modifications. The reaction did not occur in the absence of light or the amine. The fluorescence of **1** was quenched by the amines and the Stern–Volmer plots were linear but no exciplex emission was observed. The Stern–Volmer constants are shown in Table I. The rates of quenching calculated from the known lifetime of singlet **1**[7] are approximately diffusion controlled but somewhat dependent on the ionization potential of the amine used. It is concluded from this result that the initial step of the reaction is electron transfer from amine to **1** via an encounter complex or exciplex.[8]

Participation of water in the reaction was also demonstrated; when the acetonitrile was rigorously dried on phosphorus pentoxide,[9] its photochemical reaction with **1** in the presence of triethylamine did not give **2**.[10] On the other hand, irradiation of **1** with triethylamine in 90% aqueous acetonitrile for 9 h gave **2** in a high yield (95%), indicating that water is essential for the formation of **2**. When the reaction was interrupted after 3 h, an unstable intermediate **3a**, *m/e* 244 (M^+), was obtained in addition to **2**, but it was converted into **2** by chromatography on silica gel. Since **3a** was readily hydrolyzed to **2** and, moreover, acetaldehyde was detected in the reaction mixture, the structure of **3a** is deduced as a Schiff base. When trideuterioacetonitrile was used in place of acetonitrile, the mass spectra of the reaction product **3b** exhibited the molecular ion at *m/e* 247, three mass units higher than that of **3a**. When 1 drop of D_2O was added to the starting mixture of **1**, triethylamine, and dry acetonitrile, the photochemical reaction gave **3c** of which mass spectra showed its molecular ion at *m/e* 245, one mass unit higher than that of **3a**, indicating participation of a proton-transfer step in the reaction. When acetonitrile-^{15}N was used in place of ordinary acetonitrile as mentioned before, the mass spectra of the intermediate **3d** exhibited the molecular ion at *m/e* 245, again one mass unit higher than that of **3a**. The mass spectra of **3a–d** also exhibited strong fragment ions at *m/e* 229 ($M - CH_3$), 229 ($M - CD_3$), 230 ($M - CH_3$), and 230 ($M - CH_3$), respectively, which correspond to characteristic fragment ions of anils,[11] supporting the proposed structures of these intermediates.

Table I. Quenching of the Fluorescence of **1** by Amines[a]

	Et_3N	Et_2NH	$BuNH_2$
$k_q\tau$, M^{-1}	270	220	120
k_q, $M^{-1}\ s^{-1}$	1.8×10^{10}	1.4×10^{10}	7.9×10^9

[a] A solution of **1** (1.8×10^{-4} M) in dry acetonitrile was used. The amine concentration range and the correlation coefficients are as follows: 1.4×10^{-3}–7.1×10^{-3} M (0.997), 3.8×10^{-3}–1.1×10^{-2} M (0.985), and 6.4×10^{-3}–3.2×10^{-2} M (0.999) for the primary, secondary, and tertiary amines, respectively.

When isobutyronitrile was used instead of acetonitrile, a similar reaction took place. As an example, irradiation of a mixture of **1** (74 mg), triethylamine (20 mL), isobutyronitrile (250 mL), and water (10 mL) with a Pyrex-filtered medium-pressure mercury arc (100 W) for 5 h under nitrogen gave **2** in 57% yield through an intermediate **5**, *m/e* 272 (M^+), together with a small amount (26%) of an alkylated compound, 9-cyano-10-isopropylanthracene (**6**).[12]

Although the anthracene cation radical has been known to react with acetonitrile,[13] the present reaction must be the first example where the anion radical of an anthracene derivative reacts with aliphatic nitriles. We propose tentatively the mechanism shown in Scheme I for this unique reaction.[14]

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(5) On irradiation of 1-$BuNH_2$–methanol and 1-Et_2NH–benzene systems, **4** was obtained in 34 and 38% yields, respectively. **4** was also detected by mass spectrometry in the reaction products of the 1-Et_3N-benzonitrile–H_2O system.
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(14) Since the alkylated product **6** in the case of 1-Et_3N-isobutyronitrile seems to be produced through a S_N2-type reaction of the nitrile with an aromatic anion, anion b is assumed as a common intermediate to produce **3** and **5**. Processes from 1 to b are analogous to those of photoinduced Birch reduction proposed by Barltrop.[6a] The rearrangement processes from c to **3** are somewhat analogous to those of the photochemical rearrangement of 9-nitroanthracene: O. L. Chapman, D. C. Heckert, J. W. Reasoner, and S. P. Thackaberry, *J. Am. Chem. Soc.*, **88**, 5550 (1966).

Mamoru Ohashi,* Hitoshi Kudo, Shuzo Yamada
Department of Materials Science
The University of Electro-Communications
Chofu, Tokyo 182, Japan

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