chemical lability of the intervening epoxide and the overall molecular strain induced by bridgehead O-oxidation appears to be an essential element for the antibiotic's function. Epoxide relocation offers novel opportunities to examine and alter it.

Acknowledgment. Thanks to Professor Kosta Steliou (University of Montreal) for providing continuing stimulation on this problem. Professor Lester Mitscher (University of Kansas) kindly brought us in touch with key citations in the literature.

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Cooperative Reactivity in Photogenerated Radical Ion Pairs: Photofragmentation of Amino Ketones

William R. Bergmark* and David G. Whitten*

Department of Chemistry, University of Rochester
Rochester, New York 14627

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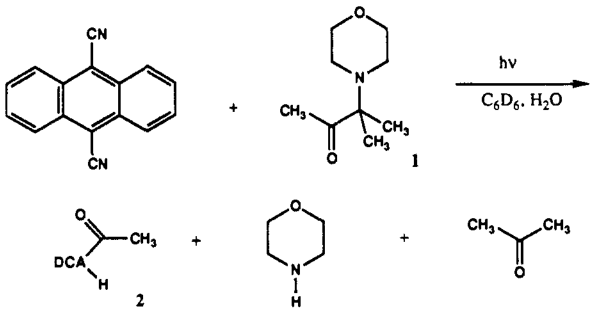
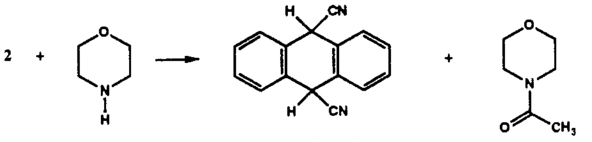
A number of instances of fragmentation (or cleavage) have recently been noted for certain electron donors when activated by photoinduced single electron transfer (SET) reactions.[1-6] In some cases the occurrence of fragmentation is attributed chiefly to a greatly reduced carbon-carbon bond energy in the donor cation radical compared to the corresponding neutral molecule.[2,7] Studies in our laboratories have focused on electron-transfer quenching of excited singlet acceptors by amino alcohols and diamines in nonpolar solvents. For the former we have shown that moderately efficient (in some cases) and chemically clean reaction occurs in nonpolar solvents within contact ion pairs in which *both* donor cation-radical (dcr) and acceptor anion-radical (aar) play important roles. The crucial step competing with reaction-limiting back electron transfer is the concerted fragmentation and deprotonation of the dcr with the aar acting as a base. Herein we report a novel reaction in which scission of a strong carbon-carbon bond in an unexcited donor can be brought about via quenching of an excited acceptor. In this case, the aar seems to function as a nucleophile in a displacement within the contact ion pair; the net reaction involves a chemically clean and yet unprecedented ketone to amide interconversion. This kind of reactivity fits well into an emerging pattern of contact ion pair reactivity.

Irradiation (with a high-pressure mercury lamp filtered to pass light from 400 to 440 nm) of 9,10-dicyanoanthracene (DCA) in the presence of amino ketone **1** in deuterated benzene (freeze-pump-thaw vacuum degassed solution) with a trace of water (0.011%) leads to a bleaching of the long-wavelength absorption of DCA together with formation of photoproducts, which are indicated by NMR and GC-MS analysis to be acetone, morpholine, and an acylated form of DCA (eq 1). In a subsequent dark reaction over several hours, **2** and morpholine undergo further reaction to produce 4-acetylmorpholine and 9,10-dihydro-9,10-dicyanoanthracene, $DCAH_2$ (eq 2). The overall result of the reaction is a net two-electron reduction of DCA concurrent with an oxidative conversion of the amino ketone to an amide and a ketone. The reaction occurs relatively cleanly with the indicated stoichiometry and overall 90% chemical yield and a modest quantum efficiency ($\Phi = 0.038$) under conditions where quenching of the fluorescence of DCA is nearly complete. The initial photolysis produces a singlet at 1.69 ppm in the NMR spectrum, consistent with either structure **2a** or **2b**.

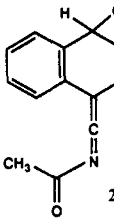


(1)

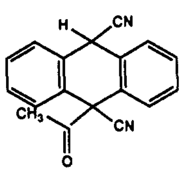


(cis and trans)

(2)

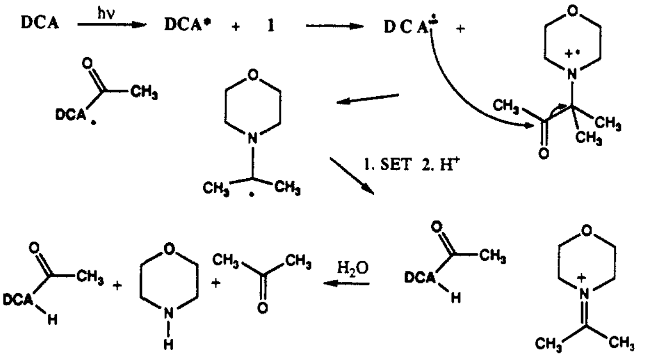


2a



2b

A reasonable mechanism for the overall conversion described in eq 1 is given below: The initially formed amino radical has a low oxidation potential and would be expected to undergo a second electron transfer.[4,8]



While an unassisted cleavage of $1^{\bullet+}$ could be proposed to yield the same products, thermochemical cycle estimation of the carbon-carbon bond energy in $1^{\bullet+}$ of ca. 30 kcal/mol suggests that the aar-assisted path is more probable.[8]

In contrast to the amino alcohol cleavage processes mediated by photoinduced electron transfer which occur in a wide range of solvents, the present reaction has been found to occur cleanly in benzene, but in more polar solvents, such as acetonitrile and methanol, both the quantum yield and the chemical yield are decreased. Thus, in the present case, the reaction is evidently governed both by the generation of reactive partners as a contact ion pair or exciplex and also by the absence of appreciable solvent stabilization of the potential nucleophile and substrate. Other

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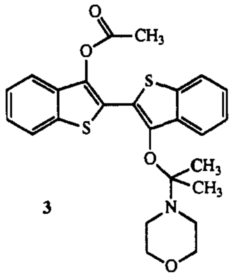
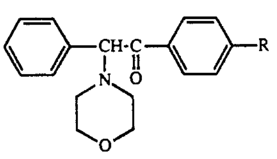
products, as yet unidentified, are produced in the much more complex reactions occurring under comparable photolysis in the absence of water or in more polar solvents; these products could result from "radical-like" reactivity of the partners such as has been observed in photoinduced electron transfer reactions of cyanoaromatics with donors such as triethylamine in studies by Ohashi,[9] Arnold,[10] and others.[11]

Related reactions have been observed with other donor–acceptor combinations, suggesting that this reaction path may be fairly general for photogenerated contact ion pairs in nonpolar solvents. Irradiation of thioindigo in the presence of **1** in degassed benzene solution leads cleanly to a metastable adduct whose NMR and visible spectra are consistent with the structure **3**, which could by formed by a comparable aar-induced cleavage of $\mathbf{1}^{\bullet+}$. Irradiation of DCA in the presence of amino ketones **4** and **5** also leads to amide and carbonyl products; in both cases, the corresponding 4-benzoylmorpholine, benzaldehyde, benzoin, and deoxybenzoin products are formed.



3



4 R=H
5 R=CH3

Acknowledgment. We thank the Department of Energy (Grant No. DE-FG02-86ER13504) for support of this research. W.R.B. is pleased to acknowledge a Faculty Development Fellowship from the Charles A. Dana Foundation.

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Interception of Copper Polysulfide Clusters in the Reaction of Copper and Sulfur in Donor Solvents: Polysulfide Complexes as the Link between Molecular and Nonmolecular Metal Sulfides

Emannuel Ramli, Thomas B. Rauchfuss,* and
Charlotte L. Stern

School of Chemical Sciences and
Materials Research Laboratory, University of Illinois
505 South Mathews Street, Urbana, Illinois 61801

Received January 12, 1990

We report a simple and potentially powerful entry into metal sulfide chemistry which involves donor solvent-assisted synthesis from the elements. The new methodology has synthetic and mechanistic implications bearing on the relationship of metal polysulfides[1] to solid-state materials.

With an interest in layered, mixed valent copper chalcogenides, we sought to develop a low-temperature synthesis of CuS (covellite).[2] We prepared covellite by the reaction of 200-mesh copper powder (928 mg, 14.6 mmol) and sulfur (458 mg, 14.3 mmol) in refluxing pyridine (py, 30 mL). After 12 h, the colorless supernatant was removed, leaving a 95% yield of covellite, pure by powder X-ray diffraction. If the same reaction is conducted at room temperature, the formation of CuS is accompanied by the appearance of an orange soluble species. After 12 h, the solution was filtered and diluted with hexanes, to give a 10–15% yield of orange crystalline $[CuS_{2.5}(py)]_n$ (**1**).[3] Compound **1** was identified as $Cu_4(S_5)_2(py)_4$ by a single-crystal X-ray diffraction study[4] of its pyridine solvate (Figure 1). This cluster consists of a compressed tetrahedral array of four copper atoms bound together by two pentasulfido chains.[5,6] The cluster has ap-

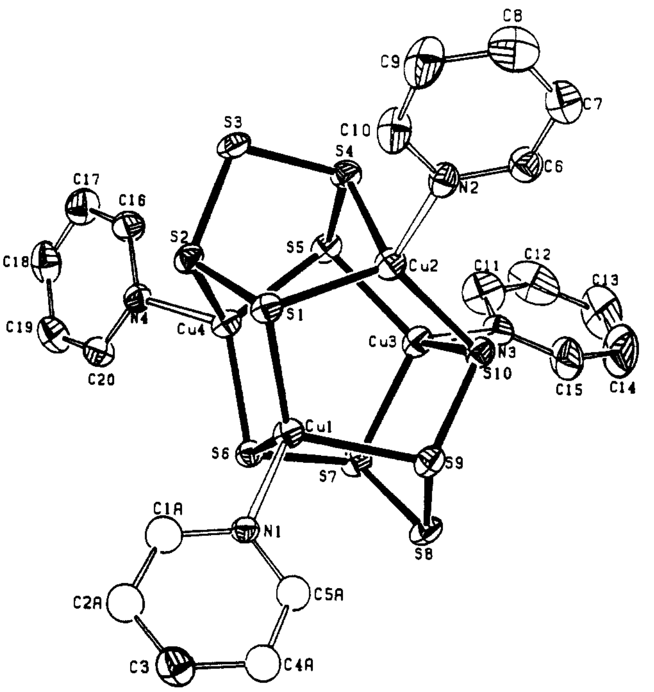
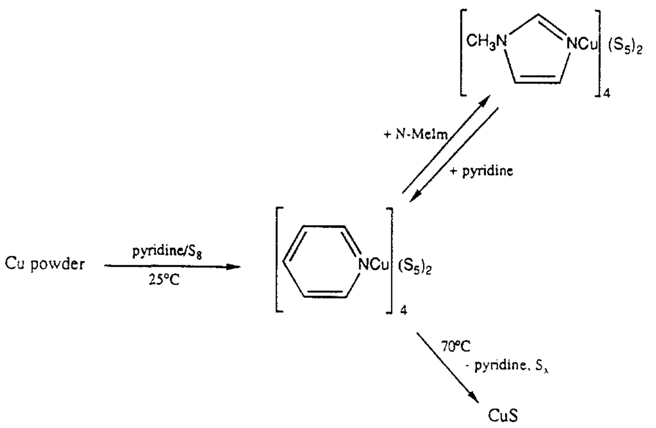


Figure 1. The structure of the $Cu_4(S_5)_2(NC_5H_5)_4$ molecule with thermal ellipsoids drawn at the 35% probability level. Representative distances (Å): Cu(1)S(1) = 2.286 (2), Cu(1)-S(6) = 2.304 (2); Cu⋯Cu distances fall into two categories, four distances at 3.206 (1)–3.309 (1), the two others at 3.881 (2) and 3.917 (1); Cu(1)-S(9) = 2.361 (2), Cu-N(1) = 2.074 (6); S-S distances range from 2.055 (3) to 2.081 (3). L-Cu-L angles range from 101.45 (8) to 120.85 (8)°.

Scheme I



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(3) Anal. Found (Calcd): C, 27.37 (26.95); H, 2.49 (2.27); N, 6.44 (6.29); Cu, 28.05 (28.52); S, 34.65 (35.97).

(4) $[Cu_4(S_5)_2py_4]\cdot 1.5py$ crystallizes from pyridine/hexane in the monoclinic space group $P2_1/n$ with $\alpha = 90°$, $\beta = 93.35$ (2)°, $a = 9.200$ (2) Å, $b = 21.839$ (4) Å, $c = 18.754$ (2) Å, $Z = 4$, and $\rho_{calcd} = 1.783$ g/cm^3. Using Mo Kα radiation, 5890 reflections were collected (−70 °C), of which 3418 were observed ($I > 2.58\sigma(I)$). The structure was solved by SHELX-86 and refined to a final $R = 0.040$, $R_w = 0.046$. Further details are provided in the supplementary material.

(5) For a recent discussion of copper polysulfide anions, see: Kanatzidis, M. G.; Park, P. *J. Am. Chem. Soc.* **1989**, *111*, 3767.

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