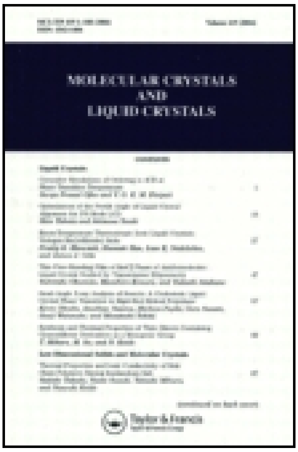

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Fragmentation of Amino Ketones by Photoinduced Electron Transfer

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FRAGMENTATION OF AMINO KETONES BY PHOTOINDUCED ELECTRON TRANSFER

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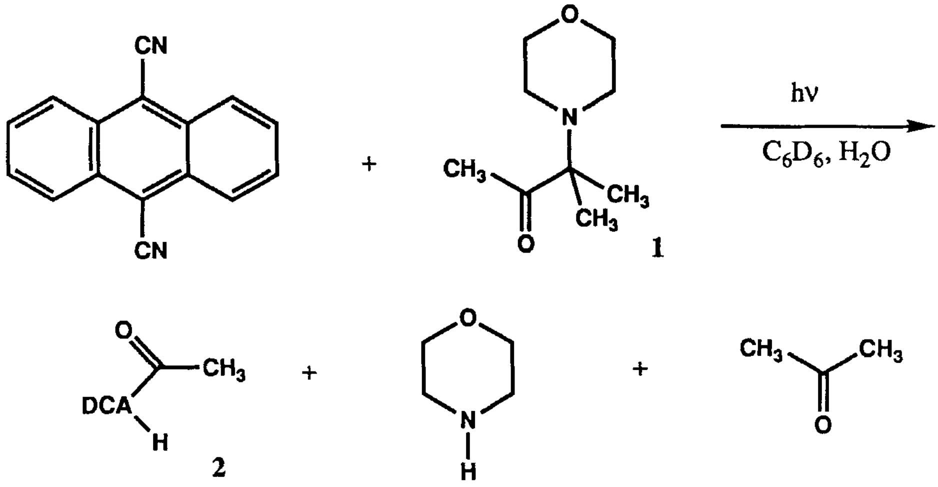
Abstract. Irradiation of electron acceptors such as 9,10-dicyanoanthracene (DCA) in the presence of the amino ketone 3-methyl-3-(4-morpholinyl)-2-butanone and water in nonpolar solvents leads to an oxidative cleavage of the amino ketone to form ultimately 4-acetylmorpholine and acetone together with 9,10-dihydro-9,10-dicyanoanthracene. A mechanism can be developed whereby single-electron transfer quenching of the excited DCA is followed by a nucleophilic attack on the acyl carbon of the cation radical; an intermediate acyl-DCA adduct has been detected and its thermal decomposition to the final products observed. The net result is an unprecedented ketone to amide interconversion in which a strong carbon-carbon bond in the donor is selectively cleaved. Related reactions are observed with other acceptors (thioindigo) and other amino ketones.

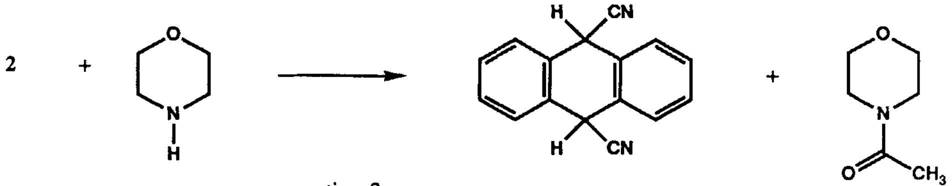
Keywords: Fragmentation, electron transfer, 9,10-dicyanoanthracene, anion-radical, cation-radical

Herein we report a novel reaction in which scission of a strong carbon-carbon bond in a unexcited donor can be brought about *via* quenching of an excited acceptor. In this case the acceptor anion-radical 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.

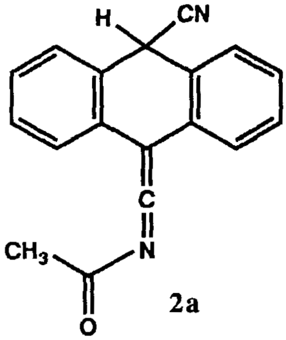
Irradiation (with a high pressure mercury lamp filtered to pass light from 400nm to 440nm) of 9,10-dicyanoanthracene (DCA) in the presence of amino ketone **1** in deuterated benzene (freeze-pump-thaw vacuum degassed solution) with a trace of water (0.011%) leads to a bleaching of the long wavelength 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 (equation 1). On a subsequent dark reaction over several hours **2** and morpholine undergo further dark reaction to produce 4-acetylmorpholine and 9,10-dihydro-9,10-dicyanoanthracene, $DCAH_2$ (equation 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 (Φ=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**:



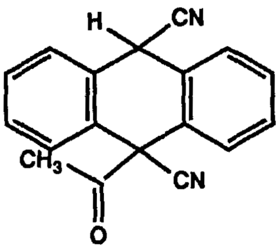
equation 1



equation 2

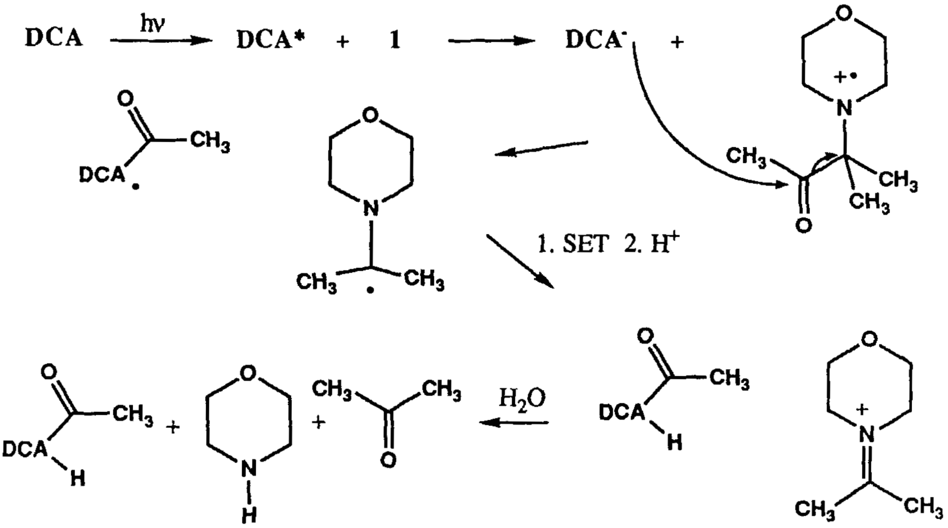


2a



2b

A reasonable mechanism for the overall conversion described in equation 1 is given below:

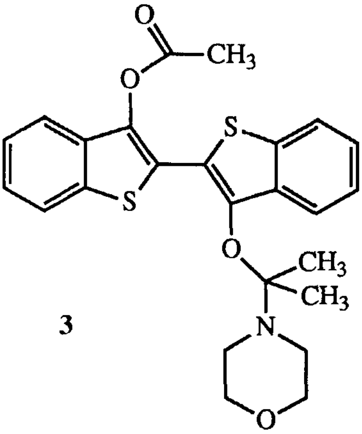


The initially formed amino radical has a low oxidation potential and would be expected to undergo a second electron transfer.[4,8]

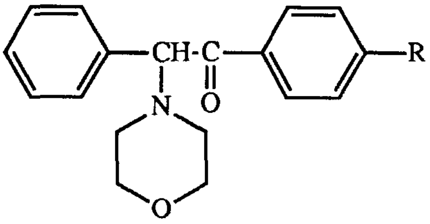
While an unassisted cleavage of $1^{+\bullet}$ could be proposed to yield the same products, thermochemical cycle estimation of the carbon-carbon bond energy in $1^{+\bullet}$ of *ca.* 30 kcal/mole suggests that the aar-assisted path is more probable.[1]

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 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[2], Arnold[3] and others[4].

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 with 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.

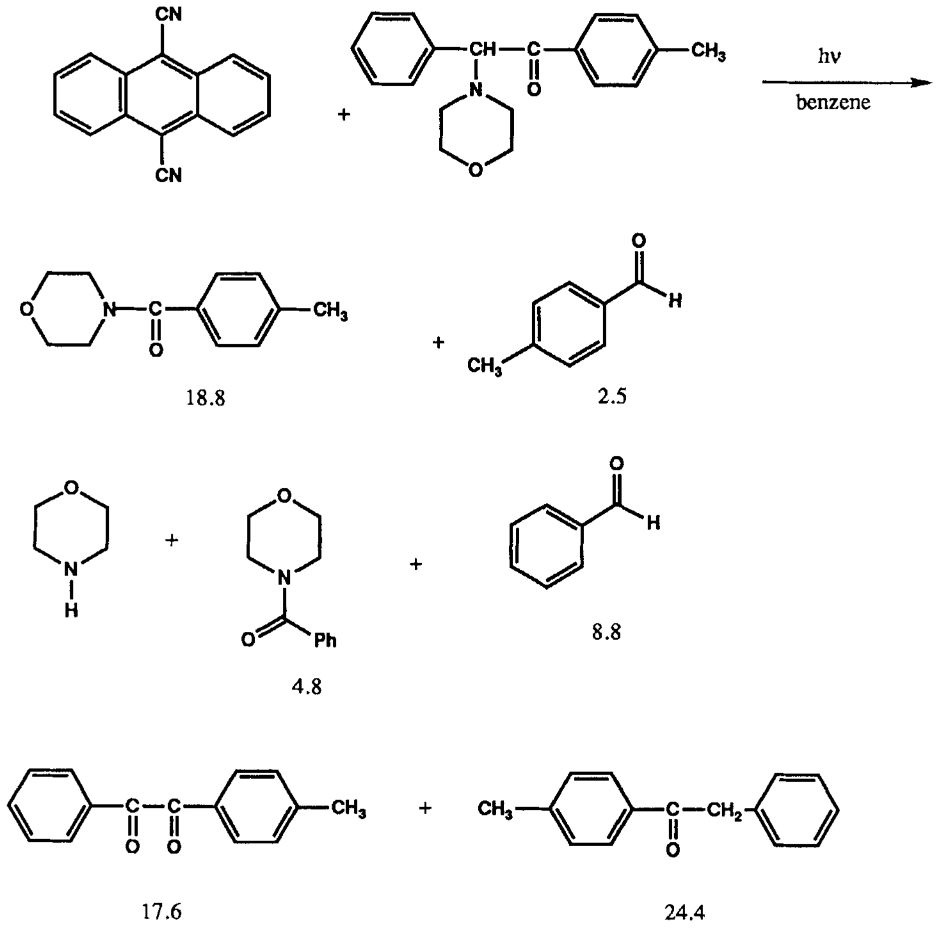


3

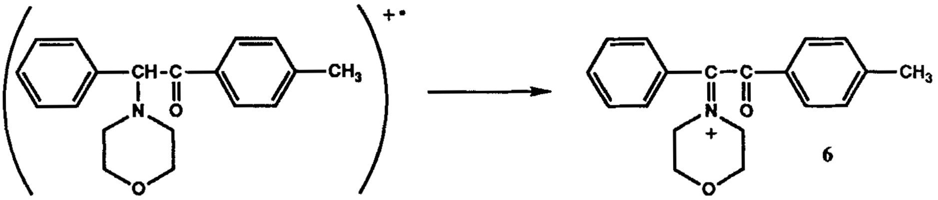


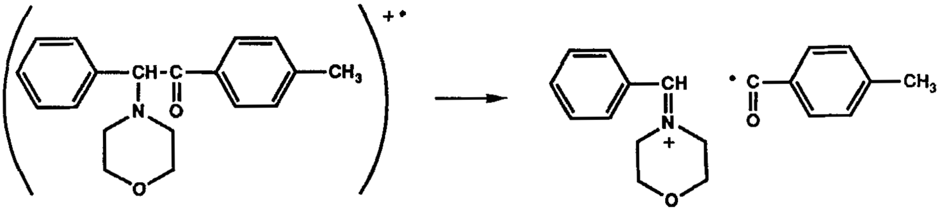
4 R=H
5 $R=CH_3$

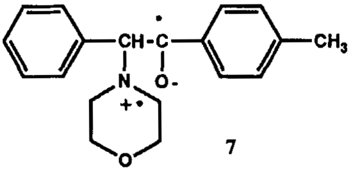
The accompanying scheme illustrates the product distribution


CN
CN
+
CH
C
N
O
O
CH₃
hv
benzene
O
N
C
O
CH₃
18.8
+
O
H
CH₃
2.5
O
N
H
+
O
N
O
Ph
4.8
+
O
H
8.8
C
C
O
O
CH₃
17.6
+
CH₃
C
CH₂
O
24.4

for the reaction with **5**. The more complex reaction can be attributed to two factors: the presence of an α-hydrogen and the possibility of deprotonation and subsequent electron transfer to produce **6**, and, secondly, the lower bond dissociation energy of the radical cation of **5** and consequent ease of fragmentation. The only product unaccounted for by these considerations is the substituted deoxybenzoin. This product might arise from sensitized Type II process involving zwitterion **7**. These processes are depicted below.







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[1] Bond dissociation energy for the radical cation was taken to be equal to the ionization potential of the radical (5.7 eV, Wayner, D. D. M.; McPhee, D. J.; Griller, D. J. Am. Chem. Soc. **1988,** 110, 132) minus the ionization potential of the neutral (7.9 eV) plus the bond dissociation energy of the neutral (81 kcal/mol).

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