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PHOTOCHEMICAL ELECTRON TRANSFER REACTIONS OF 4-TRICHLOROMETHYL-4-METHYL-2,5-CYCLOHEXADIEN-1-ONES[1]

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Abstract: Ultraviolet irradiation of the title compounds in amine solvents results in transformations attributed to initial formation of radical ions by electron transfer, the quantum efficiency of reaction depending on the ionization potential of the amine.

Cross-conjugated cyclohexadienones have been the subject of intensive photochemical investigation for many years.[2] In this laboratory, dienones 1a and 1b have been shown to undergo a variety of phototransformations, depending on the reaction conditions, including H-abstraction from the solvent followed by expulsion of $Cl_3C^\cdot$ to give phenols, photorearrangement to isomeric lumiketones via zwitterionic intermediates, nucleophilic trapping of zwitterions followed by Grob-type anionic fragmentations, as well as more complex transformations.[3] We now report new reaction pathways observed on irradiation of dienones 1a and 1b and 1c in the presence of amines involving intermediate radical ions.

When dienones 1a-c were irradiated in a variety of amine solvents (see Table I), reaction occurred to give phenols 2a-c, hexachloroethane, amine hydrochloride and a new series of dienones 3a-c in which one of the chlorines has been replaced by hydrogen. No lumiketone photoisomers could be detected in any of the photolysates by GC/MS analysis.* The products were identified by spectral analysis and independent synthesis. Although all the amines in Table I induced photoreduction of the dienones to the phenols 2, the quantum efficiency of the reaction of 1b is dependent on the ionization potential of the amine (Table I). Furthermore, those amines lacking α-hydrogens give much poorer yields of 2b from 1b compared to the yields observed when amines of similar ionization potentials possessing α-hydrogens were utilized.

The photoreduction of aromatic ketones by amines has been extensively studied,[4,5] and has been proposed to proceed via initial charge transfer interactions between the excited ketone and the amine in an exciplex, leading ultimately to the production of the amine radical cation and the ketyl radical anion. In the present instance, the n,π* triplet excited state of the dienone, which under normal circumstances decays to a zwitterionic intermediate,[3] appears to be intercepted by the amine. The rate constant k_{ir} for formation of the triplet dienone-amine exciplex should be correlated by the well-known Weller equation (eq. 1),[5,6] where ΔG is the Gibbs free energy for electron transfer from the amine to the excited ketone, E_T is the triplet excitation energy of the ketone, $E\ (D/D^+)$ is the oxidation potential of the donor (which in general correlates with its ionization potential IP_D), $E\ (A^-/A)$ is the reduction potential of the acceptor, and C is a constant. This equation can be simplified as shown in equation 2, where C' is a constant for a reaction for a given acceptor with a series

$$\ln k_{ir} \propto \Delta G \approx E_T + E\ (D/D^{+}) - E\ (A^{-}/A) + C \qquad (1)$$

$$-\ln k_{ir} = \beta \cdot IP_D \approx C' \qquad (2)$$

of amine donors. A proposed reaction mechanism is shown in Scheme I, involving irreversible electron transfer from the amine to the electronically excited ketone to give a dienone radical anion (A) which proceeds to phenol 2 with an efficiency F_A by abstraction of a proton from the α-carbon of the amine radical cation to give a ketyl radical (B), which then expels $Cl_3C^{\cdot}$ with efficiency F_B to give phenol 2 and hexachloroethane. The quantum efficiency of phenol formation would then be given by equation 3, where the second term in the denominator represents the sum of all the first order rate constants for reaction and decay modes of the triplet excited dienone which compete with electron transfer, and ϕ_{ST} is the triplet yield, which is known to be unity for these compounds.[3] For the series of amines studied possessing α-H, one would expect variations in F_A and F_B to be small. Taking the case where all quenches result in fragmentation, i.e., $F_A = F_B =$ unity, combination of equations 2 and 3 leads to equation 4, which directly relates the quantum efficiency of phenol formation to the ionization potential of the electron donor (amine).

$$\phi_{phenol} = \frac{\phi_{ST}\ k_{ir}\ [\text{Amine}]\ F_A F_B}{k_{ir}\ [\text{Amine}] + \Sigma k_i} \qquad (3)$$

$$\ln\ (1/\phi_{phenol} - 1) = \beta \cdot IP_D + \text{constant} \qquad (4)$$

This relationship was shown to be closely obeyed for a series of five amines possessing α-hydrogens whose ionization potentials varied over a 2.5 eV range (Figure 1). The linearity of this plot (r = 0.993) supports the proposed mechanism for phenol formation given in Scheme I. In the absence of an appropriate proton donor, as with aniline and tert-butylamine, the radical ion presumably reverts to ground state dienone, and relationship (4) is not obeyed.

Experiments designed to elucidate the mechanism of formation of dienones 3 under these reaction conditions are presented in the accompanying paper.

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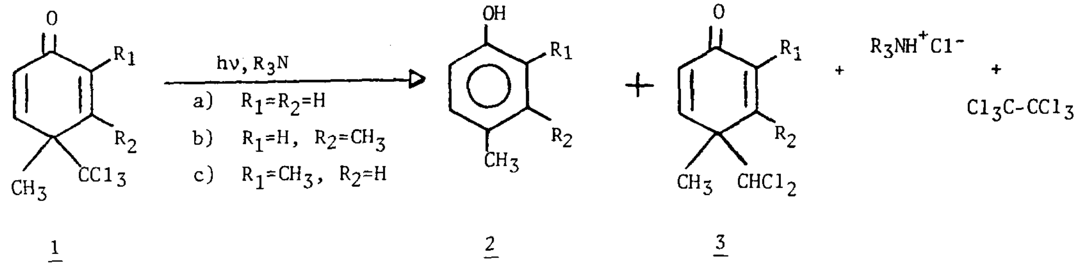
*Note: Lumiketone (see structure 5b following paper) has been detected in trace amounts in photolysis in t-butyl amine (I.P. 8.64 eV). However, it has been found that authentic lumiketone undergoes photochemical decomposition in neat amine solvents.



Scheme 1

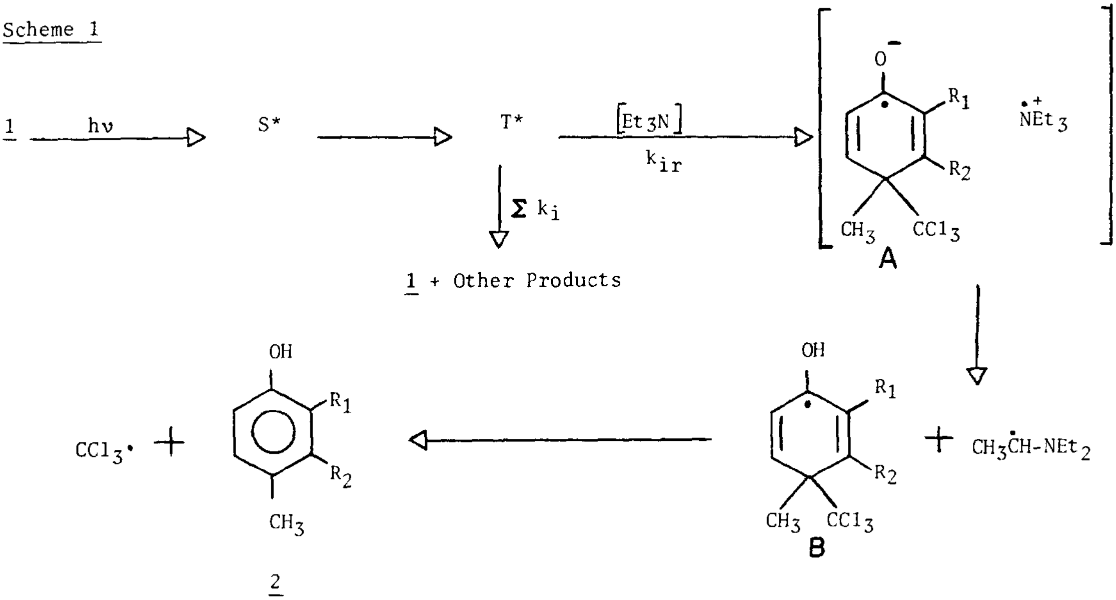


Figure 1

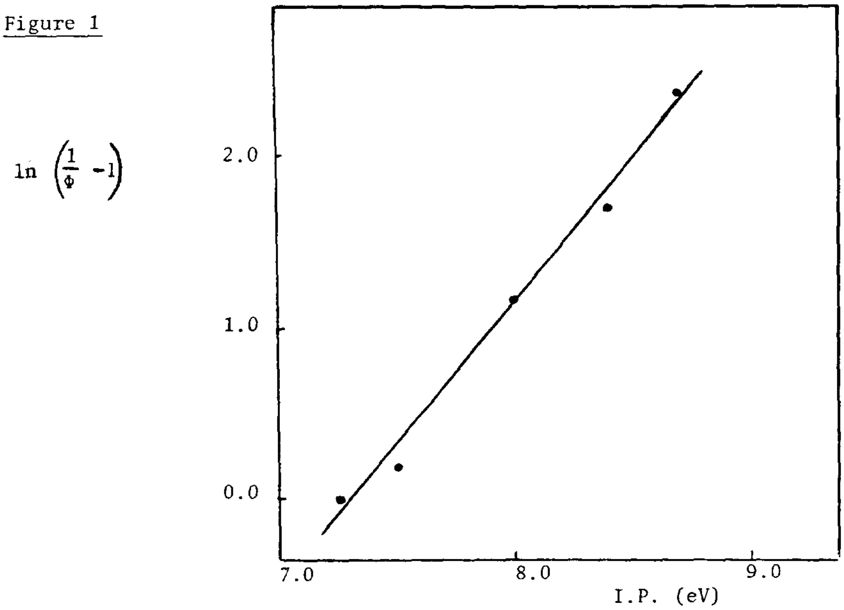


Table I

Quantum Efficiencies for Formation of Phenol 2b Upon Irradiation of Dienone 1b in Amine Solvents[a]

Amine	Ionization Potential (eV)[b]	ϕ_{2b} [c]
Tri-n-propylamine	7.23	0.50
Triethylamine	7.50	0.45
Aniline	7.70	0.056
Diethylamine	8.01	0.24
Pyrrolidine	8.40	0.16
tert-Butylamine	8.64	0.026
iso-Butylamine	8.70	0.09

a) Irradiation of 0.1 M solutions of dienone 1b in the amines as solvent in pyrex test tubes in a rotating turntable, cooled in a water bath at room temperature, using a 250-W high pressure mercury lamp (Quantum Yield Photoreactor, Applied Photophysics, Ltd., London).

b) Handbook of Chemistry and Physics, 60th Edition. R. Weast, ed., CRC Press, Inc., Boca Raton, 1980, p. E-75.

c) Quantum efficiencies determined relative to that for formation of 2b from 1b in ethyl ether, determined previously (ref. 3) to be 0.47 at 366 nm.

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