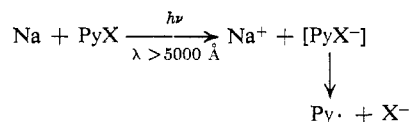


and the spectra in Figures 1–3 are due to 2-, 3-, and 4-pyridyl radicals, respectively. The plausibility of the an-



ion formation under the circumstance has been already demonstrated.² The splittings resolved in Figures 1–3, however, suggest hyperfine coupling interactions which are much larger than those expected for an anionic π radical. They can be easily understood if it were a σ radical, $\text{Py}\cdot$, resulting from a spontaneous decomposition of the anion as indicated above.

Depicted below the observed spectra in Figures 1–3 are the spectral patterns of the pyridyl radicals calculated by the INDO molecular orbital theory.⁴ The general agreement between the calculated pattern and the observed spectra strongly substantiates our proposed assignments. Thus the triplet pattern with a spacing of 27 G seen with 2-pyridyl radical (Figure 1) is attributed to the hyperfine structures (hfs) due to the ¹⁴N nucleus, and the doublet pattern of 22 G separation observed with 3-pyridyl radical is assigned to the hfs with the 4 proton. As expected, the triplet-of-triplets pattern observed with 4-pyridyl radical (Figure 3) is very similar to that observed with phenyl radical.⁵ The larger triplet with a spacing of 19 G is assigned to the hfs with the 3 and 5 protons, and the smaller triplet of 9 G to the 2 and 6 protons.

No explicit attempt to generate pyridyl radicals in order to examine their esr spectra has been reported previously. The esr signal detected in γ -irradiated solid pyridine was initially assigned to pyridine cations,^{6,7} but was later reinterpreted as arising from 2-pyridyl radicals.⁸ Our present result strongly supports the latter assignment.

In our earlier attempts to generate pyridyl radicals by direct uv photolysis ($\lambda < 4000 \text{ \AA}$) of pyridyl iodides, we observed only the radicals which can only result from a process involving a rupture of the aromatic ring. Corresponding irradiation of a matrix containing pyridyl radicals generated by the photoelectron transfer process led to disappearance of the spectrum reported here and appearance of the spectrum identical with that obtained by direct photolysis. Thus the rupturing of the ring appears to be a result of a photolytic process imposed on pyridyl radicals. Detailed analysis of the esr spectra of the pyridyl radicals and their photolysis sequence under uv irradiation will be reported soon.

Acknowledgments. We thank Dr. L. Skattebøl for his synthesis of 4-iodopyridine used in this study.

(4) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967); *J. Amer. Chem. Soc.*, **90**, 4201 (1968).

(5) P. H. Kasai, E. Hedaya, and E. B. Whipple, *ibid.*, **91**, 4364 (1969).

(6) C. David, G. Geuskens, A. Verhazzelt, and J. F. M. Oth, *Mol. Phys.*, **11**, 257 (1966).

(7) K. Tsuji, H. Yoshida, and K. Hayashi, *J. Chem. Phys.*, **45**, 2894 (1966).

(8) H. J. Bower, J. A. McRae, and M. C. R. Symmons, *Chem. Commun.*, 542 (1967).

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A New Quenching Mechanism of the (π - π^*) Ketone Triplet State

Sir:

We herein wish to describe some unusual observations encountered during a photochemical study of 1-benzoyl-8-benzyl-naphthalene (**1**).¹ Photolysis (366 nm)² of **1** ($\epsilon_{366 \text{ nm}} 140$) in degassed³ benzene solution ($9.5 \times 10^{-2} M$) gave, in an extremely clean reaction, a 1.4:1 mixture of the alcohols **2** (mp 110–115°) and **3** (mp 147–148°), respectively (91% isolated yield).⁴ A quantum yield of 0.30 was obtained for the reaction at 7% conversion.⁵ The structures of **2** and **3** were confirmed not only by their well-defined nmr and mass spectra but also by their facile acid-catalyzed dehydration into the hydrocarbon 1,2-diphenylacene.⁶

Ketone **1** sensitizes the isomerization of *trans*- to *cis*-stilbene. In addition, the photoreaction of **1** (formation of **2** and **3**) is quenched by *trans*-stilbene as well as by oxygen. Using the benzophenone-sensitized isomerization of *trans*-stilbene as a standard,⁷ the intersystem crossing efficiency of **1** was found to be unity. Stern–Volmer treatment of **1** using *trans*-stilbene as the quencher gave a linear plot with a slope of $5.4 \times 10^4 M^{-1}$ (Figure 1). A limiting value of $9.3 \times 10^4 \text{ sec}^{-1}$ for k_r was determined from the expression $\Phi_0/\Phi_Q = [k_q/k_r][Q] + 1$, assuming $k_q = 5 \times 10^9 \text{ l./mol sec}$.⁸ This low value for k_r rules out reaction from either the excited singlet state of **1**⁹ or a higher triplet state of **1**.¹⁰

Phosphorescence spectra of **1** have been measured at 77°K in several solvents.¹¹ A small bathochromic shift (characteristic of π - π^* triplet states)¹² was observed for the 0–0 band of **1** on changing from methylcyclohexane to EPA glass. The spectra of **1** closely resemble those (recorded in the same solvents)¹¹ of 1-naphthyl phenyl ketone, a substance whose triplet state has been assigned the π - π^* configuration.¹³ Irradiation of ketone **1** at 77°K in either methylcyclohexane or EPA glasses leads to the formation of alcohols **2** and **3**. These data strongly suggest that the lowest

(1) A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **90**, 5314 (1968).

(2) A water-cooled Hanovia Type L 450-W medium-pressure lamp fitted with Corning color filters 0–52 and 7–54 was employed as the 366-nm light source.

(3) All reactions were run in sealed Pyrex tubes degassed by four freeze–thaw cycles at 10^{-5} Torr.

(4) All melting points are uncorrected. Satisfactory analyses and spectral data were obtained for all new compounds.

(5) The actinometer used for these measurements was the 0.1 M benzophenone-sensitized isomerization of 0.1 M *trans*-stilbene. Several different quantum yields have been reported for this actinometer. We have chosen the value $\Phi = 0.56$ reported by H. A. Hammond, D. E. DeMayer, and J. H. R. Williams, *J. Amer. Chem. Soc.*, **91**, 5180 (1969). The same quantum yield was obtained for the photoconversion of **1** into **2** and **3** when methanol was used as the reaction solvent.

(6) G. Wittig, M. Leo, and W. Wiemer, *Ber.*, **64**, 2405 (1931).

(7) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

(8) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

(9) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1967, pp 280–281, and references cited therein.

(10) R. S. H. Liu and J. R. Edman, *J. Amer. Chem. Soc.*, **90**, 213 (1968).

(11) Luminescence spectra determinations were carried out at the Eastman Kodak Company Research Laboratories.

(12) For examples, see (a) H. McConnell, *J. Chem. Phys.*, **21**, 700 (1952); (b) G. Porter and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

(13) C. Parkanye, E. J. Baum, J. Wyatt, and J. N. Pitts, Jr., *J. Phys. Chem.*, **73**, 1132 (1969).

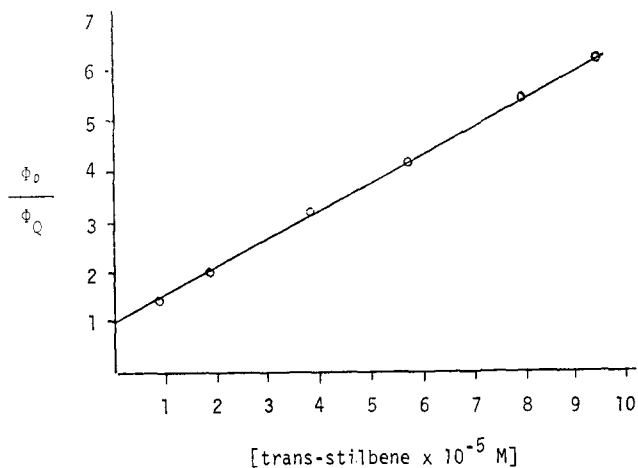


Figure 1. Stern-Volmer plot of the quenching of ketone 1 by *trans*-stilbene (Q).

triplet state of 1 ($E_T = 58.2 \text{ kcal mol}^{-1}$) is $\pi-\pi^*$ in character and also that the spectroscopically observed $^3(\pi-\pi^*)$ state is the reactive species both at 77°K and at room temperature. Hence, the photoconversion of 1 into 2 and 3 is unusual since it involves hydrogen abstraction by a $^3(\pi-\pi^*)$ ketone via a seven-membered ring transition state.¹⁴ The low value of k_r for the photoreaction is consistent not only with the supposition that hydrogen abstraction in 1 occurs via a $^3(\pi-\pi^*)$ state but also occurs through a seven-membered ring transition state. Rate constants for hydrogen abstraction by $^3(\pi-\pi^*)$ ketones through six-membered ring transition states range from $1 \times 10^8 \text{ sec}^{-1}$ to $1 \times 10^9 \text{ sec}^{-1}$.¹⁵

We have examined the effect of a variety of triplet-state sensitizers on the photoreaction of 1. Michler's ketone ($E_T = 61 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 1.00$),¹⁶ 2-methylanthraquinone ($E_T = 63 \text{ kcal mol}^{-1}$),¹⁷ and thioxanthone ($E_T = 65 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 1.00$)¹⁶ all show a marked concentration dependence, sensitizing the reaction at low concentrations but quenching the reaction at high sensitizer concentrations. A detailed plot of this effect for Michler's ketone is given in Figure 2. Benzophenone ($E_T = 69 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 1.00$)¹⁶ at high concentrations smoothly sensitizes the photoreaction of 1 while carbazole ($E_T = 70 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 0.36$)¹⁶ at high concentrations efficiently quenches the photoreaction of 1.

The behavior of naphthalene ($E_T = 61 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 0.39$),¹⁶ acetophenone ($E_T = 74 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 0.99$),¹⁶ and acetone ($E_T = 76 \text{ kcal mol}^{-1}$, $\Phi_{ST} = 1.00$)¹⁶ have also been studied. Since these compounds have no significant absorption at 366 nm, their effect on the photoreaction of 1 was examined in two different ways. In the first case, solutions of 1 and naphthalene, acetophenone, or acetone in molar ratios of 1:5, respectively, were directly irradiated at 366 nm (all of the incident light was absorbed by ketone 1). In the second set of experiments, Michler's

(14) For other examples of homo type II reactions, see P. Yates and J. M. Pal, *Chem. Commun.*, 553 (1970), and references cited therein.

(15) J. A. Barltrop and J. D. Coyle, *Tetrahedron Lett.*, 3235 (1968).

(16) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 132, and references cited therein.

(17) W. C. Neely and H. H. Dearman, *J. Chem. Phys.*, **44**, 1302 (1966). The authors wish to thank Mr. H. Gruen for a sample of 2-methylanthraquinone.

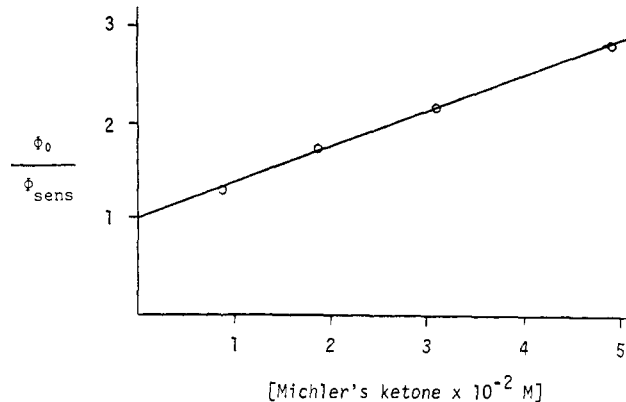
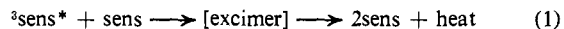


Figure 2. Plot of the quantum yield of the photoreaction of ketone 1 as a function of sensitizer concentration (Michler's ketone).

ketone ($1.72 \times 10^{-3} \text{ M}$) was added to absorb 90% of the incident light (at this concentration Michler's ketone sensitizes the photoreaction of 1). Under all of these conditions, neither naphthalene, acetophenone, nor acetone showed any quenching effect on the photoreaction of 1.

Two possibilities that could account for the above observations are: (1) the quenching is caused by a ground-state complex between ketone 1 and the sensitizer. (2) There is a chemical quenching reaction between the excited triplet state of ketone 1 and the sensitizer. For these reasons, absorption spectra were determined for mixtures of 1 and those sensitizers which act as quenchers (Michler's ketone, 2-methylanthraquinone, and thioxanthone). These spectra were simply the sum of the individual components and no charge-transfer complex bands were detected. Additionally, careful examination of these mixtures, after irradiation, gave no evidence of hydrogen transfer from ketone 1 to these quenching sensitizers.

Chapman and Wampfler have recently reported a concentration dependence for energy transfer from $^3(\pi-\pi^*)$ aromatic ketones, and have proposed that inefficiency may arise from sensitizer self-quenching (eq 1).¹⁸ We have found that efficient energy transfer



from a quenching sensitizer (Michler's ketone) to ketone 1 does occur, even at high sensitizer concentrations. This was determined by the following photostationary state measurements. Irradiation of mixtures of *trans*-stilbene ($1.03 \times 10^{-1} \text{ M}$) and ketone 1 ($2.17 \times 10^{-2} \text{ M}$) in benzene solution from 0 to 20 hr establishes the photostationary state of stilbene, as sensitized by 1, to be 81.9% *cis*-stilbene. The reported photostationary state of stilbene isomerization, sensitized by Michler's ketone, is 63.2% *cis*-stilbene.¹⁹ In our hands, values of 61.9 and 61.3% *cis*-stilbene were obtained (benzene solution) for the photostationary state using Michler's ketone ($1.63 \times 10^{-1} \text{ M}$) and *trans*-stilbene in concentrations of $1.02 \times 10^{-1} \text{ M}$ and $1.02 \times 10^{-2} \text{ M}$, respectively. Mixtures of Michler's ketone ($1.63 \times 10^{-1} \text{ M}$), ketone 1 ($4.75 \times 10^{-2} \text{ M}$),

(18) O. H. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969).

(19) G. S. Hammond, J. Saitli, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

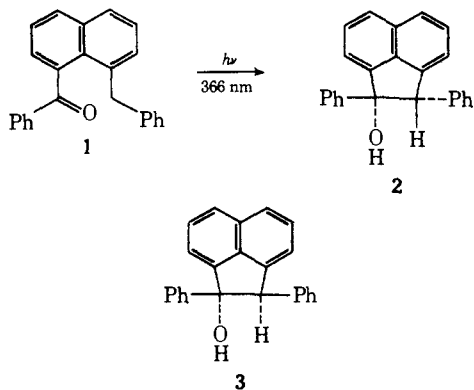
and *trans*-stilbene ($1.02 \times 10^{-1} M$) in benzene gave a stilbene photostationary state of 68.8% *cis*-stilbene.²⁰ A tenfold decrease in the stilbene concentration ($1.02 \times 10^{-2} M$) gave a photostationary state of 78.0% *cis*-stilbene. Clearly, the excitation energy of the Michler's ketone is transferred at the same rate to both ketone 1 and *trans*-stilbene in these experiments. Additional experiments show that, relative to 0.1 *M* benzophenone, the quantum yields for stilbene isomerization are the same at both high and low concentrations of Michler's ketone and thioxanthone. The same relative quantum yield was also found for high concentrations of Michler's ketone in the presence of ketone 1. Thus, sensitizer inefficiency *via* eq 1 does not seem to be an important process in the photoreaction of ketone 1. We suggest that the concentration-dependent sensitizer quenching observed for 1 is due to a reaction between ground-state sensitizer and the $^3(\pi-\pi^*)$ state of the ketone yielding the vibrationally excited ground states of the sensitizer and ketone 1 (eq 2).²¹ Interestingly,



the quenching phenomena observed for 1 shows no correlation with sensitizer lifetimes as found by Chapman and Wampfler in their system.¹⁸

A singlet-state reaction analogous to eq 2 has recently been reported.²² Vibrational quenching of a triplet state has also been suggested to account for the reduced efficiency of the sensitized isomerization of *cis*-piperylene in the presence of 1,4-cyclohexadiene.²³

Further work on the intriguing implications of the process described in eq 2 are currently being investigated.



Acknowledgment. We are grateful for support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation.

(20) 99.8% of the incident light is absorbed by Michler's ketone under these conditions.

(21) A referee has suggested that charge-transfer exciplex quenching may also account for these concentration effects.

(22) R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, **90**, 2058 (1968), and references cited therein.

(23) A. M. Braun, W. B. Hammond, and H. G. Cassidy, *ibid.*, **91**, 6196 (1969).

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Thallium in Organic Synthesis. XIX. Photochemical Phenylation. An Effective Synthesis of Unsymmetrical Biphenyls from Arylthallium Ditrifluoroacetates¹

Sir:

Unsymmetrical biaryls are customarily prepared by the Gomberg reaction and variations thereof,² or by arylations by free radicals generated through the decomposition of peroxy intermediates.² However, symmetrical biaryls as well as mixtures of isomeric unsymmetrical biaryls are formed, and in yields usually well below 50%. The most attractive alternate procedure is photolysis of aromatic iodides in benzene solution, giving yields which range from 40 to 80%.³

We report a new aromatic phenylation reaction which involves photolysis of the readily accessible arylthallium ditrifluoroacetates⁴ in benzene. Products are formed in high yield and in a high state of purity. Thus, 0.01 mol of an arylthallium ditrifluoroacetate is suspended in 600 ml of benzene in a quartz vessel, nitrogen bubbled through for 15 min, and the suspension then irradiated (Rayonet photochemical reactor, 3000-Å tubes) for 18 hr.⁵ The benzene solution is evaporated to dryness; the residue is taken up in 100 ml of 1:1 ether-hexane and extracted twice with 30-ml portions of water. The dried organic layer is decolorized with charcoal, filtered through a short column of silica gel, and evaporated to yield the unsymmetrical biphenyl. Representative conversions are listed in Table I.

The above results are in agreement with a free-radical pathway which we suggest is initiated by a photolytically induced homolysis of the aryl C-Tl bond.⁶ Capture of the resulting aryl radical by benzene would lead to the observed unsymmetrical biphenyl; spontaneous disproportionation of the initially formed Tl²⁺ species [$\cdot\text{Tl}(\text{OCOCF}_3)_2$] to thallium(I) trifluoroacetate (isolated) and trifluoroacetoxy radicals,⁸ followed by reaction of the latter with aryl radicals, would account for the small amounts of aryl trifluoroacetates formed.¹⁰

(1) Part XVIII: A. McKillop, J. D. Hunt, and E. C. Taylor, *J. Organometal. Chem.*, in press.

(2) See, for example: (a) W. E. Bachmann and R. A. Hoffman, *Org. React.*, **2**, 224 (1944); (b) O. C. Dermer and M. T. Edison, *Chem. Rev.*, **57**, 77 (1957); (c) D. R. Augood and G. H. Williams, *ibid.*, **57**, 123 (1957).

(3) W. Wolf and N. Kharasch, *J. Org. Chem.*, **30**, 2493 (1965).

(4) (a) A. McKillop, J. S. Fowler, M. J. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Lett.*, 2423 (1969); (b) E. C. Taylor, F. Kienzle, R. L. Robey, and A. McKillop, *J. Amer. Chem. Soc.*, **92**, 2175 (1970).

(5) Most of the suspended solid dissolves after 1 hr. In some cases a considerably shorter irradiation time appears to be sufficient, but prolonged photolysis has no adverse effect upon the eventual yield of biaryls formed.

(6) The photolytic synthesis of aromatic nitriles from arylthallium ditrifluoroacetates in aqueous potassium cyanide solution has also been found to be a free-radical process.⁷

(7) E. C. Taylor, H. W. Altland, R. H. Danforth, G. McGillivray, and A. McKillop, *J. Amer. Chem. Soc.*, **92**, 3520 (1970).

(8) Thallium(III) carboxylates upon photolysis are known to yield intermediate thallium(II) carboxylates, which decompose spontaneously to thallium(I) carboxylates and carboxylate radicals.⁹

(9) J. K. Kochi and T. W. Bethea, III, *J. Org. Chem.*, **33**, 75 (1968).

(10) Trifluoroacetoxy radicals would be expected to decompose rapidly to trifluoromethyl radicals and CO₂.⁹ There was no evidence, however, for the formation of any trifluoromethylated aromatic hydrocarbons. The water extracts (see the experimental procedure described above) were strongly acidic, suggesting that the necessary hydrogen abstraction from the radical species formed by addition of the aryl radicals to benzene might have been effected by trifluoroacetoxy radicals.