were due to some contaminant in their sample of I. Indeed, the racemic phenanthrone in their study was utilized as obtained from the supplier (Aldrich) without further purification. We found that the melting point of I was raised from 84.5–85.5° to 90–90.5° on recrystallization of the same commercial material. Accompanying the change in melting point was a substantial decrease in the ultraviolet absorption of I in the long-wavelength band at 345 nm, where the flash excitation of I had been performed.[2] While no impurity was detectable in I by nmr, analysis by gas chromatography indicated some minor contaminants not found in the purified sample.

The flash photolytic behavior of I in the microsecond and millisecond time range was studied using standard techniques.[8] The behavior reported by RSR[2] could be quantitatively reproduced using the commercial, impure sample of I. However, no transients could be observed in flashing purified samples of I in benzene, 2-propanol, and carbon tetrachloride, monitoring from 40 μsec after the flash at wavelengths from 350 to 430 nm, working at very high sensitivity.[9] Furthermore, with the impure samples in 2-propanol a gradual decrease in the amount of the short-lived transient was observed, suggesting gradual consumption of the impurity by hydrogen abstraction reactions. Surprisingly, there was only a slight decrease in the amount of the long-lived transient under these conditions.

There is no doubt that the transients observed by RSR[2] are due in fact to some contaminating impurity, which can be removed by recrystallization. The exact nature of the impurity is purely conjecture at this time, but from its triplet energy (<61 kcal/mol) and rate of disappearance in hydrogen-donating solvents, a reasonable candidate is a substituted 1,2- or 1,4-naphthoquinone.[10,11]

The most important conclusion is that the observations of RSR[2] have absolutely no bearing on the photochemistry of I in particular and cyclohexenones in general.

Acknowledgment. We gratefully acknowledge partial support of this study by the Petroleum Research Fund, administered by the American Chemical Society.

[8] Experiments were made on an FP-2R apparatus supplied by Northern Precision Co., Ltd., London, using a krypton-filled flash lamp without filters. The data were obtained with 360-J flashes. Solutions were exhaustively degassed at high vacuum by the freeze–thaw technique.

[9] The sensitivity was much higher than that needed to detect transients with impure I.

[10] Triplet-state energies of 1,2- and 1,4-quinones are usually 50–57 kcal/mol above the ground state. See A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969, pp 93 and 239.

[11] Transient absorption has been found on flash photolysis of some 1,2- and 1,4-quinones in the 400–500-nm region, attributed to the triplet state and/or the semiquinone radical. For leading references, see: D. R. Kemp and G. Porter, *Chem. Commun.*, 1029 (1969); P. A. Carapellucci, H. P. Wolf, and K. Weiss, *J. Amer. Chem., Soc.*, 91, 4635 (1969); E. J. Land, *Trans. Faraday Soc.*, 65, 2815 (1969).

[12] Fellow of the Alfred P. Sloan Foundation, 1967–1969.

* Address correspondence to this author.

David I. Schuster,*,[12] Bruce M. Resnick
Department of Chemistry, New York University
University Heights, New York, New York 10453

Received August 29, 1970

A Photochemical Exchange Reaction of Michler's Ketone

Sir:

Michler's ketone, 4,4′-bis(*N*,*N*-dimethylamino)benzophenone, is reported to be photochemically reactive in cyclohexane solvent ($\phi_{\text{disappearance}} = 0.3$) but unreactive in isopropyl alcohol.[1,2] The solvent effect was attributed to a change in configuration of the reactive triplet state from n,π^* to π,π^*. Reactivity in cyclohexane was characterized as hydrogen atom abstraction by the nonbonding orbital of the carbonyl; however, characterization of the products has not been achieved. Other investigators agree that Michler's ketone is photoreactive in cyclohexane but conclude that the photoprocess does not involve hydrogen atom abstraction leading to pinacol.[3,4]

We have observed a photochemical exchange reaction of Michler's ketone which we feel describes the primary photochemical process. When Michler's ketone (0.010 *M*) is irradiated in benzene solution in the presence of ethanethiol (0.32 *M*), the quantum yield of disappearance of Michler's ketone is retarded by a factor of 3. Irradiation of Michler's ketone (0.01 *M*) in the presence of ethanethiol-*S-d* (0.32 *M*) exchanges up to 12 hydrogens of Michler's ketone for deuterium, ϕ_{exchange} equal to 0.09. The nmr spectrum of recovered Michler's ketone indicates that the methyl hydrogens are exchanged. In the absence of light no exchange is observed. The quantum yield for hydrogen–deuterium exchange is dependent on Michler's ketone concentration.[5] A plot of reciprocal of quantum yield *vs.* reciprocal of Michler's ketone concentration is linear, with least-squares slope and intercept of 0.047 ± 0.003 *M* and 5.3 ± 1.3, respectively. The reaction is efficiently quenched by 1,3-cyclohexadiene, giving a linear Stern–Volmer plot, least-squares slope 275 ± 46 l./mol.

The two quantum yield plots indicate that the primary photochemical process initiating the observed hydrogen–deuterium exchange is a reaction of excited-triplet-state Michler's ketone with ground-state Michler's ketone. Since the intercept of the plot of reciprocal of quantum yield *vs.* reciprocal of Michler's ketone concentration is greater than unity beyond experimental error, an energy wasting step must be included in a description of the mechanism. Bimolecular energy wasting (self-quenching) has been reported for several aromatic ketones with lowest energy π,π^* triplet states.[8] A general mechanism consistent with the data is presented in Scheme I,

[1] G. Porter and P. Suppan, *Trans. Faraday Soc.*, 61, 1664 (1965); 62, 3375 (1966).

[2] P. Suppan, *Ber. Bunsenges. Phys. Chem.*, 72, 321 (1968).

[3] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 87, 3361 (1965).

[4] E. J. Baum, J. K. S. Wan, and J. N. Pitts, Jr., *ibid.*, 88, 2652 (1966).

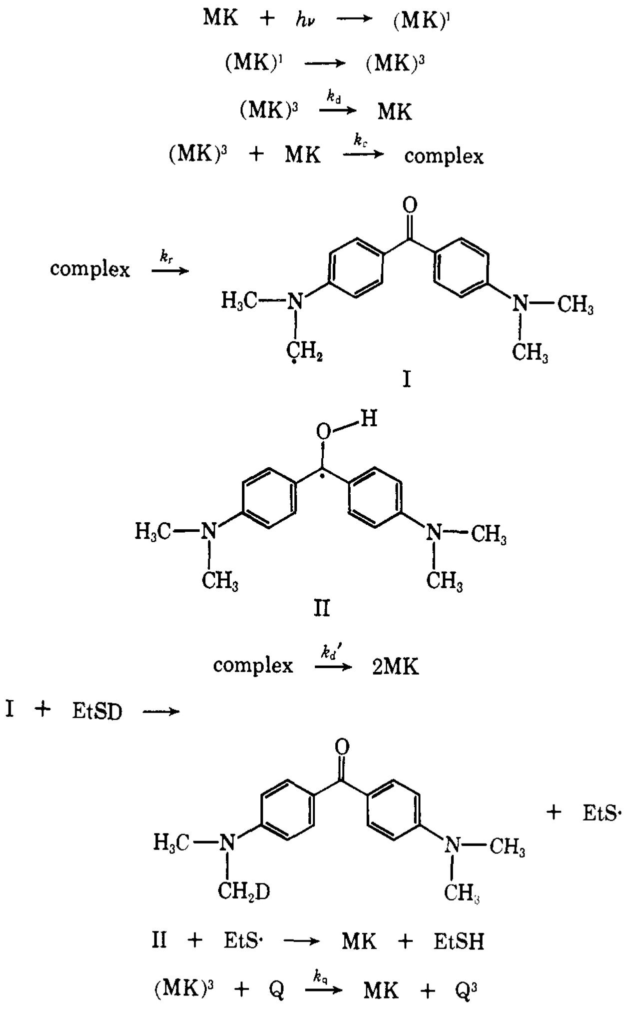
[5] Quantum yield measurements were conducted at 28° with a rotating photochemical apparatus[6] at 366 nm using potassium ferrioxalate actinometry.[7] The per cent deuterium incorporation was measured by mass spectrometry at 13 eV.

[6] F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, 1, 245 (1969).

[7] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, 235, 518 (1956).

[8] O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, 91, 5390 (1969).

Scheme I



$$MK + h\nu \longrightarrow (MK)^1$$

$$(MK)^1 \longrightarrow (MK)^3$$

$$(MK)^3 \xrightarrow{k_d} MK$$

$$(MK)^3 + MK \xrightarrow{k_c} \text{complex}$$

$$\text{complex} \xrightarrow{k_r} \text{I} + \text{II}$$

$$\text{complex} \xrightarrow{k_d'} 2MK$$

$$\text{I} + EtSD \longrightarrow + EtS\cdot$$

$$\text{II} + EtS\cdot \longrightarrow MK + EtSH$$

$$(MK)^3 + Q \xrightarrow{k_q} MK + Q^3$$

where MK = Michler's ketone and Q = 1,3-cyclohexadiene.

$$1/\phi = \left(\frac{k_r + k_d'}{k_r}\right)(1/\phi_{isc})\left(1 + \frac{k_d}{k_c[MK]}\right)$$

$$\phi/\phi_q = 1 + \frac{k_q[Q]}{k_d + k_c[MK]}$$

From the slope and intercept of the plot of reciprocal of quantum yield of exchange *vs.* reciprocal of Michler's ketone concentration, k_d (the rate of Michler's ketone triplet decay) and k_c (the rate of complex formation) are calculated to be 9×10^6 sec^{-1} and 1.0×10^9 l./(mol sec^{-1}), respectively.[9] From the intercept of the plot of reciprocal of quantum yield *vs.* reciprocal of Michler's ketone concentration, the rate of complex decay (k_d') is four times the rate of formation of radicals I and II (k_r). The magnitude of the rate constants k_d and k_c and the relationship between k_d' and k_r are consistent with the observed quantum yield of exchange (ϕ at 0.010 *M* Michler's ketone calculated from rate constants, 0.12; observed, 0.09).

We have considered two possible descriptions of the complex. One possibility is that the complex is an excited-state species, an excimer, not quenched by 1,3-cyclohexadiene. The decay process then would be excited-state decay and the reaction would be hydrogen atom transfer, giving radicals I and II. Another possibility is that the complex is an electron-transfer complex. In this case decay would occur by back electron transfer and the reaction to give radicals I and II would be proton transfer. Cohen[12] and others[13] have proposed electron transfer as an initial process in the photoreactions of ketones with amines. We cannot distinguish between these two processes at this time; however, it is interesting to note that the rate of complex formation is 100 times the rate of electron transfer from triethylamine to excited *p*-aminobenzophenone reported by Cohen.[14]

The exchange reaction does not exhibit the dramatic solvent effect reported earlier for Michler's ketone destruction.[1,2] Irradiation of Michler's ketone (0.010 *M*) in a polar solvent, spectrograde acetonitrile, in the presence of 0.32 *M* ethanethiol-*S-d* results in no deuterium exchange; however, irradiation in acetonitrile-d_3 in the presence of 0.32 *M* ethanethiol gives deuterium exchange, ϕ equal to 0.07. Apparently, acetonitrile is serving as the hydrogen atom source for the regeneration of Michler's ketone from radicals I and II. The lack of photodestruction reported in isopropyl alcohol can be explained likewise. Since photoreactivity is similar in both polar and nonpolar solvents, we conclude that the configuration of the reactive triplet state does not change dramatically as a function of solvent polarity. Even though the lowest energy triplet excited state of Michler's ketone is probably of π,π^* configuration,[15,16] the π,π^* excited triplet state cannot be assigned as the reactive excited state with certainty. Wagner has recently shown that the n,π^* triplet state, an upper triplet state, is the reactive state for several *p*-methoxyphenyl ketones in the type II photoelimination reaction.[17]

The mechanism of the exchange reaction suggests an explanation for the photodestruction of Michler's ketone in cyclohexane and benzene solution. Cyclohexane and benzene, not being particularly good hydrogen atom sources, are not capable of regenerating Michler's ketone from the radical species I and II. Combination of geminate radicals I and II producing a dimeric species III should be a favorable alternative reaction in the absence of a good hydrogen atom source. The dimeric species III contains essentially the same chromophore as Michler's ketone and should be capable of further photochemical reactivity. Irradiation

---

[9] For the calculation of k_d and k_c, the intersystem crossing efficiency of Michler's ketone was taken as unity.[10] A rate constant of 5×10^9 l./(mol sec^{-1}) was used for the rate of energy transfer in benzene, k_q.[11]

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

[11] H. J. L. Backstrom and K. Sandros, *Acta Chem. Scand.*, 16, 958 (1962); W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, 88, 4769 (1966).

[12] S. G. Cohen and J. I. Cohen, *ibid.*, 89, 164 (1967); S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, 72, 3782 (1968); S. G. Cohen and J. B. Guttenplan, *Tetrahedron Lett.*, 5353 (1968).

[13] A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, 91, 1857 (1969); A. Padwa and R. Gruber, *ibid.*, 92, 107 (1970); R. S. Davidson and P. F. Lambeth, *Chem. Commun.*, 1265 (1967); G. A. Davis, P. A. Carapellucci, K. Szoc, and J. D. Gresser, *J. Amer. Chem. Soc.*, 91, 2264 (1969).

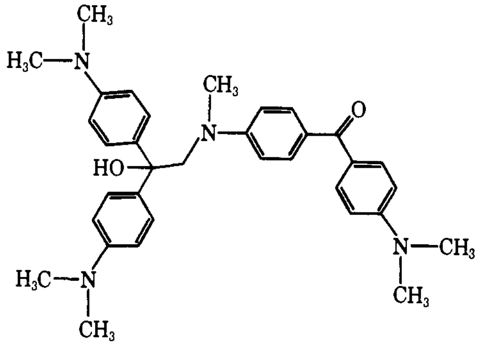
[14] S. G. Cohen and N. Stein, *ibid.*, 91, 3690 (1969).

[15] N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, 89, 5466 (1967); N. C. Yang and R. L. Dusenbery, *ibid.*, 90, 5899 (1968).

[16] P. J. Wagner and A. E. Kemppainen, *ibid.*, 90, 5898 (1968); J. N. Pitts, Jr., D. R. Burley, J. C. Mani, and A. D. Broadbent, *ibid.*, 90, 5902 (1968).

[17] P. J. Wagner, A. E. Kemppainen, and H. N. Schott, *ibid.*, 92, 5280 (1970).

of Michler's ketone in benzene solution at 350 nm gives a precipitate which collects on the walls of the irradiation vessel. The precipitate is not Michler's hydrol or Michler's pinacol and is not soluble in acetone, chloroform, or methanol. Like Michler's hydrol, the precipitate is soluble in 3 *N* hydrochloric acid, giving a blue solution. In the infrared the precipitate shows an OH stretching vibration at 3300 cm^{-1} and no distinct carbonyl absorption. Further photochemical reaction of dimeric species III, forming a high molecular weight polyhydroxy compound, is consistent with physical properties of the precipitate and our understanding of the photoreactivity of the Michler's ketone chromophore.



III

In conclusion, we note that Michler's ketone is commonly employed as a sensitizer for photoreactions because of its ideal absorption properties and high intersystem crossing efficiency. It should be an effective sensitizer provided energy transfer is exothermic and the concentration of the acceptor is sufficiently high to quench photoreaction of Michler's ketone with itself. The actual acceptor concentration required will depend upon the concentration of Michler's ketone and the quantum yield for the subsequent reaction of the triplet state of the acceptor.[18]

(18) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

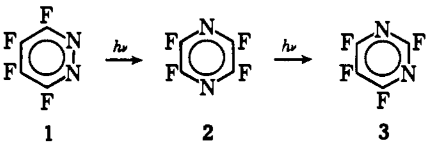
* Address correspondence to this author.

T. H. Koch,* A. H. Jones
Department of Chemistry, University of Colorado
Boulder, Colorado 80302
Received August 5, 1970

The Pyridazine–Pyrazine Photorearrangement[1]

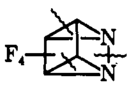
Sir:

Ultraviolet irradiation of tetrafluoropyridazine (**1**) in the vapor phase or in solution yields tetrafluoropyrazine (**2**),[2,3] which photoisomerizes much more slowly to tetrafluoropyrimidine (**3**).[3] The second transformation finds analogy in the photochemistry of pyrazine itself and methyl-substituted pyrazines.[4] The first transformation is unique, however, in that net 1,3 rearrangement of skeletal atoms occurs to the exclusion of 1,2 (generally the dominant mode in phototranspositions of benzenoid compounds[4-6]).

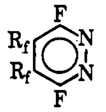


1 **2** **3**

An appealing rationalization for the pyridazine–pyrazine conversion entails valence isomerization to diazaprismane **4**, rearomatization of which should yield exclusively the pyrazine owing to the weakness of the N–N bond. To test this hypothesis, Musgrave's group irradiated the doubly labeled pyridazine **5**.[2]



4

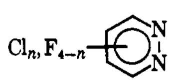


5, $R_f = -CF(CF_3)_2$

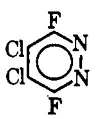
6

They obtained pyrazine **6**, whereas the diazaprismane mechanism requires formation of the 2,3-difluoro isomer. The English group nonetheless maintained their preference for this mechanism, and postulated that the initially formed 2,3 isomer suffered anionic rearrangement to the observed 2,5 compound. Although we considered the reaction conditions inauspicious for such an anionic rearrangement, it seemed possible that the bulky, neighboring perfluoroisopropyl groups had altered the course of the photoreaction itself. Hence we continued efforts then in progress to prepare a more subtly double-labeled pyridazine.

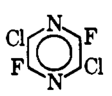
Our finding that tetrachloropyridazine[7a] in inert solvents photoisomerizes in high yield to the pyrazine[7b] suggested use of a dichlorodifluoropyridazine in the double-labeling experiment.[8] Treatment of tetrachloropyridazine with potassium fluoride at 200° yielded a mixture containing at least nine of the ten substances represented by formula **7**.[9] In contrast, brief treatment of tetrafluoropyridazine with excess lithium chloride



7, $n = 0–4$



8



9

---

[1] Presented in major part at the Symposium on Theoretical and Physical Organic Chemistry, Joint Conference of the Canadian Institute of Chemistry and the American Chemical Society, Toronto, Canada, May 1970, ORGN 12.

[2] C. G. Allison, R. D. Chambers, Yu. A. Cheburkov, J. A. H. McBride, and W. K. R. Musgrave, *Chem. Commun.*, 1200 (1969).

[3] V. Austel, C. L. Braun, and D. M. Lemal, Abstracts of Papers Presented at the Autumn Meeting of the National Academy of Sciences, Hanover, N. H., Oct 1969 (*Proc. Nat. Acad. Sci. U. S.*, **64**, 1423 (1969)).

[4] (a) F. Lahmani, N. Ivanoff, and M. Magat, *C. R. Acad. Sci., Ser. C*, **263**, 1005 (1966); F. Lahmani and N. Ivanoff, *Tetrahedron Lett.*, 3913 (1967); (b) for a review of related photochemistry, see P. Beak and W. R. Messer in "Organic Photochemistry," Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, pp 117–167.

[5] The photointerconversion of 2- and 4-picolines has the earmarks of a dissociation–recombination process, not a skeletal rearrangement: O. S. Pascual and L. O. Tuazon, *Philipp. Nucl. J.*, 1, 49 (1966); *Chem. Abstr.*, **66**, 115127 (1967). NOTE ADDED IN PROOF. A recent report presents evidence for skeletal reorganization in the photochemistry of picolines and lutidines (S. Caplain and A. Lablache-Combier, *Chem. Commun.*, 1247 (1970)).

[6] K. E. Wilzbach, A. L. Harkness, and L. Kaplan, *J. Amer. Chem. Soc.*, 90, 1116 (1968), and references cited therein.

[7] (a) R. D. Chambers, J. A. H. McBride, and W. K. R. Musgrave, *J. Chem. Soc. C*, 2116 (1968); (b) *Chem. Ind.* (*London*), 1721 (1966).

[8] Photorearrangement to a pyrazine was not found with 3,6-difluoro-, 3,6-dichloro-, 3,6-dihydroxy-, tetrakis(pentafluoroethyl)-, or unsubstituted pyridazine. The relationship between structure of a pyridazine and its susceptibility to isomerization remains mysterious.

[9] This is the method, in milder form, used by Chambers to prepare tetrafluoropyridazine (ref 7a).