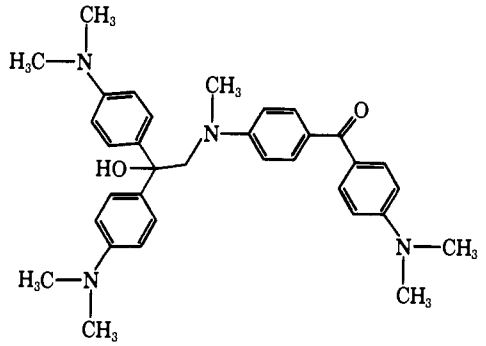
of Michler's ketone in benzene solution at 350 nm gives a precipitate which collects on the walls of the irradiation vessel. The precipitate is not Michler's hydrol or Michler's pinacol and is not soluble in acetone, chloroform, or methanol. Like Michler's hydrol, the precipitate is soluble in 3 *N* 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]

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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]).

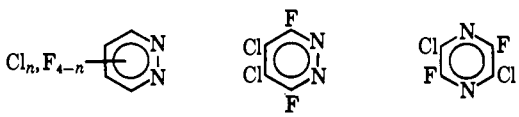
1 **2** **3**

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).

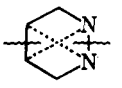
(8) Photorearrangement to a pyrazine was not found with 3,6-difluoro-, 3,6-dichloro-, 3,6-dihydroxy-, tetrakis(pentafluoroethyl)-, or unsubstituted pyridazine. The relationship between structure of a pyridazine and its susceptibility to isomerization remains mysterious.

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

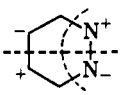
in dimethylformamide at 100° produced a single, crystalline dichlorodifluoropyridazine (**8**) in high yield:[10] mp 50–52°; uv (cyclohexane) λ_{max} (ϵ) 228 (8650), 263 (2340), 305 nm (177); ir (KBr) λ_{max} 6.49, 8.58, 8.68, 10.35, 11.52 μ; nmr 81.3 ppm;[11] mass spectrum *m/e* 184, 156, 125, 121, 106. Selective dehalogenation of **8** was accomplished with hydrogen over 10% palladium-on-charcoal in ether containing triethylamine, and the resulting difluoropyridazine was found to be identical with the authentic 3,6 isomer (prepared from its dichloro analog by heating with potassium fluoride). Irradiation of **8** in Freon 114 at 254 nm gave a single dichlorodifluoropyrazine: mp 80–82°; uv (cyclohexane) λ_{max} (ϵ) 224 (11,000), 252 (1300), 297 nm (10,600); nmr 81.0 ppm;[11] mass spectrum *m/e* 184, 149, 78. Reductive dechlorination in the manner described yielded a difluoropyrazine, purified by vapor chromatography: uv (cyclohexane) highly structured band centered at 272 nm (4550); ir (neat) λ_{max} 6.81, 7.40, 8.00, 8.56, 9.79, 11.14, 13.10 μ; mass spectrum *m/e* 116, 89, 44. This difluoropyrazine was very clearly different in its infrared, ultraviolet, and mass spectra from authentic samples of the 2,3 and 2,6 isomers which had been synthesized from their known dichloro counterparts[12] (again using potassium fluoride at elevated temperatures).

On the basis of this and other[13] evidence, the photoproduct can be assigned structure **9** with confidence; hence the results of our double-labeling experiment are in accord with those of Musgrave's group. Since the significance of the present experiment is not subject to the doubts surrounding its earlier counterpart, the diazaprismane mechanism can be eliminated from consideration.

The bond-making and -breaking processes (see **10**) revealed by the labeling experiments are not accommodated by "conventional" pathways for phototransposition of benzenoid rings.[6] Quantum yield measurements at different wavelengths have indicated that rearrangement requires only n → π^*, not the higher energy $\pi \rightarrow \pi^*$ excitation.[14] Sensitization and quenching studies, though not yet definitive, suggest that rearrangement originates in the n,π^* singlet state. Interestingly, bonding and antibonding interactions in the occupied π^* level **11** of this state[15] match neatly the requirements summarized in **10**. Although the timing of bond-making and -breaking events remains a matter for speculation, the fact that rearrangement proceeds even at 77°K without detectable accumulation of an intermediate reveals that no step requiring significant activation intervenes along the pathway.



10



11

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(16) Alfred P. Sloan Foundation Research Fellow, 1968–1970.
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Interception of Hydrogen Cyanide Precursor(s) in the Reaction of Active Nitrogen with Alcohols in Aqueous Solution

Sir:

The literature records very few reports[1,2] of the reactions of active nitrogen in aqueous solution. We initiated investigation of such reactions with organic solutes in order to determine whether a solvent which itself appears to be only slightly reactive[3] to active nitrogen could serve as a moderator and inhibit the deep-seated degradation, largely to HCN, which is characteristic[4] of the reactions of organic substrates with active nitrogen in gaseous and condensed phases. The work communicated here has been largely devoted to investigation of products formed by the reaction of active nitrogen with 10^{-2}–10 *M* aqueous methanol and the effect of approximately 10^{-2} *M* tetranitromethane (TNM) on these products. Under the conditions employed, the concentrations of substrate and scavenger did not change significantly during an experiment. More limited data have also been obtained for the analogous reactions of ethyl, isopropyl, and *tert*-butyl alcohols. These studies show that HCN is an important product formed from all the alcohols but that its yield is suppressed below its threshold of detection by tetranitromethane. The extensive data obtained with methanol[5] lead to the conclusion that *TNM acts by intercepting a precursor of HCN.* A mechanism based

(1) P. Harteck and E. Roeder, *Z. Phys. Chem., Abt. A*, 178, 389 (1937).
(2) N. N. Lichtin, S. E. Juknis, R. Melucci, and L. Backenroth, *Chem. Commun.*, 283 (1967).
(3) I. M. Campbell and B. A. Thrush, *Trans. Faraday Soc.*, 64, 1275 (1968), conclude that $N_2(A^3\Sigma_u^+)$ is responsible for slight decomposition of water vapor. See also S. V. Vadlamudy and C. A. Winkler, *Can. J. Chem.*, 45, 2463 (1967).
(4) See A. N. Wright and C. A. Winkler, "Active Nitrogen," Academic Press, New York, N. Y., 1968, pp 412–467.
(5) HCN is the only carbonaceous product observed in the gas-phase reaction of methanol; see M. J. Sole and P. A. Gartaganis, *Can. J. Chem.*, 41, 1097 (1963).

(10) Selective displacement of the 4- and 5-fluorines by other nucleophiles has been accomplished by Chambers (ref 7a).
(11) ^{19}F chemical shifts are in parts per million upfield from solvent trichlorofluoromethane.
(12) A. A. Miller, U. S. Patent 2,573,268 (1951); *Chem. Abstr.*, 46, 7594*c* (1952); K. H. Collins, U. S. Patent 3,291,802 (1966); *Chem. Abstr.*, 66, 95086*g* (1967); French Patent 1,457,963 (1966); *Chem. Abstr.*, 68, 2917*g* (1968).
(13) The photoproduct from **8** was not identical with 2,6-dichloro-3,5-difluoropyrazine: C. G. Allison, R. D. Chambers, J. A. H. MacBride, and W. K. R. Musgrave, *J. Chem. Soc. C*, 1023 (1970). Moreover, its ^{19}F resonance appeared at too low field for the 2,3-dichloro-5,6-difluoro structure, as judged from the spectra of model compounds.
(14) This finding contrasts sharply with the requirement for $\pi \rightarrow \pi^*$ excitation in the rearrangement of pyrazine and methyl-substituted pyrazines (ref 4a).
(15) Here the most naïve representation of the lowest n,π^* singlet state is assumed.