anchimeric assistance in *meta*-substituted phenyl azide[1,2] provide a convincing kinetic argument that singlet aryl nitrenes are formed initially, no intermolecular reaction has been demonstrated to be one of a singlet aryl nitrene. Instead, aryl nitrenes appear to be related to a multitude of other reactive intermediates on singlet surfaces[3-6] which isomerize to stable compounds, or react with other species in solution. On the other hand, the participation of singlet aryl nitrene in intramolecular C–H bond insertion gains support from the formation of (−)-2-ethyl-2-methylindoline from (+)-2-azido-1-(2-methylbutyl)benzene.[7] In contrast, evidence has been accumulating that the insertion of phenylnitrene into the C–H bond of hydrocarbons is actually due to the triplet.[8]

Photolysis of *p*-methoxyphenyl azide and *p*-chlorophenyl azide in dimethylamine yields the corresponding products, 2-dimethylamino-5-methoxy-3H-azepine and 5-chloro-2-dimethylamino-3H-azepine, along with minor yields of the anilines. These results are in accord with those reported for phenyl azide in amines and liquid ammonia.[9] In contrast, a similar reaction with *p*-cyanophenyl azide gave a 70% yield of 1,1-dimethyl-2-(4-cyanophenyl)hydrazine and a 5% yield of *p*-cyanoaniline. The structural assignment of the hydrazine is in accord with its elemental analysis and its ir and nmr spectra. The nmr data are particularly significant in this respect. The spectrum has a six-proton singlet at τ 7.45 (dimethylamino) and a broad one-proton singlet at τ 5.09 (amino). The ring-proton portion consists of two two-proton doublets centered at τ 3.15 (*ortho* to the hydrazino group) and 2.60 (*ortho* to the cyano group), with a coupling constant of 8.5 Hz. The chemical shifts and coupling constant agree with those reported for *p*-dimethylaminobenzonitrile.[10]

Photolysis of *p*-cyanophenyl azide in the presence of the triplet sensitizer, xanthen-9-one, which absorbs essentially all of the light, causes reversal of product yields, 70% of *p*-cyanoaniline and 6% of hydrazine. Significantly, no loss of xanthen-9-one occurs until most of the azide is consumed. Thus, the normal reaction of xanthen-9-one, the formation of the pinacol,[11] is quenched by the azide. Xanthen-9-one has a triplet energy of 71–74 kcal/mol, depending on solvent,[12] which is comparable to sensitizers used by Lewis and Saunders[13] who report close to diffusion-controlled energy transfer to azides with sensitizers of approximately 75 kcal. Clearly, in the sensitized experiments, triplet azide is formed on energy transfer and a triplet species, presumably triplet nitrene, is mostly reduced to the amine, a result in agreement with the observation of Splitter and Calvin[3] for phenyl azide. By implication, the large yield of hydrazine in the absence of sensitizer is due to the singlet nitrene.

Interestingly, the reaction of *p*-nitrophenyl azide might be expected to be analogous to the cyano compound, but this is not the case. Photolysis of the nitro compound in dimethylamine produces *p*-nitroaniline in better than 90% yield and no other products of comparable molecular weight. This is not surprising as nitro groups are known to enhance intersystem crossing, as shown in the complete suppression of fluorescence of aromatic hydrocarbons on substitution of a nitro group, with concomitant phosphorescent quantum yield of the nitro aromatic approaching unity.[14]

The *p*-cyanophenyl nitrene must differ from other aryl nitrenes because one or both of two possible effects of the *p*-cyano group are operating. The rate of ring closure of the singlet nitrene to a 7-azabicyclo[4.1.0]hepta-2,4,6-triene may decrease and the rate of reaction of the singlet nitrene with amine may increase. The reaction of the nitrene with amine, if visualized as a simple acid–base type, should be facile. The surprising thing is that amines do not capture singlet aryl nitrenes more often.

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(13) F. D. Lewis and W. H. Saunders, *J. Amer. Chem. Soc.*, **90**, 7033 (1968).

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Novel Photoaddition Reactions of Acyclic Olefins. Nucleophilic Photohydration

Sir:

Acyclic olefins characteristically undergo *cis–trans* isomerization as their chief reaction on photochemical activation. Cyclic olefins, which have difficulty adopting a twisted configuration, undergo a variety of reactions from their excited states, including dimerization and various addition reactions.[1] An example of the latter which has received much attention is the photosensitized addition of water and alcohols to six- and seven-membered ring olefins.[2] These reactions apparently involve photochemical carbonium ion formation. In the present communication we report efficient photoaddition reactions which, though formally analogous to the above, differ in that (a) electron-deficient acyclic olefins are photohydrated, (b) the excited state involved is a singlet, and (c) the reaction appears to be initiated by nucleophilic attack on the excited olefin.

The present photohydration appears to be fairly general for quaternary salts of pyridyl-substituted ethylenes.[3] The following are typical, well-behaved ex-

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(1) For recent summaries see: G. J. Fonken in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 197; P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

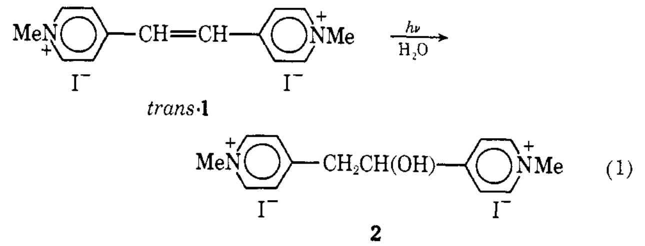
(2) (a) J. A. Marshall, *Accounts Chem. Res.*, **2**, 33 (1969), and references therein; (b) P. J. Kropp, *J. Amer. Chem. Soc.*, **89**, 3650 (1967); **89**, 5199 (1967); **88**, 4091 (1966).

(3) The reaction is complicated in several cases, especially for the stilbazoles, by concurrent photodimerization and isomerization.[4,5]

(4) J. L. R. Williams, J. M. Carlson, G. A. Reynolds, and R. E. Adel, *J. Org. Chem.*, **28**, 1317 (1963), and references therein.

(5) D. G. Whitten and M. T. McCall, *J. Amer. Chem. Soc.*, **91**, 5097 (1969).

amples. Irradiation of an aqueous solution of the dimethiodide of *trans*-1,2-bis(4-pyridyl)ethylene (**1**)[6] with the 3130-Å line of a medium-pressure lamp[7] leads to efficient (φ = 0.41) and quantitative production of the dimethiodide of 1,2-bis(4-pyridyl)ethanol (**2**) (eq 1).

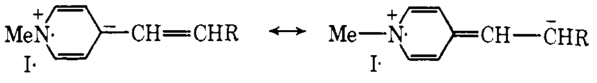

trans-**1**

2

(1)

The reaction is conveniently followed *via* spectral changes in the uv. No isomerization to the *cis* isomer is detected.[9] Product **2** melts at 240° dec and has in the nmr (D_2O) δ 8.33 (m, 8, aromatic), 5.42 (t, 1, $ArC\mathit{H}(OH)CH_2$–), 4.40 (s, 3, N-methyl), 4.37 (s, 3, N-methyl), and 3.50 (d, 2, $ArCH(OH)C\mathit{H}_2Ar$).[10] Irradiation of the dimethiodide of *trans*-1,2-bis(3-pyridyl)ethylene (**3**) under the same conditions leads to the corresponding ethanol **4** but with lower efficiency (φ = 0.04). Ethers are formed by reaction of **1** and **3** with alcohols. The reactions apparently originate from excited singlets of **1** and **3** since sensitizers such as benzophenone and Michler's ketone fail to promote the reaction. Triplet-energy transfer apparently does occur in these systems since **1** quenches the photopinacolization of benzophenone in methanol.[11]

To postulate electrophilic attack[2] on electron-deficient olefins such as **1** and **3** is unattractive. One mechanistic possibility for the photohydration is electron or charge transfer from iodide ion to the olefin in the excited state. A species such as **5** might be expected[12] to add alcohol or water *via* proton abstraction and subsequent nucleophilic attack. Many pyridine methiodides show charge-transfer transitions in the region 3500–5000 Å.[12] We do not detect such transitions in acetonitrile or aqueous solutions of **1** and **3**; however they may be buried under the stilbene-like $\pi \rightarrow \pi^*$ transitions.[13] Evidence against a charge-transfer mechanism comes from our finding that the dihydrochloride of *trans*-1,2-bis(4-pyridyl)ethylene, for which charge-transfer processes should be unlikely, photohydrates efficiently under conditions used for **1** and **3**.


5

The probable mechanism for the photohydration consists of nucleophilic attack on the excited olefin and subsequent proton abstraction. This mechanism seems especially reasonable since we find that the intense fluorescence of **1** and **3** in acetonitrile is quenched by several nucleophiles, including water, ethanol, and pyridine. Data for quenching of the fluorescence of **1** and **3** by water are given in Table I. The values in Table I indicate that water quenching is about an order of magnitude slower than diffusion controlled.[14] Although water-quenching constants for **1** and **3** are comparable, quantum efficiencies for photohydration of the two differ considerably. This difference is probably related to stabilities of the intermediate (ground-state) olefin–nucleophile adducts; the adduct from **1** should be considerably stabilized relative to that from **3**. Dissociation of the nucleophile–olefin adduct probably lowers the quantum efficiency from unity in both cases.[9] These reactions are somewhat similar to the photohydration reactions reported for the pyrimidines;[16] it is possible that a similar mechanism is operative for the cyclic DNA bases.

Table I. Quenching of Fluorescence of **1** and **3** by Water

Compd	Slope[a]	$\varphi^0{}_f$[b]	τ_s[c]	k_q, l. mol^{-1} sec^{-1}
1	0.25	0.06	1.1×10^{-10}	2.3×10^9
3	4.4	0.95	1.6×10^{-9}	2.7×10^9

[a] Slope from a linear Stern–Volmer plot of φ^0/φ *vs.* (H_2O). [b] Fluorescence quantum efficiency determined with *trans*-stilbene as a standard (see ref 5). [c] Calculated singlet lifetime in seconds.

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[6] Satisfactory analyses were obtained for all new compounds.

[7] Irradiations carried out in a "merry-go-round" apparatus[8] using glass and solution filters; concentration of **1**, 4 × 10^{-4} *M*.

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

[9] The *cis* isomer of **1** undergoes concurrent photohydration and isomerization to *trans*.

[10] The nmr spectrum of **2** showed splitting beyond those listed which are perhaps caused by the nitrogen. The spectrum of the free base, *vide infra*, is better resolved.

[11] We thank one of the referees for suggesting this experiment.

[12] E. M. Kosower, *Progr. Phys. Org. Chem.*, **3**, 81 (1965), and references therein.

[13] The fact that **1** and **3** fluoresce rather efficiently (*vide infra*) may indicate that iodide ion is not close enough to the olefin in dilute aqueous or acetonitrile solutions to perturb electronic transitions.

[14] k_{diff} for acetonitrile is calculated[15] to be 1.9 × 10^{10} l. mol^{-1} sec^{-1}.

[15] F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964).

[16] J. G. Burr, *ibid.*, **6**, 193 (1968).

[17] National Aeronautics and Space Administration Predoctoral Fellow, 1966–present.

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The Stereoelectronic Course of the Triene–Sulfur Dioxide Reaction

Sir:

Examples of antarafacial[1] (conrotatory) cycloaddition are rare.[2] We[3a] and others[3b] have previously shown

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[1] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968). The terms antarafacial and suprafacial, introduced originally to describe sigmatropic hydrogen migration, are extended here in obvious fashion to cycloadditions in preference to the previously used[3] descriptors, conrotatory and disrotatory, respectively. The new terms apply more literally to cases in which no actual rotation takes place. For a comprehensive review of orbital symmetry control, see G. B. Gill, *Quart. Rev.* (London), **22**, 338 (1968).

[2] R. B. Woodward, in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 217, cites but one example, which need not be concerted.

[3] (a) W. L. Mock, *J. Amer. Chem. Soc.*, **88**, 2857 (1966); (b) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).