100° with exclusion of moisture. The reaction mixture was chromatographed on SilicAR-7GF and the salt-like product, uv max (MeOH) 269 mμ, was eluted with methanol. Identical treatment of nucleocidin[14] gave similar material, uv max (MeOH) 272 mμ, and 5′-*O*-tosyladenosine[15] (**4**) gave the $N^3 \rightarrow 5'$-cyclonucleoside, uv max (MeOH) 271 mμ. This parallel behavior of **1**, **2**, and **4** defines the stereochemistry of the 1′-adenine and 4′-sulfamoyloxymethyl substituents of nucleocidin as *cis*.[11]

The circular dichroism curves of nucleocidin[14] and **2** in water are identical within experimental error throughout the range 230–290 mμ and are similar to that of adenosine.[16] This indicates that the adenine ring is above the sugar plane.[16,17] Thus, structure **1** for nucleocidin[5] is consistent with the present data.

It is of interest that 5′-*O*-sulfamoyladenosine (**2**) produces 50% inhibition of *S. faecalis* at 4×10^{-6} *M* compared to a similar inhibition by nucleocidin at 5×10^{-7} *M*.[18] Compound **2** also has been found to exhibit pronounced *in vitro* inhibition of *Trypanosoma rhodesiense* at 10^{-9} *M*.[19] 5′-*O*-Sulfamoyladenosine (**2**) may be viewed[20] as an analog of adenosine 5′-phosphate (AMP) which, however, should readily cross cellular membranes due to the nonionic character of the sulfamoyl ester group.

(14) We thank Dr. J. S. Webb, Lederle Laboratories, for a sample of nucleocidin.
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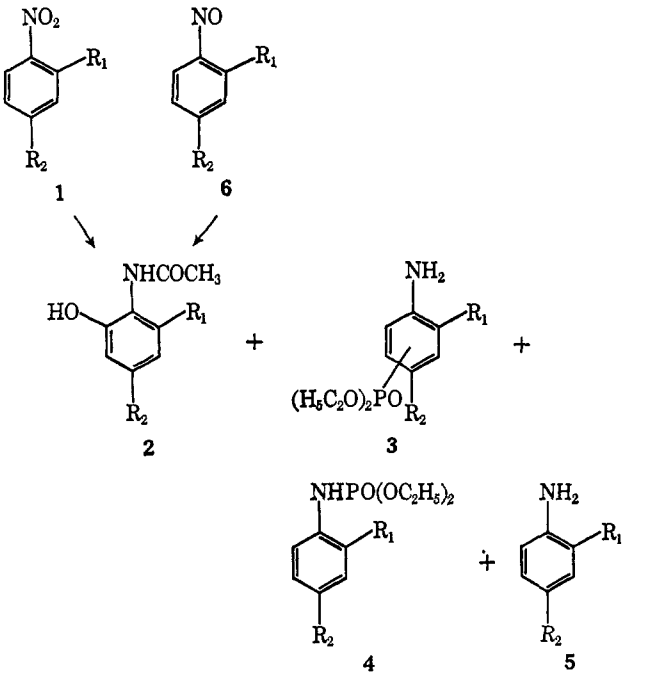
Generation of Aryl Nitrenes in the Presence of Acetic Acid by Deoxygenation of Aromatic Nitro and Nitroso Compounds[1]

Sir:

We wish to report that the presence of acetic acid (5% by volume) in triethyl phosphite solutions employed for photochemical deoxygenation of aromatic nitro compounds[2] or deoxygenation of aromatic nitroso compounds[3] profoundly affects the nature of the reaction products. Our results suggest that a substantial fraction of the aryl nitrenes generated under these conditions are converted to aryl nitrenium ions. This result implies that aryl nitrenes are relatively basic, a conclusion which is of significance to the interpretation of the chemistry of aryl nitrenes in general.

The product mixtures from photochemical deoxygenation of aromatic nitro compounds in the presence of acetic acid include significant amounts of *o*-hydroxyacetanilides (**2**) and diethyl aminophenylphosphonates



(**3**). Diethyl N-arylphosphoramidates (**4**) are also formed but in yields generally lower than those observed in the absence of acetic acid. Anilines are also found. The formation of N-aryl 2-acetimidylpyridines from *o*-methylnitrobenzenes, which is an important process in the absence of acetic acid,[2] is completely suppressed. Diethyl aminophenylphosphonates are not formed in the absence of acetic acid. Nonphotochemical deoxygenation of aromatic nitroso compounds is also believed[4] to generate aryl nitrenes, and the product composition from deoxygenation of nitroso compounds is affected in a similar way when acetic acid is present. Table I summarizes the data. Structural assignments for the new compounds *o*-**3a**, *o*-**3b**, *p*-**3b**, *o*-**3c**, *o*-**3d**, and *m*-**3d** rest on correct elemental analyses and definitive infrared and nmr spectral data. The known compounds **2a–d**, *p*-**3a**, **4b–d**, and **5a–d** show spectral data in accord with expectation and physical constants in agreement with literature data.

Table I. Product Distribution from Deoxygenations

	% yields[a]					
		3[b]				
Reactant	**2**	*o*	*m*	*p*	**4**	**5**
1a	6	8	*c*	8	*c*	4
6a	11	3	*c*	6	3	*c*
1b	*c*	2	*c*	10	7	2
6b	*c*	2	*c*	9	12	2
1c	27	11	*c*		2	10
6c	23	9	*c*		3	2
1d	14	6	6		9	4

[a] Yields are isolated yields, normally after column chromatography. [b] The designations *o*, *m*, and *p* denote the relationship between the amino and phosphoryl substituents. [c] Not definitively characterized; yield is less than 3%.

Aryl nitrenium ions are expected to undergo nucleophilic attack principally at the *ortho* and *para* carbon atoms[5] and can be invoked as intermediates in the

(1) Supported by National Institutes of Health Grant 14344.
(2) R. J. Sundberg, B. P. Das, and R. H. Smith, Jr., *J. Am. Chem. Soc.*, **91**, 658 (1969).
(3) R. J. Sundberg, *ibid.*, **88**, 3781 (1966).
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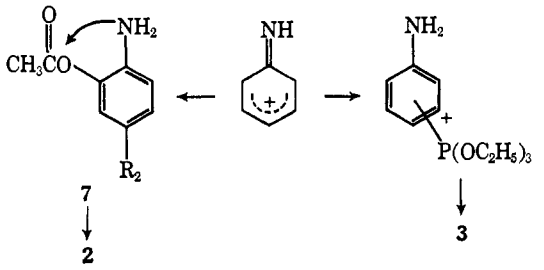
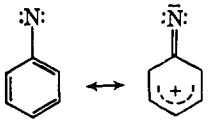
(5) P. G. Gassman, G. Campbell, and R. Frederick, *J. Am. Chem. Soc.*, **90**, 7377 (1968); P. A. S. Smith, "Open Chain Nitrogen Com-

formation of **2** and **3**. The specific introduction of the acetoxy substituent in the *ortho* position in the case of **1a** and **6a** suggests an ion-pair effect and indicates that the protonation step must immediately precede product formation.[6]



Deoxygenation of aromatic nitroso compounds at 0° in solutions of triethyl phosphite containing 50% by volume acetic anhydride gives *o*-acetoxyacetanilides (**8**) as significant products (**8a**, 6%; **8b**, 16%; **8c**, 46%). While this result suggests that aryl nitrenes may be acylated by acetic anhydride, an alternative possibility involving formation of **7a–c** by reaction of the nitrene with traces of acetic acid followed by acylation of **8a–c** cannot be ruled out at present.

Extended Hückel calculations confirm the intuitive expectation that there would be extensive delocalization of the electron deficiency in phenyl nitrene and show an appreciable negative charge on nitrogen. Such delocalization would rationalize the apparent basicity of



the nitrogen atom of phenyl nitrene. Extensive delocalization of the electron deficiency at nitrogen may explain the apparent failure[9] of singlet phenyl nitrene to undergo intermolecular C–H insertion reactions. In contrast to cyanonitrene[10] or carbethoxynitrene,[11] in which the substituent groups are electron withdrawing, singlet phenyl nitrene may be less electrophilic at nitrogen than the triplet species. In the triplet species only one of the half-filled orbitals can interact with the phenyl π system to delocalize electron deficiency to the carbon atoms. Singlet phenyl nitrene may have substantial nucleophilic or dipolar properties as well as basic character, and we are investigating this possibility.

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(6) An alternative mode of formation of aryl nitrenium ions in this system could involve protonation of the intermediate in the oxygen-transfer reaction, prior to expulsion of triethyl phosphate. Photolysis of aryl azides in acidic media also leads to products resulting from nucleophilic ring substitution,[7] although azides are weakly basic,[8] and protonation prior to photolytic expulsion of nitrogen is unlikely.

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(10) A. G. Anastassiou, *ibid.*, **89**, 3184 (1967).

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(12) National Defense Education Act Fellow, 1966–present.

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Ligand Photoisomerization in Metalloporphyrin Complexes. A Possible Case of Photocatalysis

Sir:

Metalloporphyrins complex with a variety of axial ligands such as pyridine, ethanol, and other bases.[1] We thought that complexes containing a metalloporphyrin with the metal bound to stilbene-like ligands such as 1-(α-naphthyl)-2-(4-pyridyl)ethylene (NPE) might exhibit unusual energy-transfer phenomena. Particularly intriguing was the possibility that efficient "nonvertical" energy transfer might occur with the porphyrin as donor and the higher energy olefinic ligand as acceptor. We wish to report highly efficient photoisomerization processes for these complexes which are best described by mechanisms not involving specific electronic energy transfer.

Wavelength shifts in absorption and emission spectra indicate that *cis*- and *trans*-NPE[2] coordinate to zinc and magnesium etioporphyrin I in both ground and excited states in several solvents much the same as does pyridine.[1,3] Spectral similarities suggest that excitation in all of the complexes is largely localized in the porphyrin π electron system. The olefins quench neither the room-temperature fluorescence nor the low-temperature (EPA, 77°K) phosphorescence of the porphyrin. Irradiation of benzene solutions of *cis*- or *trans*-NPE and zinc etioporphyrin I with light absorbed only by the metalloporphyrin causes surprisingly efficient *cis–trans* isomerization of the ligand as the only detectable reaction (Table I). Similar, but less dramatic, results are obtained with magnesium etioporphyrin I–NPE solutions and with 4-stilbazole complexes. The photoisomerization is first order in light intensity; the quantum yields increase with increasing NPE concentration but show little temperature effect in the range 20–50°.[4] The isomerization is quenched by low concentrations of *p*-benzoquinone and by moderate concentrations of pyridine, which competes with NPE as a ligand. The greater than unit value for $\Phi_{c\rightarrow t}$ indicates that the reaction does not involve simple transfer of excitation from porphyrin to ligand. The strong preference for forming *trans*-NPE

Table I. Photoisomerization of Zinc Etioporphyrin I–Olefin Complexes

Sample[a]	$\Phi_{c\rightarrow t}$	$\Phi_{t\rightarrow c}$
Zn etio I–NPE[b]	6.6 ± 1	0.2
Zn etio I–stilbene	0.01	0.001
Zn etio I–NPE with 0.5 *M* pyridine[b]	0.37 ± 0.05	
Zn etio I–NPE with 10^{-4} *M* quinone[b]	0.055	

[a] Degassed benzene solutions irradiated using 405–408- and 436-nm regions of a mercury arc; porphyrin concentration 5×10^{-5} *M*; olefin concentration 5×10^{-3} *M*; temperature 25–28°; vpc analyses. [b] Photostationary state of 96% *trans*-NPE obtained.

(1) See, for example: A. H. Corwin, *et al.*, *J. Am. Chem. Soc.*, **88**, 2525 (1966); **85**, 3621 (1963); *J. Org. Chem.*, **27**, 3344 (1962); B. D. McLees and W. S. Caughey, *Biochemistry*, **7**, 642 (1968), and references therein.

(2) Satisfactory analyses and spectral data were obtained for all new compounds.

(3) D. G. Whitten, I. G. Lopp, and P. D. Wildes, *J. Am. Chem. Soc.*, **90**, 7196 (1968).

(4) The lack of a temperature effect probably indicates that increases in the rates of isomerization and ligand exchange are offset by decreases in the excited-state lifetime.