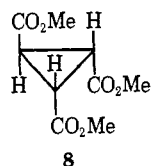


Interestingly, trimethyl cyclopropane-1,*cis*-2,*trans*-3-tricarboxylate (**8**) was produced in 34% yield when methylmonochloroacetate was treated with the copper(I) oxide-isonitrile system in the absence of olefin under the conditions of Table I. Probably fumarate was first formed from monochloroacetate and then fumarate participated in the formation of cyclopropanetricarboxylate.



Comparison of this reaction with the synthesis of cyclopropanes from α -halo ester and α,β -unsaturated ester in the presence of a strong base such as sodium alkoxide and sodium hydride² suggests two prominent differences. First, the reaction with strong base is not stereoselective; for example, the reaction of ethyl monochloroacetate and methyl acrylate with sodium methoxide yields 26% *cis* and 22% *trans* isomers.² The basic reactions carried out in dimethylformamide or in hexamethylphosphoramide-benzene mixtures gave predominantly the more stable isomer, usually the *trans* isomer. However, the stereoselectivity was not high. Second, the reaction utilizing strong base is not applicable to maleate and fumarate, whereas that with the copper(I) oxide-isonitrile system can successfully be applied to these olefin 1,2-dicarboxylates to produce cyclopropanetricarboxylic esters.

(2) L. L. McCoy, *J. Amer. Chem. Soc.*, **80**, 6568 (1958); **82**, 6416 (1960); **84**, 2246 (1962).

T. Saegusa,* Y. Ito, K. Yonezawa
Y. Inubushi, S. Tomita

Department of Synthetic Chemistry, Faculty of Engineering
Kyoto University, Kyoto, Japan
Received May 3, 1971

Spin State of Photogenerated Phenylnitrene

Sir:

The decomposition of organic azides results in the elimination of nitrogen and the formation of a nitrene. In the thermal reactions of azides the nitrene appears at first in an excited singlet state (spin conservation) which may either react with the solvent or decay by spin inversion to the triplet ground state.^{1,2} In photolysis, nitrenes can be formed from both the singlet and the triplet excited states of the azide and may therefore appear either as singlets or as triplets.³ Hydrazoic acid has been shown to produce exclusively the singlet-excited-state HN ($c^1\Pi$) of the imino radical on irradiation in the vacuum uv,^{4,5} and cyano azide, N₃CN, behaves in a similar way.^{6,7} In contrast, irradiation of ethyl azidoformate results in a mixture of singlet and triplet ethoxycarbonylnitrene⁸ in the approximate ratio 2:1.

- (1) R. A. Abramovitch and B. A. Davies, *Chem. Rev.*, **64**, 149 (1964).
- (2) R. S. Berry in "Nitrenes," W. Lwowski, Ed., Interscience, New York, N. Y., 1970, pp 34-41.
- (3) A. Reiser and R. Marley, *Trans. Faraday Soc.*, **64**, 1806 (1968).
- (4) K. H. Welge, *J. Chem. Phys.*, **45**, 4373 (1966).
- (5) H. Okabe, *ibid.*, **49**, 2726 (1968).
- (6) A. G. Anastassiou, *J. Amer. Chem. Soc.*, **89**, 3184 (1967).
- (7) H. W. Kroto, *J. Chem. Phys.*, **44**, 831 (1966).
- (8) W. Lwowski, *Angew. Chem., Int. Ed. Engl.*, **6**, 897 (1967).

In the present communication an attempt is made to establish the spin state of photogenerated phenylnitrene, using its reactions with CH bonds to distinguish between the singlet and the triplet species.

Singlet nitrenes insert into CH bonds producing secondary amines; triplet nitrenes abstract hydrogen and may produce both primary and secondary amines, the first by successive hydrogen abstraction, the second by hydrogen abstraction and subsequent radical coupling.⁹ If the radical concentration is kept low (low azide concentrations, low intensity of photolytic radiation), the formation of secondary amines from triplet nitrene can be minimized. Under these conditions the yield of primary and secondary amine is indicative of the spin state of the nitrene intermediate. Finally, it is recalled that both singlet and triplet nitrenes will react with lone electron pairs, an important reaction of this kind being the attack of nitrenes on azido groups with the formation of azo compounds and nitrogen.¹⁰

Dilute solutions (10^{-2} M) of phenyl azide in degassed solvents were irradiated with the 313-nm mercury line. Photolysis was stopped at an azide conversion of 2% and the products were analyzed by a combination of thin-layer chromatography, vpc, solvent extraction, and fluorescence spectrophotometry. The results are summarized in Table I. It can be seen that in hydrocarbon

Table I. Product Distribution in the Photolysis of Phenyl Azide

Solvent	Mol % product			
	Azobenzene	Aniline	Insertion into solvent	Polymer
Benzene ^a	50 ± 3	5 ± 2	<3	50 ± 7
<i>b</i>	97 ± 3	3 ± 2	<3	0
Cyclohexane ^a	51 ± 3	4 ± 2	<3	48 ± 7
2,2,4-Trimethylpentane ^a	46 ± 3	8 ± 2	<3	48 ± 7
Methanol ^a	5 ± 3	7 ± 2	~80	0
<i>b</i>	55 ± 3	12 ± 2	0	0
2-Propanol ^a	3 ± 3	12 ± 2	~80	0
<i>b</i>	45 ± 10	27 ± 2	0	0
<i>tert</i> -Butyl alcohol ^a	55 ± 5	5 ± 2	0	30 ± 10

^a Direct photolysis of a 10^{-2} M solution of azide; irradiation with the 313-nm mercury line. ^b Sensitized photolysis with acetophenone; irradiation with the 365-nm mercury line.

solvents the main reaction products are azobenzene and a polymer. Small amounts of aniline are obtained, but no insertion into the solvent is observed. The polymers obtained in different hydrocarbons appear to be identical. Their infrared spectra indicate only the presence of aromatic CH groups and -NH linkages, but no aliphatic CH and no unreacted azide. It is thought that the polymer arises by insertion of the singlet nitrene into the aromatic ring of phenyl azide, followed by decomposition of the azido group, further insertion, etc. This view is in complete agreement with recent work by Abramovitch and Scriven,¹¹ who observed the insertion of (we believe, singlet) 4-cyanophenyl nitrene into the para position of dimethylaniline. It is also

(9) J. H. Hall, J. W. Hill, and J. M. Fargher, *J. Amer. Chem. Soc.*, **90**, 5313 (1968).

(10) L. Horner, A. Christmann, and A. Gross, *Chem. Ber.*, **96**, 399 (1963).

(11) R. A. Abramovitch and E. F. V. Scriven, *Chem. Commun.*, 787 (1970).

supported by the fact that no polymer is obtained in the photolysis of phenyl azide sensitized by acetophenone (items marked with *b* in Table I), where the nitrene must be in the triplet state. Assuming then that the polymer is an insertion product of singlet nitrene, that aniline is a product of the nitrene triplet, and that azobenzene is not specific for either species, it may be concluded that in the photolysis of phenyl azide at least 50%, but possibly up to 95%, of the nitrene is produced in the singlet state.

The large margin of uncertainty in this estimate is due to the presence of azobenzene in the products. This difficulty can be overcome by using alcohols as substrates. Photolysis of phenyl azide in methanol and in 2-propanol produces little azobenzene, only small amounts of aniline, no polymer, and a major product which is unstable on the chromatographic plates and turns rapidly into several colored compounds and form-anilide. This product is not found in the sensitized photolysis (acetophenone) of phenyl azide in alcohols and is also absent in the direct photolysis of phenyl azide in *tert*-butyl alcohol; it is therefore thought to arise by insertion of the nitrene singlet into the α -CH bond of the alcohol.

A series of experiments in alcohol-hydrocarbon mixtures was carried out. The results obtained in the system benzene-methanol are shown in Figure 1.

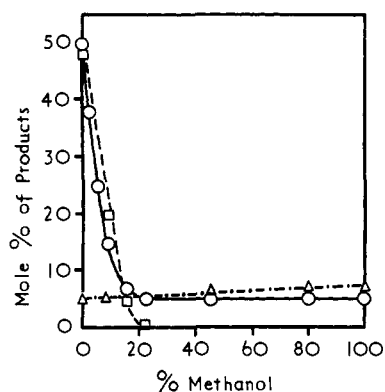


Figure 1. Effect of solvent composition on product yield in the direct photolysis of phenyl azide in benzene-methanol mixtures: O, azobenzene; □, polymer; Δ, aniline.

With increasing alcohol content, the yield of azobenzene decreases rapidly to a limiting value of 5%, the polymer disappears altogether, and the yield of aniline remains virtually unchanged. This indicates that in pure methanol all singlet nitrenes have been intercepted, and that under these conditions both azobenzene and aniline are products of triplet nitrene. Similar results were obtained with isopropyl alcohol as solvent.

It is concluded that in the photolysis of phenyl azide the nitrenes appear predominantly in the excited singlet state and only 12–13% are generated directly in the triplet ground state.

A. Reiser,* L. J. Leyshon
 Research Laboratory, Kodak Limited
 Wealdstone, Harrow, Middlesex, England
 Received April 28, 1971

Hydrogen Bonding.¹ VI. A Dramatic Difference between Proton Transfer and Hydrogen Bonding

Sir:

A number of years ago, Gordy and Stanford² reported for a variety of compounds a good correlation between their ability to accept protons from aqueous acid (pK_a) and their hydrogen-bonding acceptor ability, as represented by their effect on the O–D stretching frequency of deuteriomethanol. In the ensuing years many authors³ have implied that hydrogen bonding and proton transfer could be used almost interchangeably as measures of the same property—“basicity.” Work cited here and reported below indicates that important differences in these properties may arise. In previous papers in this series⁴ we have developed with our collaborators (Taft and Schleyer) a variety of methods for determining thermodynamic properties for hydrogen bonding using *p*-fluorophenol, PFP, in carbon tetrachloride as solvent at 25°. These methods give results which are not only self-consistent (usually within 0.1 kcal), but which also agree with the best data from other laboratories. We have also demonstrated the failure of the Badger–Bauer relation to correlate $\Delta\nu$ with heats of hydrogen bonding, ΔH_f , for some compounds.^{4a} Neither is there a general correlation of $\Delta\nu$ with the free energy of hydrogen bond formation. In another series of papers⁵ we have developed the use of ΔH_i , the heat of transfer from carbon tetrachloride (or some other inert solvent), to high dilution in fluoro-sulfuric acid at 25° as a useful criterion of Bronsted

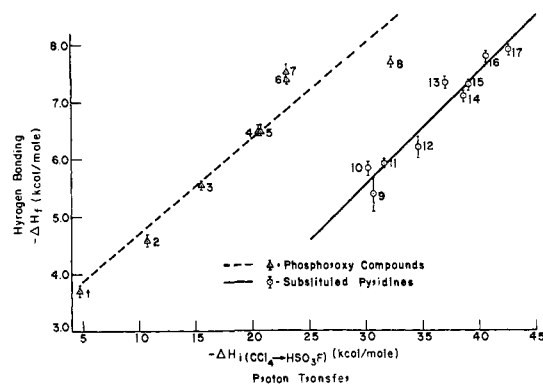


Figure 1. Relationships between hydrogen bonding and proton transfer for the compounds in Table I.

basicity. This criterion has the advantage over pK_a that all measurements are made under the same conditions in the same medium by the same method, thereby avoiding many of the difficulties which surround determination of the pK_a 's of weak bases through the Hammett acidity function method.⁶ Figure 1, therefore,

(1) Supported by NSF Grant No. GP-6550-X and in part by the Office of Saline Water.

(2) W. Gordy and S. C. Stanford, *J. Chem. Phys.*, **9**, 204 (1941).

(3) See, however, W. Tamres, S. Searles, E. M. Leighly, and D. M. Mohrman, *J. Amer. Chem. Soc.*, **76**, 3983 (1954).

(4) (a) E. M. Arnett, L. Joris, E. Mitchell, T. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *ibid.*, **92**, 2365 (1970); (b) D. Gurka and R. W. Taft, *ibid.*, **91**, 4794 (1969); (c) R. W. Taft, D. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *ibid.*, **91**, 4801 (1969).

(5) (a) E. M. Arnett, R. P. Quirk, and J. J. Burke, *ibid.*, **92**, 1260 (1970); (b) E. M. Arnett, R. P. Quirk, and J. W. Larsen, *ibid.*, **92**, 3977 (1970).

(6) E. M. Arnett, *Progr. Phys. Org. Chem.*, **1**, 223 (1963).