

sistent with the small isotropic nmr shift for the resonance of the corresponding proton in pyridine. An EHMO calculation for the phenyl radical is again in poor agreement with experiment for the γ proton where a hyperfine constant somewhat larger than for the α proton is predicted. The approximate MO treatment of Dixon¹⁶ for the phenyl radical predicts A_i 's for the α , β , and γ protons of 23.3, 4.2, and 17.9 gauss, respectively. However, he states that if negative overlap integrals are neglected the constants become 19.2, 3.1, and 0.1 for the protons in the above order. This latter result is more in agreement with the phenyl radical esr¹⁶ and the present pyridine nmr data.

We must conclude that EHMO calculations yield inaccurate σ -orbital eigenvectors, that the σ contribution to the isotropic shift at the γ position is actually quite small, and that the indirect π -delocalization mechanism predominates here, at least for methyl substitution. It is apparent that the mode of spin delocalization, in pyridine-type ligands at least, is more a function of the ligand than of the symmetry of the complex as a whole. The relative energies and perhaps overlap characteristics of the ligand and metal orbitals probably determine the mode of spin delocalization. This conclusion is in accord with ideas presented recently concerning spin density transferral in octahedral transition metal acetylacetonate complexes.¹⁷

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(17) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

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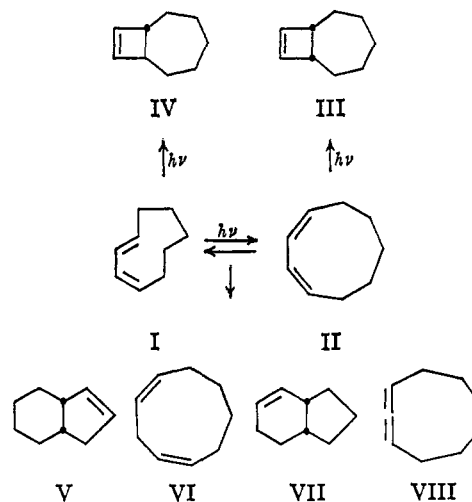
Photochemical Reactions of Medium Ring 1,3-Dienes

Sir:

Having recently¹ noted the unusual electrocyclic reactions of medium ring conjugated dienes in the electronic ground state, we now wish to report on processes which are presumed to arise from the electronic excited state of such systems.

Irradiation of ether solutions of *cis,trans*-1,3-cyclononadiene (I) with ultraviolet light of $<3000 \text{ \AA}$ gives rise to rapid isomerization to an approximate steady state in which the isomeric *cis,cis*-1,3-cyclononadiene predominates. Slower processes which accompany the *cis-trans* isomerization lead to the formation of a complex mixture of III, IV, V, VI, VII, and VIII in the approximate distribution ratio of 25:14:23:4:6:1.

(1) K. M. Shumate, P. N. Neuman, and G. J. Fonken, *J. Am. Chem. Soc.*, **87**, 3996 (1965).



Structures have been assigned on the basis of physical property and spectral identity with authentic samples of III,¹ VI,² VII,³ and VIII.⁴ The structure of IV is assigned on the basis of its nmr spectrum (τ 3.90, 7.1, 8.5; area ratio 2:2:10) and hydrogenation to the known⁵ *trans*-bicyclo[5.2.0]nonane. The structure of V is assigned on the basis of its identity with the primary olefin obtained by a Bamford-Stevens reaction⁶ of the tosylhydrazone of *cis*-2-hydrindanone and its hydrogenation to *cis*-hydrindane.

It is our conviction that III results from a disrotatory cyclization arising from the excited state of II, and that IV arises similarly from the excited state of I. Such stereoselectivity would be in complete accord with the postulated⁷ orbital symmetry control of such electrocyclic reactions and would bear witness of the anticipated reversal of stereochemistry of such cyclizations upon proceeding from the ground state to the excited state. In this respect 1,3-cyclononadiene is the first example of a diene system in which the complimentary modes of electrocyclic cyclization have been observed in both the electronic ground and excited states.

The formation of V, VI, VII, and VIII are postulated to result from photochemically induced hydrogen shifts and cyclizations of the sigmatropic type.⁸ The photochemically induced formation of V and VII from cyclononadiene is without precedent, and the process accordingly represents a new photochemical process. The complexity of the photochemistry of cyclononadiene is unrivaled among dienes heretofore studied. Preliminary studies of the photolysis of higher members of the medium ring conjugated diene suggest that these may rival the C₉ diene in product complexity and afford similar structurally altered products.

(2) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *ibid.*, **85**, 1553 (1963).

(3) C. Foote and R. B. Woodward, *Tetrahedron*, **20**, 687 (1964). We are indebted to Professor Foote for the infrared spectrum of *cis*-bicyclo[4.3.0]non-2-ene.

(4) P. D. Gardner and N. Narayana, *J. Org. Chem.*, **26**, 3518 (1961). The authors are indebted to Professor Gardner for authentic samples of VI and VIII.

(5) N. Allinger, M. Nakasak, and V. Zalkow, *J. Am. Chem. Soc.*, **81**, 4074 (1959). We are indebted to Professor Allinger for assistance in obtaining the infrared spectrum of the isomeric bicyclo[5.2.0]nonanes.

(6) W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, 4735 (1952). Details of this synthesis will be reported in the completed manuscript.

(7) R. B. Woodward and R. Hoffman, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(8) R. B. Woodward and R. Hoffman, *ibid.*, **87**, 2511 (1965).

The details of the precise photochemical origin of the described photoproducts is under further investigation.

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An Unusual Photochemical Rearrangement in the Synthesis of Adenine from Hydrogen Cyanide¹

Sir:

We have described the syntheses of aminomalononitrile and 4-amino-5-cyanoimidazole and discussed the relevance of these intermediates to the prebiological synthesis of adenine and other heterocyclics.² Further study shows: (1) the reaction of 4-amino-5-cyanoimidazole (II) (0.05 *M*) with formamidine acetate (0.1 *M*) in aqueous solution (pH 8–8.5) proceeds slowly at 30° and yields only adenine (III) and 4-aminoimidazole-5-carboxamide in the ratio of about 100:1. After 5 days about 3% of adenine had been formed in a typical experiment. Little or no reaction occurred if formamidine was replaced by 0.1 *M* cyanide or 0.1 *M* cyanide–0.1 *M* ammonia mixtures. Ultraviolet irradiation (253 μ) did not accelerate any of the above reactions.

(2) The slow addition (5 hr) of aminomalononitrile (0.01 *M*) to formamidine acetate (0.1 *M*) at 25–30° and pH 8–8.5 gives a 5% yield of 4-amino-5-cyanoimidazole (II) with the remainder of the aminomalononitrile apparently giving polymeric material. A 50% yield of 4-amino-5-cyanoimidazole is obtained when the aminomalononitrile (0.01 *M*) is added over a 24-hr period to 0.1 *M* formamidine acetate at 50°. However, the reaction of aminomalononitrile with cyanide to give HCN tetramer (diaminomaleonitrile, I) is much more rapid; if aminomalononitrile (0.01 *M*) is added to a solution 0.1 *M* in both cyanide and formamidine the yield of HCN tetramer (I) exceeds that of aminoimidazolenitrile (II) by about 100:1.

It is apparent that the prebiotic formation of adenine (III) could proceed by the reaction of a dilute solution of formamidine with 4-amino-5-cyanoimidazole (II) (0.001 *M* formamidine should give comparable rates of hydrolysis and adenine synthesis). The formation of 4-amino-5-cyanoimidazole from aminomalononitrile, however, would not proceed efficiently under these circumstances and the alternative reaction with cyanide ion to give the HCN tetramer would surely be more important under plausible prebiotic conditions.

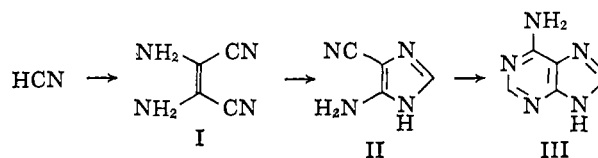
We therefore investigated the reactions of the HCN tetramer (I). Direct reaction of formamidine with I gives a very poor yield of II, but when an aqueous solution of HCN tetramer (10^{-4} *M*) is irradiated at 25° with a 350 μ lamp a 77–82% yield of 4-cyano-5-aminoimidazole (II) is obtained. The identity of the product with an authentic specimen of II was confirmed by chromatography, ultraviolet spectroscopy, and quantitative hydrolysis to the well-known 5-aminoimidazole-4-carboxamide. Yields were estimated from the intensity of the 247 μ peak of II.

Preliminary studies on the scope of this photochemical rearrangement at 253 μ show that 1,1-diamino-2,2-

dicyanoethylene³ in tetrahydrofuran solution, but not in water, also yields 4-amino-5-cyanoimidazole along with other products. 3-Aminocrotononitrile is converted to 4-methylimidazole in 50–60% yield. Aminomethylenemalononitrile,⁴ *o*-aminobenzonitrile,⁵ and 1,1-dimorpholino-2,2-dicyanoethylene⁶ do not rearrange to imidazoles.

3-Amino-4-cyanopyrazole also rearranges to II, but only when irradiated by lamps emitting at 253 μ .^{7,8} Since the rearrangement of the HCN tetramer proceeds readily with lamps emitting mainly at 350 μ , the pyrazole cannot be an intermediate. Pathways for the photochemical rearrangement of I involving the formation of intermediates containing either a three-membered or a four-membered ring⁹ can be written, but at present we have no evidence for or against either intermediate.

The most plausible route to adenine from HCN under prebiotic conditions which can be proposed at the moment appears to be



However, we shall not indulge in detailed speculation until we have investigated other routes.

(3) B. C. McKusick, R. E. Heckert, T. L. Cairns, D. D. Coffman, and H. F. Mower, *ibid.*, 80, 2806 (1958).

(4) A. Ishiwata, *Takamine Kenkyukusho Nempo*, 9, 21 (1957); *Chem. Abstr.*, 55, 1439c (1961).

(5) J. Pinnow and C. Samann, *Ber.*, 28, 151 (1895).

(6) J. P. Ferris and L. E. Orgel, *J. Org. Chem.*, 30, 2365 (1965).

(7) R. K. Robins, *J. Am. Chem. Soc.*, 78, 784 (1956).

(8) H. Tiefenthaler, W. Dorscheln, H. Goth, and H. Schmid, *Tetrahedron Letters*, 2999 (1964).

(9) A similar intermediate was postulated for the reverse reaction in the photochemical isomerization of cytosine: K. L. Wierzchowski and D. Shugar, *Photochem. Photobiol.*, 2, 377 (1963). (No cytosine was formed on the irradiation of aminomethylenemalononitrile.)

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The Oxidative Dealkylation of Mesityl with Activated Manganese Dioxide

Sir:

During the course of a survey of the reactions of phenols with hydrogen peroxide and acidified ferrous sulfate, Cosgrove and Waters¹ reported the formation of 4,4'-dihydroxy-3,3',5,5'-tetramethyldiphenylmethane (VIII) from mesityl (I) in low yield. Bacon and Munro² observed this same product in 13% yield in the silver persulfate oxidation of I. A loss of a methyl group was inferred by Becconsall, *et al.*,³ during an electron spin resonance study of the lead dioxide oxidation of 4-methyl-2,6-di-*t*-butylphenol. In this communication, we wish to report results which not only expand the scope of this curious reaction to another oxidant,

(1) S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 1726 (1951).

(2) R. G. R. Bacon and D. J. Munro, *ibid.*, 1339 (1960).

(3) J. K. Becconsall, S. Clough, and G. Scott, *Proc. Chem. Soc.*, 308 (1959).

(1) This work was supported by Grant GB-3152 from the National Science Foundation.

(2) J. P. Ferris and L. E. Orgel, *J. Am. Chem. Soc.*, 87, 4976 (1965).