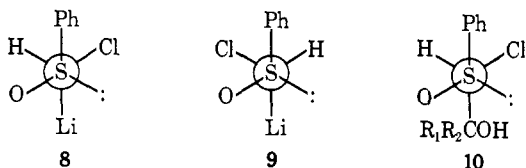


methyl phenyl sulfone¹² with the corresponding ketone.

The benzophenone adduct **5**, mp 128°, when heated to 130° for 1 min underwent a clean thermal decomposition to afford 2-chloro-1,1-diphenylethylene in 92% yield. A similar decomposition has been observed for the β -hydroxy sulfoxide obtained from the addition of methylsulfinyl carbanion to benzophenone.¹³ In contrast to the thermal instability of **5**, the adducts **3** and **4** were stable at temperatures up to 180°.

The unusually high stereoselectivity in the formation of the adducts from **1** and ketones is probably due to a free energy difference of at least 2 kcal/mol at -60° between the diastereomeric lithio derivatives **8** and **9**; the activation energy differences for the reaction of **8** and **9** with a ketone should be quite small. These lithio derivatives, which can be obtained by abstraction of the hydrogen bisecting the oxygen-sulfur-lone pair angle in two of the rotomers of chloromethyl phenyl sulfoxide, should, according to theory, be readily equilibrated by the carbanion inversion mechanism.¹⁴ On the basis of steric and dipole-dipole interactions, one could suggest that **8** should be more stable than **9** and thus the adducts would possess the stereochemistry shown in **10**.



Preliminary experiments¹⁵ on the metalation of sulfoxides of the general formula $\text{RSOCH}_2\text{R}'$ (R or $\text{R}' = \text{alkyl}$ or aryl) followed by reaction with symmetrical ketones indicate that these reactions also display significant stereoselectivity. Refinement of the results and the stereochemistry of the adducts will be reported shortly.

Acknowledgment. Support of this research by the Department of University Affairs of the Province of Ontario is gratefully acknowledged.

(12) T. Durst, unpublished observations.

(13) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, **88**, 5656 (1966).

(14) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.

(15) T. Durst and M. M. McClory, unpublished observation.

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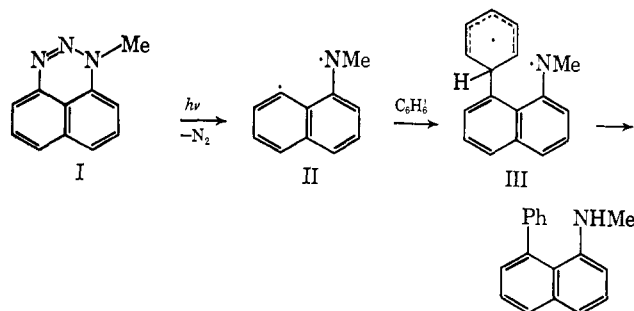
A Novel Heterocyclic Transformation

Sir:

We wish to report a one-step photochemical transformation of a 1,2,3-triazine ring to a pyridine ring and its application to the synthesis of a novel heteroaromatic system.

In the course of investigations of the chemistry of

peri-fused naphtho heterocycles,¹⁻³ we have turned our attention to photolysis of 1-methylnaphtho[1,8-*de*]triazine (**I**)¹ and related compounds. The products from photolysis⁴ of **I** in cyclohexane included 1-methylaminonaphthalene and bicyclohexyl, as expected for a homolytic reaction following extrusion of nitrogen. The photolysis of **I** in benzene gave 1-methylamino-8-phenylnaphthalene⁵ as the sole detectable product, suggesting that an initial diradical (**II**)⁶ adds to benzene *via* its reactive aryl radical center, and that this is followed by intramolecular hydrogen transfer in the diradical adduct **III**.



It seemed possible that in a diradical adduct to an olefin, cyclization would compete effectively with hydrogen migration; in particular, the adduct **IV** with vinyl bromide⁸ might cyclize with subsequent elimination of hydrogen bromide assisted by the residual nitrogen atom. Such a reaction, the net result of which is replacement of nitrogen (N_2) by the elements of acetylene, has now been effected, both with triazine **I** (to give *N*-methyl-1-azaphenylene, **V**)² and with the acenaphthylene analog **VI**.²

(1) M. J. Perkins, *J. Chem. Soc.*, 3005 (1964).

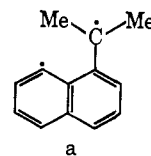
(2) A. R. J. Arthur, P. Flowerday, and M. J. Perkins, *Chem. Commun.*, 410 (1967).

(3) P. Flowerday and M. J. Perkins, *Tetrahedron Letters*, 1261 (1968).

(4) Irradiations employed a Phillips MLU 300-W lamp with a Pyrex filter. Reactions were carried out in an atmosphere of nitrogen; the experiments with vinyl bromide were conducted at 0° and employed a 20% solution of olefin in benzene containing *ca.* 2.5% triethylamine to remove hydrogen bromide.

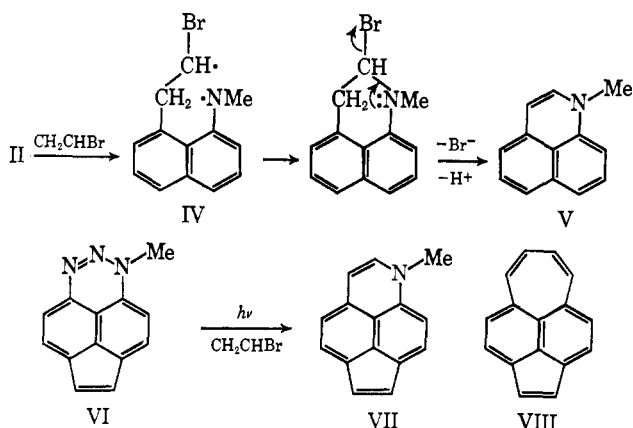
(5) Satisfactory elemental analyses and spectroscopic data (ir, nmr, mass) were obtained for all new compounds, with the exception of the azaphenylene **V**. This compound was isolated as a crystalline solid after chromatography of reaction mixtures on basic alumina in yields of 30-40%, but samples deteriorated rapidly during attempts at further purification, and satisfactory analytical figures were not obtained. However spectroscopic data including a molecular weight of 181 (mass spectrometry) together with the close similarity of the uv and visible absorptions with those of 1-azaphenylene itself (D. C. C. Smith and S. O'Brien *J. Chem. Soc.*, 2907 (1963)) left no doubt as to the identity of the product.

(6) We could find no evidence for intramolecular hydrogen transfer in **II** to give an azomethine, nor was such a reaction evidenced in photolysis of the *N*-isopropyl analog⁵ of **I**. Possibly there exists an appreciable barrier to rotation about the naphthyl-nitrogen bond in **II**, as hydrogen migration appears to be the preferred reaction path open to diradical **a**.⁷



(7) E. M. Burgess, R. Carrithers, and L. McCullagh, *J. Am. Chem. Soc.*, **90**, 1923 (1968).

(8) Addition to vinyl bromide would be expected at the unsubstituted carbon atom, as shown.



Yellow N-methylacenaphtho[5,6-*bc*]pyridine (VII),⁵ mp 126–127°, derived from VI in *ca.* 30% yield, is the simplest heterocyclic analog of the nonbenzenoid aromatic hydrocarbon VIII⁹ so far recorded.¹⁰ The aromaticity of VII is reflected in a substantial downfield shift in the nmr spectrum relative to that of V (e.g., protons on C₂ and C₃ appear at τ 3.78 and 4.38 in V and τ 2.69 and 3.00 in VII; *cf.* ref 2 and 3).

Our results supplement data on the photolysis of cyclic diazoamino compounds communicated recently by Burgess, Carrithers, and McCullagh.⁷ We are currently exploring extensions of these photolyses in the presence of vinyl bromide and other halo olefins.

Acknowledgment. We are grateful to the Science Research Council for the award of a Research Studentship (to P. F.).

(9) V. Boekelheide and G. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

(10) Examples of other heterocycles related to hydrocarbon VIII are described in ref 2 and 3, and by I. S. Ponticello and R. H. Schlessinger, *J. Am. Chem. Soc.*, **90**, 4190 (1968).

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The Photoreduction of Desmethoxypyrodelphinine

Sir:

Eight years ago we showed¹ that pyrodelphinine (Ia) and pyroneoline (Ib) display an unexpected ultraviolet absorption spectrum [Ia, λ_{max} 245 m μ ($\log \epsilon$ 3.8); Ib, λ_{max} 236 m μ ($\log \epsilon$ 3.85)] which disappears on acidification. We postulated at that time that the free electron pair of the nitrogen, the σ bond marked by an arrow in formula I, and the π -electron pair of the double bond are part of the unprecedented chromophore and that the excited state of this system may be portrayed as a mesomeric hybrid between the limiting structures I and II. Six years later Cookson and his collaborators published a paper² entitled " σ -Coupled π Electron Systems. A New Type of Chromophore," in which several more examples of such chromophoric systems

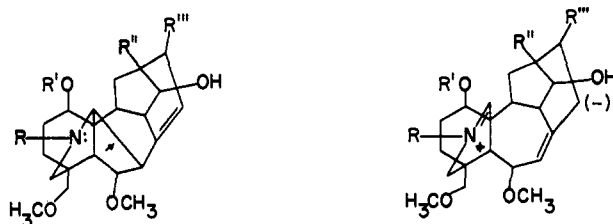
(1) K. Wiesner, H. W. Brewer, D. L. Simmons, D. R. Babin, F. Bickelhaupt, J. Kallos, and T. Bogri, *Tetrahedron Letters*, No. 3, 17 (1960).

(2) R. C. Cookson, J. Henstock, and J. Hudec, *J. Am. Chem. Soc.*, **88**, 1060 (1966).

are given, but the authors claim that this type has "remained previously unrecognized."³

It appeared to us probable that if the excited state of the pyro compounds resembles II, it might be reducible with sodium borohydride. Since, however, many reactions of the pyrodelphinine system involve the R''' methoxyl,⁴ we wished to perform our photochemical experiments on compound Ic in which this group is missing. The desired derivative was readily accessible from compound III. The preparation of the N-formyl analog of III (*i.e.*, V) from α -oxopyrodelphinine is known,⁵ and we have prepared compound III itself by the same sequence of steps starting from pyrodelphinine.⁶ Pyrolysis of compound III followed by alkaline hydrolysis yielded the desired product Ic [amorphous glass homogeneous in thin-layer chromatography; uv λ_{max} 231 m μ ($\log \epsilon$ 3.96); nmr poorly resolved quadruplet (1 H), τ 4.86 (vinylic hydrogen); molecular ion found at *m/e* 405.2524 (calcd 405.2515)]. Compound Ic was completely stable in methanolic solution in the presence of an excess of sodium borohydride at room temperature in the dark.

When the same solution was irradiated at 0° with a quartz mercury vapor lamp (100 W) for 4.5 hr a mixture of products was formed. The major component of this mixture was isolated by preparative thin-layer chromatography, and it was the expected product IV



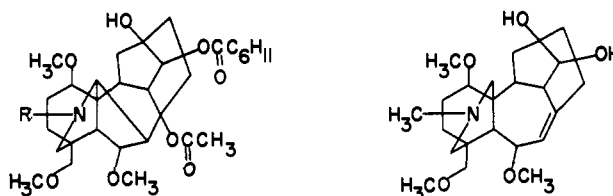
I a, b, c

II a, b, c

a (R = CH₃, R' = CH₃, R'' = OH, R''' = OCH₃)

b (R = CH₃-CH₂, R' = H, R'' = H, R''' = OCH₃)

c (R = CH₃, R' = CH₃, R'' = OH, R''' = H)



III (R = CH₃)

V (R = CHO)

[amorphous glass homogeneous in tlc; nmr broad singlet (1 H), τ 4.61 (vinylic hydrogen); molecular ion found at *m/e* 407.2666, (calcd 407.2671)]. If our views are correct and the excited state resembling IIC

(3) In a letter to K. W., Professor Cookson admitted that we have "expressed¹ in valence-bond language much the same thought about the spectrum of our pyro alkaloids" as Cookson, *et al.*²

(4) K. Wiesner, D. L. Simmons, and R. H. Wightman, *Tetrahedron Letters*, No. 15, 23 (1960).

(5) K. Wiesner, F. Bickelhaupt, D. R. Babin, and M. Gotz, *Tetrahedron*, **9**, 254 (1960).

(6) To be described in a full paper.