

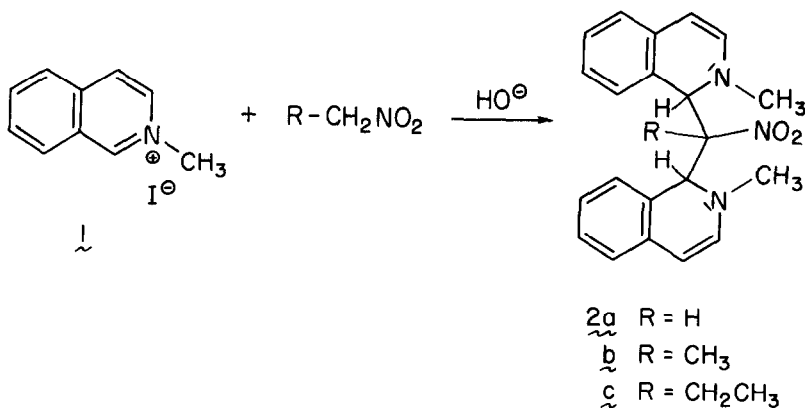
A NOVEL RING SYSTEM FROM ISOQUINOLINE METHIODIDE
AND ACTIVE METHYLENE COMPOUNDS. I.

W. R. Schleigh

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

(Received in USA 10 January 1969; received in UK for publication 12 March 1969)

In 1949, N. J. Leonard and G. W. Leubner (1) reported the synthesis of the bis[1-(2-methyl-1,2-dihydroisoquinoly)]nitroalkanes (2) from the alkaline condensation of various nitroalkanes and isoquinoline methiodide (1). Structure assignments were based on infrared spectra and elemental analyses.



We should like to present the preliminary results of a reinvestigation of this reaction. Employing a slight modification of the published procedure (1,2), we prepared compounds with the same physical and chemical properties as 2a and 2b. However, the NMR spectra (3) (Fig. 1) were inconsistent with the original structural assignments. We have interpreted the NMR spectra in terms of structure 3 on the basis of the following experiment and from extensive spin-decoupling experiments (4). First order analysis of the coupling constants was consistent with that predicted from Dreiding models (5).

Isoquinoline-1-d methiodide was prepared and condensed with nitromethane-d₃ in methanol-d solution in the presence of sodium methoxide. On concen-

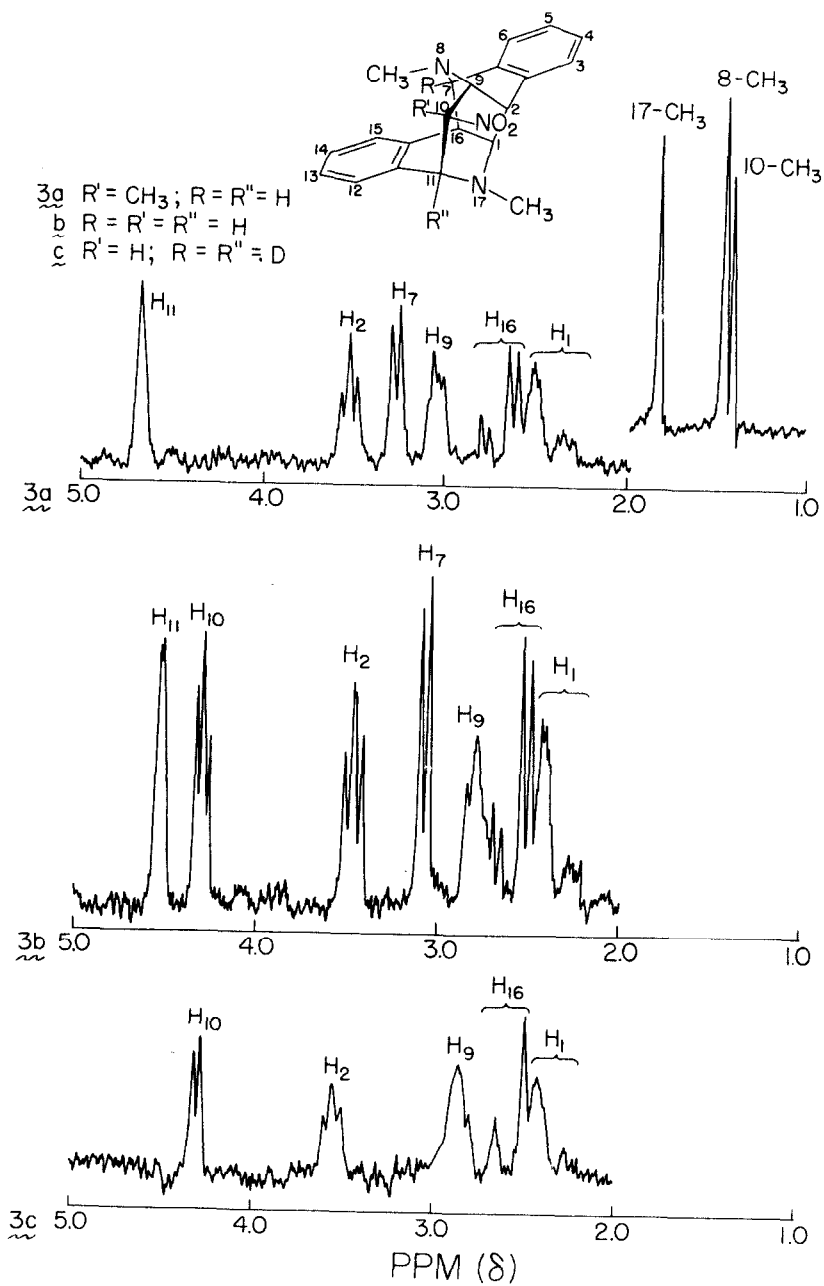
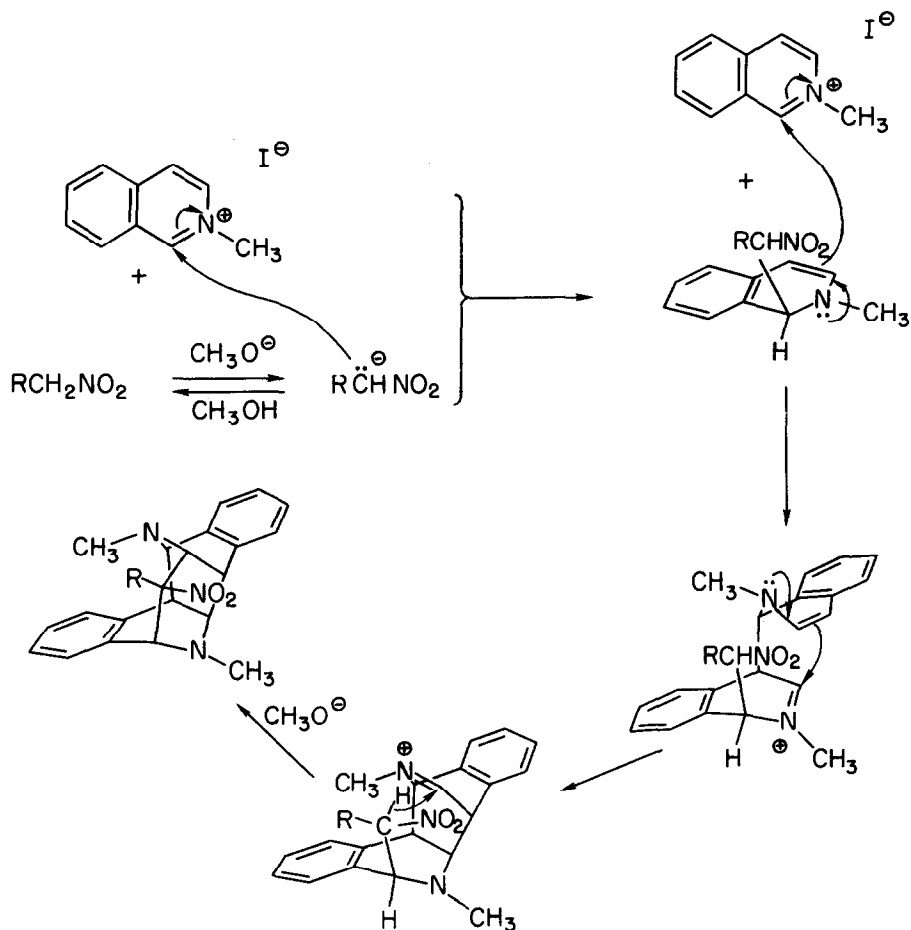


Fig. 1: NMR Spectra of 10-substituted 8,17-dimethyl-8,17-diazadibenzo[*c,j*]-tetracyclo[7.3.1.0^{2,9}.0^{7,16}]tridecanes

tration of the reaction mixture and dilution of the dark solution with water, a colorless crystalline material separated. Comparison of the NMR spectrum of 3c with that of 3b indicated that signals originally at 4.71 δ and 3.26 δ



were no longer present in the NMR spectrum of the deuterated compound. These protons were assigned to the 1-position of the isoquinoline fragments. The other outstanding feature of this spectrum was the doublet centered at 4.32 δ ($\text{H}-\text{C}-\text{NO}_2$). This indicated that nitromethane had condensed at the 1-position of only one isoquinoline fragment and not at both as suggested previously (1).

The formation of 3 has been rationalized as indicated in the scheme.

The transformations involved find some precedent in the alkaloid field and related areas (Cf. 6,7,8,9).

Further labeling experiments and an extension of this reaction are in progress.

Acknowledgment. The author thanks Dr. T. H. Regan for NMR spectra, Mr. D. P. Maier for mass spectra, and Mr. D. F. Ketchum for microanalytical data.

References

1. N. J. Leonard and G. W. Leubner, J. Am. Chem. Soc., **71**, 3405 (1949).
2. H. A. DeWalt, Jr., Ph.D. Thesis, University of Illinois, 1950, p. 33.
3. NMR spectra were determined in C₆D₆-TMS on a Varian Associates A60 spectrophotometer.
4. The results of these experiments will be discussed in detail in a later publication.
5. (a) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, Vol. 1, pp. 160-199. Pergamon Press, New York (1965). (b) N. S. Bhacca and D. H. Williams, Applications of NMR Spectroscopy in Organic Chemistry, pp. 49-61. Holden-Day, Inc., San Francisco (1964).
6. M. Sainsbury, S. F. Dyke, D. W. Brown, and W. G. D. Lugton, Tetrahedron, **24**, 427 (1968).
7. E. E. van Tamelen, V. B. Haarstad, and R. L. Orvis, Tetrahedron, **24**, 687 (1968).
8. E. Wenkert, K. G. Dave, C. T. Gnewuch, and P. W. Sprague, J. Am. Chem. Soc., **90**, 5251 (1968).
9. H. Zinnes, F. R. Zuleske, and J. Shavel, Jr., J. Org. Chem., **33**, 3605 (1968).