Tetrahedron Letters No.52, pp. 4539-4542, 1970. Pergamon Press. Printed in Great Britain.

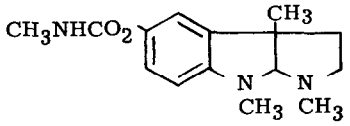
NITROGEN PHOTOCHEMISTRY VIII. PHOTODECARBAMATION A NEW REACTION ON PHYSOSTIGMINE

Enrique F. Travecedo[1] and Virgil I. Stenberg[2]

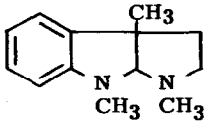
Department of Chemistry, The University of North Dakota
Grand Forks, North Dakota 58201

(Received in USA 6 October 1970; received in UK for publication 12 October 1970)

Physostigmine(I), or eserine, a biologically active alkaloid of the calabar bean, Physostigma venenosum, has been reported to be photochemically active,[3] however the products have not been isolated and identified. With our current interest in developing and understanding the photochemistry of alkaloids, the structure of the photoproducts were sought. A 24 hour irradiation of a 3.9 x 10^{-3}M 2-propanol solution of I with the 300 nm low pressure lamps of the Rayonet reactor produced a 10% yield of deoxyeseroline(II) together with a not-readily-purified oil. The transformation occurred in both Pyrex and quartz vessels. The reaction progress was monitored by silica gel tlc (7.5 benzene:



I



II

$2CHCl_3$:0.5 $(C_2H_5)_2NH$), and its separation was effected on alumina chromatography (benzene).

The ir spectrum of II was clearly lacking the carbamate carbonyl stretching frequency and phenolic hydroxyl bands. The reported uv spectrum[4] of deoxyeseroline, λ_{max}^{EtOH} 251 nm (log ϵ = 4.03); 303 nm (log ϵ = 3.47), agrees with that of the photoproduct, λ_{max}^{EtOH} 250 nm (log ϵ = 4.01); 302 (log ϵ = 3.43). The mass spectra of physostigmine and the photoproduct exhibited in Figure 1 demonstrate conclusively that the carbamate group has been removed during irradiation. The characteristic 16 unit difference of the bands of II from the already assigned principal bands[5,6] of physostigmine can be attributed to the

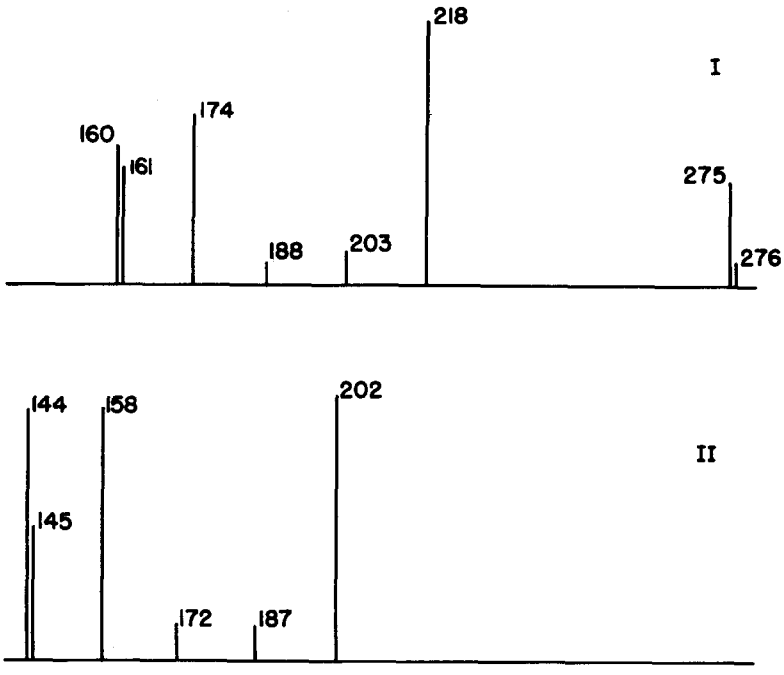


Figure 1. Mass spectra of physostigmine(I) and the photoproduct, deoxyeseroline-(II).

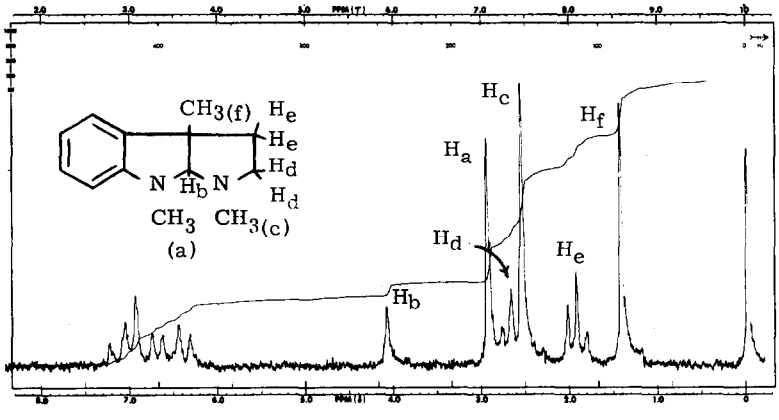
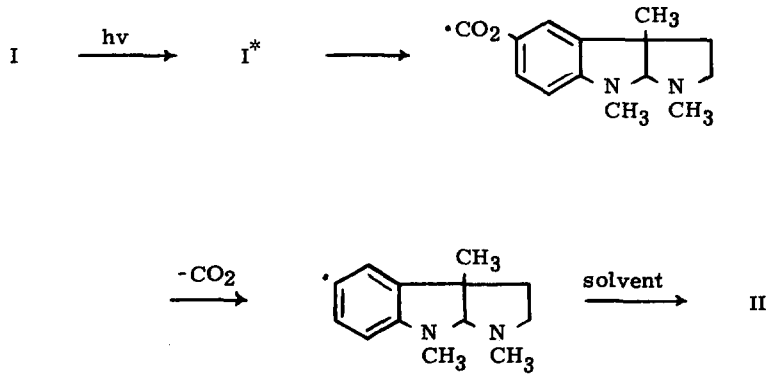


Figure 2. Nmr spectrum of the photoproduct II in $CDCl_3$.

lack of oxygen in II. The nmr illustrated in Figure 2 can readily be interpreted in terms of the assigned structure for II.

Neither benzophenone nor acetone was effective as a sensitizer for the formation of II though the decomposition of I was greatly enhanced. Quenching studies with biacetyl and piperylene were both unsuccessful because these molecules reacted during the irradiation. It is difficult to draw valid conclusions concerning the nature of the excited states on the basis of these data. A rationalization for the formation of II is proposed in Scheme I.



Potentially this new reaction offers a tool for converting phenols to the corresponding benzene compounds via their carbamate esters.

Acknowledgement: This investigation was supported by a research grant 1-R01-AI-08138-03 from the National Institutes of Health, United States Public Health Service and in part by a Public Health Service Research Career Development Award (No. 1 K 04 GM 09888-01) from the National Institute of General Medical Services. We are also grateful to Mr. Vernon Feil of the U. S. Radiation and Metabolism Laboratory for obtaining the mass spectral analysis.

REFERENCES

1. Present address: Department of Chemistry, University of Antioquia, Medellin, Columbia, South America.

2. To whom inquiries should be made.

3. J. Buchi and H. Welti, Pharm. Acta Helv., 16, 67 (1941); Chem. Abstr., 36, 220 (1942).

4. S. Yamada, T. Hino, and K. Ogawa, Chem. Pharm. Bull. (Tokyo), 11, 674 (1963).

5. E. Clayton and R. I. Reed, Tetrahedron, 19, 1345 (1963).

6. G. Spiteller and M. Spiteller-Friedmann, Tetrahedron Lett., 147 (1963).