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THE PHOTOCHEMICAL FRAGMENTATION OF N-CHLOROCONIINE

Edward Leete and Alan R. Hargens

School of Chemistry, University of Minnesota, Minneapolis.

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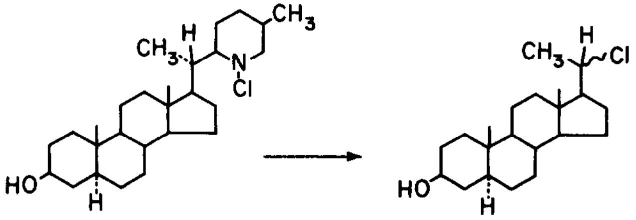
Recently Adam and Schreiber (1), on attempting to apply the Hofmann-Löffler reaction (2) to the N-chloro compound I, discovered a new type of fragmentation, the main products obtained on UV irradiation being the 20(R) and 20(S)-chloro-5α-pregnane-3β-ol (II). We have now shown that this same type of fragmentation occurs on the UV irradiation of N-chloroconiine (III) yielding propyl chloride and Δ^1-piperideine. Hofmann (3) found that the thermal decomposition of N-bromoconiine afforded 1-azabicyclo[4,3,0]nonane (IX) in 40 % yield, and we have shown that this compound is also one of the products of the photolysis of III .



I II

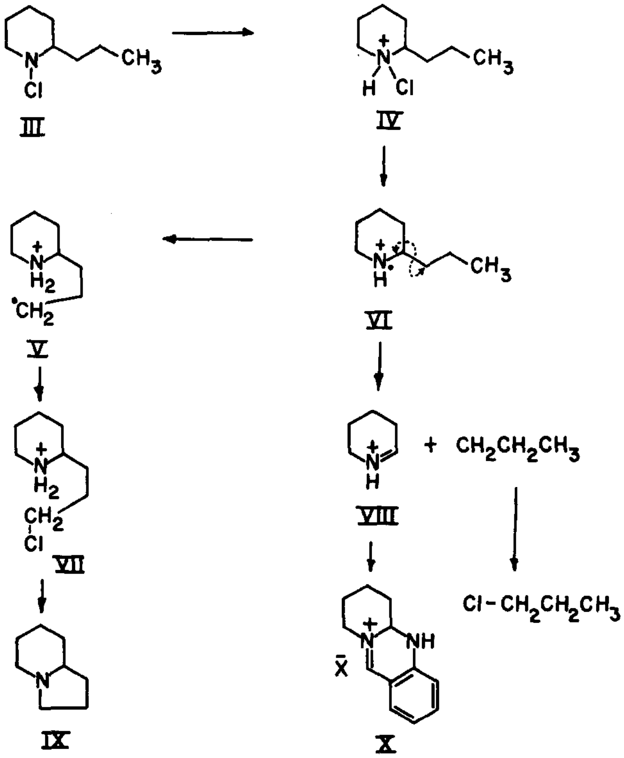


Figure 1. Photochemical decomposition of N-chloroconiine

N-Chloroconiine (a pale yellow oil, picrate, m.p. 224-225°), was obtained in 95 % yield by adding sodium hypochlorite solution to a cooled aqueous solution of DL-coniine hydrochloride. The N-chloroconiine , dissolved in concentrated sulfuric acid in a quartz flask, was irradiated with an Hanovia high pressure mercury lamp, Model 16200, for nine hours, keeping the solution below 30°. The brown solution was then added to ice and the mixture extracted with ether . Evaporation of the dried ether extract afforded propyl chloride in 25-35 % yield. Its identity was established by determination of its infrared spectrum and by gas chromatography*. The acid solution from which the propyl chloride had been extracted was made basic with sodium hydroxide and extracted with ether . Δ^1-Piperideine was detected in the extract by condensation with o-aminobenzaldehyde which affords a 2,3-tetramethylene-1,2-dihydroquinazolinium salt (X), isolated as its picrate, m.p. 169-171° (lit.(4), m.p. 170-172°). The estimated yield of Δ^1-piperideine based on the yield of this derivative was only 6-8 %, considerably less than the yield of propyl chloride. However this low yield may be due to the fact that Δ^1-piperideine readily undergoes self condensation to yield tetrahydroanabasine and isotripiperideine (4). Concentration of the solution from which the picrate X had been removed yielded crystals of the picrate of 1-azabicyclo[4,3,0]nonane (22-38 % yield), m.p. 226° (lit.(5), m.p. 226°). The identity of this compound was confirmed by the preparation of its hydrochloride, m.p. 202° (lit. (6), m.p. 202-203°).

The products obtained by the photolysis of N-chloroconiine in concentrated sulfuric acid can be rationalized on the basis of conclusions which Corey and Hertler (7) reached as a result of their investigations on the mechanism of the Hofmann-Löffler reaction. It is considered that the protonated N-chloroconiine

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*A solution of the reaction product in carbon tetrachloride (b.p. 76.8°) was chromatographed in a Perkin-Elmer Vapor fractometer, Model 154, with a polypropylene glycol-LB 550-X column at 40°. Authentic propyl chloride (b.p. 47.2°) and the reaction product had identical retention times of 7 min. 54 sec., compared with a retention time of 23 min. 48 sec. for the solvent carbon tetrachloride.

(IV) decomposes yielding the aminium radical VI, which can undergo reactions by two routes . A 1-5 hydrogen migration yields V, which on reaction with a second molecule of the protonated N-chloroconiine affords the chloro derivative VII and the aminium radical. Azabicyclo[4,3,0]nonane is formed when the reaction mixture is made alkaline . An alternate mode of decomposition of the aminium radical (indicated by dotted lines in Fig. 1) yields the protonated Δ^1-piperideine (VIII) and a propyl radical which then affords propyl chloride by reaction with IV . A similar type of mechanism has been suggested for the photolytic decomposition of tertiary hypochlorites (8). The yields of pyrrolidine derivatives in the Hofmann-Löffler reaction are often quite low (2), and it is possible that the fragmentation which we have described here is a common side reaction.

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References

1. G. Adam and K. Schreiber, Tetrahedron Letters, 923 (1965); cf. also : Chem. and Ind. (London), 989 (1965).
2. M. E. Wolff, Chem. Rev., **63**, 55 (1963).
3. A. W. Hofmann, Ber., **18**, 5, 109 (1885).
4. C. Schöpf and K. Otte, Ber., **89**, 335 (1956).
5. K. Löffler and H. Kaim, Ber., **42**, 94 (1909).
6. K. Löffler and M. Flügel, Ber., **42**, 3420 (1909).
7. E. J. Corey and W. R. Hertler, J. Am. Chem. Soc., **82**, 1657 (1960).
8. C. Walling and A. Padwa, J. Am. Chem. Soc., **85**, 1597 (1963); cf. also : F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. N. Zanet, J. Org. Chem., **28**, 55 (1963) ; M. Akhtar and D. H. R. Barton, J. Am. Chem. Soc., **83**, 2213 (1961).