−8.5 ± 0.3° (*c* 1.90, chloroform). The compound did not depress the melting point of an authentic sample, isolated[22] from *Himantandra baccata* and purified to a constant m.p. of 132.6–133.4° cor. (lit.[22] 135° uncor.), $[\alpha]^{21}\text{D}$ −8.5 ± 0.2° (*c* 1.92, chloroform) (lit.[22] −8.0°). Both had identical infrared spectra.

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.22; H, 7.62.

Isogalbulin (VII, R = H).—In view of the easy decomposition of the ditosylate VII (R = OTs), it was considered desirable to start the reaction at a low temperature. Therefore the suspension of lithium aluminum hydride was cooled in Dry Ice–acetone while the solution of the ditosylate was added. It was then allowed to come to room temperature gradually, stirred for one hour, finally refluxed during three hours. The mixture was worked up as usual, except that chloroform and neutral alumina[34] were used in the chromatography. Crystallization from methanol yielded 59% of material, m.p. 85–98°. Two further recrystallizations gave colorless needles, m.p. 87–89° and 87.8–89.6°, respectively. A third recrystallization provided what appeared to be a polymorphic modification, also needles, m.p. 100.5–101.5°. The lower-melting form could not be obtained again. Material recovered from the mother liquors melted at 100–101.5°. The final product had $[\alpha]^{21}\text{D}$ +48 ± 2° (*c* 0.296, chloroform). The compound was quite soluble even in cold methanol. In an attempt to prepare it from the dimesylate (VII, R = OMs), several zones were detected on the chromatogram by examination under ultraviolet light. No isogalbulin could be isolated. It appears that reduction of the dimesylate may have led mainly to the diol (VII, R = OH), which in turn may have undergone partial dehydration[13] to VII (RR = O). Formation of the alcohol rather than the hydrocarbon in sulfonic ester reductions has been observed with other classes of compounds.[21a]

Anal. Calcd. for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.14; H, 8.07.

Acknowledgments.—The authors are greatly indebted to Prof. L. H. Briggs for a supply of (−)-matairesinol dimethyl ether, to Prof. G. K. Hughes for a sample of galbulin and to Dr. W. M. Hearon and Dr. W. L. Shilling for large amounts of α-conidendrin dimethyl ether and β-conidendrin, as well as samples of α-retrodendrin dimethyl ether and α-retrodendric acid dimethyl ether. We also wish to express our thanks to Mrs. Iris J. Siewers and Miss Fleur C. Bateman for the infrared spectra and to Dr. W. C. Alford and collaborators for the microanalyses.

BETHESDA 14, MD.

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[34] An excellent grade, produced by M. Woelm in Eschwege (Germany), is now available from Alupharm Chemicals, 54 C Street, Elmont, Long Island, N. Y.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Unsaturated Amines. II. Determination of the Proximity of Nitrogen to a Double Bond by Ultraviolet Absorption Spectra[1]

BY NELSON J. LEONARD AND DAVID M. LOCKE[2]

RECEIVED JUNE 23, 1954

The ultraviolet absorption spectra have been determined for several groups of α,β-unsaturated, β,γ-unsaturated and related saturated tertiary amines. A definite shift toward longer wave length and higher intensity of absorption is observed consistently with the introduction of α,β-unsaturation. Thus, comparison of the ultraviolet absorption spectrum of an unsaturated tertiary amine with that of the corresponding saturated amine provides a convenient empirical method for differentiating between an α,β-unsaturated amine and one in which the double bond is further removed from the nitrogen.

The previous paper in this series[1] has demonstrated the use of infrared absorption spectra in differentiating between an α,β-unsaturated tertiary amine and one in which the double bond is further removed from the nitrogen. The present paper is devoted to the application of ultraviolet absorption spectra for the solution of the same structural problem. The method is most safely employed when the spectra of both the unsaturated and the corresponding saturated amines are obtained for comparison.

Studies on the vacuum ultraviolet spectra of certain primary amines,[3] cyclic secondary amines,[4] and related primary, secondary and tertiary aliphatic amines[5] indicate that the tertiary amines absorb at longer wave lengths than do the less substituted amines. Unsaturation adjacent (α,β) to the tertiary amine nitrogen induces ultraviolet absorption in a range more readily measurable in solution. Thus, the wave length of the absorption maximum for 1-butenylpiperidine (in hexane) is 228 mμ,[6,7] indicating that the amino group possesses a conjugating power similar to that of C=C, by interaction of the unshared pair of electrons on the nitrogen with the π-electrons of the multiple bond.[8] Maxima in the region 229–236 mμ (in ether) have been used by Herr and Heyl[9,10] to characterize the α,β-unsaturated amines obtained on condensation of certain steroidal aldehydes and ketones with piperidine and pyrrolidine. In the cases cited,[6–10] neither related saturated amines nor unsaturated amines other than the $\Delta^{\alpha,\beta}$-type have been used for spectral comparison. In the present investigation, ultraviolet maxima (or apparent maxima)[11–14] are

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[1] Paper I in this series, N. J. Leonard and V. W. Gash, THIS JOURNAL, **76**, 2781 (1954).

[2] National Science Foundation Fellow, 1953–1954.

[3] St. Vencov, *Bull. sect. sci. acad. roumaine*, **26**, 89 (1943).

[4] Lucy W. Pickett, Mary E. Corning, Grace M. Wieder, Dorothy A. Semenov and Jean M. Buckley, THIS JOURNAL, **75**, 1618 (1953); λ_{max} for piperidine <200 mμ.

[5] E. Tannenbaum, E. M. Coffin and A. J. Harrison, *J. Chem. Phys.*, **21**, 311 (1953); λ_{max} for triethylamine 212 mμ.

[6] E. A. Braude, *Ann. Reps. Chem. Soc.*, **42**, 105 (1945).

[7] K. Bowden, E. A. Braude, E. R. H. Jones and B. C. L. Weedon, *J. Chem. Soc.*, 45 (1946).

[8] K. Bowden, E. A. Braude and E. R. H. Jones, *ibid.*, 948 (1946).

[9] M. E. Herr and F. W. Heyl, THIS JOURNAL, **74**, 3627 (1952).

[10] F. W. Heyl and M. E. Herr, *ibid.*, **75**, 1918 (1953).

[11] L. J. Saidel, A. R. Goldfarb and W. B. Kalt, *Science*, **113**, 683 (1951).

[12] J. M. Vandenbelt, C. Heinrich and S. L. Bash, *ibid.*, **114**, 576 (1951).

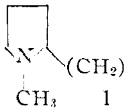
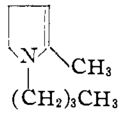
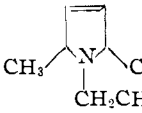
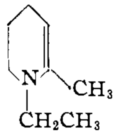
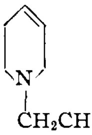
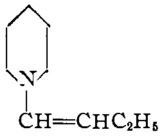
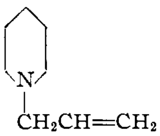
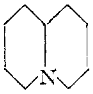
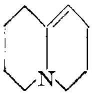
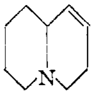
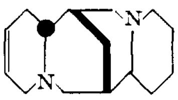
[13] P. Bladon, H. B. Henbest and G. W. Wood, *J. Chem. Soc.*, 2737 (1952).

[14] G. Eglinton, E. R. H. Jones and M. C. Whiting, *ibid.*, 2873 (1952).

recorded for several groups of α,β-unsaturated, β,γ-unsaturated and related saturated tertiary amines (Table I).[15]

TABLE I

ULTRAVIOLET ABSORPTION MAXIMA

Saturated amines	λmax, mμ	εmax (±200)	α,β-Unsaturated amines	λmax	εmax	β,γ-Unsaturated amines	λmax	εmax
 I	214	2300	 II	238	7200	 III	215	2600
 IV	213	1600	 V	231	5100	 VI	218	1700
			 VII	228	7500	 VIII	213	2600
 IX	215	3100	 X	228	5600	 XI	214	2800
 XII	214	5100	 XIII	~225[16] 216	7200 7800	 XIV or	218	5600
 XV	216	6100	 XVI	225	9600			

From the data recorded in Table I, it is immediately apparent that the introduction of α,β-unsaturation into tertiary amine molecules produces a clearly recognizable bathochromic shift in the wave length of the ultraviolet absorption maximum,[17] and has a definite hyperchromic effect on the intensity of the absorption. By contrast, the introduction of β,γ-unsaturation into the same tertiary amine molecules produces no appreciable change in either the wave length or the intensity of the ultraviolet absorption. Thus, a convenient method is made available for differentiating between an α,β-unsaturated tertiary amine and one in which the double bond is further removed from the nitrogen. The combined bathochromic and hyperchromic effect of the α,β-unsaturation is observed in amines of quite varied structure (Table I): monocyclic five- and six-membered rings, acyclic unsaturates, and fused bicyclic and tetracyclic systems. The method promises to be generally applicable for the characterization of α,β-unsaturated tertiary amines in which the steric requirements do not prevent[18] the interaction of the unshared pair of electrons on the nitrogen with the π-electrons of the multiple bond.

Experimental[19]

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined using a Cary recording spectrophotometer, model 11. The solvent used was diethyl ether, dried over sodium hydride and distilled, or (preferably) Mallinckrodt white-label anhydrous ether, used directly. When run against a blank cell, the solvent (1-cm. cell) showed appreciable absorption starting about 215 mμ. This is the region of the spectrum in which the saturated and β,γ-unsaturated tertiary amines exhibited their absorption maxima; thus, the solvent absorption may have affected the intensity of these maxima. However, several runs of ether against ether indicated an uncertainty of only *ca.* ±0.05 optical density unit due to absorption by solvent in this region. In most cases this caused an uncertainty in the extinction coefficients of *ca.* ±200 units. Normally, the wave length values are considered accurate to ±1 mμ, but in the region below 220 mμ, with ether as the solvent, the

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[15] Ultraviolet absorption has been shown to permit differentiation between C=C and C=C—O—,[14] also presumably between -O- and C=C—O— (Lucy W. Pickett, Nancy J. Hoeflich and Tien-Chuan Liu, THIS JOURNAL, **73**, 4865 (1951); J. R. Platt, H. B. Klevens and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1949)). The bathochromic effect of α,β-unsaturation on a sulfide linkage[6] has been recognized for some time (H. Mohler and J. Sorge, *Helv. Chim. Acta*, **23**, 1200 (1940); E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 84 (1949); H. P. Koch, *J. Chem. Soc.*, 387 (1949); C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950)).

[16] The total absorption appears to be roughly the sum of the saturated and α,β-unsaturated amine absorptions. The (apparent) maximum occurs at 216 mμ, with a slight shoulder at 225 mμ. Subtraction of one-half the extinction coefficient of sparteine XII at 225 mμ from that of the dehydrosparteine XIII at the same wave length gives a value of 5500 for the contribution of the α,β-unsaturated amine to ε in this region. The value is in the range of the figure observed for the dehydroquinolizidine X and that of $^1/_2\epsilon$ recorded for the didehydrosparteine XVI.

[17] The maxima reported above 220 mμ (center column of Table I) are real maxima. Those below 220 mμ (left and right columns of Table I) may be apparent maxima due to scattered light effects,[11-14] although the suggestion that these are equally real maxima is supported by the finding of Tannenbaum, Coffin and Harrison[8] that triethylamine exhibits a maximum at 212 mμ in the vacuum ultraviolet.

[18] B. M. Wepster, *Rec. trav. chim.*, **71**, 1159, 1171 (1952).

[19] The authors are indebted to Miss Geraldine Meerman for determination of the absorption spectra.

readings may not be as accurate as this, especially since the slit opens to its maximum (*i.e.*, 3.0 mm.) at 213–215 mμ.

The values reported in Table I are all observed with diethyl ether as the solvent. In addition, diethylamine and triethylamine, whose spectra have been determined previously in the vacuum ultraviolet,[5] were run in solution under the same conditions used for the cyclic amines. Neither showed a maximum at or above 215 mμ; their extinction coefficients at 215 mμ were, respectively, 350 and 1600.

Absorption spectra were determined for several compounds in cyclohexane as well as in ether. The cyclohexane was purified by shaking with concentrated sulfuric acid, then with water, followed by drying over magnesium sulfate and distilling. With this solvent, the slit width was a maximum at 208 mμ. At 228 mμ, solvent seemed to have little effect on the maxima, since 1-butenylpiperidine (VII) exhibited $\epsilon_{\max.}$ 7800 at 228 mμ in cyclohexane.[6,7] The (apparent) maximum for Δ^3 (or Δ^{13})-dehydrosparteine (XIV), however, was shifted in cyclohexane to 208 mμ and $\epsilon_{\max.}$ 6900, and quinolizidine failed to show any maximum in cyclohexane at or above 208 mμ (ϵ 4600 at 208 mμ).

Purification of Compounds.—All compounds were of analytical purity.

Diethylamine: redistilled, b.p. 55–55.5°, n^{20}D 1.3869.

Triethylamine: redistilled, b.p. 86.5–87°, n^{20}D 1.4003.

1-Methyl-2-*n*-butylpyrrolidine (I)[20]: redistilled, b.p. 40–41° (28 mm.).[21]

1-*n*-Butyl-2-methyl-Δ^2-pyrroline (II)[20]: redistilled under nitrogen, b.p. 65–66° (17 mm.).

1-Ethyl-2,5-dimethyl-Δ^3-pyrroline (III)[20]: redistilled under nitrogen, b.p. 64.5–66° (85 mm.), n^{20}D 1.4440.

1-Methylpiperidine (IV)[22]: redistilled, b.p. *ca.* 25° at 20 mm.

1-Ethyl-2-methyl-Δ^2-tetrahydropyridine (V)[20]: redistilled under nitrogen, b.p. 57–57.5° (16 mm.).

1-Ethyl-Δ^3-tetrahydropyridine (VI)[1]: redistilled under nitrogen, b.p. 35–36° (28 mm.).

1-Butenylpiperidine (VII)[23]: redistilled under nitrogen, b.p. 84–85° (20 mm.), n^{20}D 1.4810.

1-Allylpiperidine (VIII)[20]: redistilled, b.p. 44–45° (18 mm.), n^{20}D 1.4584.

Quinolizidine (IX)[24]: redistilled, b.p. 75–75.5° (18 mm.), n^{20}D 1.4793.

$\Delta^{1(10)}$-Dehydroquinolizidine (X)[25]: purified through the perchlorate salt, m.p. 232–233° dec.; distilled under nitrogen, b.p. 80° (18 mm.), n^{28}D 1.5116.

Δ^1-Dehydroquinolizidine (XI)[25]: redistilled under nitrogen, b.p. 75–76° (20 mm.), n^{28}D 1.4917.

***l*-Sparteine** (XII): purified through the sulfate salt; distilled, b.p. 102–103° (0.3 mm.).

Δ^5-Dehydrosparteine (XIII)[26,27]: purified through the perchlorate salt, d.p. 243°; distilled under nitrogen, b.p. 83–84° (0.2 mm.).

Δ^3(or Δ^{13})-Dehydrosparteine (XIV)[27,28]: recrystallized from chloroform–acetone, m.p. 168–169°.

***l*-α-Isosparteine** (XV)[26,29–31]: resublimed at 75–85° (0.1 mm.), m.p. 107–115° (softens at 95°), partially hydrated.

$\Delta^{5,11}$-Didehydrosparteine (XVI)[26,27]: resublimed at 110–115° (0.1 mm.), m.p. 104–106°.

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(20) R. Adams and J. E. Mahan, THIS JOURNAL, **64**, 2588 (1942).

(21) The liquid samples were distilled through a modified Holzman column, and the boiling points recorded when very small amounts were distilled may be lower than the literature values.

(22) N. J. Leonard, S. Swann, Jr., and H. L. Dryden, Jr., THIS JOURNAL, **74**, 2871 (1952).

(23) C. Mannich and H. Davidsen, *Ber.*, **69**, 2106 (1936).

(24) V. Boekelheide and S. Rothchild, THIS JOURNAL, **69**, 3149 (1947).

(25) N. J. Leonard, A. S. Hay, R. W. Fulmer and V. W. Gash, *ibid.*, **77**, 439 (1955).

(26) K. Winterfeld and C. Rauch, *Arch. Pharm.*, **272**, 273 (1934).

(27) N. J. Leonard, P. D. Thomas and V. W. Gash, THIS JOURNAL, in press.

(28) Structure is uncertain. P. D. Thomas, Ph.D. Thesis, University of Illinois, 1954.

(29) N. J. Leonard and R. E. Beyler, THIS JOURNAL, **72**, 1316 (1950).

(30) L. Marion and N. J. Leonard, *Can. J. Chem.*, **29**, 355 (1951).

(31) Maria Przybylska and W. H. Barnes, *Acta Cryst.*, **6**, 377 (1953).

URBANA, ILLINOIS

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Unsaturated Amines. III. Introduction of α,β-Unsaturation by Means of Mercuric Acetate: $\Delta^{1(10)}$-Dehydroquinolizidine[1,2]

BY NELSON J. LEONARD, ALLAN S. HAY, RICHARD W. FULMER AND VIRGIL W. GASH

RECEIVED AUGUST 12, 1954

The mild dehydrogenation of the representative saturated bicyclic tertiary amine, quinolizidine (I), by means of mercuric acetate results in $\Delta^{1(10)}$-dehydroquinolizidine (II), which forms salts of the $\Delta^{5(10)}$-dehydroquinolizidinium type (III). The establishment of the structures is based upon data accumulated from infrared spectra, ultraviolet spectra, pK'_a measurements, Zerewitinoff active hydrogen determinations, reduction with lithium aluminum hydride, and Grignard reaction with the α,β-unsaturated (enamine) salt. The action of methylmagnesium iodide on $\Delta^{1(10)}$-dehydroquinolizidinium perchlorate results in the introduction of a bridgehead methyl group and the formation of 10-methylquinolizidine. The structure of this compound was proved by comparison with the isomeric methylquinolizidines, all of which have now been characterized.

Now that satisfactory diagnostic methods[2–4] exist for differentiating between an α,β-unsaturated tertiary amine and one in which the double bond is further removed from the nitrogen, we are able to proceed more effectively with an examination of various means of introducing a double bond into a saturated amine. Mercuric acetate was selected as the first reagent to be studied because fundamental knowledge concerning its dehydrogenating action was lacking, despite its occasional employment in the modification of alkaloid structures.[5] The saturated bicyclic tertiary amine, quinolizidine

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(1) Presented at the 5th Summer Seminar in the Chemistry of Natural Products at the University of New Brunswick, Fredericton, N. B., Canada, August 19, 1953.

(2) Paper II in this series, N. J. Leonard and D. M. Locke, THIS JOURNAL, **77**, 437 (1955).

(3) R. Adams and J. E. Mahan, *ibid.*, **64**, 2588 (1942).

(4) N. J. Leonard and V. W. Gash, *ibid.*, **76**, 2781 (1954).

(5) *E.g.*, (a) J. Tafel, *Ber.*, **25**, 1619 (1892); (b) A. Reissert, *ibid.*, **27**, 2244 (1894); (c) J. Gadamer, *Arch. Pharm.*, **253**, 274 (1915); (d) N. V. Subba Rao and T. R. Seshadri, *Proc. Indian Acad. Sci.*, **11A**, 23 (1940); (e) H. Legerlotz, *Arch. Pharm.*, **256**, 123 (1918); (f) J. Gadamer and H. Kollmar, *ibid.*, **261**, 153 (1923); (g) H. Dieterle and P. Dickens, *ibid.*, **264**, 257 (1926); (h) K. Winterfeld, *ibid.*, **266**, 299 (1928); (i) K. Winterfeld and C. Rauch, *ibid.*, **272**, 273 (1934); (j) L. Marion and N. J. Leonard, *Can. J. Chem.*, **29**, 355 (1951); (k) A. R. Battersby and H. T. Openshaw, *J. Chem. Soc.*, S67 (1949); (l) A. R. Battersby, H. T. Openshaw and H. C. S. Wood, *Experientia* ,**5**, 114 (1949); (m) P. Karrer and O. Rüttner, *Helv. Chim. Acta*, **33**, 291 (1950); (n) R. N. Hazlett and W. E. McEwen, THIS JOURNAL, **73**, 2578 (1951); (o) H. T. Openshaw and H. C. S. Wood, *J. Chem. Soc.*, 391 (1952); (p) R. F. Tietz and W. E. McEwen, THIS JOURNAL, **75**, 4945 (1953).