[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NEW MEXICO]

ULTRAVIOLET ABSORPTION SPECTRA STUDIES OF 2-IMIDAZOLINES AND IMIDAZOLIDINES

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A. 2-IMIDAZOLINES

While 2-imidazolines have been obtained by a variety of synthetic approaches (1–9), little additional evidence has been offered to support their accepted structural formulas. The 2-imidazoline structure has been cited (10) as an example of one of the few types of compounds containing a double bond which resists catalytic hydrogenation completely. Interest in this carbon to nitrogen double bond has prompted the present ultraviolet absorption spectra studies. A summary of the data obtained is given in Table I.

Curve A of Figure 1 shows that for 4,4-dimethyl-1-isopropyl-2-imidazoline a single maximum absorption occurred at 230 mμ, which is in agreement with the accepted value for the nitrogen to carbon double bond. Curve B of Figure 1 for 1-isopropyl-2,4,4-trimethyl-2-imidazoline shows that replacement of the hydrogen in the 2-position by a methyl group caused a slight shift, maximum absorption occurring at 227 mμ. Examination of other 4,4-dimethyl-1-isopropyl-2-alkyl-2-imidazolines (Table I) indicates that increase in the length of the alkyl group has no appreciable effect on the point of maximum absorption.

The general tendency upon acidification of the 2-imidazolines as shown in Table I for 1-isopropyl-2,4,4-trimethyl-2-imidazoline, is to give a single maximum due to the presence of the carbon to nitrogen double bond in the acidified structure.

Curve A of Figure 2 for 4,4-dimethyl-1-isopropyl-2-phenyl-2-imidazoline shows that substitution of a phenyl for an alkyl group in the 2-position caused a hypsochromic shift to 222 mμ which may be due to resonance involving the carbon to nitrogen double bond and the benzene ring. Curve B of Figure 2 shows that upon acidification this resonance is minimized and absorption occurs at 230 mμ. Curve C of this same figure illustrates that when two insulating methylene groups are placed between the imidazoline ring and the phenyl group maximum absorption takes place at 231 mμ which is essentially in agreement with that obtained for 1,2,4,4-tetraalkyl-2-imidazolines.

When a hydrogen instead of an alkyl group was attached to the 2-imidazoline ring-nitrogen, as in 2-methyl-2-imidazoline, maximum absorption was found at 221 mμ. Upon acidification the spectrum of this compound remained substantially unchanged.

Curve A of Figure 3 shows that maximum absorption for 2-cyanomethyl-

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[1] This publication was abstracted from the thesis presented by Dr. Ferm to the graduate faculty of the University of New Mexico in partial fulfillment of the requirements for the Ph.D. degree. Dr. Ferm's present address is, Standard Oil Co. of Indiana; Sugar Creek, Missouri.

4,4-dimethyl-1-isopropyl-2-imidazoline occurred at 258 mμ. An acidified sample, however, showed maximum absorption at 231 mμ which is in agreement with 1,2,4,4-tetraalkyl-2-imidazolines. No satisfactory explanation has been found to explain the absorption maximum obtained for the free imidazoline.

TABLE I

THE ULTRAVIOLET ABSORPTION SPECTRA OF 2-IMIDAZOLINES

2-IMIDAZOLINES	B.P., °C./MM.	CONC'N. Moles/liter[a]	MAX. ABS., mμ	TRANSMISSION AT MAX. ABS., %	ϵ_{max}
4,4-Dimethyl-1-isopropyl-2-imidazoline	81–82/19	6.48×10^{-5}	230	71.6	2,250
1-Isopropyl-2,4,4-trimethyl-2-imidazoline	89–90/26	7.62×10^{-5}	227	32.1	6,490
1-Isopropyl-2,4,4-trimethyl-2-imidazoline (acidified)	—	7.62×10^{-5}	226	29.3	6,830
4,4-Dimethyl-2-ethyl-1-isopropyl-2-imidazoline	92/22	8.04×10^{-5}	227	29.2	6,650
4,4-Dimethyl-2-*n*-propyl-2-imidazoline	93–95/15	7.80×10^{-5}	228	30.1	6,680
2-*n*-Butyl-4,4-dimethyl-1-isopropyl-2-imidazoline	108–112/15	8.45×10^{-5}	228	28.1	6,520
4,4-Dimethyl-1-isopropyl-2-phenyl-2-imidazoline	163–166/28	4.76×10^{-5}	222	36.4	9,240
4,4-Dimethyl-1-isopropyl-2-phenyl-2-imidazoline (acidified)	—	4.76×10^{-5}	231	28.8	11,400
4,4-Dimethyl-1-isopropyl-2-β-phenylethyl-2-imidazoline	171.5/15	8.59×10^{-5}	231	32.1	5,740
2-Methyl-2-imidazoline	M.p. 103	8.04×10^{-5}	221	40.2	4,930
2-Methyl-2-imidazoline (acidified)	—	8.04×10^{-5}	220	42.9	4,570
2-Cyanomethyl-4,4-dimethyl-1-isopropyl-2-imidazoline	M.p. 197	2.00×10^{-5}	258	31.5	25,100
2-Cyanomethyl-4,4-dimethyl-1-isopropyl-2-imidazoline (acidified)	—	2.00×10^{-5}	231	73.0	6,890
Ethyl (4,4-dimethyl-1-isopropyl-2-imidazolinyl-2)-acetate	M.p. 58	1.98×10^{-5}	222 271	76.8 28.4	5,820 27,700
Ethyl (4,4-dimethyl-1-isopropyl-2-imidazolinyl-2)-acetate (acidified)	—	1.98×10^{-5}	231	71.3	7,480

[a] All solutions studied contained 95% ethanol as solvent.

When an acidified sample of the above named compound was examined, abnormalities in structure appeared to be inhibited, since maximum absorption was found at 231 mμ, which is in agreement with that expected for the acidified 2-imidazoline ring.

The absorption spectrum of ethyl (4,4-dimethyl-1-isopropyl-2-imidazolinyl-2)-acetate, Curve C of Figure 3, shows absorption at 222 mμ and also unexpectedly

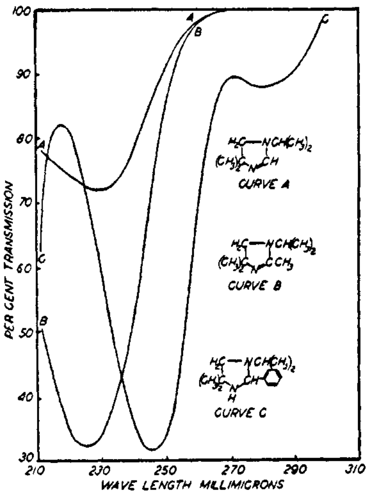


FIG. 1

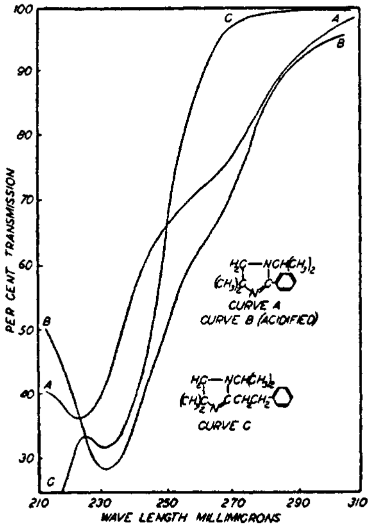


FIG. 2

FIG. 1. ABSORPTION SPECTRA OF 4,4-DIMETHYL-1-ISOPROPYL-2-IMIDAZOLINE (CURVE A), 1-ISOPROPYL-2,4,4-TRIMETHYL-2-IMIDAZOLINE (CURVE B), AND 4,4-DIMETHYL-1-ISOPROPYL-2-PHENYLIMIDAZOLIDINE (CURVE C)

FIG. 2. ABSORPTION SPECTRA OF 4,4-DIMETHYL-1-ISOPROPYL-2-PHENYL-2-IMIDAZOLINE (CURVE A), ACIDIFIED 4,4-DIMETHYL-1-ISOPROPYL-2-PHENYL-2-IMIDAZOLINE (CURVE B), AND 4,4-DIMETHYL-1-ISOPROPYL-2-β-PHENYLETHYL-2-IMIDAZOLINE (CURVE C)

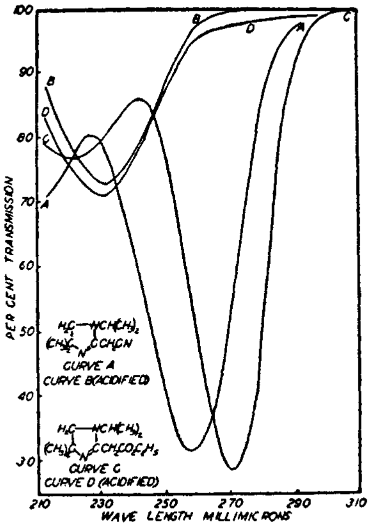
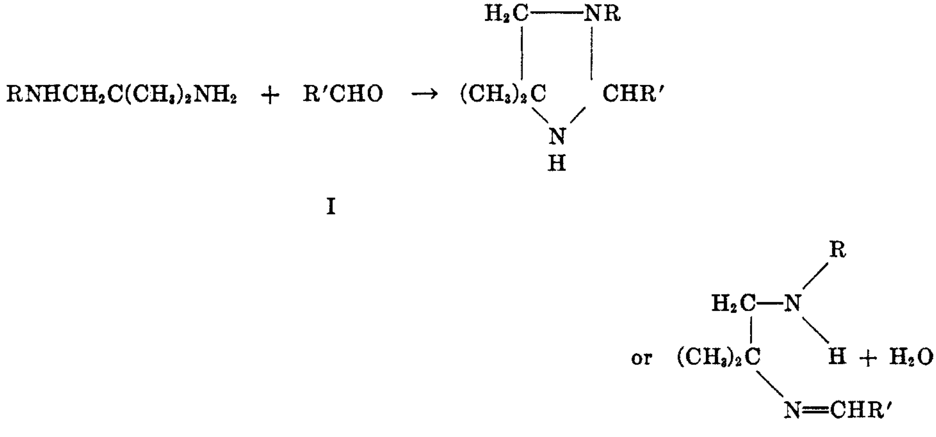


FIG. 3. ABSORPTION SPECTRA OF 2-CYANOMETHYL-4,4-DIMETHYL-1-ISOPROPYL-2-IMIDAZOLINE (CURVE A), ACIDIFIED 2-CYANOMETHYL-4,4-DIMETHYL-1-ISOPROPYL-2-IMIDAZOLINE (CURVE B), ETHYL (4,4-DIMETHYL-1-ISOPROPYL-2-IMIDAZOLINYL-2)ACETATE (CURVE C), AND ACIDIFIED ETHYL (4,4-DIMETHYL-1-ISOPROPYL-2-IMIDAZOLINYL-2)ACETATE (CURVE D)

at 271 mμ. Curve D of this same figure shows that this compound upon acidification, (Curve D, Figure 3) behaved in a manner comparable to the nitrile.

B. IMIDAZOLIDINES

The preparation of imidazolidines from aldehydes and 1,2-diamines in which both amino groups are secondary has been widely demonstrated (11–14). If, however, in this same type of reaction both amino groups are primary a Schiff's base is obtained (15–17). The reaction of aldehydes with 1,2-diamines containing one secondary and one primary group has received but little attention (18, 20). In a preceding paper (20) it was shown that a 1,2-diamine of this type reacts with aldehydes to yield compounds which are most likely imidazolidines such as (I), rather than their isomeric Schiff's bases (II):



I

II

In the present work ultraviolet absorption studies of such imidazolidines were made in order to furnish additional proof of their structures. A summary of the data is given in Table II.

It was possible to confirm the structures of 1-isopropyl-2,4,4-trimethylimidazolidine (I, $R' = CH_3$) and of 4,4-dimethyl-1-isopropyl-2-*n*-propylimidazolidine (I, $R' = n\text{-}C_3H_7$). These compounds were prepared from *N*-(2-aminoisobutyl)isopropylamine and acetaldehyde and *n*-butyraldehyde respectively. Continuous absorption curves were obtained for these compounds while the alternate Schiff's base structures (II) would have given absorption at 230 mμ corresponding to the carbon to nitrogen double bond.

The structures of 1-phenyl-2,4,4-trimethylimidazolidine and 4,4-dimethyl-1-phenyl-2-*n*-propylimidazolidine, which were obtained by the reaction of acetaldehyde and of *n*-butyraldehyde with N-(2-aminoisobutyl)aniline, were also confirmed since these compounds as expected gave absorption spectra similar to that of N,N-dimethylaniline (11) with no absorption at 230 mμ.

It was not possible to use the ultraviolet absorption spectra of the remaining imidazolidines listed in Table II as a means of confirmation of structure since the corresponding Schiff's bases would contain a phenyl or furyl group next to the carbon to nitrogen double bond, and they would be expected to give absorption spectra similar to that obtained for the imidazolidines. This is demonstrated by the case of 4,4-dimethyl-1-isopropyl-2-phenylimidazolidine, Curve C of Figure 1, for which maximum absorption was obtained at 247 mμ, while the corresponding Schiff's base would be expected to absorb at the same wave length.

TABLE II

THE ULTRAVIOLET ABSORPTION SPECTRA OF IMIDAZOLIDINES

IMIDAZOLIDINES	B.P., °C./MM.	CONC'N Moles/liter[a]	MAX. ABS, mμ	TRANSMISSION AT MAX. ABS., %	ϵ_{max}
1-Isopropyl-2,4,4-trimethylimidazolidine	72–74/24	2.55×10^{-5}	—	—	—
4,4-Dimethyl-1-isopropyl-2-*n*-propylimidazolidine	93–94/18	3.76×10^{-5}	—	—	—
1-Phenyl-2,4,4-trimethylimidazolidine	124–126/3	4.16×10^{-5}	252	28.6	13,100
			296	81.7	2,120
4,4-Dimethyl-1-phenyl-2-*n*-propylimidazolidine	134–135/3	4.65×10^{-5}	249	24.2	13,200
			296	78.6	2,250
4,4-Dimethyl-1-isopropyl-2-phenylimidazolidine	144/10	4.16×10^{-5}	247	31.8	12,000
			280	87.9	1,350
4,4-Dimethyl-1,2-diphenylimidazolidine	M.p. 96–97	2.62×10^{-5}	249	37.8	16,100
			298	86.4	2,410
4,4-Dimethyl-2-(2-furyl)-1-isopropylimidazolidine	128–129/22	3.14×10^{-5}	217	73.7	4,240
			273	39.6	12,800
4,4-Dimethyl-2-(2-furyl)-1-phenylimidazolidine	157–159/4	3.95×10^{-5}	248	33.0	12,200

[a] All solutions studied contained 95% ethanol as solvent.

EXPERIMENTAL

All ultraviolet absorption studies were made with a Model DU Beckman spectrophotometer and a pair of 1-cm. matched silica cells. Samples (20 to 45 mg. weighed to ±0.5 mg.) were diluted with 95% ethanol in volumetric flasks. The acidified samples were made by adding an excess (2 drops) of concentrated hydrochloric acid to the alcohol solution just before a final tenfold dilution. The 95% ethanol in the standard silica cell was always acidified in the same manner as was the sample. All compounds were investigated between the range of 210 to 310 mμ using a slit width of 1.5 mm. Observations with concentrated samples showed stray light effects to be negligible over this range. Readings of per cent transmission were taken at 5 mμ wave length intervals except at points of inflection or deflection when points were taken at each millimicron. The methods of preparation of the 2-imidazolines (4, 19), and of the imidazolidines (20), studied were those described in preceding publications.

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SUMMARY

1. The ultraviolet absorption spectra of the carbon to nitrogen double bond in a series of 2-imidazolines have been determined.

2. Confirmation of the structures of imidazolidines, which were prepared from 1,2-diamines and aliphatic aldehydes, was obtained through their ultraviolet absorption spectra. This method of confirmation of structure could not be extended to imidazolidines prepared from 1,2-diamines and benzaldehyde or furfural.

Albuquerque, N. M.

REFERENCES

(1) Sprung, *Chem. Revs.*, **26,** 306 (1940).
(2) Radziszewski, *Ber.*, **15,** 1493 (1882).
(3) Diels, *Ber.*, **51,** 965 (1918).
(4) Riebsomer, *J. Am. Chem. Soc.*, **70,** 1629 (1948).
(5) Clayton, *Ber.*, **28,** 1665 (1895).
(6) Drozdov and Kekhli, *J. Gen. Chem. (U.S.S.R.)*, **14,** 480 (1944).
(7) Hofman, *Ber.*, **15,** 1493 (1882).
(8) Hawkins and Biggs, *J. Am. Chem. Soc.*, **71,** 2530 (1949).
(9) Johnson and Edens, *J. Am. Chem. Soc.*, **64,** 2706 (1942).
(10) Adkins, *Reactions of Hydrogen with Organic Compounds Over Copper-Chromium Oxide and Nickel Catalysts*, p. 120, The Univ. of Wis. Press, Madison, Wis., 1937.
(11) Moos, *Ber.*, **20,** 732 (1887).
(12) Lob, *Rec. trav. chim.*, **55,** 859 (1936).
(13) Rameau, *Rec. trav. chim.*, **57,** 194 (1938).
(14) Van Alphen, *Rec. trav. chim.*, **54,** 93 (1935); and **55,** 669 (1936).
(15) Mason, *Ber.*, **20,** 270 (1887).
(16) Strache, *Ber.*, **21,** 2361 (1888).
(17) Kolda, *Monatsh.*, **19,** 610 (1898).
(18) Van Alphen, *Rec. trav. chim.*, **55,** 412 (1936).
(19) Pachter and Riebsomer, *J. Org. Chem.*, **15,** 909 (1950).
(20) Riebsomer, *J. Org. Chem.*, **15,** 237 (1950).