[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, EATON LABORATORIES, INC.]

Furans. I. The Ultraviolet Absorption of Isomeric Furaldoximes

BY ROBERT F. RAFFAUF

Though ultraviolet absorption studies often have aided in assigning configurations to pairs of *cis–trans* isomers in the ethylene series, few cases are recorded in which such studies have been of value for the analogous oximes and semicarbazones. The absorption curves for the semicarbazones of mesityl oxide are shifted with respect to each other though are "practically identical as is to be expected from a case of pure N stereoisomerism."[1] A similar displacement was noted by Bruzau[2] for the isomeric semicarbazones of α-dimethyl-α-phenylacetone. Brady and Grayson[3] observed slight differences in the absorption of the isomers of anisaldoxime, and the acetyl derivatives and O-methyl ethers of *p*-nitrobenzaldoxime. Hantzsch[4] recorded a difference in the absorption characteristics of the *p*-nitrobenzaldoximes, benzilmonoximes and their alkali salts, of sufficient magnitude to differentiate the isomers of these compounds by this means. It is now shown that the isomeric furaldoximes can be distinguished by their ultraviolet absorption spectra, and that on this basis the configurations of the known[5] but previously unassigned 5-nitrofuraldoximes have been determined.

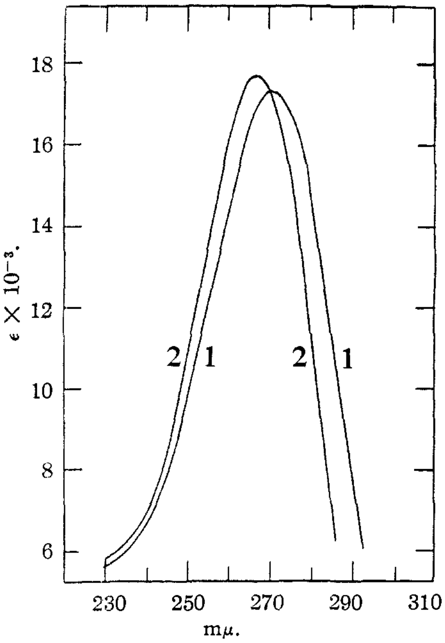

Fig. 1.—Ultraviolet absorption spectra of the furaldoximes: curve 1, *syn;* curve 2, *anti;* determinations in water, c = 9 mg./l.

Discussion

Hughes and Johnson[6] have shown that furan derivatives do not exhibit an absorption band in the near ultraviolet unless an α,β-unsaturated group is present in the 2-position of the furan ring. Since furaldoxime fulfills these conditions, an absorption peak at 265 mμ was not unanticipated, but it was also observed that the *syn* isomer gave maximum absorption at a wave length 50 Å. nearer the visible than did its *anti* analog (Fig. 1). If the unsaturation is supplied by an α nitro group, the absorption maximum falls quite regularly above 300 mμ regardless of the nature of the substituent in the α'-position.[7] In the case of the nitrofuraldoximes, a second absorption band with a maximum at 232 mμ was introduced, but only the band in the 300 mμ region reflected the isomerism of these derivatives after the fashion of the unsubstituted compounds (Fig. 2). That the isomer which absorbed at the higher wave length had the *syn* configuration was demonstrated by the traditional treatment of the oxime acetates

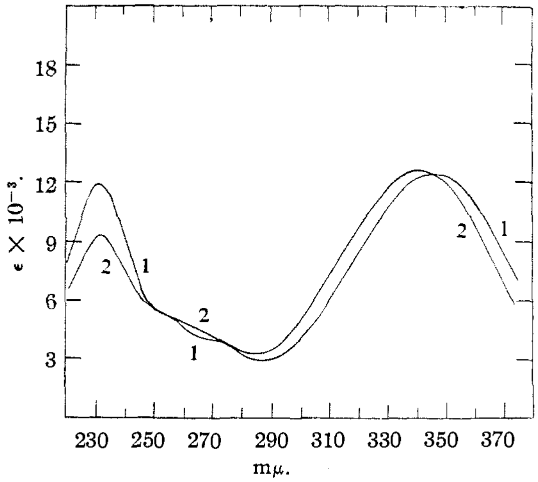

Fig. 2.—Ultraviolet absorption spectra of the 5-nitrofuraldoximes: curve 1, *syn;* curve 2, *anti;* determinations in water, c = 10.4 and 10.2 mg./l., respectively.

TABLE I

Solvent is water.

Compound	max₁	max₂	ϵ_1	ϵ_2
Furaldoxime, *syn*	270	...	17400	...
anti	265	...	17800	...
5-Nitrofuraldoxime, *syn*	230	345	11900	12500
anti	230	340	9500	12700
5-Nitrofuraldoxime acetate, *syn*	230	330	15200	14600
anti	230	325	11700	15400

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[1] Wilson and Heilbron, *J. Chem. Soc.*, **103**, 377 (1913).

[2] Bruzau, *Ann. chim.*, (11) **1**, 257 (1934).

[3] Brady and Grayson, *J. Chem. Soc.*, 1037 (1933).

[4] Hantzsch, *Ber.*, **43**, 1651 (1910).

[5] Gilman and Wright, THIS JOURNAL, **52**, 2553 (1930).

[6] Hughes and Johnson, *ibid.*, **53**, 737 (1931).

[7] Unpublished studies conducted in these Laboratories.

with basic reagents.[8] That the configurations about the >C=N— bond were not disturbed during conversion to the acetates was shown by the absorption curves for these compounds (Fig. 3). The data obtained for the three pairs of isomers are given in Table I.

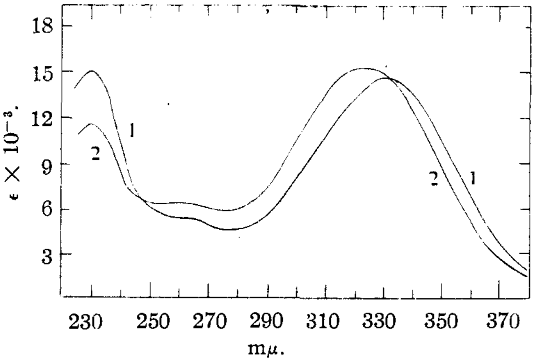

Fig. 3.—Ultraviolet absorption spectra of the 5-nitrofuraldoxime acetates: curve 1, *syn;* curve 2, *anti;* determinations in water, c = 10.2 mg./l.

Experimental

Furaldoxime.—The isomers were prepared by the method of Brady and Goldstein[9]: α-form (*anti*), m. p. 90–91°; β-form (*syn*), m. p. 75–76°.

5-Nitrofuraldoximes.—These were prepared according to the directions of Gilman and Wright[5]: α-form, m. p. 159–161°; β-form, m. p. 121°.

5-Nitrofuraldoxime Acetates.—The oximes were dissolved in warm acetic anhydride in which they were readily soluble. Sufficient water was then added to hydrolyze the excess acetic anhydride, and the products were allowed to crystallize from the warm liquors. Each was then recrystallized from dilute methanol: α-form, light yellow powder, m. p. 107–109°; β-form, colorless needles, m. p. 169–170°.

Anal. Calcd. for $C_7H_6N_2O_5$: C, 42.4; H, 3.03. Found: (α) C, 42.5; H, 2.94; (β) C, 42.9; H, 3.35.

Treatment of the Oxime Acetates with Pyridine.—The α-oxime acetate was dissolved in warm pyridine, and the mixture was then diluted with an equal volume of water and refrigerated. The solid which separated was crystallized from dilute methanol; colorless needles, m. p. 63–65° alone and when mixed with an authentic specimen of 5-nitrofuronitrile. Under identical conditions, the β-oxime acetate was recovered unchanged; m. p. and mixed m. p. 169–170°.

5-Nitrofuronitrile.—This was prepared according to the procedure used by Williams[10] for the tetrahydro compound. The product was not distilled, but was twice crystallized from dilute methanol; yield 78%, colorless needles, m. p. 63–65°.

Anal. Calcd. for $C_5H_2N_2O_3$: C, 43.5; H, 1.45. Found: C, 43.6; H, 1.70.

Absorption Spectra.—Spectral data were taken, using aqueous solutions, in the region 220–400 mμ, on a Beckmann Model D Quartz Spectrophotometer with a hydrogen source. $\log_{10} I_0/I$ was read directly from the instrument, and the extinction coefficients were then calculated from the concentrations of the solutions.

Summary

Isomerism about the >C=N— bond in the furaldoximes is reflected by consistent differences in the ultraviolet absorption spectra of these compounds.

On this basis configurations have been assigned to the 5-nitrofuraldoximes and their acetates, and the validity of the method was checked by an accepted chemical procedure.

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[8] Gilman, "Organic Chemistry," Vol. I, 2nd ed., John Wiley and Sons, New York, N. Y., 1943, p. 468.

[9] Brady and Goldstein, *J. Chem. Soc.*, 1959 (1927).

[10] Williams, *Ber.*, **60**, 2509 (1927).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Action of Copper Sulfate on the Phenylosazones of the Sugars. III. The D-, L- and D,L-Arabinose Phenylosotriazoles[1]

BY W. T. HASKINS, RAYMOND M. HANN AND C. S. HUDSON

In the previous articles[2] concerning the transformation of sugar phenylosazones to the corresponding phenylosotriazoles through the action of copper sulfate, no mention was made of the behavior of arabinose phenylosazone because the corresponding arabinose phenylosotriazole was not obtained in crystalline condition. Lately we have found that arabinose phenylosazone can be purified so that its melting point (171–172°, with decomposition) is approximately ten degrees higher than the values that have been reported by previous investigators.[3] The mutarotations of the purified L-arabinose phenylosazone were $[\alpha]^{20}\text{D} + 60.5° \rightarrow + 31.0°$ (forty-eight hours, constant value) in a mixture of four parts by volume of pyridine and six parts of absolute alcohol, and $+33.3° \rightarrow +20.4°$ (twenty-four hours, constant

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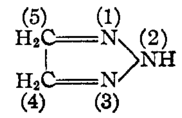
[1] We named the first member of this group of sugar derivatives *phenyl-D-glucosotriazole.* However, it now seems preferable to change the name to read D-*glucose phenylosotriazole* in order that the form may be similar to that of D-*glucose phenylosazone,* which has come into general use. The substance which has the formula



was named by its discoverer, von Pechmann, [*Ann.*, **262**, 265 (1891)] *osotriazole;* it has subsequently been assigned the indicated numbering and the systematic name *2,1,3-triazole* [*C. A.*, **39**, 6541 (1945)]. The systematic name of D-glucose phenylosotriazole is accordingly 2-phenyl-4-(D-*arabino*-tetrahydroxybutyl)-2,1,3-triazole and that of D-arabinose phenylosotriazole 2-phenyl-4-(D-*erythro*-trihydroxypropyl)-2,1,3-triazole.

This paper was presented in part at a meeting of the Washington Section of the American Chemical Society, May 9, 1946.

[2] (I) Hann and Hudson, THIS JOURNAL, **66**, 735 (1944); (II) Haskins, Hann and Hudson, *ibid.*, **67**, 939 (1945).

[3] Kiliani, *Ber.*, **20**, 339 (1887); Ruff, *ibid.*, **31**, 1573 (1898); Levene and LaForge, *J. Biol. Chem.*, **20**, 429 (1915).