The Resolution of 1-Ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetimide

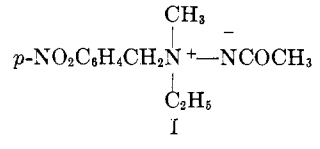
S. WAWZONEK, J. CHUA,[1] E. L. YEAKEY,[1] AND W. MCKILLIP

Department of Chemistry, University of Iowa, Iowa City, Iowa

Received November 20, 1962

1-Ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetimide has been prepared in crystalline form and resolved through its salt with L-dibenzoyltartaric acid. Other asymmetrically substituted aminimides derived from a series of 1-ethyl-1-methyl-1-*n*-butyl-2-acylhydrazonium salts in which the acyl group was acetyl, 3,5-dinitrobenzoyl, and *p*-nitrophenylacetyl also were prepared, but could not be obtained crystalline. Prior resolution of one of these, 1-ethyl-1-methyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazonium iodide, did not effect crystallization of the corresponding aminimide.

The preparation of optically active compounds containing a quaternary nitrogen atom has been reported for ammonium salts,[2] amine oxides,[3] and hydrazonium salts.[4] This property now has been found to be also a characteristic of aminimides, the nitrogen analogs of amine oxides, and has been demonstrated by the resolution of 1-ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetimide (I).



I

The aminimide I was prepared from ethylmethylamine by a similar synthesis to that reported previously for 1,1-dimethyl-1-*p*-nitrobenzylamine-2-acetimide,[5] and had an infrared spectrum similar to the latter in the 6.2–6.6-μ region.

This compound I formed a crystalline L-dibenzoyltartrate which could be separated into diastereoisomeric salts by repeated crystallizations from ethanol. The corresponding salts with L-tartaric, *d*-α-bromo-π-camphorsulfonic, and *d*-β-camphorsulfonic acids were glassy and could not be obtained crystalline.

The more insoluble L-dibenzoyltartrate upon decomposition with base gave the *d*-aminimide I with a specific rotation of +98.3°. The soluble isomeric salt which was more difficult to purify, gave the *l*-aminimide with a specific rotation of −80.3°. This isomer is obviously not pure and could be made to crystallize only by seeding with the *d*-isomer.

A number of other asymmetrically substituted aminimides were prepared from a series of 1-ethyl-1-methyl-1-*n*-butyl-2-acylhydrazonium salts in which the acyl group was acetyl, 3,5-dinitrobenzoyl, and *p*-nitrophenylacetyl, by treatment with alkali or silver oxide but could not be obtained crystalline. Crystallization of the last example could not be effected by a prior resolution of the hydrazonium iodide. Treatment of the optically active hydrazonium iodide with base in methanol gave an optically active solution but removal of the solvent gave an oil which could not be crystallized.

The presence of the 1-ethyl-1-methyl-1-*n*-butylamine-2-*p*-nitrophenylacetimide in this oil was demonstrated by a reductive cleavage with zinc dust and acetic acid to *p*-aminophenylacetamide and ethylmethyl-*n*-butylamine.

Experimental[6]

1-Ethyl-1-methylhydrazine.—A mixture of N-nitrosoethylmethylamine[7] (182 g.) and zinc dust (525 g.) in water (2.3 l.) was treated with vigorous stirring at 25–30° with 800 ml. of 85% acetic acid in the course of 2.5 hr. After completion of the addition, the mixture was stirred for 1.5 hr. at room temperature and at 60° for 30 min. Filtration of the excess zinc dust was followed by treatment with base of the filtrate and steam distillation. The last step was continued until the distillate no longer reduced Fehling's solution. The distillate was neutralized with hydrochloric acid and evaporated to dryness. Distillation of the crude hydrochloride from a concentrated potassium hydroxide solution gave 1,1-ethylmethylhydrazine which was purified by distillation from solid potassium hydroxide; yield, 83 g.; b.p. 79.5–80°; n^{23}D 1.4035; d^{25}_4 0.795.

Anal. Calcd. for $C_3H_{10}N_2$: C, 48.64; H, 13.61. Found: C, 48.45; H, 13.52.

The picrate when recrystallized from ethanol melted at 106–107°.

Anal. Calcd. for $C_9H_{13}N_5O_7$: C, 35.61; H, 4.29; N, 23.09. Found: C, 35.75; H, 4.20; N, 23.17.

1-Ethyl-1-methyl-2-acetylhydrazine.—A solution of 50 g. of 1-ethyl-1-methylhydrazine in 100 ml. of dry benzene was treated slowly with 80 g. of acetic anhydride. The temperature rose rapidly and was controlled by cooling in ice. The resulting pale yellow solution was refluxed for 1 hr., and the volatile materials were then removed under reduced pressure. The residual yellow oil was distilled through a 25-cm. Vigreux column; yield, 57.6 g. of a colorless liquid; b.p. 108° (14 mm.); n^{30}D 1.4461.

Anal. Calcd. for $C_5H_{12}N_2O$: C, 51.74; H, 10.35. Found: C, 51.65; H, 10.20.

***dl*-1-Ethyl-1-methyl-1-*p*-nitrobenzyl-2-acetylhydrazonium Bromide.**—A solution of 1-ethyl-1-methyl-2-acetylhydrazine (94 g.) and *p*-nitrobenzylbromide (181 g.) in 500 ml. of dry benzene was refluxed for 8 hr. and cooled. The crystals formed were recrystallized from a mixture of absolute ethanol and ether; yield, 140 g.; m.p. 144–145°.

Anal. Calcd. for $C_{12}H_{18}N_3O_3Br$: C, 43.31; H, 5.42; N, 12.65. Found: C, 43.51; H, 5.32; N, 13.07.

***dl*-1-Ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetimide.**—The hydrazonium bromide (140 g.) dissolved in a minimum of water was titrated to a phenolphthalein end point with a solution of 16.8 g. of sodium hydroxide in 50 ml. of water. The resulting solution was evaporated to dryness and the residue was extracted with three 100 ml. portions of chloroform. Removal of the chloroform gave an oil (87 g.), which was recrystallized from a mixture of acetonitrile and ether; m.p. 126–127°.

Anal. Calcd. for $C_{12}H_{17}N_3O_3$: C, 57.18; H, 6.77; N, 16.73. Found: C, 57.38; H, 6.67; N, 16.65.

Salts of the aminimide with *d*-β-camphorsulfonic acid, *d*-α-bromo-π-camphorsulfonic acid, and L-tartaric acid were obtained as glasses which could not be crystallized.

***dl*-1-Ethyl-1-methyl-1-*p*-nitrobenzylhydrazonium L-Dibenzoyltartrate.**—A hot solution of the *dl*-aminimide (62.5 g.) in ethanol (700 ml.) was treated with 94 g. of L-dibenzoyltartaric acid monohydrate and allowed to cool. Crystallizations from 95%

(1) Abstracted in part from the Ph.D. theses of J. Chua (February, 1959) and E. Yeakey (August, 1960).
(2) W. J. Pope and S. J. Peachy, *J. Chem. Soc.*, **75**, 1127 (1899).
(3) J. Meisenheimer, *Ber.*, **41**, 3966 (1908).
(4) B. K. Singh, *J. Chem. Soc.*, **103**, 604 (1913).
(5) S. Wawzonek and E. L. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).
(6) Boiling points and melting points are not corrected.
(7) J. Graymore, *J. Chem. Soc.*, 1311 (1938).

ethanol gave 21 g. of the less soluble salt; m.p. 139–140° dec.; $[\alpha]^{23}D$ −31.2° (95% ethanol).

Anal. Calcd. for $C_{30}H_{31}N_3O_{11}$: C, 57.41; H, 5.30; N, 6.89. Found: C, 57.49; H, 5.02; N, 6.98.

The combined filtrates were concentrated and gave 77 g. of the more soluble dibenzoyltartrate. Two crystallizations from absolute ethanol gave 45 g. of the diastereoisomer; m.p. 146–148° dec.; $[\alpha]^{23}D$ −91.2° (95% ethanol).

Anal. Calcd. for $C_{30}H_{31}N_3O_{11}$: C, 57.41; H, 5.30; N, 6.89. Found: C, 57.76; H, 5.09; N, 7.05.

d-1-Ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetimide.—The 139–140° melting salt (20 g.) was dissolved in a minimal amount of ethanol and treated with a solution of 3.36 g. of sodium hydroxide in water (20 ml.). The resulting solution was allowed to stand for 30 min. and then evaporated to dryness under reduced pressure. The residue obtained was extracted several times with chloroform. Removal of the chloroform gave a yellow oil which was dissolved in benzene (100 ml.). Partial removal of the benzene gave an anhydrous homogeneous solution which was treated with ethyl acetate. The crystals formed after several hours of standing were recrystallized from ethyl acetate; yield, 6.8 g.; m.p. 110–110.5°; $[\alpha]^{23}D$ +98.3° (95% ethanol).

Anal. Calcd. for $C_{12}H_{17}N_3O_3$: C, 57.18; H, 6.77; N, 16.73. Found: C, 56.88; H, 6.77; N, 17.13.

l-1-Ethyl-1-methyl-1-*p*-nitrobenzylamine-2-acetimide.—The 146–148° melting salt (17.2 g.) was treated in a manner similar to that described for the lower melting isomer. The resulting benzene–ethyl acetate solution, however, did not crystallize. Seeding with a crystal of the *d*-aminimide gave a product (3.7 g.) melting at 108–110°; $[\alpha]^{23}D$ −80.3°.

Anal. Calcd. for $C_{12}H_{17}N_3O_3$: C, 57.18; H, 6.77. Found: C, 56.98; H, 6.55.

N-Nitrosoethyl-*n*-butylamine.—An aqueous solution of ethyl-*n*-butylamine hydrochloride prepared by the addition of 101.1 g. of ethyl-*n*-butylamine to 193 ml. of 5.175 *N* hydrochloric acid solution was added to a solution of 72 g. of sodium nitrite in 90 ml. of water. The mixture was rapidly distilled under reduced pressure and the nitrosoamine was separated from the aqueous solution. The aqueous layer was saturated with solid potassium carbonate and extracted several times with ether. The combined ether extracts and the nitrosoamine were dried over anhydrous potassium carbonate. Removal of the ether was followed by fractional distillation of the nitrosoamine under reduced pressure. The yield of N-nitrosoethyl-*n*-butylamine which boiled at 89° (8 mm.)[8] was 120.7 g.; $d^{23.5}_4$ 0.907; $n^{24}D$ 1.4471.

Anal. Calcd. for $C_6H_{14}N_2O$: C, 55.35; H, 10.84; N, 21.52. Found: C, 55.44; H, 10.92; N, 21.46.

1-Ethyl-1-*n*-butylhydrazine.—N-Nitrosoethyl-*n*-butylamine (5 ml.) was added to a slurry of lithium aluminum hydride (12 g.) in absolute ether (150 ml.) and the mixture was stirred vigorously until the reaction started (about 1 hr.). The remainder of the nitrosoamine (26.2 g.) dissolved in 200 ml. of absolute ether was then added at a rate that gave a constant reflux. After completion of the addition, the mixture was stirred for an additional 2 hr. and decomposed by successive additions of water (36 ml.), 15% sodium hydroxide (12 ml.), and water (12 ml.). The ether layer was filtered by suction from the inorganic precipitate and the latter was washed several times with ether. The combined ether solutions, after drying over anhydrous magnesium sulfate, were evaporated to dryness. The resulting product was fractionated through an eight-plate column. The fraction boiling at 140–147° was refractionated under reduced pressure. The yield of 1-ethyl-1-*n*-butylhydrazine which boiled at 52.5° (25 mm.) was 14.04 g. (60%).

Anal. Calcd. for $C_6H_{16}N_2$: C, 62.07; H, 13.88. Found: C, 62.47; H, 13.89.

1-Ethyl-1-*n*-butyl-2-acetylhydrazine. A solution of 1-ethyl-1-*n*-butylhydrazine (38.3 g.) in benzene (50 ml.) was added slowly with stirring to 41 g. of acetic anhydride. The temperature increased rapidly and was moderated by cooling in ice. The resulting solution was refluxed for 15 min. and the volatile materials were then removed under reduced pressure. Fractional distillation under reduced pressure gave 1-ethyl-1-*n*-butyl-2-acetylhydrazine boiling at 110° (2 mm.); yield, 39 g.

Anal. Calcd. for $C_8H_{18}N_2O$: C, 60.70; H, 11.45; N, 17.69. Found: C, 60.47; H, 11.35; N, 17.43.

1-Ethyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazine.—One mole of acid chloride dissolved in 600 ml. of ether was added slowly to a solution of 1 mole of 1-ethyl-1-*n*-butylhydrazine and 1 mole of triethylamine in 200 ml. of ether with vigorous stirring. The temperature of the mixture was kept below 5° during the addition. After completion of the addition, the mixture was stirred for an additional hour and the triethylamine hydrochloride formed was filtered and washed several times with ether. The combined ether solutions were washed with 5% sodium bicarbonate and with water. Removal of the ether gave the hydrazide. Recrystallization was effected with aqueous ethanol and hexane and gave a 76% yield of the hydrazide; m.p. 85–86°.

Anal. Calcd. for $C_{14}H_{21}N_3O_3$: C, 60.25; H, 7.59. Found: C, 59.95; H, 7.06.

1-Ethyl-1-*n*-butyl-2-(3,5-dinitrobenzoyl)hydrazine.—This compound was prepared in a 76% yield by the method given for the *p*-nitro derivative; m.p., 115–116°.

Anal. Calcd. for $C_{13}H_{18}N_4O_5$: C, 50.31; H, 5.85. Found: C, 50.19; H, 5.96.

1-Ethyl-1-methyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazonium Iodide.—This compound was prepared by refluxing the hydrazide (5.0 g.) in excess methyl iodide for 24 hr. Purification was accomplished by successive recrystallizations from mixtures of ethanol and ether, methanol and ether, and from ethyl acetate; m.p. 121–122°; yield, 6.55 g.

Anal. Calcd. for $C_{15}H_{24}N_3O_3I$: C, 42.76; H, 5.75; N, 9.99; neut. equiv., 421.2. Found: C, 42.85; H, 5.70; N, 9.97; neut. equiv., 420.9; 421.6.

1-Ethyl-1-methyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazonium *d*-Camphor-β-sulfonate.—A solution of 1-ethyl-1-methyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazonium iodide (17 g.) in ethanol (200 ml.) was stirred with 20 g. of silver oxide for 1 hr. The silver iodide formed and the excess silver oxide were filtered and the iodide free filtrate was treated with 9.4 g. of *d*-camphor-β-sulfonate. The resulting solution upon evaporation to dryness gave 20 g. of the camphorsulfonate; m.p. 85–96°. Eight crystallizations from ethyl acetate gave a salt (1.8 g.), which was more soluble in ethyl acetate and was precipitated by the addition of ether; m.p. 137–138°; $[\alpha]^{26}D$ +27.7° (chloroform).

Anal. Calcd. for $C_{25}H_{39}N_3O_7S$: C, 57.22; H, 7.48; N, 7.99. Found: C, 57.24; H, 7.53; N, 8.34.

d-1-Ethyl-1-methyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazonium Iodide.—A solution of 1.5 g. of *d*-1-ethyl-1-methyl-1-*n*-butyl-2-*p*-nitrophenylacetylhydrazonium *d*-camphor-β-sulfonate was stirred with 0.428 g. of sodium iodide in a minimal amount of anhydrous acetone. The precipitation of sodium *d*-camphor-β-sulfonate was quantitative after 6 hr. Removal of the acetone gave a solid which was recrystallized twice from a mixture of acetone and ether and twice from ethyl acetate; yield, 0.5 g.; m.p. 91–93°; $[\alpha]^{25}D$ +2.78° (methanol).

Anal. Calcd. for $C_{15}H_{24}N_3O_3I$: C, 42.76; H, 5.74. Found: C, 42.63; H, 5.66.

Neutralization of the *d*-hydrazonium iodide in methanol gave a solution which retained its optical activity; $[\alpha]^{25}D$ +3.86°.

Treatment of the *d*-hydrazonium iodide with excess silver oxide in methanol followed by removal of the silver iodide, excess silver oxide, and methanol gave an oil which would not crystallize.

Reduction of 1-ethyl-1-methyl-1-*n*-butylamine-2-*p*-nitrophenylacetimide.—A solution of 1-ethyl-1-methyl-1-*n*-butylamine-2-*p*-nitrophenylacetylhydrazonium iodide (2.8 g.) in water (50 ml.) was converted to the aminimide by stirring with excess silver oxide for 1 hr. The resulting solution after filtration was concentrated to 20 ml. and refluxed with 13 g. of zinc dust and 10 ml. of glacial acetic acid for 5 hr. Removal of the excess zinc dust was followed by treatment with 20% sodium hydroxide and steam distillation. The basic distillate upon treatment with hydrochloric acid gave ethylmethyl-*n*-butylamine hydrochloride (0.65 g.). Identification was made as ethylmethyl di-*n*-butylammonium iodide by conversion to the free amine and refluxing in ethanol with *n*-butyl iodide for 6 hr. The iodide melted at 176–178° after recrystallization from ethyl acetate and did not depress the melting point of a sample prepared from methyl di-*n*-butylamine and ethyl iodide.

Anal. Calcd. for $C_{11}H_{26}NI$: C, 44.10; H, 8.70; N, 4.68. Found: C, 44.27; H, 8.83; N, 4.56.

The steam distillation residue was filtered, neutralized, and evaporated to dryness The solid residue upon solution in

(8) R. Preussmann, *Ber.*, **95**, 1571 (1962). This investigator reports a boiling point of 94–96° (14 mm.). No other physical constants are given.

minimal amount of hot water and cooling gave 0.5 g. or *p*-aminophenylacetamide; m.p., 160–162° (lit.[9] m.p. 161–162°).

1-Ethyl-1-methyl-1-*n*-butyl-2-(3,5-dinitrobenzoyl)hydrazonium *p*-Toluenesulfonate.—A solution of the hydrazine (5.92 g.) and methyl *p*-to'uenesulfonate (3.54 g.) in acetonitrile (100 ml.) was refluxed for 48 hr. Removal of the solvent under reduced pressure gave a solid which was recrystallized from a mixture of ethanol and ether; yield, 9.4 g.; m.p., 174–175°.

Anal. Calcd. for $C_{21}H_{28}N_4O_8S$: C, 50.79; H, 5.68; N, 11.28. Found: C, 51.26; H, 5.85; N, 11.47.

(9) I. Heilbron and H. H. Bunburg, "Dictionary of Organic Compounds," Vol. I, Eyre and Spottisworde, London, 1953, p. 123.

Acknowledgment.—Support of this research by the National Science Foundation is gratefully acknowledged.

Imidazoimidazoles. I. The Reaction of Ureas With Glyoxal. Tetrahydroimidazo[4,5-*d*]imidazole-2,5-diones[1,2]

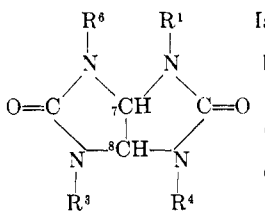
JAY NEMATOLLAHI AND ROGER KETCHAM[3]

Department of Pharmaceutical Chemistry, School of Pharmacy, University of California Medical Center, San Francisco, California

Received January 14, 1963

The acid-catalyzed condensations of a variety of substituted ureas with glyoxal have been shown to yield tetrahydroimidazo[4,5-*d*]imidazole-2,5-diones. With aryl substituted ureas, 1-arylhydantoins were obtained as side products.

Earlier investigations of the urea–glyoxal condensation to give tetrahydroimidazo[4,5-*d*]imidazole-2,5-diones[4–8] (I) left several questions unanswered. Identities of isomeric products Ib,c obtained from methylurea and glyoxal[6,7] have not been established. No condensations with arylureas have been reported. That the reactions of urea,[9] methylurea, and 1,3-dimethylurea all lead to the same carbon–nitrogen skeleton has not been established and the existence of the fused bicyclic system is open to some objection on the basis of strain.[10] Finally, if the structure is correct, it could conceivably have either the *cis* or the *trans* configuration.



Ia, $R^1 = R^3 = R^4 = R^6 = H$
b, $R^1 = R^4 = CH_3$, $R^3 = R^6 = H$
c, $R^1 = R^6 = CH_3$, $R^3 = R^4 = H$
d, $R^1 = R^3 = R^4 = R^6 = CH_3$
e, $R^1 = R^4 = C_6H_5$, $R^3 = R^6 = H$
f, $R^1 = R^4 = CH_3$, $R^3 = R^6 = C_6H_5$
g, $R^1 = R^6 = CH_3$, $R^3 = R^4 = C_6H_5$

Repetition of the condensations of urea[4,5] and 1,3-dimethylurea[8] confirmed the earlier reports. The urea product Ia was converted by exhaustive methylation to the same tetramethyl derivative Id as obtained by condensation of 1,3-dimethylurea with glyoxal, thus indicating that these substances have a common carbon–nitrogen skeleton. Neither the urea nor the 1,3-dimethylurea–glyoxal condensation product show significant ultraviolet absorption above 210 mμ.[11,12] The n.m.r. spectrum of the urea condensation product shows only one sharp peak and that of the tetramethyl

(1) This work was supported, in part, by a grant from the National Institutes of Health (training grant 2 G-728 Cl) and an American Cancer Society Institutional grant IN 33D, no. 3. The nuclear magnetic resonance spectrometer used in this work was provided by a grant (NSF G 21268) from the National Science Foundation.

(2) The nomenclature requires comment. *Chemical Abstracts* uses either glycoluril, the trivial name, or tetrahydroimidazo[4,5-*d*]imidazole-2,5(1*H*,3*H*)-dione. The systematic name seems preferable, but raises two questions. The (1*H*,3*H*) part of the name appears unnecessary. The propriety of considering the dione rather than imidazo[4,5-*d*]imidazole as the parent system seems questionable. The *Chemical Abstracts* systematic name with omission of the (1*H*,3*H*) portion is used throughout this paper.

(3) To whom inquiries should be directed.

(4) (a) H. Schiff, *Ann.*, **189**, 157 (1877); (b) U. Schiff, *Gazz. chim. ital.*, **7**, 351 (1877); (c) L. Siemonsen, *Ann.*, **333**, 101 (1904); (d) R. Behrend, E. Meyer and F. Rusche, *ibid.*, **339**, 4 (1905); (e) H. Biltz, *ibid.*, **368**, 243 (1909); (f) C. Böttinger, *Ber.*, **10**, 1923 (1877).

(5) (a) F. B. Slezak, H. Bluestone, T. A. Magee, and J. H. Wotiz, *J. Org. Chem.*, **27**, 2181 (1962); (b) F. B. Slezak, A. Hirsch, and I. Rosen, *ibid.*, **25** 660 (1960).

(6) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 12 (1887).

(7) E. Weitzner, *Ann.*, **362**, 125 (1908).

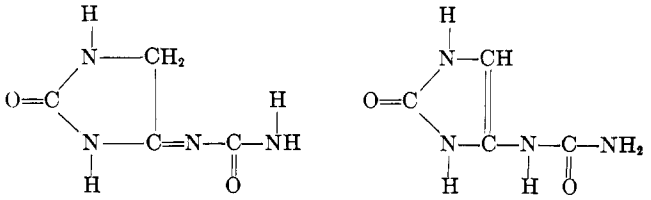
(8) A. P. N. Franchimont and E. A. Klobbie, *Rec. trav. chim.*, **7**, 236 (1887).

(9) Unsubstituted tetrahydroimidazo[4,5-*d*]imidazole-2,5-dione had been obtained earlier by reduction of allantoin with sodium amalgam. H. Rheineck, *Ann.*, **134**, 219 (1865).

(10) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 436, 612 (1935).

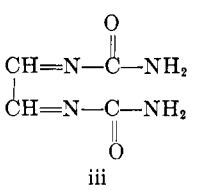
(11) We are indebted to Mr. Harold D. Aylor of Beckman Instruments, Inc., for extending our measurements to the far-ultraviolet. The 1,3,4,6-tetramethyl derivative shows a shoulder at 187 mμ, but the 1,4-dimethyl derivative and the unsubstituted condensation product show only end absorption above 185 mμ. These spectra were determined on a Beckman far-ultraviolet DK-2A spectrophotometer.

(12) The only alternate isomeric structures which were considered are the two monocyclic structures, i and ii, and the open chain system, iii.



i

ii



iii

Of these, only ii could have been converted to a tetramethyl derivative identical with the 1,3-dimethylurea-glyoxal condensation product. However, it should have produced a pentamethyl derivative on exhaustive methylation.

These structures contain chromophoric systems which should absorb above 210 mμ. The amidine system present in i exhibits an ultraviolet maximum at about 230 mμ.[13] 2,3-Dihydro-2-oxo-4-imidazolecarboxylic acid, a model compound for structure ii, has an absorption maximum at 250 mμ.[14] Glyoxime, a model compound for structure iii, absorbs at 329 mμ.[15] However, the relative complexity of these structures and the presence of cross conjugated systems renders conclusions based on the simple model systems subject to some doubt.

(13) (a) J. C. Gage, *J. Chem. Soc.*, 221 (1949); (b) S. F. Mason, *ibid.*, 2071 (1954).

(14) K. Ditmar, M. F. Ferger, and V. du Vigneaud, *J. Biol. Chem.*, **164**, 19 (1946).

(15) H. Schmid and W. Bencze, *Helv. Chim. Acta*, **36**, 205 (1953).