nite progression in intensities of certain bands. As the alkyl chain length increases from 1 to 18 carbons, the intensity of the entire group of bands from 6.94 to 9.12 μ decreases from, *e.g.*, 46% transmission at 9.12 μ to 68%. This suggests a possible aid in the identification of the alkyl radical of an unknown sebacate by comparison of its % transmission under specified conditions at selected wave lengths with values taken from prepared plots of % transmission *vs.* number of skeletal carbon atoms at corresponding wave lengths.

Acknowledgment.—The authors are grateful to Miss D. A. Wiener for obtaining the infrared spectrograms and Mr. Sam Cohen for his help in their interpretation.

Philadelphia, Penna.

[Contribution from the Basic Sciences Research Department, U. S. Naval Civil Engineering Research and Evaluation Laboratory]

The Mechanism of the Reaction of Aniline with Furfural in the Presence of Acid[1]

By William M. Foley, Jr., Guy E. Sanford and Herbert McKennis, Jr.

Received May 22, 1952

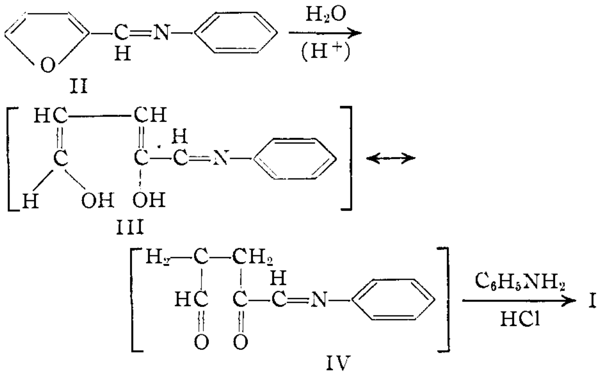
A study has been made of the Stenhouse reaction in which aniline and furfural react in the presence of acid to form a deep purple compound, the corresponding acid salt of 1-phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene. Evidence is presented to show that the intermediation of water is not necessary for the reaction. A mechanism involving a 1,6-addition of the acid component to an anil followed by attack of aniline to give the resultant diene is proposed.

Stenhouse[2] observed that aniline, aniline hydrochloride and furfural react in alcohol to form a deep purple compound. Zincke and Mulhausen[3] found that the latter can be converted to 3-hydroxy-N-phenylpyridinium salts and suggested structure I[4] for the original condensation compound.

$$\mathrm{Ar{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}C(OH){\cdot}CH{:}N{\cdot}Ar.HCl}$$

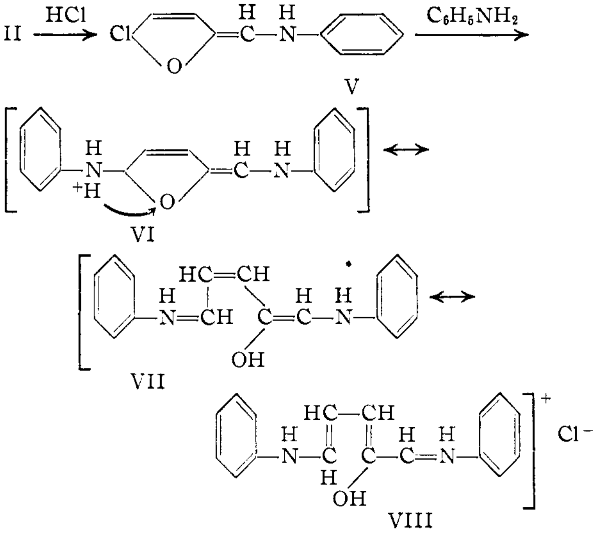
I

An examination of structure I and the work of Pummerer and co-workers[5] on cleavages of furfuryl alcohol suggests in a general sense a mechanism which involves the intermediation of water:



Aniline and furfural react to form the furfural anil, II, which could then be hydrolytically cleaved to yield a 1,4-diol, III, which is tautomeric with the 1,4-dial, IV. Reaction of the hypothetical intermediate IV with aniline hydrochloride could then lead to the condensation compound, I.

Since no previous workers had reported success or failure in preparing I under anhydrous conditions, an alternate mechanism in which the anil II reacts directly with hydrogen chloride and then with aniline could not be excluded from consideration. In the reactions shown below, hydrogen chloride adds 1,6 to the anil II. The intermediate V, which bears an allylic chloride, is represented as reacting with aniline to form an intermediate salt VI. A subsequent proton transfer to the ring oxygen and ring cleavage results in the formation of the resonance structures, VII and VIII. The final product as represented by VII and VIII affords a more convenient picture of some of the resonance possibilities than does the classical formula employed by Zincke and others. The hypothetical intermediate V, in addition, offers a possible explanation for the decomposition observed when the anil of furfural is treated with a catalytic amount of hydrogen chloride.



To test the possibility of the mechanism II–VIII, both aniline hydrochloride and the anil of furfural were prepared in anhydrous condition and mixed in the presence of anhydrous solvent. The immedi-

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[1] Presented before the Division of Organic Chemistry, American Chemical Society, 121st Meeting, Buffalo, N. Y., March, 1952.

[2] J. Stenhouse, *Ann.*, **156**, 197 (1870).

[3] T. H. Zincke and G. Mulhausen, *Ber.*, **38**, 3824 (1905).

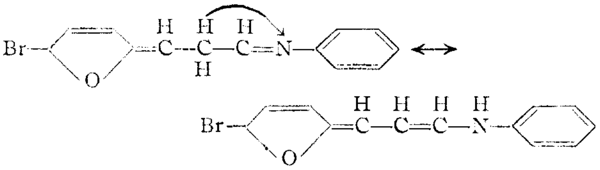
[4] A previous paper, R. W. Drisko and H. McKennis, Jr., This Journal, **74**, 2626 (1952), cites other references.

[5] R. Pummerer and W. Gump, *Ber.*, **56**, 999 (1923); R. Pummerer, O. Guyot and L. Birkofer, *ibid.*, **68**, 480 (1935).

ate formation of a purple dye was noted. The reaction product was isolated and purified, and the properties of the product were identical with those of the material formed under hydrous conditions, or under conditions where water could reasonably be expected to be present. The fact that the isolated products are identical suggests that the intermediation of water is not necessary, but does not definitely exclude its participation.

Additional support for the proposed mechanism which involves a 1,6-addition of hydrogen chloride can be found in the numerous 1,6-additions in the literature. Malonic ester adds 1,6 to unsaturated esters of the $CH_3CH:CHCH:CHCOOR$ type, according to Kohler and Butler.[6] Bromine and hydrogen bromide add 1,6 to 2,4,6-hexatriene to give a 1,6-dibromide, according to Kuhn and Winterstein.[7]

König[8] described an interesting extension of the Stenhouse reaction in which furylacrolein, aromatic amines and hydrogen bromide react with cleavage of the furan ring to form colored salts. This may be explained by the above 1,5-addition mechanism and the tautomeric shift[9]



Stenhouse[2] prepared from aniline and furfural, the chloride, sulfate, oxalate and nitrate salts of 1-phenylimino-5-phenylamino-2-hydroxy-penta-2,4-diene by the reaction in the presence of the corresponding acids. König and co-workers[10] treated the compound which gives the correct analysis for the perchlorate salt of furfural anil with aniline and obtained the perchlorate salt of the substituted pentadiene, VII–VIII.

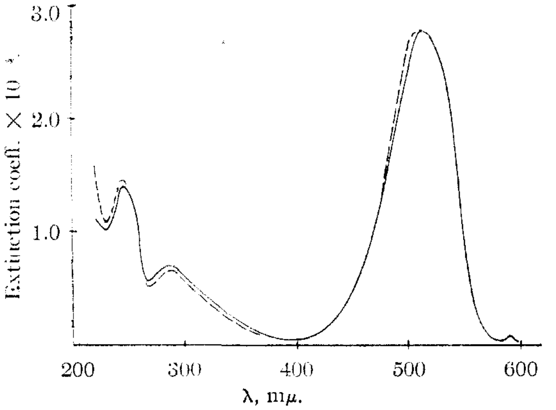


Fig. 1.—Absorption spectra of the chloride and nitrate salts of 1-phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene in ethanol. Observations were made at 10 mμ intervals, using a Beckman DU spectrophotometer: ——, chloride salt; ----, nitrate salt.

As part of the present study the absorption spectra of the chloride I and nitrate salts of the dianil of 2-hydroxyglutaconaldehyde were determined in ethanol (Fig. 1). These were found to be substantially identical with a maximum in the region of 520 mμ. The acid sulfate showed a similar maximum. König[8,10] has investigated the absorption spectra of analogous compounds in alcohol. In our investigation a very rapid bleaching of the colored solutions of the salts of 1-phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene was noted. All spectra must be determined immediately after mixing. The observed fading was provisionally attributed to a reaction between the acid component and ethanol. Increased stability of the solution and enhancement of the 520 mμ peak of the acid sulfate salt was achieved by carrying out the determination in a solution of ethanol and an amount of sulfuric acid calculated for an 0.024 *M* solution (if no reaction occurred between sulfuric acid and ethanol) (Fig. 2).

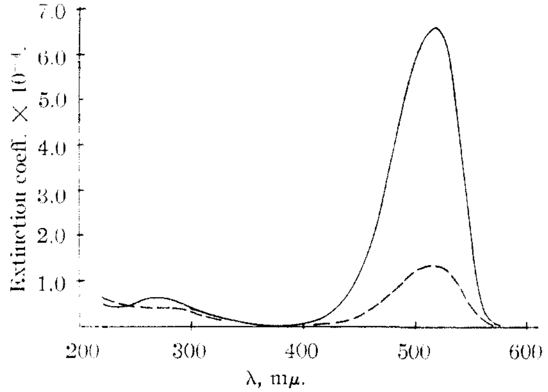


Fig. 2.—Absorption spectra of the acid sulfate salt of 1-phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene, in ethanol, 0.024 *M* in H_2SO_4. Observations were made every 10 mμ, using a Beckman DU spectrophotometer: ——, fresh solution; ----, solution after 24 hr.

One possible explanation for the loss of maximum at 520 mμ lies in a cyclization reaction leading to N-phenyl-2-phenylamino-3-hydroxydihydropyridine and N-phenyl-6-phenylamino-3-hydroxydihydropyridine. McGowan[11] has described cyclizations of 1-phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene upon neutralization of the hydrochloride. The instability of the salts in ethanol as contrasted with the relative stability in ethanol–sulfuric acid can, therefore, be tentatively attributed to ring closures which proceed as acid is depleted in reaction with ethanol. The lesser instability under the more acidic conditions may reside in cyclizations leading to N-phenyl-3-hydroxypyridinium salts which have been studied by Zincke and Mulhausen[3] and subsequently by others.[12]

The similarity of the absorption spectra of the various salts affords additional confirmation of a

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(6) E. P. Kohler and F. R. Butler, THIS JOURNAL, **48**, 1036 (1926).

(7) R. Kuhn and A. Winterstein, *Helv. Chim. Acta*, **11**, 123 (1928).

(8) W. König, *J. prakt. Chem.*, **88**, 193 (1913).

(9) Other transformations in the furan series, *e.g.*, the conversion of 2-acetofuran to 4,5-dioxo-2-hexenal-1-acetal (L. Vargha, J. Ramonczai and P. Bite, *Nature*, **159**, 744 (1947); THIS JOURNAL, **70**, 371 (1948)) can be formally treated in terms of 1,6-addition mechanisms.

(10) W. König, K. Hey, Fr. Schulze, E. Silberkweit and K. Trautmann, *Ber.*, **67**, 1274 (1934).

(11) J. C. McGowan, *J. Chem. Soc.*, 777 (1949).

(12) C. F. Koelsch and J. J. Carney, THIS JOURNAL, **72**, 2285 (1950).

general acid-catalyzed reaction and suggests that in processes leading to the formation of salts of the dianil of 2-hydroxyglutaconaldehyde, VII–VIII, a generalized 1,6-addition may occur.

Representation of the reaction mechanism as involving the intermediate formation of the anil is based in part on the early studies of de Chalmot[13] who reported that aniline hydrochloride and furfural anil reacted to form the purple compound described by Stenhouse.[2] The work of König, *et al.*,[8,10] is similarly suggestive. In addition to the preparation of the chloride and nitrate salts of VII–VIII from the anil for this study, a variety of similar compounds, unsymmetric anils of 2-hydroxyglutaconaldehyde, have been prepared from substituted-anils of furfural and various aromatic amines in the presence of acid.[14]

Borsche and co-workers[15] have proposed a mechanism for the formation of the substituted dienes in which hydrogen chloride cleaves the furan ring of the anil at the 1- and 5-positions. This is followed by a 1,6-addition of aniline to the intermediate and subsequent 1,6-elimination of hydrogen chloride to give structure I. The mechanism of Borsche, *et al.*, involves the reaction of a vinylic chloride with an amine, whereas the mechanism proposed here invokes reaction of an allylic chloride or α-chloroether. Both of the latter species are notably reactive.

Experimental

Preparation of 1-Phenylimino-5-phenylamino-2-hydroxypenta-2,4-diene Hydrochloride (Under Anhydrous Conditions).—The anhydrous anil of furfural[13] (5.64 g.) was mixed with 4.23 g. of anhydrous aniline hydrochloride in 30 ml. of anhydrous ethanol under an atmosphere of dry nitrogen. The solvent was removed under diminished pressure. The residue, m.p. 166.5–167.5°, weighed 9.21 g. (93%). Recrystallization from anhydrous ethanol gave a product, m.p. 169° (dec.). Williams and Wilson[16] reported a melting point of 166–167° (dec.). The melting point of this and related compounds varies with the rate of heating. The hydrochloride is hygroscopic and decomposes under the influence of subdued light.

Anal. Calcd. for $C_{17}H_{17}N_2OCl$: C, 67.8; H, 5.64; N, 9.28; Cl, 11.8. Found: C, 67.5; H, 5.7; N, 9.01; Cl, 11.9.

Preparation of the Nitrate.—Aniline nitrate (1.42 g.) and 1.71 g. of the anil of furfural were dissolved in 17 ml. of anhydrous ethanol. The product, 1.91 g. (61%) formed and was removed by filtration and dried under diminished pressure, m.p. 124–126° (dec.). The salt is very hygroscopic and extremely sensitive to light.

Anal. Calcd. for $C_{17}H_{17}N_3O_4$: N, 12.85. Found: N, 12.85.

Preparation of the Acid Sulfate.—The method of Stenhouse[2] was employed. It was found that purification could best be effected by dissolving the compound in warm ethanol (not over 50°) and chilling as soon as possible. The product was dried under diminished pressure. In common with the other salts it is hygroscopic and decomposes in the presence of light.

Acknowledgment.—The authors wish to thank Dr. Carl T. Redemann and Mr. Robert J. Brotherton for the microanalyses, and Mr. Elmer Streed, all of this Laboratory, for determination of the absorption spectra.

PORT HUENEME, CALIFORNIA

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[13] G. de Chalmot, *Ann.*, **271**, 11 (1892).

[14] W. M. Foley, Jr., C. V. Brouillette, G. E. Sanford and H. McKennis, Jr., THIS JOURNAL, in preparation.

[15] W. Borsche, H. Leditschke and K. Lange, *Ber.*, **71B**, 957 (1938).

[16] G. Williams and C. L. Wilson, *J. Chem. Soc.*, 506 (1942).

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

Ultraviolet Spectra and Structures of the Pyrido[1,2-a]pyrimidones

BY ROGER ADAMS AND IRWIN J. PACHTER

RECEIVED JUNE 16, 1952

The ring nitrogen of 2-aminopyridine adds to acrylic acid, ethyl acrylate and α-bromoacrylic acid; on the other hand, the amino nitrogen adds to ethoxymethylenemalonic ester. These facts were established by determination of the structure of the addition products. Pyrido[1,2-a]pyrimidin-4-one was synthesized and its ultraviolet absorption spectrum compared with that of pyrido[1,2-a]pyridin-2-one. The differences were sufficiently great to permit these spectra to be used as models in a reconsideration of the structures assigned to several pyridopyrimidones reported in the literature.

The chemistry of 2-aminopyridine is complicated by the presence in the molecule of two nitrogen atoms of similar reactivity, and it is frequently difficult to present unequivocal proof of structure of the reaction products of the base. In the present paper the structures of the pyrido[1,2-a]pyrimidones derived from 2-aminopyridine will be considered.

When 2-aminopyridine was heated with α-bromoacrylic acid in chloroform, the hydrobromide of 2H-pyrido[1,2-a]pyrimidin-2-one (I) was obtained in 45% yield. The intermediate II (or its zwitterionic tautomer) was probably formed and then eliminated hydrogen bromide and water. The free base (I) was obtained from the hydrobromide by treatment with either silver oxide or sodium hydroxide. The structure of I was established previously and it was also synthesized by another route.[1]

Acrylic acid and ethyl acrylate reacted with 2-aminopyridine to give the previously characterized compounds[1] III and IV, respectively.

These reactions involved attachment of the ring nitrogen of 2-aminopyridine to the β-carbon atom of acrylic acid, its ethyl ester and its α-bromo derivative. Previously, Lappin[2] described the reactions of several 2-aminopyridine derivatives with ethoxymethylenemalonic ester to give products in which he assumed that the amino nitrogen atom of 2-aminopyridine had become attached to the carbon atom β to the carbethoxy groups. The condensation products derived from certain 6-substituted 2-

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[1] R. Adams and I. J. Pachter, THIS JOURNAL, **74**, 4906 (1952).

[2] G. R. Lappin, *ibid.*, **70**, 3348 (1948).