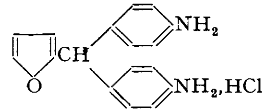
92. *Reactions of Furan Compounds. Part I. Constitution of the Coloured Condensation Product from Furfural, Aniline, and Aniline Hydrochloride.*

By Gerald Williams and Christopher L. Wilson.

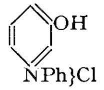
The evidence for the structure of the condensation product from furfural, aniline, and aniline hydrochloride is summarised and discussed. It has been shown that reaction with nitrous acid liberates aniline. Subsequent coupling reactions produce benzeneazo-derivatives. This demonstration would appear to discredit recent conclusions by Riegel and Hathaway (*J. Amer. Chem. Soc.*, 1941, **63**, 1835) in favour of a triphenylmethane structure (I). The glutaconic dialdehyde structure (II) is still, therefore, to be preferred.

When furfural, aniline, and aniline hydrochloride are mixed in equimolecular amounts in alcoholic solution, a deeply coloured condensation product rapidly crystallises. After purification the material forms prismatic crystals, almost like potassium permanganate in appearance, melts at 166—167° (decomp.), and gives the analytical figures required for a hydrochloride, $C_{17}H_{16}ON_2$,HCl. Schiff (*Annalen*, 1880, **201**, 355; 1887, **239**, 349) thought the substance had a triphenylmethane structure (I), but later investigators (Zincke and Mülhausen, *Ber.*, 1905, **38**, 3824; König, *J. pr. Chem.*, 1905, **72**, 555; Dieckmann and Beck, *Ber.*, 1905, **38**, 4122) preferred an open-chain representation (II), based on glutaconic dialdehyde. The reasons for this change were briefly as follows : the substance readily loses a molecule of aniline on heating to give 3-hydroxy-1-phenylpyridinium chloride (III), a reaction which would necessitate a simple cyclisation of (II) but a complex rearrangment of (I).

(I.)

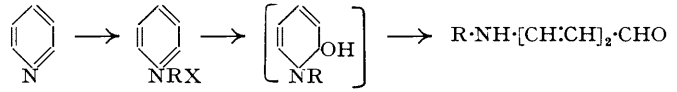


Ph·NH·CH:CH·CH:C(OH)·CH:NPh,HCl (II.)



(III.)

Further support for (II) is afforded by the similarity in properties, particularly colour, between the furfural derivative and a series of compounds obtainable from pyridine for which a glutaconic dialdehyde structure is generally assumed. These reactions comprise the addition of molecules such as 2 : 4-dinitrochlorobenzene (Zincke, *Annalen*, 1903, **330**, 361; 1904, **333**, 296; **338**, 107; 1905, **341**, 365; 1915, **408**, 285), cyanogen bromide (König, *J. pr. Chem.*, 1904, **69**, 105; **70**, 19; 1911, **83**, 406), phosphorus pentachloride (Reitzenstein and Breuning, *J. pr. Chem.*, 1911, **83**, 97), or ethyl chlorosulphonate (Baumgarten, *Ber.*, 1924, **57**, 1622; 1925, **58**, 2018; 1926, **59**, 11) to pyridine to produce, most probably, a type of quaternary salt, which, on treatment with alkali or aniline, gives derivatives of glutaconic dialdehyde. The reaction may be represented by the following formulæ, which, in part, recall the behaviour of a *ψ*-base such as cotarnine :



Baumgarten (*loc. cit.*) has shown that the reverse process to give pyridine may be realised and has thus provided an interesting analogy for the reaction (II) ⟶ (III).

There is much more evidence of a similar nature which, although indirect, supports (II). It was, therefore, with considerable interest that we noticed that Riegel and Hathaway (*loc. cit.*) have recently concluded that, in spite of previous evidence, the triphenylmethane structure (I) is most probably correct. In the present paper we wish to reinterpret the evidence presented by these authors.

Riegel and Hathaway's contention was based essentially on the observation that the furfural product reacted with nitrous acid (2 equivs.), giving a solution of a diazonium salt which could be coupled with hydroxy- and amino-naphthalenesulphonic acids and the like to produce wool dyes. These compounds were analysed, but only for nitrogen, and the figures were shown to compare favourably with those required for bisazo-compounds derived from (I). We have repeated these experiments and have shown that the condensation product does indeed react with nitrite as R. and H. say. The resulting solution, however, on reaction with β-naphthol (not investigated by R. and H.) produces benzeneazo-β-naphthol. Identity was shown by analysis and mixed melting point with an authentic specimen. In the reaction with nitrous acid it appears, therefore, that aniline is liberated. Further confirmation was provided by analogous experiments with the condensation product of furfural and *p*-toluidine, which gave tolueneazo-β-naphthol. Fission of aniline from (II) is not surprising in view of the known sensitivity of Schiff's bases towards acids. We have also shown that aniline is liberated by reaction of the furfural derivative with aqueous sodium bisulphite. The fate of the remainder of the molecule in these two reactions is not known.

Having disposed of the main difficulty, we are now in a position to deal with the rest of Riegel and Hathaway's argument. Viewed impartially, most of this really supports (II). For instance, their reaction scheme for the conversion of (I) into (III) is so highly imaginative as to condemn it; the failure to bring about reaction between furfural, dimethylaniline, and dimethylaniline hydrochloride in alcoholic solution suggests that a primary amino-group and not a reactive *p*-position is essential for the condensation; and lastly, their reference, in order to illustrate the stability of the furan ring, to the formation (Renshaw and Naylor, *J. Amer. Chem. Soc.*, 1922 , **44**, 862; Mahood and Harris, *ibid.*, 1924, **46**, 2810; Mahood and Aldrich, 1930, **52**, 4477) of a true malachite-green analogue by reaction between furfural and dimethylaniline under the influence of zinc chloride, followed by oxidation with lead dioxide, serves only to stress the improbability of (I) being formed under milder conditions in the absence of zinc chloride. Furthermore it would be surprising if (I), which is a leuco-compound, possessed much colour at all, and it is interesting that Renshaw and Naylor (*loc. cit.*) have demonstrated that the *NN'*-tetramethyl derivative of (I) is only faintly yellow.

Riegel and Hathaway, by the reaction between furfural, dimethylaniline, and aniline hydrochloride, obtained a coloured condensation product which they considered to be an *N*-dimethyl derivative of (I). We have repeated this reaction and have been able to isolate only small amounts of the simple unmethylated compound derived from furfural, aniline, and aniline hydrochloride.

So far we have ignored the table of nitrogen analyses recorded by Riegel and Hathaway for the wool dyes referred to above. It does not seem possible to assume that these were simple benzeneazo-derivatives, since the latter would require nitrogen figures which are up to 1 unit higher than those listed. Nevertheless we think that nitrogen analyses on complex dyes, which are notoriously difficult to purify, are hardly sound criteria to apply in the present connection. In the case of α-naphthol (recorded in R. and H.'s list) we have shown that the product from both diazotised aniline and the furfural compound is a complex mixture, as is frequently the case with α-naphthol as second diazo-component. We have also been able to show, by spotting on filter-paper, that, if the solutions are equally concentrated, the colours produced, as well as the shade changes caused by acid and alkali treatment afterwards, in the coupling reactions tabulated by Riegel and Hathaway are remarkably similar to those given by the simple benzeneazo-compounds.

With this material before us we think the balance of evidence is strongly in favour of (II).

EXPERIMENTAL.

The Condensation Product.—An almost quantitative yield was obtained by mixing redistilled furfural (21 c.c.; 0·25 mol.) and aniline (45·5 c.c.; 0·5 mol.) in ethyl alcohol (150 c.c.) and adding 10N-hydrochloric acid (25 c.c.; 0·25 mol.) in ethyl alcohol (25 c.c.). Recrystallisation from glacial acetic acid gave small, almost black, prisms which, after drying in a vacuum, had m. p. 166—167° (decomp.) (Found: C, 67·7; H, 5·9. Calc. for $C_{17}H_{16}ON_2,HCl$: C, 67·8; H, 5·65%).

Reaction with Nitrous Acid.—The above compound (3·05 g.; 0·01 mol.) was suspended in ethyl alcohol (200 c.c.), concentrated hydrochloric acid (2 c.c.) added, and the mixture cooled in ice while N-sodium nitrite was run in and more acid added from time to time to maintain acidity to Congo-red. An immediate positive starch–iodide reaction was obtained only after much more than two equivalents of nitrite had been added. The solution was rapidly filtered to remove the suspended brown solid material.

Coupling with β-Naphthol.—The diazonium solution obtained above was added to β-naphthol dissolved in excess of 2N-sodium hydroxide. The solid obtained corresponded in amount to slightly less than one mol.-equiv. of aniline; recrystallised from petrol (b. p. 60—80°), it formed red needles, m. p. 130—131° (Found: C, 77·35; H, 5·0; N, 11·6. Calc. for $C_{16}H_{12}ON_2$: C, 77·3; H, 4·8; N, 11·3%), not depressed by the product from benzenediazonium chloride and β-naphthol (m. p. 130—131°).

A similar result was obtained, although purification of the product was rendered more difficult by the presence of other substances, when exactly 2 equivs. of sodium nitrite were added in the original diazotisation.

Coupling with α-Naphthol.—The diazonium solution both from the furfural product and from aniline gave a mixture of substances. From the former, after recrystallisation from butyl acetate, a small amount of a product, m. p. 178° (decomp.) (Found: C, 70·45; H, 4·25; N, 10·85%), was obtained. Riegel and Hathaway give a nitrogen figure of 9·91%. Their calculated figure (10·22%) would appear to be in error; we find 9·76%. The triphenylmethane structure (I) would necessitate C, 77·3; H, 4·6% for the bisazo-derivative.

Coupling Products from the Toluidine Condensation Product.—The procedure was as described for aniline. The condensation product after recrystallisation from glacial acetic acid formed almost black prisms with a bluish-grey reflex, m. p. 159—161° (decomp.) (Found: C, 69·1; H, 6·8; N, 8·35. Calc. for $C_{19}H_{20}ON_2,HCl$: C, 69·4; H, 6·4; N, 8·5%). After coupling with β-naphthol the product separated from petrol (b. p. 60—80°) in red needles, m. p. 130—131° (Found: C, 77·55; H, 5·75; N, 10·7. Calc. for $C_{17}H_{14}ON_2$: C, 77·8; H, 5·4; N, 10·7%). The substance did not depress the m. p. of an authentic specimen from diazotised *p*-toluidine and β-naphthol. It did, however, depress the m. p. of benzeneazo-β-naphthol, which has the same m. p.

Reaction of Dimethylaniline, Aniline Hydrochloride, and Furfural.—Equimolecular amounts of the reactants were mixed in methyl alcohol. After some time a small amount of crystalline material had separated. Recrystallisation from glacial acetic acid gave almost black prisms, m. p. 166—167° (decomp.), not depressed by the aniline–aniline hydrochloride product. Identity was further supported by analysis (Found: C, 68·35; H, 6·0. Calc. for $C_{17}H_{16}ON_2,HCl$: C, 67·8; H, 5·65%. Calc. for $C_{19}H_{20}ON_2,HCl$: C, 69·4; H, 6·4%).

The authors wish to thank I.C.I. (Dyestuffs), Ltd., for permission to publish the work.

RESEARCH DEPARTMENT, I.C.I. (DYESTUFFS), LTD., BLACKLEY, MANCHESTER, 9. [*Received, March* 31*st*, 1942.]