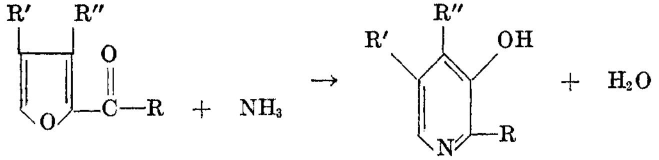
[Contribution from the Department of Chemistry and Chemical Engineering, Stanford University]

THE REARRANGEMENT OF ACYLFURANS TO 3-HYDROXYPYRIDINES[1]

HOMER WILLIAMS,[2] PAULA KAUFMANN,[3] and HARRY S. MOSHER

Received May 19, 1955

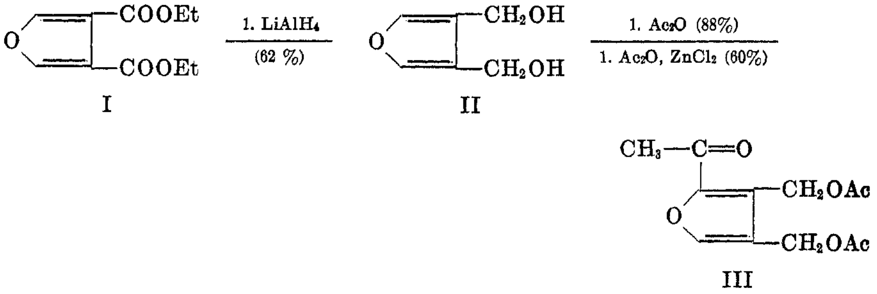
Since the first report by Aso (1) of the conversion of furfural to 3-hydroxypyridine and of 5-methylfurfural to 2-methyl-5-hydroxypyridine by treatment with ammonium sulfate at 152–153°, several investigators (2–4) have demonstrated that this is a general reaction and that 2-acylfurans can be converted into the corresponding 2-substituted 3-hydroxypyridines by treatment with ammonia alone or in the presence of ammonium salts according to the following equation where R′ and R″ are hydrogen.



1.

In these previous studies no report was made on the application of this reaction to a 2-acylfuran which was also substituted in the 3-, 4-, or 3,4-positions. Since an appropriately substituted 2-acetylfuran could, according to this reaction (equation 1), give pyridoxine, or an intermediate readily converted to pyridoxine, we have studied the reaction further to see if the rearrangement still takes place when the 2-acylfuran has substituents in the 3- and 4-positions of the furan ring.

The intermediate of major importance in these studies was 2-acetyl-3,4-bis(acetoxymethyl)furan which was made from 3,4-dicarbethoxyfuran by lithium aluminum hydride reduction of the corresponding ester followed by acetylation and a Friedel-Crafts reaction using acetic anhydride and zinc chloride.



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When this investigation was started two methods had been reported for the preparation of the necessary furan-3,4-dicarboxylic acid or its ester (I). Reich-

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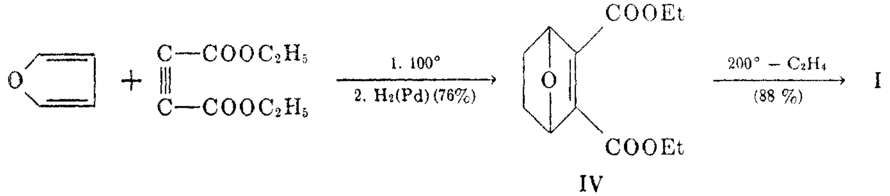
[1] This paper is an abstract in part of the Ph.D. Thesis of HRW, Stanford University, 1953.

[2] Parke, Davis and Co. Graduate Fellow, 1952–1953.

[3] Parke, Davis and Co. Postdoctorate Fellow, 1953–1954.

stein and co-workers (5) prepared this acid by partial decarboxylation of furantetracarboxylic acid and Alder and Rickert (6) prepared the impure ethyl ester in unstated yield by the thermal decomposition of the partially reduced Diels-Alder adduct from furan and ethyl acetylenedicarboxylate. Both of these methods were investigated from a preparative standpoint. Although the furantetracarboxylic acid could be made in good yield (5, 7), an extensive study of the partial decarboxylation of this acid was made without finding conditions which gave more than a trace of the desired furan-3,4-dicarboxylic acid. The Alder and Rickert (6) procedure was investigated and was developed into a satisfactory synthetic route for the preparation of 3,4-dicarbethoxyfuran (I) according to the following equations.



IV

3.

A series of attempts at the conversion of 2-acetyl-3,4-bis(acetoxymethyl)furan (III) or 2-acetyl-3,4-bis(hydroxymethyl)furan (V) into pyridoxine by treatment with ammonia alone or in the presence of ammonium acetate, or ammonium chloride were completely unsuccessful at temperatures ranging from 237° for ten hours to 180° for two hours. It was determined that pyridoxine would, at least in part, survive these latter conditions. During the course of this work, and previous to the publications of Gruber (3), and Dunlop and Swadesh (4), the conversion of 2-acetylfuran (10) into 2-methyl-3-hydroxypyridine was studied to test the feasibility of this approach to the synthesis of pyridoxine. The best conditions found (10% alcoholic ammonia in the presence of ammonium chloride for two hours at 204°) gave a 43% yield of the desired product.

A method of protecting the hydroxymethyl groups other than acetylation then was sought. 3,4-Bis(hydroxymethyl)furan (II) was methylated in 59% crude yield to 3,4-bis(methoxymethyl)furan (VI) which, however, could not be successfully acetylated in the Friedel-Crafts reaction. The methylation of 2-acetyl-3,4-bis(hydroxymethyl)furan (V) which was obtained by hydrolysis of III, then was studied by preparing the sodium salt with excess sodium hydride and treating with methyl iodide. The product from several such experiments was always incompletely methylated as shown by infrared spectra and analyses. A Shotten-Baumann methylation with excess dimethyl sulfate gave a product in poor yield which showed absorption at 2.92μ and failed to give a positive iodoform test. When equimolar amounts of dimethyl sulfate and 2-acetyl-3,4-bis-(hydroxymethyl)furan (V) were allowed to react, the product gave a positive iodoform test and the analysis corresponded to that expected for 2-acetyl-3-(or 4)-(hydroxymethyl)-4(or 3)(methoxymethyl)furan. From the above and the following investigation of the ethylation of 2-acetyl-3,4-bis(hydroxymethyl)-

furan, it appeared that C-methylation on the acetyl group took precedence over O-methylation of the second hydroxyl group. It seems logical to assume that it was the more hindered 3-hydroxymethyl group which was resistant to alkylation but no specific information is available on this point. This substance was not converted to a pyridine compound according to equation 1 when treated with alcoholic ammonia.

The ethylations of 2-acetyl-3,4-bis(hydroxymethyl)furan followed a similar course; the best results were obtained with potassium amide and ethyl iodide in liquid ammonia (11). Two ethyl groups were introduced into the molecule but a Zeisel determination showed the presence of a single ethoxy group in the product. The infrared spectra showed the presence of hydroxyl and carbonyl groups, and the product failed to give an iodoform reaction. It was therefore assumed that the second ethyl group was introduced on the methyl of the 2-acetyl function and the infrared spectra were compatible with this interpretation. This product, 2-(butyryl)-3(or 4)-(hydroxylmethyl)-4(or 3)-(ethoxymethyl)furan (VIII) was not converted to a pyridine compound according to equation 1 when treated with ammonia.

The unstable 2-acetyl-3,4-bis(chloromethyl)furan (IX) could be obtained in poor yield. Immediate treatment with methyl alcohol gave a product which corresponded in its properties to 2-acetyl-3,4-bis(methoxymethyl)furan (VII). In a single experiment this product was treated with ammonia and failed to give a pyridine derivative.

2-Acetyl-3,4-dicarbethoxyfuran (X) was prepared according to the method of Alder and Rickert (6) starting with 2-acetylfuran (12) instead of furan in reaction 3. This appears to be the first instance of such a negatively substituted furan undergoing the Diels-Alder reaction (13). The possible conversion of this substance or its derivatives into pyridine compounds was not studied.

Acknowledgment. We wish to thank Parke, Davis and Company for fellowship support which made these studies possible.

EXPERIMENTAL[4]

The partial decarboxylation of furantetracarboxylic acid. Furantetracarboxylic acid (5, 7), 121 mg., (0.492 m. mole), was heated in a test tube immersed in an oil-bath at 200–240° until the volume of evolved gas measured 21 ml. (0.9 m. mole). During the decarboxylation, the mixture darkened rapidly. The residue was sublimed in a vacuum to give a very small amount of crystals which on recrystallization from ethyl acetate gave furan-3,4-dicarboxylic acid (5), m.p. 204–207°. In another trial the decarboxylation of 2 g. of furantetracarboxylic acid was run at 275–285° for 20 minutes, the black residue was extracted with alcohol, and the soluble portion, 0.8 g., was recrystallized from ethyl acetate to give crude 3-furancarboxylic acid, m.p. 116–119°. Other decarboxylations were conducted in which the furan tetracarboxylic acid was heated in quinoline, quinoline and copper powder, and in phenyl ether and copper powder; but a satisfactory yield of the desired furan-3,4-dicarboxylic acid was not obtained in any case.

3,4-Dicarbethoxyfuran (I). This procedure was a modification of that reported by Alder

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[4] All melting points are uncorrected. Microanalyses by C. Koch, Microchemical Specialties Co., Berkeley, California. The infrared spectra of each compound was taken and found to be compatible with the structures reported.

and Rickert (6). A mixture of ethyl acetylenedicarboxylate (12) (72 g., 0.42 mole), and furan (29 g., 0.42 mole), was heated in a sealed tube at 100° for 18 hours and the product was dissolved in 75 ml. of ethyl acetate and hydrogenated in the presence of 1 g. of palladium on calcium carbonate (14) at 10–35 p.s.i. over a two-hour period. The hydrogenation was interrupted several times to prevent overheating during the exothermic reaction. After 0.415 mole of hydrogen had been absorbed, the catalyst and solvent were removed and the residue was distilled to give the main fraction, b.p. 96–106° (0.7 mm.) 68.0 g. (76%) of IV with a smaller amount, 13.3 g., boiling from 106–173°. A 20% excess of furan reduced the yield of the lower-boiling material to 52% and increased that of the higher-boiling component. From 10.85 g. of the higher-boiling component there was isolated by crystallization from ethyl acetate-petroleum ether, 2.8 g. of colorless crystals, m.p. 113–115°.

Anal. Calc'd for $C_{16}H_{22}O_6$: C, 61.93; H, 7.15.
Found: C, 62.63; H, 7.39.

This material did not decolorize bromine in carbon tetrachloride. Its structure was not investigated further; it may have been the reduced product from the condensation of two molecules of furan with one of ethyl acetylenedicarboxylate, 4a,8a-dicarbethoxy-1,4,5,8-diepoxydecahydronaphthalene.

The crude ethyl 3,6-epoxy-3,4,5,6-tetrahydrophthalate (IV) (68 g., 0.283 mole), was heated to 200° for 40 minutes until the evolution of ethylene ceased. The minimum temperature for ethylene evolution was 175° but the rate did not become practical until the temperature reached 195–200°. The residue was distilled to give 50 g. (88% yield) of 3,4-dicarbethoxyfuran as a colorless oil, b.p. 79–83° (0.7 mm.) n_D^{20} 1.4675. When the procedure reported by Alder and Rickert (6) was followed, the decomposition was incomplete and the yield of the desired ester very low; the main material isolated was recovered ethyl 3,6-epoxy-3,4,5,6-tetrahydrophthalate (IV), b.p. 100–105° (0.7 mm.). Alder and Rickert had reported the boiling point of IV as 130–140° (11 mm.) and of I as 140–165° (11 mm.) which is the reverse of what would be expected and what was found in this work. Since this investigation was completed, an alternate route to 3,4-dicarbethoxyfuran has been described by Kornfeld and Jones[5] (8).

3,4-Bis(hydroxymethyl)furan (II). A solution of 3,4-dicarbethoxyfuran (9.45 g., 0.045 mole), in 30 ml. of anhydrous ether was added dropwise with stirring to 1.95 g. (0.0515 mole) of powdered lithium aluminum hydride in 70 ml. of anhydrous ether under a nitrogen atmosphere. The reaction mixture was refluxed for one hour, cooled, and decomposed by adding 62 g. of an ice-cold acetic acid solution. Continuous ether extraction followed by removal of the solvent and distillation gave 3.75 g. (62% yield) of II, b.p. 117–121° (1 mm.). A redistilled sample, b.p. 120° (1 mm.) n_D^{20} 1.4970, was analyzed. It was insoluble in benzene but was soluble in all proportions with ether, alcohol and water.

Anal. Calc'd for $C_6H_8O_3$: C, 56.24; H, 6.29.
Found: C, 55.92; H, 6.42.

The infrared spectra showed that in certain runs the crude product obtained by this method contained some acid. This could be removed by redistillation or the crude material could be used directly since the acid was removed by extraction from basic solution in the next step.

3,4-Bis(acetoxymethyl)furan. After a mixture of 3,4-bis(hydroxymethyl)furan (3.50 g., 0.0273 mole), acetic anhydride (10.0 g., 0.0980 mole), and sodium acetate (0.1 g.) had been refluxed for one hour, the acetic acid and excess acetic anhydride were removed under a vacuum and the residue was distilled to give 5.12 g. (88.5% yield) of 3,4-bis(acetoxymethyl)furan, b.p. 96–100° (1 mm.). A redistilled sample b.p. 96° (1 mm.), n_D^{20} 1.4675 was analyzed.

Anal. Calc'd for $C_{10}H_{12}O_5$: C, 56.60; H, 5.70.
Found: C, 56.60; H, 5.92.

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[5] We wish to thank Dr. Kornfeld and Dr. Jones for the opportunity to read their manuscript prior to publication and to learn of their parallel experiments on the attempted conversion of 2-acylfurans to 3-hydroxypyridines in the accompanying paper (9).

2-Acetyl-3,4-bis(acetoxymethyl)furan (III). A mixture of acetic anhydride (6.0 g., 0.059 mole), 3,4-di(acetoxymethyl)furan (3.0 g., 0.014 mole), and zinc chloride (0.2 g.) was heated on the steam-bath for 45 minutes. Ether was added and after washing with two 5-ml. portions of water the solvent and excess acetic acid were removed at reduced pressure and the residue was distilled to give 2.18 g. (60% yield) of III, b.p. 136–139° (0.8 mm.). A redistilled sample, b.p. 137° (0.8 mm.), n_D^{20} 1.4925 was analyzed. This product crystallized, m.p. 51–52° when seeded with a sample furnished by Kornfeld and Jones (9).

Anal. Calc'd for $C_{12}H_{14}O_6$: C, 56.69; H, 5.55.
Found: C, 56.30; H, 5.76.

2-Acetyl-3,4-bis(hydroxymethyl)furan (V). 2-Acetyl-3,4-bis(acetoxymethyl)furan, 18.5 g., was hydrolyzed by shaking with 100 ml. of 7% sodium hydroxide solution at room temperature for 30 minutes. The reaction mixture was neutralized with acetic acid and was extracted continuously with ether. The ether extracts were dried over sodium sulfate, concentrated, and distilled to give 10 g. (82% yield) of product, b.p. 160–162° (2 mm.), m.p. 35–40°, which gave a positive iodoform reaction and showed strong infrared absorption at 2.96, 6.00, 6.24, and 6.54 microns indicative of hydroxyl, carbonyl and furan functions, respectively.

Anal. Calc'd for $C_8H_{10}O_4$: C, 56.46; H, 5.92.
Found: C, 56.20; H, 6.20.

3,4-Bis(methoxymethyl)furan. To a suspension of sodium hydride (1.76 g., 0.0733 mole) in ether (40 ml.), was added 3,4-bis(hydroxymethyl)furan (4.68 g., 0.0366 mole), and the mixture was refluxed until the formation of the cream-colored sodium salt was complete. Methyl iodide (30 g., 0.21 mole), was added and the mixture was refluxed for 72 hours; the mixture was filtered, the filtrate was concentrated, and the residue was distilled to give 3.45 g. (59% crude yield) of 3,4-bis(methoxymethyl)furan, b.p. 98–104° (19 mm.). Infrared spectra showed that this product still contained unmethylated product. Therefore it was treated with phthalic anhydride, washed with sodium bicarbonate solution, and redistilled to give a product b.p. 96° (20 mm.) n_D^{20} 1.14611. This absorbed strongly at 5.97, 6.24, and 6.52 microns, characteristic of carbonyl and furan ring but did not absorb significantly in the region 2.8 microns characteristic of hydroxyl absorption.

Anal. Calc'd for $C_8H_{12}O_3$: C, 61.44; H, 7.75.
Found: C, 61.65; H, 8.09.

When the methylation was carried out on 3,4-bis(hydroxymethyl)furan with excess dimethyl sulfate and sodium hydroxide the infrared spectra showed that the product still contained free hydroxy function. Seven attempted Friedel-Crafts reactions on 3,4-bis(methoxymethyl)furan under a variety of conditions failed to produce any of the desired 2-acetyl derivative.

Similar methylations of 2-acetyl-3,4-bis(hydroxymethyl)furan with sodium amide or sodium hydride and excess methyl iodide gave products which still possessed free OH function as shown by the infrared spectra. The same was true when excess dimethyl sulfate was used as the methylating agent. The results paralleled those described in the following ethylation experiment.

Reaction of 2-acetyl-3,4-bis(hydroxymethyl)furan (V) *with potassium amide and ethyl iodide.* Potassium (10 g.) was converted to potassium amide by dissolving in liquid ammonia, about 300 cc., in the presence of a trace of iron oxide. 2-Acetyl-3,4-bis(hydroxymethyl)furan (22 g.) and ethyl iodide (41 g.) were added to this solution and the mixture was allowed to stand overnight. After the ammonia had evaporated, water was added and the mixture was extracted with ether. Evaporation of the solvent and distillation of the residue at 1 mm. pressure gave three fractions: (a), b.p. 110–126°, 4.5 g., n_D^{20} 1.5015; (b) b.p. 126–136°, 7 g., n_D^{20} 1.5029; (c) b.p. 137–152°, 8.15 g., n_D^{20} 1.5170. Only slight differences were detectable in the infrared spectra of these cuts and all showed strong absorption at 2.92μ. Fraction 2 above was redistilled and the first fraction from this, b.p. 123–126° (1 mm.) 1.15 g., n_D^{20} 1.5019 was analyzed.

Anal. Calc'd for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02.
Found: C, 63.70; H, 8.04.

This cut gave a negative iodoform test, had strong absorption at 2.92μ and 6.00μ characteristic of the hydroxy and carbonyl functions[6], and at 6.26μ and 6.56μ characteristic of the furan nucleus. It gave a Zeisel ethoxy determination of 19.6% as compared to a calculated value of 19.9% for 2-butyryl-3-(hydroxymethyl)-4-(ethoxymethyl)furan. The higher-boiling cuts gave analyses indicating further C-alkylation but no further O-alkylation. Thus one of the hydroxymethyl groups, presumably the one situated in the 3-position, is resistant to alkylation.

2-Acetyl-3,4-bis(chloromethyl)furan (IX). 2-Acetyl-3,4-bis(hydroxymethyl)furan (15 g.) was dissolved in anhydrous ether (25 ml.) and pyridine (17 g.) and slowly added with stirring to thionyl chloride (15 ml.) in hexane 35 ml. at 0°. The mixture was stirred for one-half hour after the addition was complete and was decomposed by addition of 2 *N* hydrochloric acid at 0°. The ether layer was washed with a cold sodium carbonate solution and water until the washings were neutral and then was dried over sodium sulfate. After the solvent was removed the product was distilled to give 6.0 g., b.p. 120–122°, n_{D}^{20} 1.5420.

Anal. Calc'd $C_8H_8Cl_2O_2$: C, 46.40; H, 3.88.
Found: C, 46.65; H, 4.17.

The major portion of the product was a black tar resulting from decomposition during distillation. The product rapidly darkened on standing and was a lacrymator and vesicant. Attempts to methylate this with methanol and potassium hydroxide were unsuccessful.

2-Acetyl-2,4-bis(methoxymethyl)furan (?) (VII). A sample of freshly prepared undistilled 2-acetyl-3,4-bis(chloromethyl)furan (4.5 g.) was heated in a sealed tube at 110° for 24 hours with 80 ml. of absolute methanol. The contents of the tube were neutralized with sodium hydroxide solution, poured into water, and extracted with ether. After the ether extracts were dried and concentrated, the residue was distilled to give 0.65 g. of product, b.p. 88–119° (3 mm.). A redistilled sample, b.p. 95–99° (3 mm.) n_{D}^{20} 1.4950 showed characteristic carbonyl absorption at 6.00μ[6] and was essentially transparent in the hydroxyl region at 2.8–3.0μ. It gave a negative halogen test and positive iodoform reaction.

Anal. Calc'd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12.
Found: C, 59.45; 6.79.

Although the carbon analysis was not satisfactory for the desired product, this material was treated with alcoholic ammonia at 155° for 13 hours on the assumption that it was 2-acetyl-3,4-bis(methoxymethyl)furan. No basic organic material could be detected in the reaction product.

2-Acetyl-3,4-dicarbethoxy furan (X). 2-Acetylfuran (10) (8.5 g.) and ethyl acetylenedicarboxylate (13.1 g.) were heated in a sealed tube for 18 hours at 105°. The reaction mixture was dissolved in ethyl acetate (20 ml.) and hydrogenated in the presence of palladium on calcium carbonate catalyst (14) at 3 atmospheres pressure for 30 minutes. The catalyst and solvent were removed and the residue was distilled to give a viscous oil, 9.8 g., b.p. 145–150° (2 mm.), n_{D}^{20} 1.4868. This was heated at 210° for 30 minutes until evolution of ethylene was complete. Distillation of the product gave 6 g. (33% over-all yield) of material b.p. 131–134° (2 mm.), n_{D}^{20} 1.4891 which corresponded in analysis, infrared and ultraviolet spectra with the expected 2-acetyl-3,4-dicarbethoxyfuran, $\lambda_{\max}^{\text{alc}}$ 263 mμ (ϵ 10,300).

Anal. Calc'd for $C_{12}H_{14}O_6$: C, 56.67; H, 5.55.
Found: C, 56.58; H, 5.74.

2-Methyl-3-hydroxypyridine (2–4). The following were the best conditions found for the rearrangement (3, 4) of 2-acetylfuran to 2-methyl-3-hydroxypyridine. A mixture of 455 mg. (0.0041 mole) of 2-acetylfuran and 250 mg. (0.0047 mole) of ammonium chloride in 1.5 ml. of 10% alcoholic ammonia was heated at 204° for two hours in a sealed tube. The reac-

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[6] The carbonyl absorption in 2-acetylfuran is at 5.98μ; 2-acetyl-3,4-bis(hydroxymethyl)-furan, 6.02μ; 2-butyryl-3(or 4)-hydroxymethyl-4(or 3)-(ethoxymethyl)furan, 6.00μ; 2-acetyl-3,4-bis(chloromethyl)furan, 5.96μ; 2-propionyl-3(or 4)-hydroxymethyl-4(or 3)-(methoxymethyl)furan, 5.97μ; 2-acetyl-3,4-bis(methoxymethyl)furan, 6.00μ; 2-acetyl-3,4-bis(acetoxymethyl)furan, 5.98μ.

tion mixture was evaporated to dryness on the steam-bath and the residue was digested with 2 ml. of 10% hydrochloric acid. The acid solution was treated with Darco and evaporated to dryness. The crystalline residue was recrystallized from a very small amount of isopropyl alcohol after a second decolorization. The crystals were washed with ether and chloroform and dried to give 259 mg. (43% crude yield), m.p. 193–199°. Recrystallization from dioxane-alcohol solution gave a product decomposing at 212°. The free base was prepared from the hydrochloride and was purified by sublimation; m.p. 164–165°. The product gave an orange-red color with ferric chloride solution and corresponds in properties to the known (3, 4) 2-methyl-3-pyridol.

The reaction of 2-acetyl-3,4-bis(substituted)furans with ammonia and ammonium salts. Several experiments under conditions approximating the best conditions found above for the preparation of 2-methyl-3-hydroxypyridine were tried with 2-acetyl-3,4-bis(acetoxymethyl)furan (VI): heating with ammonium acetate at 237° for ten hours, with ammonium chloride and alcoholic ammonia at 197° for from 45 minutes to ten hours, and with ammonium chloride in water at 180° for two hours. Processing the reaction mixtures as indicated for 2-methyl-3-hydroxypyridine failed to give any detectable product which gave a positive ferric chloride test for a 3-hydroxypyridine derivative. The longer reaction times and higher temperatures gave mostly black solid material and the shorter reaction times gave essentially no basic organic matter.

SUMMARY

A study has been made of the synthesis of 3,4-bis(hydroxymethyl)-2-acetylfuran and several of its derivatives in a search for a new route to the synthesis of pyridoxine. The reaction of these compounds with ammonia alone and in the presence of ammonium salts at elevated temperatures failed to produce any isolable amount of the desired pyridine derivative according to equation 1 ($R = CH_3$, R' and $R'' = CH_2OH, CH_2OAc, CH_2OCH_3$). 2-Acetylfuran readily reacts to give 2-methyl-3-hydroxypyridine under the conditions studied.

STANFORD, CALIFORNIA

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