REACTION OF FURAN DERIVATIVES WITH AMMONIA

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By

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I. The Reaction of 2-Acetylfuran with Ammonia.**
II. The Reaction of 2-Furyl-ethylketone with Ammonia.
III. The Spectrum of β-Hydroxy-pyridine Derivatives.

It has been reported (1) that various kinds of β-hydroxy pyridine derivatives were formed from furan derivatives having a carbonyl group in α-position by heating with ammonium salts in an autoclave, although the yields of pyridine derivatives were comparatively not high. Preparation of 2-methyl-3-hydroxy-pyridine from 2-acetylfuran was first reported by Aso (2) and then other investigations (3, 4, 5) were carried out in the presence of water or alcohol, so it was uncertain whether the reaction was hydrolytic cleavage (1) or ammonolytic cleavage (6).

One object of the present investigation is to prove the reaction mechanism; the other object is to provide an improved process for the preparation of β-hydroxy-pyridine derivatives by reacting 2-furyl-alkylketones with ammonia.

We have found it possible to obtain in good yield 2-methyl-3-hydroxy-pyridine and 2-acetylpyrrole by reacting with ammonia under several conditions as shown in Table 1, and we have found that 2-methyl-3-hydroxy-pyridine and 2-acetylpyrrole are obtained from 2-acetylfuran with liquid ammonia without a solvent by using ammonium chloride as a catalyst. Dunlop (3) reported that 2-acetylpyrrole only was produced from 2-acetylfuran with ammonia in the absence of any solvent.

From the above work, the next investigation was subjected to a similar reaction in the hope that 2-ethyl-3-hydroxy-pyridine and 2-ethyl-pyrrylketone might be synthesized from 2-furyl-ethylketone, and 2-ethyl-3-hydroxy-pyridine and 2-ethyl-pyrrylketone were obtained by reacting 2-furyl-ethylketone with ammonia under the same condition as mentioned above. In this work, the

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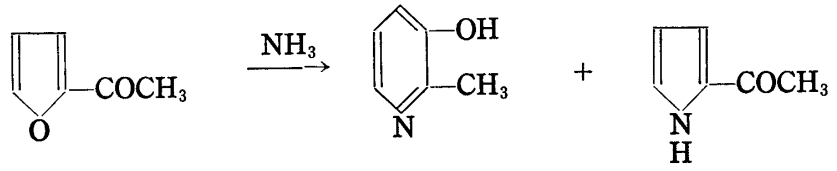
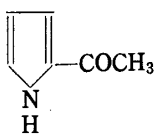
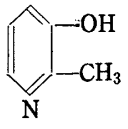
infrared spectrum of 2-alkyl-3-hydroxy-pyridines measured in solid state did not show the absorption band of free hydroxyl group near 3400 cm^{-1}, and have shown the hydroxyl group to be present in bonded form since they had two very broad bands centred at about 2500 cm^{-1} and 1800 cm^{-1}. So various kinds of β-hydroxy-pyridine having a characteristic structure have been measured in solid state and solution, and the relation between structure and hydroxyl group was discussed. Presumably, in β-hydroxy-pyridines, OH—N intermolecular hydrogen bond exists and this accounts for the wide spread of absorption. α-Hydroxy-pyridines having the tautomeric form did not show intermolecular hydrogen bond. α-Substituted pyridines had the absorption bands at 990-1000 cm^{-1} and 1045-1050 cm^{-1}, and β-substituted pyridines at 1020-1030 cm^{-1} and near 1200 cm^{-1}. In addition, all the measured compounds, α,β-disubstituted pyridines showed the two absorption bands described above. Moreover, it has been pointed out that α-hydroxy-pyridines measured in this work had a characteristic band at 780 cm^{-1}, and β-hydroxy-pyridines near 800 cm^{-1}.

I, The Reaction of 2-Acetylfuran with Ammonia. Formation of 2-Methyl-3-hydroxy-pyridine (**II**) and 2-Acetylpyrrole (**III**) from 2-Acetylfuran (**I**).



(**I**) (**II**) (**III**)

Table 1. The yields of 2-methyl-3-hydroxy-pyridine and 2-acetylpyrrole.

Reactants	Yield % (theoretical)	
		
2-Acetylfuran 2 g, Liq. NH_3 10 *ml*, NH_4Cl 0.5 g.	25	20
2-Acetylfuran 2 g, Liq. NH_3 10 *ml*, MeOH 10 *ml*.	15	40
2-Acetylfuran 2 g, 28 % NH_4OH 20 *ml*, MeOH 20 *ml*	10	55
2-Acetylfuran 2 g. 10 % alcoholic ammonia 25 *ml* NH_4Cl 0.5 g	20	60

Experimental

1) Synthesis of 2-acetylfuran (2-furyl-methylketone) (4, 7, 8) (**I**).

Furan 25 g, acetic anhydride 74 *ml* and 85 % H_3PO_4 4 g were heated slowly with stirring to 35°C for 30 min, then more rapidly to 60°C for the next 30 min and the temperature was kept at 60°C for 30 min. After cooling, 300 *ml* of water was added to the reaction mixture, extracted with ether, and the extract was washed first with Na_2CO_3 solution, and then with water, finally dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was distilled under reduced pressure, yielding 30 g of 2-acetylfuran, bp_{10} 60–65°C, mp 32°C.

2) Isolation of 2-methyl-3-hydroxy-pyridine (**II**) *and 2-acetylpyrrole (2-methyl-pyrrylketon)* (**III**).

The reactants as shown Table 1 were heated in an autoclave at 180°C for 20 hr, the reaction mixture was diluted with 50 *ml* of methanol, and treated with active carbon. After removal of the solvent and ammonia at reduced pressure, the residue was dried over $CaCl_2$. (**II**) and (**III**) were obtained from the dried material by the method of sublimation at reduced pressure. (**III**) was sublimed at 90–100°C, and then (**II**) was sublimed at 160–170°C under reduced pressure at 10 mm Hg.

3) 2-Methyl-3-hydroxy-pyridine (**II**).

(**II**) was recrystallized from benzene after sublimation, colorless prism, mp 168°C. Yield of (**II**) is shown in Table 1. Anal. Fouud; C, 65.84; H, 6.35; N, 12.84. Calcd. for C_6H_7ON C, 66.03; H, 6.47; N, 12.84 %. (**II**) indicated a deep red color by $FeCl_3$ solution, and a deep green color by the Folin-Denis reagent, the melting point of (**II**) was not depressed by admixture with authentic 2-methyl-3-hydroxy-pyridine (2). The infrared spectrum of (**II**) showed the absorption band of 2-methyl-3-hydroxy-pyridine and not the absorption band of free hydroxyl group near 3400 cm^{-1}, and has shown the hydroxyl group to be present in bonded form since it had two broad bands centred at about 2500 cm^{-1} and 1800 cm^{-1} as shown in Fig. 1. Its picrate was prepared by the usual method, recrystallized from water, yellowish needle, mp 203°C. Anal. Found: N, 16.71. Calcd. for C_{12} $H_{10}O_8N_4$ N, 16.56 %.

4) 2-Acetylpyrrole (**III**).

(**III**) was recrystallized from water after isolation by sublimation, colorless needle, mp 91°C. Anal. Found: C, 65.67; H, 6.27; N, 12.91. Calcd. for C_6H_7ON C, 66.03; H, 6.47; N, 12.84 %. The yield of (**III**) is shown in Table 1. The infrared spectrum of (**III**) was identical with that of 2-acetylpyrrole described by Eisner (9). It is shown in Fig. 2.

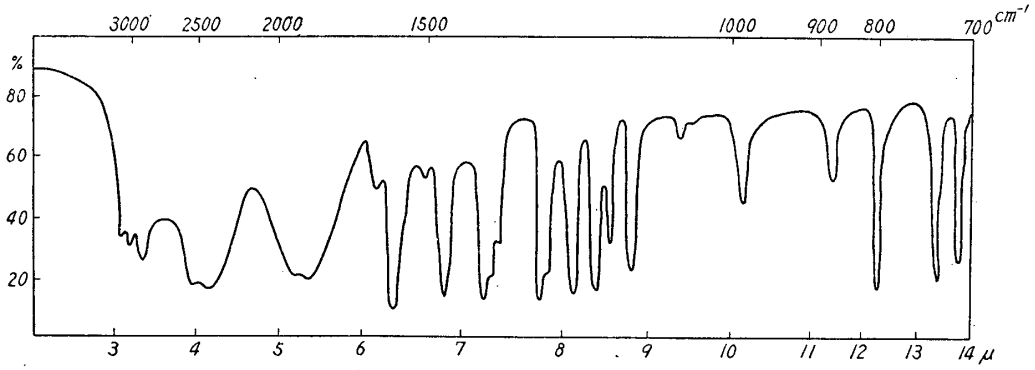


Fig. 1. The infrared spectrum of (**II**). (**C**).

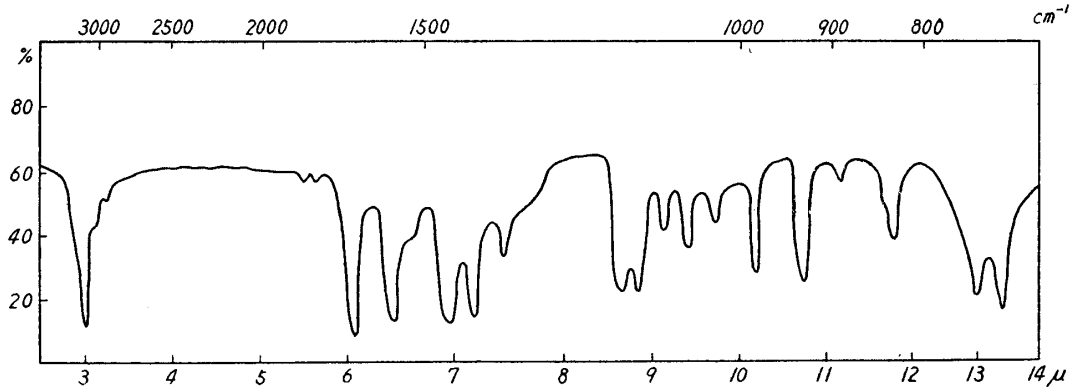
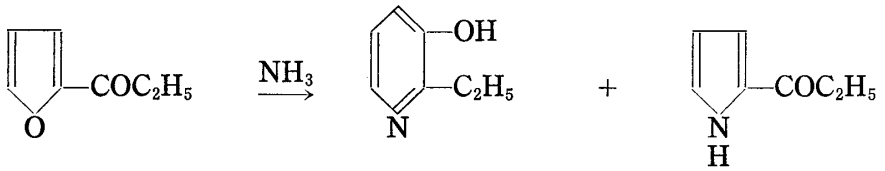


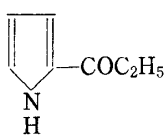
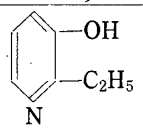
Fig. 2. The infrared spectrum of (**III**).

II. The Reaction of 2-Furyl-ethylketone with Ammonia. Formation of 2-Ethyl-3-hydroxy-pyridine (**V**) and 2-Ethyl-pyrrylketone (**VI**) from 2-Furyl-ethylketone (**IV**).



(**IV**) (**V**) (**VI**)

Table 2. The yields of 2-ethyl-3-hydroxy-pyridine and 2-ethyl-pyrrylketone.

Reactants	Yield % (theoretical)	
		
2-Furyl-ethylketone 2 g. Liq. NH_3 10 *ml*, NH_4Cl 0.5 g. 180°C, 6 hr.	70	20
2-Furyl-ethylketone 2 g, Liq. NH_3 10 *ml*, EtOH 10 *ml*.	25	40
2-Furyl-ethylketone 2 g, 28 % NH_4OH 20 *ml*, EtOH 20 *ml*.	17	20
2-Furyl-ethylketone 2 g, 10 % alcoholic ammonia 25 *ml*, NH_4Cl 0.5 g.	26	45

5) 2-Furyl-ethylketone (**IV**) (4, 10).

2-Furyl-ethylketone was prepared by Friedel-Crafts reaction using $ZnCl_2$ or 85 % H_3PO_4 as a catalyst.

a) Furan 25 g, propionic anhydride 97 g and 1.4 g of fresh $ZnCl_2$ were placed in a three-neckflask and stirred under anhydrous condition for 3 hr at room temperature, and then 100 *ml* of water was added to the reaction mixture. After stirring for 20 minutes, the reaction mixture was extracted with ether, and the extract was washed with Na_2CO_3 solution, then dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was distilled under reduced pressure, bp_{15} 75–77°C, mp 28°C. Yield 20 g.

b) 2-Furyl-ethylketone was prepared nearly by the same procedure using 85% H_3PO_4 instead of $ZnCl_2$. A well stirred mixture of furan 25g and propionic anhydride 91g was warmed to 40°C, the heat removed, and 85 % H_3PO_4 6 g was added at once. This caused a slight rise of temperature which allowed to subside and the mixture was kept at 60°C for 2.5 hr. 30 g of 2-furyl-ethylketone was obtained by the method described above, bp_{15} 75–77°C, mp 28°C.

6) Isolation of 2-ethyl-3-hydroxy-pyridine (**V**) *and 2-ethyl-pyrrylketone* (**VI**).

The reactants as shown in Table 2 were heated in an autoclave at 180°C for 20 hr. The reaction mixture was diluted with 50 *ml* of ethanol, and treated with active carbon. After removal of the solvent and ammonia, the residue was distilled under reduced pressure. (**VI**) was distilled at bp_{12} 105–110°C, the residue was extracted with 2*N*-NaOH, and NaOH solution was saturated with CO_2, and then extracted again with ether for 48 hr. (**V**) was obtained from the ether extract.

7) 2-Ethyl-3-hydroxy-pyridine (**V**).

(**V**) was recrystallized from the ether-chloroform mixture after sublimation, colorless prism, mp 134°C. The yield of (**V**) is shown in Table 2. Anal. Found: C, 68.21; H, 7.42; N, 11.74. Calcd. for C_7H_9ON C, 67.76; H, 7.43; N, 11.57 %. (**V**) indicated a deep red color by $FeCl_3$ solution, and a deep green color by the Folin-Denis reagent. This melting point was identical with that of 2-ethyl-3-hydroxy-pyridine described by Dunlop (3), and Gruber (4). When the spectrum of (**V**) was compared with that of 2-methyl-3-hydroxy-pyridin, the former had the absorption bands of ethyl group at 1463 cm^{-1} and 1368 cm^{-1}, and also showed the hydroxyl group to be present in bonded form as shown in Fig. 3. Its picrate after recrystallizing from water had a melting point of 173–174°C, yellow needle. Anal. Found: N, 15.98 Calcd. for $C_{13}H_{12}O_8N_4$ N, 15.90 %.

8) 2-Ethyl-pyrrylketone (2-propionyl-pyrrole) (**VI**).

(**V**) was recrystallized from water, colorless needle, mp 52°C. Anal. Found C, 68.21; H, 7.31; N, 11.70 Calcd. for C_7H_9ON C, 67.76; H, 7.43; N, 11.57 %. This was identical with 2-ethyl-pyrrylketone reported by Oddo (11). The

spectrum of (**VI**) is shown in Fig. 4.

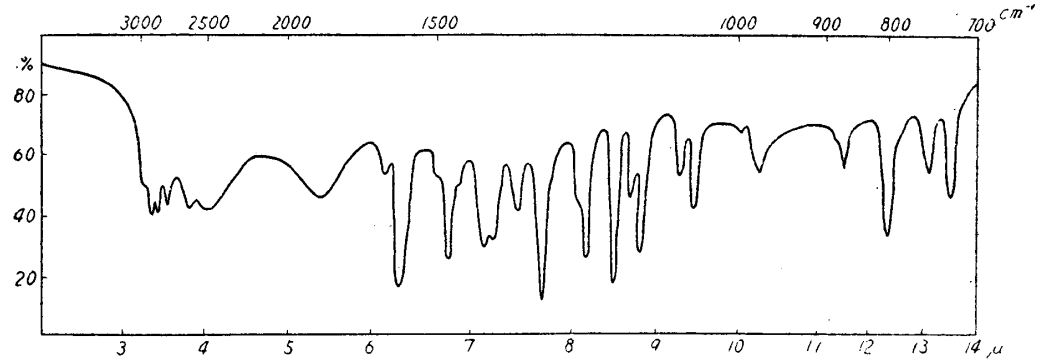


Fig. 3. The infrared spectrum of (**V**). (**D**).

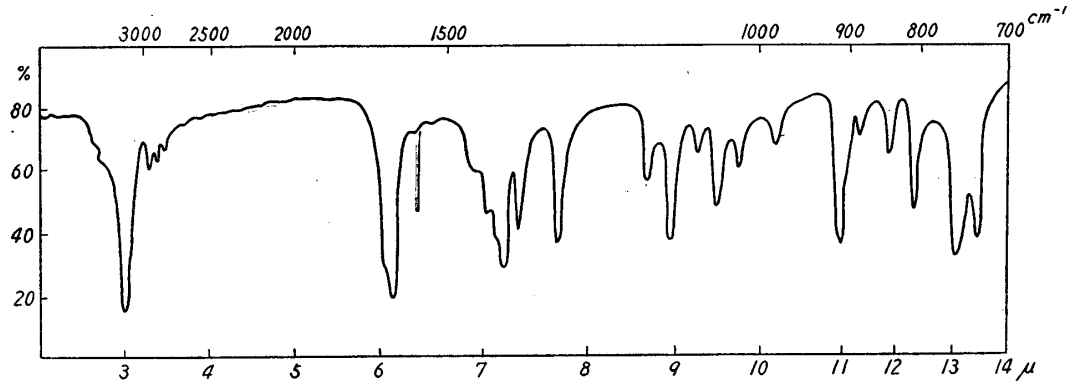


Fig. 4. The infrared spectrum of (**VI**).

III. The Infrared Spectrum of β-Hydroxy-pyridine Derivatives.

9) Infrared absorption spectrum. The spectrum was obtained with a Perkin-Elmer Model 21 spectrophotometer equipped with NaCl prism. 3-Hydroxy-pyridine (**A**) mp 127°C, 2,3-dihydroxy-pyridine (**B**) mp 248°C, 2-methyl-3-hydroxy-pyridine (**C**) mp 168°C, 2-ethyl-3-hydroxy-pyridine (**D**) mp 134°C, 2-methyl-5-hydroxy-pyridine (**E**) mp 167°C, 2-carboxyl-5-hydroxy-pyridine (**F**) mp 258°C, 2-methyl-3,6-dihydroxy-pyridine (**G**) mp 245°C, were prepared by the method (1, 2, 12, 13) described previously, and all these observations were made in KBr-disc, in addition, (**A**) was also measured in chloroform solution. The spectrum obtained are shown in the following. Absorption centres are given in cm^{-1}.

3-Hydroxy-pyridine (**A**) (14, 15). In KBr-disc: 3000, 2900, 2770, 2700, ca. 2500, 1870, ca. 1800, 1607, 1575, 1484, 1377, 1337, 1315, 1280, 1245, 1210, 1182, 1125, 1105, 1050, 1020, 975, 925, 913, 895, 847, 832, 805, 798, 703. In chloroform solution (0.4 *M*): 3600, 3050, 2960, 2560, 1800, 1585, 1480, 1460, 1370, 1315, 1280, 1250, 1195, 1120, 1103, 1050, 1020, 890; (0.02 *M*) 3595, 2980, 1582, 1460–1415 (bb), 1280, 1175, 1100.

2, 3-Dihydroxy-pyridine (**B**). In KBr-disc: 3380, 3160, 3100, 3040, 1680, 1655, 1620,

Fig. 5. The characteristic structure of β-hydroxy-pyridines.

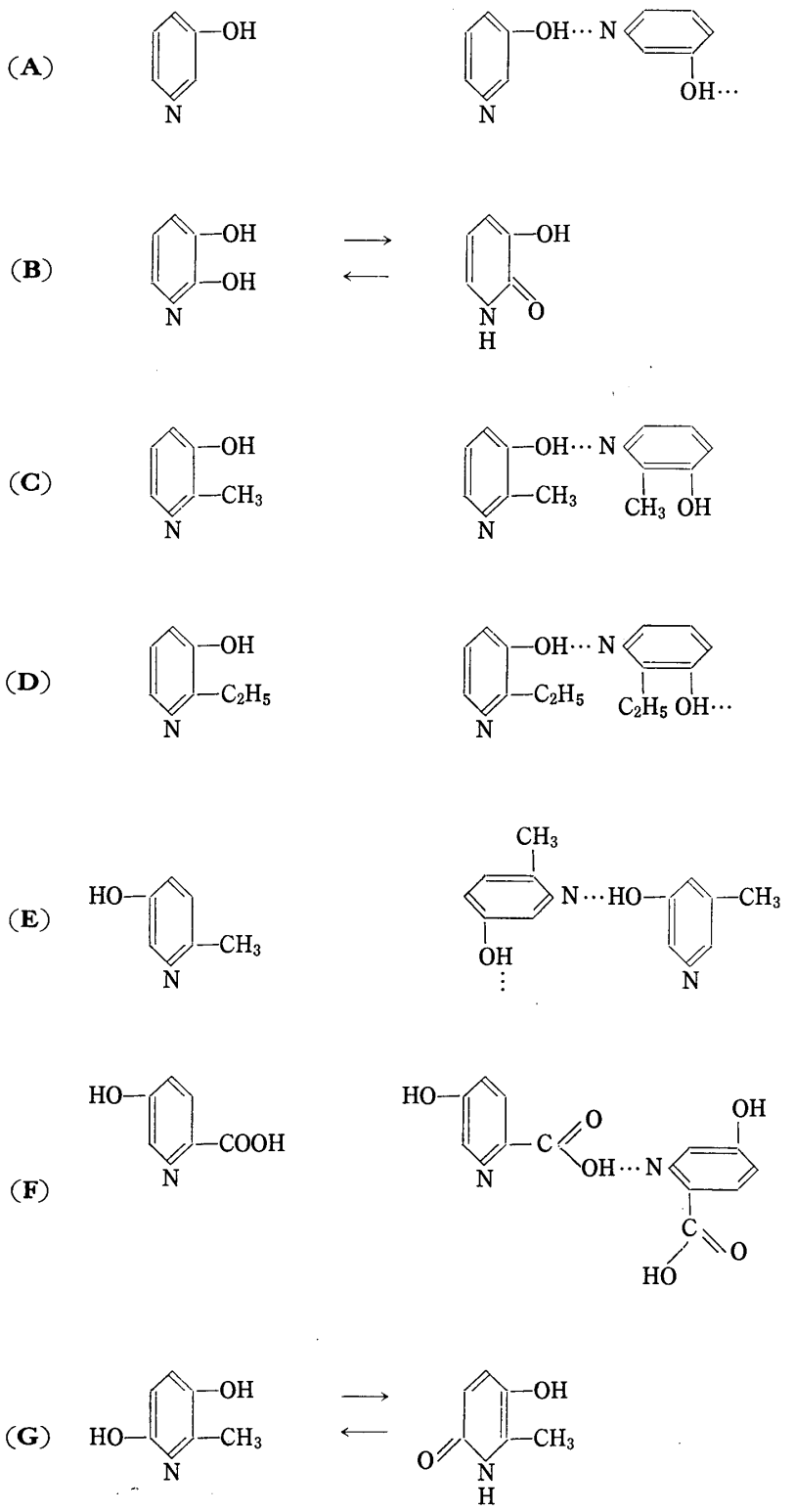


Table. 3. The relation between the absorption band and position of substituent.

Substituents	Absorption Centre cm^{-1}							
2-OH			1155s	1130sh				1008m
2-OCH_3			1140m			1044s		988m
2-CH_3			1147m			1049m		988w
2-C_2H_5			1150s			1050s		1000s
3-CH_3		1190w			1122w		1029m	
3-C_2H_5		1190m			1123m		1025m	
3-OH (A)		1182s			1125m		1020m	
3-OCH_3		1190m			1127w		1022m	
2-CH_3, 3-CH_3		1180w			1123m			990w
2-CH_3,3-OH (C)		1182s			1128s			988m
2-C_2H_5,3-OH (D)		1172s			1127s			970m
2-OH, 3-OH (B)		1187s		1135sh		1048s		
2-CH_3, 5-CH_3				1139w			1031m	
2-CH_3, 5-C_2H_5				1140m		1060w	1030m	
2-CH_3, 5-OH (E)	1224s			1133s		1045w	1031m	
2-COOH, 5-OH (F)	1230s	1175s		1132m		1065sh		1000w
2-CH_3, 3-CH_3, 6-CH_3				1130m			1025s	1000w
2-CH_3, 3-OH, 6-OH (G)	1233s	1174m			1120w		1025s	

Table 4. The chracteristic absorption band of β-hydroxy-pyridines.

H	Substituents	Absorption Centre cm^{-1}							
4	2-CH_3					749s			
	2-C_2H_5		810m			746s			
	2-OCH_3		810m		778s		735m		
	2-OH				781s		731m		
3	3-CH_3				782s			709s	
	3-C_2H_5		805s		780m			710s	
	3-OH (A)		805s	798s					703s
	2-CH_3, 3-CH_3				784s		715s		
	2-CH_3, 3-OH (C)			797s	762s		725s		
	2-CH_2H_5, 3-OH (D)			797m	763m		736s		
	2-OH, 3-OH (B)				780s	750s			690m
2	2-CH_3, 5-CH_3		814s					724s	
	2-CH_3, 5-OH (E)	826s		795w		751		721m	
	2-COOH, 5-OH (F)		809sh	800s					
	2-CH_3, 3-CH_3, 6-CH_3		814s				740m	730m	
	2-CH_3, 3-OH, 6-OH (G)	826s			787s				

w weak; m medium; s strong; sh shoulder; bb broad band.

1580, 1513, 1462, 1450, 1413, 1375, 1293, 1187, 1135, 1103, 1048, 917, 900, 845, 780. 750, 690.

2-Methyl-3-hydroxy-pyridine (**C**). 3050, 2920, 2810, 2606, 2450, 2160, 1820, 1602, 1580, 1500, 1465, 1392, 1377, 1355, 1285, 1236, 1182, 1165, 1128, 1068, 988, 872, 797, 762, 725.

2-Ethyl-3-hydroxy-pyridine (**D**). In KBr-disc: 3005, 2990, 2970, 2800, 2600, 2500, 1818, 1605, 1580, 1500, 1463, 1385, 1368, 1328, 1287, 1227, 1172, 1139, 1127, 1084, 1035, 970, 862, 797, 763, 736.

2-Methyl-5-hydroxy-pyridine (**E**). In KBr-disc: 2995, 2860, 2500, 1750, 1620, 1575, 1502, 1480, 1442, 1387, 1347, 1322, 1294, 1277, 1253, 1240, 1224, 1133, 1045, 1031, 990, 920, 863, 826, 795, 751, 721.

2-Carboxy-5-hydroxy-pyridine (**F**). In KBr-disc: 3400, 3080, 2900, 2480, 1775, 1675, 1633, 1590, 1550, 1490, 1385, 1340, 1313, 1275, 1230, 1175, 1132, 1065, 1000, 935, 887, 867, 809, 800, 682.

2-Methyl-3, 6-dihydroxy-pyridine (**G**). In KBr-disc: 3400, 3100, 2900, 2675, 1657, 1634, 1575, 1545, 1452, 1425, 1415, 1380, 1315, 1265, 1233, 1174, 1120, 1025, 940, 826, 787.

Result and Discussion

In solid state, (**A**) did not show an absorption band of an unbonded hydroxyl group stretching vibration near 3400–3500 cm^{-1} and showed two very broad bands at 2500 cm^{-1} and 1800 cm^{-1}, but in the spectrum of (**A**) in the chloroform solution there appeared the OH absorption band at 3600 cm^{-1} and the above broad bands at 2500 cm^{-1} and 1800 cm^{-1} disappeared. The spectrum of (**C**), (**D**) and (**E**) have shown the same band as that of (**A**) at 2500 cm^{-1} and 1800 cm^{-1}, and that of (**B**), (**F**) and (**G**) showed OH absorption band at 3400–3600 cm^{-1} and moreover the band of NH stretching vibration was shown at 3150–3300 cm^{-1}. The C=C and C=N vibration of the pyridine ring appears to occur in a very similar way to benzene, giving at 1650–1580 cm^{-1}, every compounds measured in this work have shown the absorption band of cyclic C=N at 1575–1580 cm^{-1}. (**B**) had the C=O band of lactam form at 1680 cm^{-1}, (**F**) had the C=O band of carboxylic form at 1675 cm^{-1}, (**G**) had the same band of lactam form as that of (**B**). In addition to the above bands, (**B**) and (**G**) showed the N–H deformation band at 1520~1540 cm^{-1}, and were indicative of the amido structure, and they have shown the keto-enol of tautomeric form as shown in Fig. 5.

In the region of ring vibration and in-plane vibration of C–H deformation, every compounds have shown a strong absorption band at 1370 cm^{-1}. Pyridine itself absorbed at 1375 cm^{-1} and various kinds of alkyl-pyridine also absorbed at the same region, so the absorption band near 1370 cm^{-1} may be a ring vibration of pyridine. (**C**), (**E**) and (**G**) showed the bands of the methyl

group in 1450–1465 range and near 1390 cm^{-1}, (**D**) has shown the bands of ethyl group at 1463 cm^{-1} and 1368 cm^{-1}. In this region, there is a reasonably close analogy between the absorption band of the substituted benzene and the position of the substituent. Cannon reported previously on their relationship in mono-substituted pyridines, but no precise remarkable data of di-substituted pyridines have been reported and the relation between the absorption band and the position of the substituent was not certain. However, it is thought that di-substituted pyridines have some regular relations in the absorption band as in mono-substituted pyridines. Shindo (16) and Bohon (17) reported on the spectrum of alkylpyridine derivatives, so the spectrum of these β-hydroxy-pyridines are compared with that of alkylpyridines, the reasonably close relation between the absorption band and the position of the substituent is evident from this work. The relations are listed in Table 3. α-Substituted pyridines had the absorption bands at 990–1000 cm^{-1} and 1045–1050 cm^{-1}, and β-substituted pyridines at 1020–1030, 1180–1190 cm^{-1} and 1220–1230 cm^{-1}. In addition, all the above compounds, α, β-disubstituted pyridines have shown the two absorption bands described above, for example, (**A**) has absorbed at 1182 cm^{-1} and 1020 cm^{-1}, (**C**) and (**D**) at 1172–1187 cm^{-1} and 970–988 cm^{-1}, (**E**) at 1224, 1045 and 1031 cm^{-1}.

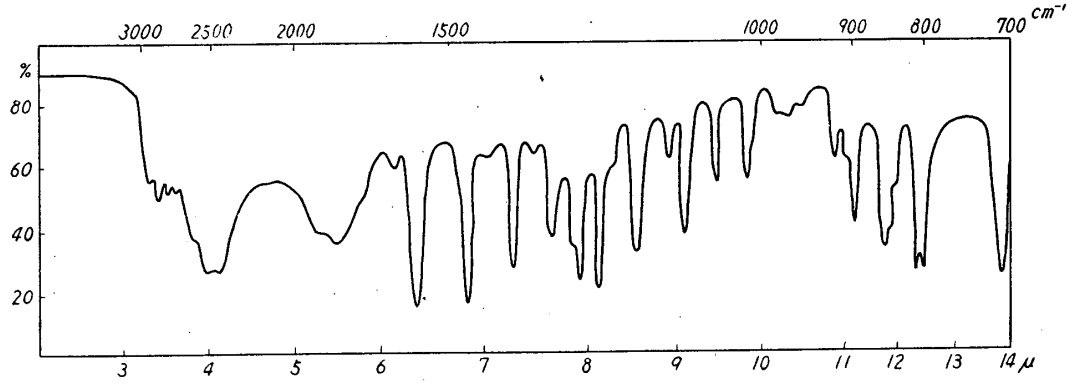


Fig. 6. The infrared spectrum of (**A**).

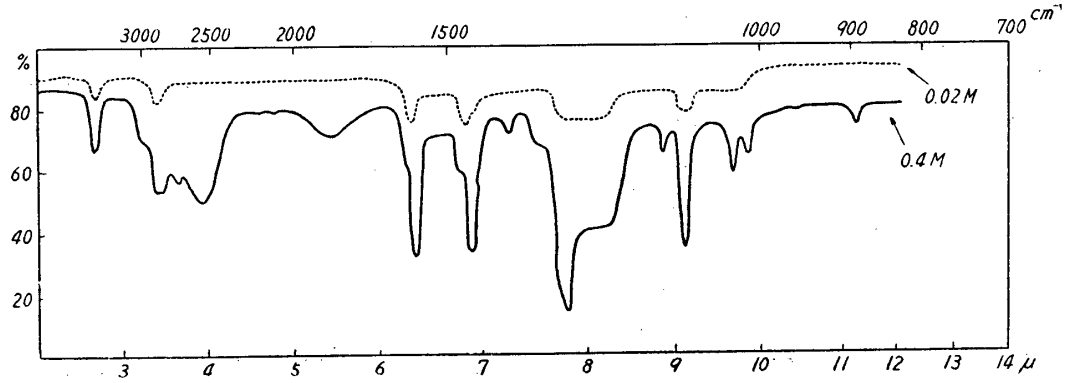


Fig. 7. The infrared spectrum of (**A**) in chloroform solution.

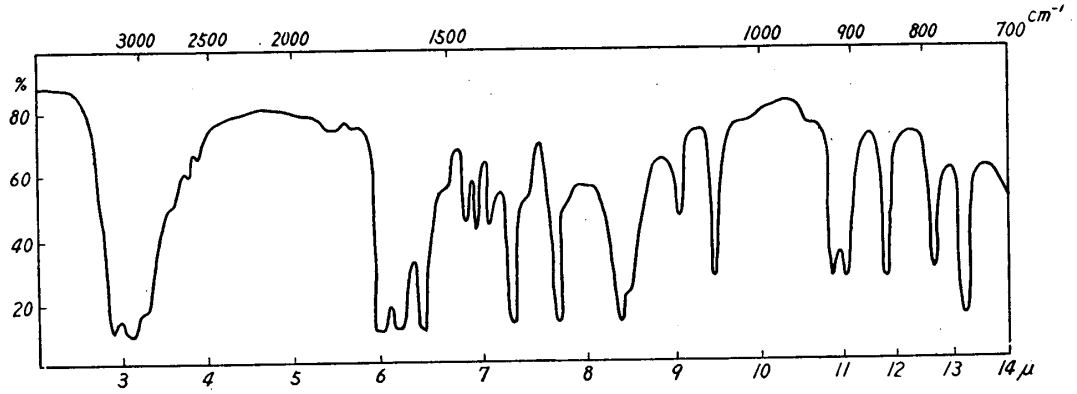


Fig. 8. The infrared spectrum of (B).

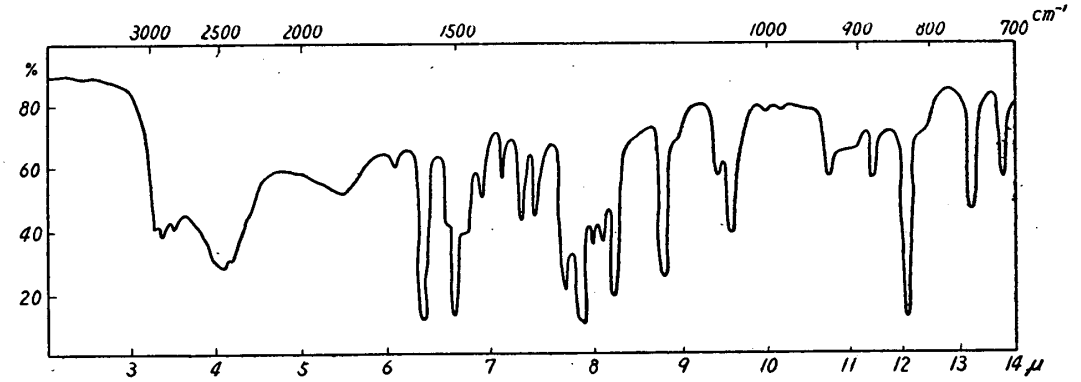


Fig. 9. The infrared spectrum of (**E**).

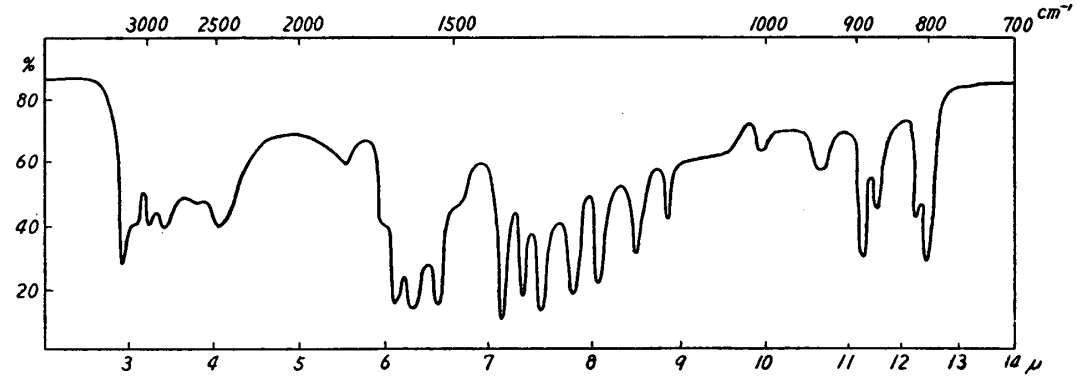


Fig. 10. The infrared spectrum of (**F**).

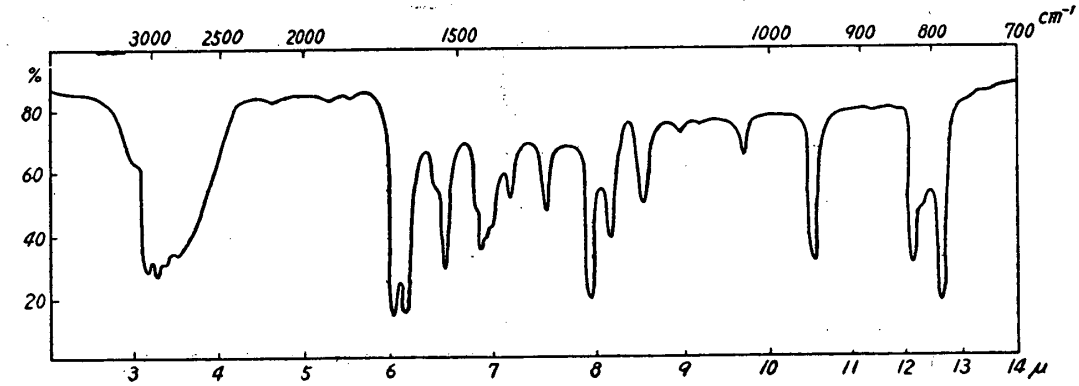


Fig. 11. The infrared spectrum of (G).

In general, aromatic compounds have the characteristic absorption band between 950 cm^{-1} and 650 cm^{-1} which C–H deformation occur, it has been shown in the case of substituted benzene that the strong band in this region originates in the out-plane vibration of unsubstituted hydrogen atoms of the ring, and that the principal factor determining the frequency is the number of such free hydrogen atoms which are adjacent to one another. A similar effect can be expected in pyridine derivatives, so that pyridine with five free hydrogen atoms is similar in this region to a mono-substituted benzene, and 3-hydroxy-pyridine having three free hydrogen atoms, for example, is similar to a meta-disubstituted benzene. (**B**), (**C**) and (**D**), which have three free hydrogen atoms, have shown the absorption band of 2,3-disubstituted compounds, (**E**) and (**F**) are also similar to para-disubstituted benzene. From the obtained data, this expectation has been realized in practice. The relations discussed are listed in the Table 4, moreover, it has been pointed out that α-hydroxy-pyridines measured in this work had the characteristic band at 780 cm^{-1}, and β-hydroxy-pyridine near 800 cm^{-1}.

Summary

There was obtained in good yield 2-methyl-3-hydroxy-pyridine and 2-acetylpyrrole by reacting 2-acetylfuran with ammonia at 180°C under several conditions as shown in Table 1, and also these compounds were obtained from the reaction of 2-acetylfuran with liquid ammonia by using ammonium chloride as a catalyst, 2-Ethyl-3-hydroxy-pyridine and 2-ethyl-pyrrylketone were obtained from 2-furyl-ethylketone by a similar reaction. The infrared spectrum of β-hydroxy-pyridines having the characteristic structure has been measured in solid state and solution, and the relation between structure and absorption band was discussed.

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