

**610.** *Synthetical Applications of Activated Metal Catalysts. Part VII.\*  
The Formation of 2,2'-Bipyridyl and 2-2'-Pyrrolylpyridine from  
Pyridine under the Influence of Degassed Raney Nickel.*

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A modified Raney nickel catalyst is described. Its action on pyridine under varied conditions is reported.

THE preparation of 2,2'-bipyridyl from pyridine by means of degassed Raney nickel<sup>1</sup> is complicated by the formation of a nickel(II) complex which contains 2,2'-bipyridyl and 2,2'-pyrrolylpyridine.<sup>2</sup> I now report some of the factors which influence the yields of these products. During this work it became necessary to alter the method of preparation of the catalyst as explosions occurred repeatedly during the degassing of the Raney

*Reaction between W7-J Raney Nickel Catalyst and Pyridine.*

No.	Time (hr.)	Pyridine (c.c.)	2,2'-Bipyridyl <sup>a</sup> (g.)	Complex <sup>b</sup> (g.)	Ratio <sup>c</sup>
1	6	250	12	0.3	2.5
2	11	250	20	0.5	2.5
3	21	250	27.5	1.2	4.4
4	46	250	30	1.5	5
5	70	250	30.5	1.8	5.9
6	187	250	30	4.0	7.5
7 <sup>d</sup>	46	250	26	2.5	9.6
8 <sup>d</sup>	53	225	3	0.8	37.5
9 <sup>d</sup>	49	250	22	2.0	9.1
10	22	89	18	1.7	9.5
11 <sup>e</sup>	28	89	3.2	0.38	11.9
12 <sup>e</sup>	27	89	3.6	0.44	12.2
13 <sup>e</sup>	27	42	1.5	0.5	33.3
14 <sup>f</sup>	44	250	26	2.5	9.6
15 <sup>d,f</sup>	46	250	4	0.005	0.125
16 <sup>g</sup>	—	150	5	0.04	0.8
17 <sup>g</sup>	—	150	16	0.8	5

Yields refer to about 1 g.-atom of nickel (prepared from 125 g. of 50 : 50 aluminium-nickel alloy).

<sup>a</sup> After chromatographic purification. <sup>b</sup> After washing with boiling light petroleum, b. p. 60—90°; dried *in vacuo*. <sup>c</sup> 100 × Weight of complex/Weight of 2,2'-bipyridyl. <sup>d</sup> Experiment with pyridine containing pyrrole. <sup>e</sup> Experiment with pyridine diluted with mesitylene. <sup>f</sup> Experiment in the presence of nickel(II) acetate. <sup>g</sup> Experiment by passing pyridine through a column packed with the catalyst.

nickel.<sup>3</sup> With the modified catalyst, named W7-J Raney nickel, the dimerisation of pyridine ceased after about 2 days, while the formation of the complex continued at an approximately constant rate for at least a week (see Table, Nos. 1—6). In the presence of a solvent the yields of both products were lower (compare No. 10 with Nos. 11, 12), but

Part VI, *J.*, 1959, 440.

<sup>1</sup> Badger and Sasse, *J.*, 1956, 616.

<sup>2</sup> Sargeson and Sasse, *Proc. Chem. Soc.*, 1958, 150.

<sup>3</sup> Cf. Smith, Chadwell, and Kirslis, *J. Phys. Chem.*, 1955, 59, 820.

the amount of complex formed relative to that of 2,2'-bipyridyl was slightly increased. A large proportion of nickel had a similar effect (Nos. 3, 10), particularly when the reaction was carried out in a solvent (Nos. 12, 13). The addition of either pyrrole (Nos. 7, 9) or nickel(II) acetate (No. 14) interfered with the dimerisation (cf. No. 4), and the yield of complex increased. Larger amounts of pyrrole (10%) (No. 8), or simultaneous addition of pyrrole and nickel(II) acetate, led to very much reduced yields of both products (No. 15). When the reaction was carried out by passing pyridine through a column packed with the catalyst, at 60–70°, the yield of the complex was more sensitive to changes in the rate of flow of the pyridine than was the formation of 2,2'-bipyridyl, and at higher rates of flow the dimerisation of pyridine could be carried out with a minimum of side reactions.

Traces of pyrrole were detected in the reaction mixture (see below), but no attempts were made to identify other pyrroles which may have been present in smaller amounts. The results obtained with W7-J Raney nickel show that the pyrrole which is formed in the reaction between the catalyst and pyridine interferes with the formation of 2,2'-bipyridyl, and as the addition of small quantities of pyrrole increases the yield of the complex (Nos. 7, 9), it seems likely that the 2,2'-pyrrolylpyridine is derived from a reaction involving pyrrole. The formation of pyrrole from pyridine under the conditions used in the present work is of interest, as earlier examples of the formation of pyrroles from pyridines during hydrogenations over nickel catalysts were observed at much higher temperatures.<sup>4</sup>

A Raney nickel catalyst which had been washed free from alkali gave the complex and 2,2'-bipyridyl in reduced yields, but in the same ratio as did the W7-J Raney nickel catalyst. When W7 Raney nickel was used no complex could be detected, and much less 2,2'-bipyridyl was isolated. However, colour tests indicated the presence of traces of pyrroles.

#### EXPERIMENTAL

*Preparation of W7-J Nickel Catalyst.*—Explosions occurred on several occasions during the degassing of the catalyst which had been prepared as described previously<sup>1</sup> from an aluminium-nickel alloy (50 : 50) with an average particle size of 4 $\mu$  (as determined with a Fisher subsieve sizer). However, this procedure could be safely used when seven non-return valves (of the type used in bicycle tubes) were incorporated in the vacuum-line close to the flask containing the nickel. Alternatively, the same alloy was satisfactory when the following modifications were adopted: The alloy was added to the aqueous solution of sodium hydroxide as described, but without external cooling. Then the catalyst was digested for 6 hr. at 100° while being gently stirred. After being kept at room temperature overnight, the nickel was washed and transferred to a three-necked round-bottomed flask (500 c.c.) equipped with a dropping funnel. This flask was connected to two 3-l. Buchner flasks which in turn were connected to two efficient water-pumps. All connections were made with short pieces of stout, large-bore rubber tubing (int. diam. 9 mm.; ext. diam. 15 mm.). After evacuation of the apparatus at room temperature, the flask containing the catalyst was slowly warmed so as to avoid losses of the nickel by vigorous boiling. After being kept at 100°/15–20 mm. for about 2 hr. the catalyst was ready for use. Pyridine was added through the dropping funnel to the cooled catalyst as previously described.

An aluminium-nickel alloy with an average particle size of 2.85  $\mu$  invariably lost hydrogen in an explosive fashion at about 80°/15–20 mm., but could be degassed with the use of non-return valves.

*Purification of Pyridine.*—Pyridine was fractionated through the column described before,<sup>5</sup> with a reflux ratio 1 : 10. When the b. p. reached 115°, anhydrous potassium hydroxide (10 g./100 c.c. of pyridine) was added. After 2 hours' heating under total reflux, fractionation (reflux ratio 1 : 10) was continued. Pyridine containing between 0.001 and 0.0001 vol.-% of pyrrole did not react with *p*-dimethylaminobenzaldehyde after this treatment. When higher concentrations of pyrrole were present the fractionation had to be repeated.

<sup>4</sup> Padoa, *Gazzetta*, 1908, **38**, 228; Granelli, *Farm. Ital.*, 1937, **5**, 708; Jones, *J.*, 1950, 1392; Jones and Lindsey, *J.*, 1952, 3261.

<sup>5</sup> Badger, Rodda, and Sasse, *J.*, 1954, 4162.

*Pyridine and W7-J Nickel Catalyst.*—With the exception of two experiments (see Table, Nos. 16, 17) all reactions were carried out by refluxing pyridine over the catalyst (in every case prepared from 125 g. of 50 : 50 aluminium–nickel alloy). The products were isolated in the way described,<sup>1</sup> and the results are summarised in the Table. The following experiments were carried out with pyridine in the presence of other compounds.

No. 7. Pyrrole was added in four portions (1 c.c. each) at intervals of 9 hr., beginning 15 min. after the reaction had been started with pyridine (250 c.c.).

No. 8. Pyrrole (25 c.c.) in pyridine (225 c.c.) was used.

No. 9. Pyridine (250 c.c.; b. p. 115°), recovered from experiment No. 3 by distillation, was used.

No. 11. Pyridine (89 c.c.) and mesitylene (89 c.c.) were used.

No. 12. Pyridine (89 c.c.) and mesitylene (267 c.c.) were used.

No. 13. Pyridine (42 c.c.) and mesitylene (126 c.c.) were used.

No. 14. A solution of nickel(II) acetate (3 g.) in pyridine (30 c.c.) was added in portions (10 c.c.) at intervals of 12 hr., beginning 1 hr. after reaction had been started with pyridine (250 c.c.).

No. 15. Pyrrole (1 c.c.) was added 1 hr. after reaction had been started with pyridine (250 c.c.). One hr. later, nickel(II) acetate (1 g.) in pyridine (10 c.c.) was added.

No. 16. After having been degassed, the catalyst was wetted with pyridine (100 c.c.) and packed into a column (ext. diam. 2 cm.), placed in a heating jacket, and the temperature kept at 60–70° while pyridine (150 c.c./hr.) was passed through it for 1 hr.

No. 17. The apparatus and conditions of experiment No. 16 were used, except for a rate of flow of 50 c.c./hr. of pyridine for 3 hr.

*Detection of Pyrrole in Pyridine.*—(a) Pyridine (0.1 c.c.) was diluted with water (0.5 c.c.). Concentrated hydrochloric acid (0.5 c.c.) was added, followed by a 5% solution (0.1 c.c.) of *p*-dimethylaminobenzaldehyde in aqueous 1.3*N*-hydrochloric acid.<sup>6</sup> In the presence of pyrrole a purple-red colour was produced (lower limit 0.0001 vol.-% of pyrrole in pyridine).

(b) Other reagents which were used for the detection of pyrrole included: isatin and concentrated sulphuric acid<sup>7</sup> (deep blue colour; lower limit 0.01 vol.-%); selenium dioxide and concentrated nitric acid<sup>7</sup> (deep purple colour; lower limit 0.1 vol.-%); phenyldiazonium chloride and aqueous sodium carbonate solution<sup>8</sup> (bright red precipitate; lower limit 0.01 vol.-%).

(c) Detection of pyrrole in pyridine by paper chromatography was difficult because of the volatility of the mixture. However, by the addition of picric acid to the spots of the mixture on Whatman paper No. 1 the picrates of the components were produced which were then developed by ascent with 2% aqueous acetic acid. The picrate of pyridine streaked, probably because of partial dissociation ( $R_F$  0.23–0.81). The picrate of pyrrole dissociated readily to give picric acid ( $R_F$  0.81) and pyrrole ( $R_F$  0.95). The latter was made visible by exposure of the paper to iodine vapour.

(d) Gas–liquid partition chromatography was used for the identification and estimation of pyrrole. A Griffin V.P.C. apparatus Mk II was used with a four ft. column packed with Celite (40–80 mesh; 20% Apiezon L). At 150° the retention times observed were for pyridine, 2.18 min., and for pyrrole, 1.71 min. (outlet pressure 139 mm.; inlet pressure 333 mm.; flow rate 1.41./hr. of nitrogen; bridge current 133 milliamp.). From the peak areas the approximate composition of the mixture could be measured.

(e) As described by Densham, Langston, and Gough,<sup>9</sup> examination of the infrared spectra of mixtures of pyridine and pyrrole in the region 9–10  $\mu$  gave results comparable with those obtained by gas-phase chromatography.

*Detection of Pyrrole in the Reaction between Pyridine and W7-J Nickel.*—Pyrrole was detected in each experiment which was conducted with pyrrole-free pyridine (see Table, Nos. 1–6, 10–14) within 5–8 min. from the beginning of refluxing, by means of *p*-dimethylaminobenzaldehyde. After 24 hr. (Nos. 4–6, 10–14) all other tests described confirmed the presence of pyrrole. Gas–liquid chromatography and infrared spectra showed the presence of pyrrole

<sup>6</sup> Fischer and Nenitzescu, *Z. physiol. Chem.*, 1925, **145**, 295.

<sup>7</sup> Fischer and Orth, "Die Chemie des Pyrrols," Vol. I, p. 25, Akademische Verlagsgesellschaft, Leipzig, 1934.

<sup>8</sup> Fischer and Hepp, *Ber.*, 1886, **19**, 2251.

<sup>9</sup> Densham, Langston, and Gough, *J.*, 1952, 2433.

after refluxing had been continued for 5 days (No. 6). After one week part of the pyridine (No. 6) was removed by filtration without dilution with fresh pyridine; after distillation from a water-bath at 20 mm. (to remove complex and 2,2'-bipyridyl), it contained  $1 \pm 0.2$  vol.-% as determined by the last-mentioned methods (checked against standard mixtures).

Nos. 16, 17. When the temperature of the column had reached 60° pyrrole was detected by means of *p*-dimethylaminobenzaldehyde in the pyridine which had been passed through the column.

*Experiments with Other Raney Nickel Catalysts.*—The conditions of experiment No. 4 (see Table) were used throughout.

(a) Neutral degassed Raney nickel was prepared by adding the alloy to the aqueous solution of sodium hydroxide in the usual way. The catalyst was then washed with distilled water (about 10 l.) until the washings were neutral and degassed as described above. This catalyst gave 2,2'-bipyridyl (24 g.) and complex (1.25 g.), equal to 5.2% of the weight of 2,2'-bipyridyl obtained.

(b) W7 Raney nickel<sup>10</sup> was freed from water with methanol and three times washed by decantation with pyridine (3 × 75 c.c.). 2,2'-Bipyridyl (3.6 g.) was obtained but no complex was isolated. Pyrrole was detected in the recovered pyridine by means of *p*-dimethylaminobenzaldehyde.

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<sup>10</sup> Billica and Adkins, *Org. Synth.*, 1949, **29**, 24.

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