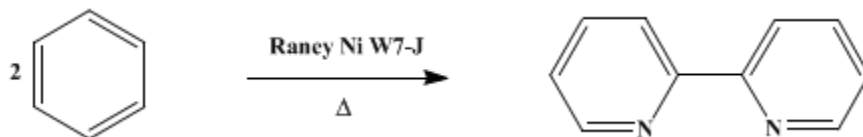


2,2'-BIPYRIDINE



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1. Procedure

A. Degassed Raney nickel catalyst (W7-J). *Caution! Raney nickel catalysts which have been prepared by the usual methods should not be heated in vacuum, as large quantities of heat and hydrogen may be given off suddenly, and dangerous explosions may result.*^{2,3}

In a hood a 2-l., wide-mouthed Erlenmeyer flask containing 600 ml. of distilled water is placed in an empty water bath and fitted with an efficient stainless steel stirrer, so that its blades are half immersed. The stirrer is started, and 160 g. of sodium hydroxide is dissolved in the water. Then 125 g. of 1:1 aluminum-nickel alloy (Note 1) is added in portions as rapidly as possible, but at such a rate that no material is lost by frothing with the stirrer running at full speed (Note 2). When all the alloy has been added the stirrer is slowed down, and the catalyst is washed down from the sides of the flask with distilled water. As soon as the reaction has subsided the water bath is filled with boiling water, and the catalyst is slowly stirred while the volume is kept up by the occasional addition of distilled water so that the catalyst is well covered at all times. After 6 hours, stirring and heating are discontinued, and the catalyst is allowed to stand at room temperature for 12–15 hours. It is then washed by decantation with ten 250-ml. portions of distilled water and transferred to a 1-l., round-bottomed, three-necked flask by means of distilled water. The total volume of catalyst and water is adjusted to 300 ml., and the flask placed in a cold water bath which is equipped with a thermometer. One side arm is fitted with a 100-ml. dropping funnel, and the other two necks are each connected to a 3-l. Büchner flask by short lengths of thick-walled, wide-bore rubber tubing (Note 3), (Note 4). One of the Büchner flasks is connected to a vacuum gauge and then to an efficient water pump. The other Büchner flask is connected directly to a second, equally efficient water pump. To control the pressure inside the apparatus, a screw clamp is placed between each Büchner flask and each pump (Note 5). With these clamps completely closed both pumps are turned on fully. The pressure inside the apparatus is now gradually reduced by opening the clamps at such a rate that no excessive frothing occurs. When both clamps are fully open, the water bath is heated slowly until the water in the reaction flask begins to boil. The bath is kept at this temperature until there is no more water left in the flask (Note 6). Then, with both clamps fully opened, the temperature of the water bath is raised to 100° during 15–20 minutes and kept at this temperature for 2 hours. After this time the catalyst is allowed to cool to 50–60°; it is now ready for use.

B. 2,2'-Bipyridine. With the apparatus set as described above, 100 ml. of pure pyridine (Note 7) is poured into the dropping funnel, and the screw clamps are completely closed. Immediately afterward about 80 ml. of the pyridine is run slowly onto the catalyst from the dropping funnel. Under no circumstances is any air allowed to enter the flask. The flask is then shaken carefully in order to wet the catalyst as much as possible with pyridine. Another 80 ml. of pyridine is added in the same way, and the flask is shaken again. Finally 40 ml. of pyridine is added, and air is allowed to enter the flask. The connections to the Büchner flask are removed, and a reflux condenser is fitted. The reaction mixture is then boiled gently under reflux (Note 8). After about 48 hours the flask is allowed to cool to about 60°, and most of the liquid is decanted (*Hood!*) and filtered through a sintered-glass funnel (Note 9) into a 500-ml. round-bottomed flask. Then 50 ml. of fresh pyridine is added to the catalyst in the reaction flask, and the mixture is heated to reflux for 10 minutes. The flask contents are allowed to cool to about 60° and the pyridine is decanted and filtered as before. This extraction is repeated two more times. The flask containing the filtrates is then equipped for vacuum distillation (Note 10), and most of the pyridine is removed on a water bath under reduced pressure (20–30 mm.) at a bath temperature not exceeding

40°. Toward the end of the distillation the bath temperature is raised to about 75° for 10 minutes (Note 11). The residue from this distillation is extracted with 100 ml. of boiling petroleum ether (Note 12), and the insoluble cream-colored material is collected by filtration and washed with three 25-ml. portions of the boiling petroleum ether (Note 13). The filtrate is chromatographed over alumina (Note 14) using petroleum ether (60–90°) for elution. The first 2 l. of eluate is collected, concentrated to 100 ml., and allowed to stand overnight in a refrigerator. The crude solid (23–24 g.) is collected and recrystallized from about 80 ml. of petroleum ether (60–90°) to give 21.0 g. of 2,2'-bipyridine as white crystals, m.p. 70–71° (Note 15), (Note 16).

2. Notes

1. The nickel-aluminum alloy used was supplied by British Drug Houses (through the Ealing Corporation in the U.S.A.). Average particle size was about 4 μ as measured by a Fisher Sub-sieve Sizer. Alloys of a finer particle size (about 2.85 μ) gave rise to considerable loss of catalyst during the washing and lost hydrogen during the degassing procedure in a much more vigorous fashion.
2. With a motor running at approximately 3500–4500 r.p.m. the addition of the alloy is completed in less than 10 minutes. Alcohol should not be added to the catalyst to control the frothing.
3. The Büchner flasks are included in the apparatus to accommodate relatively large quantities of hydrogen which are sometimes given off suddenly by the catalyst during the later stages of the degassing. Instead of Büchner flasks, strong round-bottomed flasks may be used.
4. Rubber tubing with diameters of 9 mm. I.D. and 17 mm. O.D. was used.
5. An air leak cannot be employed to regulate the vacuum inside the reaction flask since the catalyst becomes increasingly pyrophoric as the degassing progresses.
6. The average time required for the complete removal of the water from the catalyst varies from 4 to 12 hours. It is essential to evaporate the water slowly since much nickel may be lost if the water boils too vigorously. If the temperature of the bath should rise too high, the screw clamps are closed far enough to increase the pressure slightly in the apparatus. As soon as the bath has cooled to the required temperature, the clamps are reopened fully. The maximum practical temperature for the removal of the water was found to be 25–30° at pressures between 17 and 20 mm.
7. The pyridine used must be free of pyrrole since as little as 0.001% of pyrrole will markedly decrease the yield. The checkers found it most satisfactory to use spectroquality pyridine supplied by Matheson, Coleman and Bell. The submitters purified their pyridine by distillation from potassium hydroxide. To test for the presence of pyrrole, a 0.5-ml. sample of pyridine is diluted with 2.5 ml. of water, and 2 ml. of concentrated hydrochloric acid is added followed by 0.5 ml. of a 5% solution of *p*-dimethylaminobenzaldehyde in dilute hydrochloric acid (1:10 dilution of concentrated hydrochloric acid). If pyrrole is present, a red-purple color appears. Spectroquality pyridine gives a negative result in this test.
8. Excessive bumping will occur if the reaction mixture is heated too strongly.
9. A sintered-glass funnel (diameter 9 cm.) of medium porosity was used. The filtration is conveniently carried out under slightly reduced pressure, but care must be taken to keep any nickel on the funnel damp, as the catalyst is highly pyrophoric.
10. A relatively wide capillary (about 0.5 mm. I.D.) should be used to avoid blockages toward the end of the distillation.
11. The distillate contains, besides pyridine, small quantities of pyrrole, water, and 2,2'-bipyridine.
12. A petroleum fraction, b.p. 60–90° containing 5% of aromatics, was used throughout.
13. The petroleum-insoluble material is a nickel (II) complex containing 2,2'-bipyridine and 2,2'-pyrrolylpyridine.⁴ About 1.5 g. of this compound is obtained.
14. The checkers used No. 2 grade neutral alumina (Woelm) in a column 3.5 \times 20 cm. If a more active alumina is used, larger quantities of petroleum ether are needed for the elution.
15. Small quantities of 2,2',2''-tripyridine are removed by this recrystallization.
16. Similarly 3- and 4-alkylpyridines give the corresponding 5,5'-dialkyl-2,2'-bipyridines and 4,4'-dialkyl-2,2'-bipyridines, respectively, in good yield when treated with W7-J nickel.⁵ Somewhat lower yields of 2,2'-biquinolines are obtained with quinolines.^{6,7}

3. Discussion

2,2'-Bipyridine has been prepared by the action of ferric chloride,^{8,9} iodine,¹⁰ or a nickel-alumina

catalyst¹⁰ on [pyridine](#) at temperatures ranging from 300° to 400°. It has also been obtained from the reaction of [2-bromopyridine](#) and [copper](#).¹¹ The present procedure is a modification of a previously published, general method.³ The W7-J nickel catalyst was developed from the description of the W7 Raney nickel catalyst of Billica and Adkins.¹²

4. Merits of the Preparation

This procedure serves two purposes. It provides a synthesis for the important chelating reagent [2,2'-bipyridine](#), a substance of interest in several fields of chemistry, and it gives a preparation of an active, degassed [Raney nickel](#) catalyst.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 468](#)

References and Notes

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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alumina

petroleum ether

2,2',2''-tripyridine

W7-J nickel

2,2'-biquinolines

nickel-alumina

W7 Raney nickel

alcohol (64-17-5)

hydrochloric acid (7647-01-0)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

copper (7440-50-8)

nickel,
Raney nickel (7440-02-0)

iodine (7553-56-2)

pyridine (110-86-1)

potassium hydroxide (1310-58-3)

ferric chloride (7705-08-0)

Pyrrole (109-97-7)

2-Bromopyridine (109-04-6)

nickel-aluminum,
aluminum-nickel

nickel (II)

p-Dimethylaminobenzaldehyde (100-10-7)

2,2'-Bipyridine (366-18-7)

2,2'-pyrrolylpyridine