

SYNTHETICAL APPLICATIONS OF ACTIVATED METAL CATALYSTS

XVIII. THE FORMATION OF 2,2',5',2''-TERPYRIDYL IN THE REACTION OF PYRIDINE WITH DEGASSED RANEY NICKEL

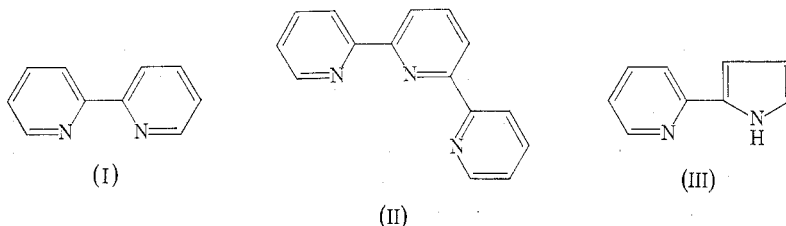
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[Manuscript received October 3, 1962]

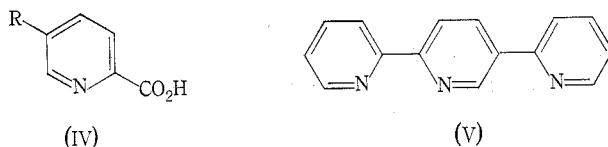
Summary

2,2',5',2''-Terpyridyl has been isolated in c. 0.1% yield from the reaction between pyridine and degassed Raney nickel. The structure of this terpyridine has been proved by degradation to picolinic acid and isocinchomeronic acid.

In the reaction of pyridine with degassed Raney nickel two products other than 2,2'-bipyridyl (I) have been identified previously. One of these is 2,2',6',2''-terpyridyl (II) which is present in the crude 2,2'-bipyridyl isolated from the reaction to the extent of about 1% (Badger and Sasse 1956). The other by-product is a nickel(II) complex containing two molecules of 2,2'-pyrrolylpyridine (III) and one molecule of 2,2'-bipyridyl for each nickel(II) ion (Sargeson and Sasse 1958). The yield of this compound amounts to about 5% of the weight of 2,2'-bipyridyl isolated (after 50 hr, using initially pyrrole-free pyridine), and some of the factors affecting the formation of this complex are known (Sasse 1959).

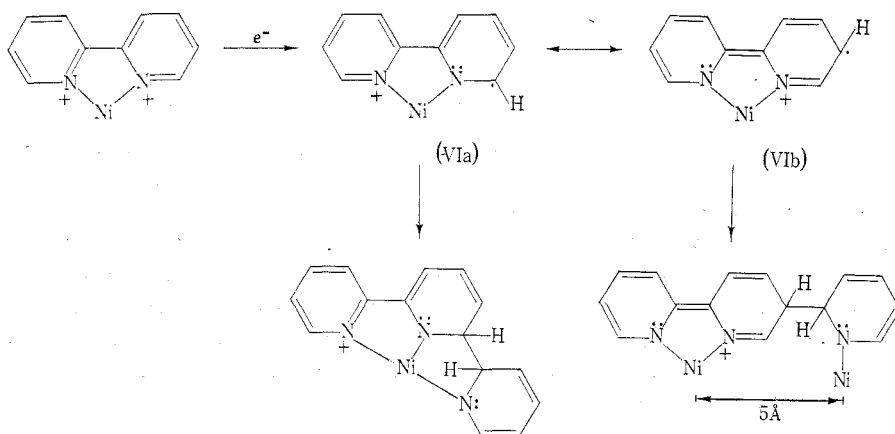


The present paper deals with another terpyridyl, m.p. 156–157.5°C, which forms a red chelate compound with ferrous ions and is present in the crude 2,2'-bipyridyl to the extent of about 0.1%. It has now been found that oxidation of this base by aqueous potassium permanganate according to Kuffner and Faderl (1956) yields picolinic acid (IV; R = H) and isocinchomeronic acid (IV; R = COOH). These acids were identified by paper chromatography using several solvent systems also developed by Kuffner and Faderl (1955). Comparison of the ultraviolet spectrum of the new terpyridyl with that of 2,2',6',2''-terpyridyl (II) reveals enhanced adsorption at longer wavelengths. On the basis of these facts, the new base is suggested to be 2,2',5',2''-terpyridyl (V).

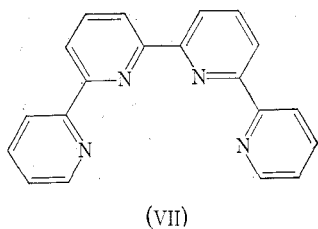


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The formation of this base as well as of the isomeric 2,2',6',2"-terpyridyl (II) probably involves as the first step the chemisorption of 2,2'-bipyridyl to the catalyst, and in the following it is assumed that both nitrogen atoms are attached to one nickel atom. Transfer of one electron from the catalyst to the bonded 2,2'-bipyridyl in the way previously discussed for pyridine (Sasse and Whittle 1963) will result in the formation of a hybrid radical, two contributing structures of which are shown (VIa) and (VIb). Provided a similarly activated molecule of pyridine is available, carbon-carbon bond formation should occur to give a dihydroterpyridyl.



The structure of the resulting terpyridyl will depend on the distance between the nickel atoms to which the component bases were initially bonded, and models suggest that the formation of 2,2',5',2"-terpyridyl is possible only if this distance is close to 5 Å. This corresponds to twice the shortest distance between nickel atoms in W6 Raney nickel (Kokes and Emmett 1959). Similarly, the formation of 2,2',6',2"-terpyridyl appears to be possible only when pyridine and 2,2'-bipyridyl are chemisorbed on the same nickel atom, or less likely, on adjacent ones. The low yield of the 2,2',5',2"-isomer suggests that pairs of nickel atoms separated by 5 Å are only rarely available on the surface of the catalyst.



and this may be surprising because of the mechanism discussed above. However, if 2,2'-bipyridyl is in fact bonded by both nitrogen atoms to the catalyst, rotation around the nickel-nitrogen bonds is impossible, in contrast to simple pyridine derivatives (Sasse and Whittle 1961). This implies that the formation of the quaterpyridyl (VII) from two molecules of 2,2'-bipyridyl can occur only when these are

In the present work traces of two other compounds (m.p. 189–191°C and 239·5–240·5°C respectively) have been isolated. Both bases appear to be derivatives of 2,2'-bipyridyl as they form red chelate compounds with ferrous ions, and their R_F values suggest that they contain three or more pyridyl groups. Neither of these compounds appears to be identical with 2,2',6',2'',6'',2'''-quaterpyridyl (VII), m.p. 219–220°C (Burstall 1938),

adsorbed on the catalyst "end-to-end" in an almost collinear configuration, an arrangement which should only rarely be achieved.

EXPERIMENTAL

(a) *General*.—Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Melting points are uncorrected. Ultraviolet spectra were determined using an Optica CF4 recording spectrophotometer. Unless otherwise stated solvent petroleum was a fraction, b.p. 60–90°C. For the paper chromatography of the polypyridyls the solvent n-butanol–concentrated hydrochloric acid–water (8:2:6) was used. The paper chromatography of the pyridine acids was carried out using solvent systems described by Kuffner and Faderl (1955).

(b) *Separation of the Polypyridyls*.—Crude 2,2'-bipyridyl (500 g) as obtained from the reaction of pyridine with W7-J Raney nickel (Sasse 1959) was distilled to give the fractions (a) b.p. 146–147°C/25 mm (404.5 g); (b) 147–151°C/25 mm (48.5 g); (c) b.p. 151–157°C/25 mm (8 g); (d) b.p. 157–159°C/25 mm (7 g); residue (25 g). Paper chromatography revealed the presence of 2,2'-bipyridyl (R_F 0.46) in fractions (a)–(d), and the presence of 2,2',6',2''-terpyridyl (R_F 0.14) in fractions (b), (c), and (d). The residue of the distillation was extracted with boiling petroleum and the soluble part (23 g) was passed through a column of alumina. Elution with petroleum and petroleum–ethanol gave mixtures containing 2,2',6',2''-terpyridyl and small quantities of 2,2'-bipyridyl. Elution with ethanol gave a fraction (2.5 g) which was rechromatographed on alumina (Spence; 75 g). Fractions (100 ml) were taken as follows; (1)–(3) petroleum b.p. 40–70°C; (3)–(11) petroleum, (12)–(15) petroleum–benzene, 3:1; (17–20) petroleum–benzene, 1:1; (21)–(23) petroleum–benzene, 1:2; (24–36) benzene; (37)–(39) benzene–ethanol, 1:1 (40)–(42) ethanol. Fractions (12) and (13) contained traces of 2,2'-bipyridyl and 2,2',6',2''-terpyridyl; (15)–(23) contained 2,2',5',2''-terpyridyl, (0.585 g) which crystallized from benzene in colourless needles, m.p. 156–157.5°C (R_F 0.12) (Found: C, 77.2; H, 4.8; N, 17.8%; mol.wt.(Rast), 238. Calc. for $C_{15}H_{11}N_3$: C, 77.2; H, 4.7; N, 18.0%; mol.wt., 233). The u.v. spectrum of this base has maxima at 254.5 and 305.5 $m\mu$ (ϵ 11,400 and 35,000), while 2,2',6',2''-terpyridyl has maxima at 235.5 and 281.5 $m\mu$ (ϵ 15,000 and 15,300).

Fractions (26)–(27) gave a base, m.p. 189–191°C, R_F 0.078, trace 0.055 (0.011 g), and fractions (28)–(30) yielded a base, m.p. 239.5–240.5°C, R_F 0.055, (0.010 g). These two compounds gave deep red coloured chelates when treated with ferrous ions.

(c) *Oxidation of 2,2',5',2''-Terpyridyl*.—This was carried out using the recrystallized base (0.025 g) and 4% aq. $KMnO_4$ soln. (6.25 ml) according to Kuffner and Faderl (1956). The resulting mixture was examined by paper chromatography on Whatman No. 1 paper using the solvent systems A7, B3, C6, and D5 of Kuffner and Faderl (1955). Using authentic specimens for comparison picolinic acid, R_F 0.47 (A7), 0.19 (B3), 0.38 (C6), 0.52 (D5) and isocinchomeric acid, R_F 0.20 (A7), 0.35 (B3), 0.03 (C6), 0.09 (D5) were identified.

ACKNOWLEDGMENTS

The authors thank Professor G. M. Badger for his interest in this work. This research was supported by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

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