259. *Synthetical Applications of Activated Metal Catalysts. Part XII.*[1] *The Preparation of Symmetrically Substituted 2,2′-Bipyridyls.*

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The action of W7-J Raney nickel catalyst on ten substituted pyridines has been examined. 3- and 4-Alkyl groups facilitate the formation of 2,2′-bipyridyls, but electron-attracting groups in these positions or 2-methyl groups have the opposite effect. The structures of 2,2′-bipyridyls derived from 3-substituted pyridines are discussed.

The formation of some disubstituted 2,2′-bipyridyls from monosubstituted pyridines under the influence of a degassed Raney nickel catalyst has been described earlier.[2] In view of the potential value of substituted 2,2′-bipyridyls as chelating agents, this work has been repeated and extended.

When refluxed over W7-J Raney nickel, β-picoline, γ-picoline, β-collidine, and 4-ethylpyridine gave biaryls in higher yields than did pyridine itself.[3] This finding agrees with

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[1] Part XI, Badger, Jackson, and Sasse, *J.*, 1960. 4438.

[2] Badger and Sasse, *J.*, 1956, 616.

[3] Sasse, *J.*, 1959, 3046.

the view that chemisorption of the simple pyridines on the catalyst precedes dimerisation,[2] as an increase in basicity will facilitate chemisorption.[4] The yields of the biaryls from the higher-boiling 4-phenylpyridine and β-collidine were higher in reactions under reduced pressure (reflux temperature, about 140°), an effect also observed in the quinoline series where secondary reactions of the biaryls occur at higher temperatures.[5] Although the yield of the diester obtained previously from ethyl nicotinate could be improved by working without a solvent and under reduced pressure, less than one-third of the quantity of biaryl obtainable from pyridine itself was isolated. 5-Benzoylpyridine (in boiling xylene) gave only traces of the bipyridyl, and no biaryl was obtained from ethyl isonicotinate, probably owing to the decreased basicity of these pyridine derivatives. The inhibiting effect of a 2-methyl group has been noted earlier,[2] but it has now been found that the small quantities of the biaryls derived from α-picoline and 2,4-lutidine are accompanied by traces of bipyridyls which do not contain 6,6′-methyl groups as they give stable iron(II) chelate compounds [6] (see Experimental part). Similarly, γ-collidine reacted under forcing conditions, to give a complex mixture from which 2,4-lutidine was separated by gas–liquid chromatography. The elimination of methyl groups from positions adjacent to the nitrogen atom occurs also in the quinoline series.[5]

All the biaryls obtained during the present work form chelate compounds with either ferrous or cuprous ions, and are therefore considered to be derivatives of 2,2′-bipyridyl. Structural ambiguities can arise only with 3-substituted pyridines which may be expected to give as many as three disubstituted 2,2′-bipyridyls. However, in each of the four cases examined, only one isomer could be detected. Of the three dimethyl-2,2′-bipyridyls which can be derived from β-picoline, the 3,5′-isomer appears to be unknown. 3,3′-Dimethyl-2,2′-bipyridyl was reported by Case to be a liquid [7] which forms a labile iron(II) chelate compound ($\lambda_{\max}$ at 526 mμ).[8] Case also prepared the 5,5′-isomer by two different routes but he did not disclose its properties; [7] however, Cagle and Smith [8] determined the absorption maximum of its iron(II) complex (at 510 mμ), and Case converted this base into dimethyl 2,2′-bipyridyl-5,5′-dicarboxylate. Our dimethyl-2,2′-bipyridyl also had these properties and is therefore regarded as the 5,5′-dimethyl isomer. Moreover, the acid obtained from it by oxidation is now found to be identical with that isolated from the reaction with nicotinic acid or its ethyl ester, thus confirming the structure suggested earlier.[2] Comparison of the ultraviolet spectra of these bipyridyls with the spectra of corresponding biphenyls supports this assignment (see Experimental part). Substitution in the 5,5′-positions is similarly indicated for the 2,2′-bipyridyls obtained from 3-benzoylpyridine and β-collidine. This substitution pattern is expected to be preferred for steric reasons, provided that there is some freedom for rotation around the nickel–nitrogen bonds in the adsorbed species.[5] The biaryls obtained from γ-picoline and β-collidine were further characterised by the preparation of bis-styryl derivatives.

Except for ethyl isonicotinate all 3- and 4-substituted pyridines gave rise to small quantities of materials containing nickel: [2,9] these substances are being examined.

EXPERIMENTAL

Starting Materials.—These were prepared by standard procedures except for the picolines, collidines, and the 2,4-lutidines. These bases were freed from pyrrolic constituents and fractionally distilled before use.[3]

Paper Chromatography.—The method described for bases in Part VIII [10] was used.

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[4] Devereux, Payne, and Peeling, *J.*, 1957, 2845.

[5] Sasse, *J.*, 1960, 526.

[6] Brandt, Dwyer, and Gyarfas, *Chem. Rev.*, 1954, **54**, 959.

[7] Case, *J. Amer. Chem. Soc.*, 1946, **68**, 2574.

[8] Cagle and Smith, *J. Amer. Chem. Soc.*, 1947, **69**, 1860.

[9] Sargeson and Sasse, *Proc. Chem. Soc.*, 1958, 150.

[10] Sasse, *J.*, 1960, 526.

Ultraviolet Spectra.—Unless otherwise stated, these were determined for EtOH solutions on an Optica CF-4 recording spectrophotometer.

General Procedure.—Unless otherwise stated, each reaction was carried out by refluxing the base (150 c.c.) over W7-J Raney nickel catalyst [3] (prepared from 125 g. of alloy) for 50 hr. The bipyridyls were isolated as described for 2,2′-bipyridyl,[2] but hot benzene was used for the extraction of the catalyst. In some experiments different procedures were used. These are described below:

α-*Picoline.* 6,6′-Dimethyl-2,2′-bipyridyl, which separated from light petroleum as colourless needles (0·9 g.), m. p. 88·5—89·5° (lit.,[2,11] m. p. 89—90°), $\lambda_{\text{max.}}$ (log ε) at 238 (3·99) and 292 mμ (4·23), reacted with cuprous ions to give an orange chelate compound, but no colour was produced with ferrous ions. However, the liquors of its crystallisation formed a red chelate compound with ferrous ions.

β-*Picoline.* 5,5′-Dimethyl-2,2′-bipyridyl (Found: C, 78·5; H, 6·5; N, 15·0. Calc. for $C_{12}H_{12}N_2$: C, 78·2; H, 6·6; N, 15·2%) crystallised in colourless needles (53 g.) (from ethanol), m. p. 114·5—115°, R_F 0·66, $\lambda_{\text{max.}}$ (log ε) at 245 (4·05) and 290 mμ (4·18). 2,2′-Dimethylbiphenyl absorbs at 227 mμ (3·78) (point of inflexion),[12] 2,4′-dimethylbiphenyl at 240 mμ (4·07),[13] and 4,4′-dimethylbiphenyl at 254·5 mμ (4·32).[11] The bipyridyl forms a stable red iron(II) chelate compound ($\lambda_{\text{max.}}$ at 510 mμ; lit.,[8] 510 mμ). It did not form a styryl derivative when heated with benzaldehyde. Oxidation with potassium permanganate and esterification with methanol and sulphuric acid yielded dimethyl 2,2′-bipyridyl-5,5′-dicarboxylate (Found: C, 61·5; H, 4·4; N, 10·3. Calc. for $C_{14}H_{12}N_2O_4$: C, 61·8; H, 4·4; N, 10·3%), m. p. 261—262° (lit.,[7] m. p. 261—262°) alone or mixed with a sample derived from the dicarboxylic acid formed by degassed Raney nickel from nicotinic acid.[2]

γ-*Picoline.* 4,4′-Dimethyl-2,2′-bipyridyl (Found: C, 78·4; H, 6·6; N, 15·3. Calc. for $C_{12}H_{12}N_2$: C, 78·2 H, 6·6; N, 15·2%) separated from ethanol in colourless needles (56 g.), m. p. 170—172° (lit.,[7] m. p. 171—172°), $\lambda_{\text{max.}}$ (log ε) at 241 (3·97) and 282·5 mμ (4·12), R_F 0·44. Condensation with benzaldehyde by the method of Staněk and Horák [14] gave 4,4′-*distyryl*-2,2′-*bipyridyl* (Found: C, 86·5; H, 5·6; N, 8·0. $C_{26}H_{20}O_2$ requires C, 86·6; H, 5·6; N, 7·8%) in 93% yield. This base formed a colourless powder, m. p. 268·5—269·5° (from ethyl benzoate–pyridine). Hydrogenation over 5% palladium–charcoal (500 lb.; 65°) in acetic acid gave 4,4′-*diphenethyl*-2,2′-*bipyridyl* (Found: C, 85·5; H, 6·4; N, 7·7. $C_{26}H_{24}N_2$ requires C, 85·7; H, 6·6; N, 7·7%), crystallising in needles, m. p. 147·5—148°, from ethanol. All three bipyridyls derived from γ-picoline reacted with ferrous ions, to give red chelate compounds.

4-*Ethylpyridine.* 4,4′-Diethyl-2,2′-bipyridyl formed a colourless oil (48 g.), b. p. 130°/0·2 mm. (lit.,[2] b. p. 210°/30 mm.). Its *monopicrate* crystallised from ethanol as yellow plates, m. p. 153—154° (decomp.), alone or mixed with a sample obtained from the bipyridyl analysed earlier [2] (Found for picrate: C, 54·65; H, 4·4; O, 25·5. $C_{20}H_{19}N_5O_7$ requires C, 54·4; H, 4·3; O, 25·4%).

β-*Collidine.* (*a*) 5,5′-*Diethyl*-4,4′-*dimethyl*-2,2′-*bipyridyl* (Found: C, 80·3; H, 8·4; N, 11·5. $C_{16}H_{20}N_2$ requires C, 80·0; H, 8·4; N, 11·7%) crystallised in colourless needles (25 g.) (from ethanol), m. p. 141·5—142°, $\lambda_{\text{max.}}$ (log ε) at 247 (4·15) and 290 mμ (4·32), R_F 0·93.

(*b*) Reaction under reduced pressure at 140° gave an improved yield of the bipyridyl (53 g.). This base with benzaldehyde gave, in 92% yield, 5,5′-*diethyl*-4,4′-*distyryl*-2,2′-*bipyridyl* (Found: C, 86·1; H, 6·8; N, 6·7. $C_{30}H_{28}N_2$ requires C, 86·5; H, 6·8; N, 6·7%), colourless plates (from ethanol), m. p. 182—183°. This derivative was hydrogenated as described above, giving in 98% yield 5,5′-*diethyl*-4,4′-*diphenethyl*-2,2′-*bipyridyl* (Found: C, 85·9; H, 7·5; N, 6·75. $C_{30}H_{32}N_2$ requires C, 85·7; H, 7·7; N, 6·7%). After crystallisation from ethanol it formed colourless dimorphic needles, m. p. 133—135° amd 142—143°. All three bipyridyls derived from β-collidine formed red iron(II) chelate compounds.

2,4-*Lutidine.* After removal of all materials boiling up to 100°/20 mm. the residue was chromatographed on alumina. All materials eluted by light petroleum were distilled. The fraction of b. p. 110—130°/1 mm. formed a colourless oil (10 g.) from which separated 4,4′,6,6′-tetramethyl-2,2′-bipyridyl (0·83 g.) (Found: C, 79·4; H, 7·7; N, 13·2. Calc. for $C_{14}H_{16}N_2$:

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[11] Willinck and Wibaut, *Rec. Trav. chim.*, 1935, **54**, 275.

[12] Johnson, *J.*, 1957, 4155.

[13] Catalogue of Ultraviolet Spectral Data of the American Petroleum Inst., Research Project 44, no. 708.

[14] Staněk and Horák, *Coll. Czech. Chem. Comm.*, 1951, **15**, 1037 (*Chem. Abs.*, 1952, **46**, 7100).

C, 79·2; H, 7·6; N, 13·2%), needles (from light petroleum), m. p. 142·5—143° (lit.,[15] m. p. 144—145°), $\lambda_{max.}$ (log ε) at 247 (4·15) and 290 mμ (4·3), R_F 0·25. This base formed an orange chelate compound with cuprous ions, $\lambda_{max.}$ 450 mμ (lit.,[15] $\lambda_{max.}$ 450 mμ), but it failed to produce a colour with ferrous ions. However, the liquors of its crystallisation gave a red colour with ferrous ions, and paper chromatography revealed the presence of a base with the R_F of 4,4′-dimethyl-2,2′-bipyridyl.

2,4,6-*Collidine*. The reaction was continued for 200 hr. After removal of the catalyst all material boiling up to 175° was distilled off (141 c.c.). Examination of the residue by paper chromatography showed the presence of at least six bases, five of which gave red stains on being sprayed with ferrous sulphate solution. The distillate was redistilled to give the fractions: (*a*) b. p. 98—100° (4 c.c.); (*b*) b. p. 140—164° (3 c.c.); (*c*) b. p. 164—167° (5 c.c.); (*d*) b. p. 167—168° (11 c.c.); and a residue (118 c.c.). Fraction (*a*) contained largely water. Gas–liquid chromatography [5] of fractions (*b*), (*c*), and (*d*) at 90° (flow-rate 1·2 l. per hr. of nitrogen) showed that, besides collidine (retention time 14·1 min.), 2,4-lutidine (retention time 9·3 min.) was present. From the areas under the peaks it was estimated that 3—4% of lutidine was formed in this reaction. Both bases were separated by gas chromatography and identified by their infrared spectra. A third component (retention time 6·3 min.) occurred in fractions (*b*) and (*c*) in quantities which did not allow its isolation.

4-*Phenylpyridine*. (*a*) 4-Phenylpyridine [16] (63 g.) gave 4,4′-diphenyl-2,2′-bipyridyl (Found: C, 85·5; H, 5·2; N, 9·0. Calc. for $C_{22}H_{16}N_2$: C, 85·7; H, 5·2; N, 9·1%) which separated from light petroleum–benzene as colourless needles (3·1 g.), m. p. 187—188° (lit.,[17] m. p. 187—188°), $\lambda_{max.}$ (log ε) 251 mμ (4·63), and formed a red iron(II) chelate compound.

(*b*) Under reduced pressure at 130—150°, 4-phenylpyridine (100 g.) gave 4,4′-diphenyl-2,2′-bipyridyl (5 g.).

Ethyl nicotinate. Under reduced pressure at 145° diethyl 2,2′-bipyridyl-5,5′-dicarboxylate (11 g.), m. p. 149° (lit.,[2] m. p. 148—149°), was obtained. It had $\lambda_{max.}$ (log ε) at 250 (4·12), 256 (4·14), and 300 mμ (4·45). The diacid absorbs at 290 mμ (4·48).[18]

3-*Benzoylpyridine*. The ketone (32 g.) was refluxed in xylene (50 c.c.) for 45 hr., to give colourless plates (0·14 g.) of *5,5′-dibenzoyl-2,2′-bipyridyl* (Found: C, 79·2; H, 4·4; N, 7·9. $C_{24}H_{16}N_2O_2$ requires C, 79·1; H, 4·4; N, 7·7%), m. p. 209·5—211° (from benzene–ethanol), $\nu_{max.}$ 1660 cm.$^{-1}$ (in Nujol), $\lambda_{max.}$ (log ε) 260 (4·21), 264 (4·23), and 311 mμ (4·48). 4,4′-Dibenzoylbiphenyl [18] has $\lambda_{max.}$ (log ε) at 250 (4·20), 256 (4·24), 262 (4·24), and 299 mμ (4·76) (in dioxan). The bipyridyl gave a blue-violet iron(II) chelate compound when dissolved in glacial acetic acid.

Ethyl isonicotinate. No derivative of 2,2′-bipyridyl could be detected after this ester had been refluxed for 76 hr. over the catalyst.

Formation of Nickel Complexes.[3]—Small quantities (1—3 g.) of nickel complexes were obtained from the reactions involving β-picoline, γ-picoline, β-collidine, 4-ethylpyridine, 4-phenylpyridine, and ethyl nicotinate. Except for the reaction with ethyl isonicotinate, *p*-dimethylaminobenzaldehyde indicated the presence of small quantities of pyrroles in every experiment.

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[15] Linell, *J. Org. Chem.*, 1957, **22**, 1691.
[16] Schmidle and Mansfield, *J. Amer. Chem. Soc.*, 1956, **78**, 1702.
[17] Case and Kasper, *J. Amer. Chem. Soc.*, 1956, **78**, 5842.
[18] Williamson and Rodebush, *J. Amer. Chem. Soc.*, 1941, **63**, 3018.
[19] Schlenk and Brauns, *Ber.*, 1915, **48**, 716.