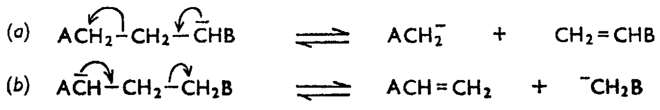
94. *Alkyl- and Alkenyl-pyridines. Part VI.*[1] *Michael Reactions of Vinylpyridines with Alkylpyridines: Reversal and Resynthesis of the* 1,3-*Dipyridylpropane System.*

By J. MICHALSKI and H. ZAJĄC.

Alkylpyridines have been added to vinylpyridines in the presence of alkali metals. The products indicate a breakdown and resynthesis of 1,3-dipyridylpropanes and lead to an assessment of the relative nucleophilicities of the anions of various alkylpyridines. The reactions are the first examples of a Michael addition in which the product-determining factor is a re-addition of primary donors to secondary acceptors, the latter being formed from the primary adduct.

IN connection with work on the 1,3-dipyridylpropanes, we began several years ago to study the preparation of 1-2′-pyridyl-3-4′-pyridyl-, 1-(6-methyl-2-pyridyl)-3-2′-pyridyl-, and 1-(6-methyl-2-pyridyl)-3-4′-pyridyl-propane. The first was ascribed by Magnus and Levine [2] to the product of addition of 2-picoline to 4-vinylpyridine or of 4-picoline to 2-vinylpyridine; we sought to obtain the remaining two in analogous ways. In all these cases we used the alkylpyridine in considerable excess. Two different products were obtained in reactions which should have yielded the same products. Thus, 1-2′-pyridyl-3-4′-pyridylpropane was produced in the reaction between 2-picoline and 4-vinylpyridine, but not from 4-picoline and 2-vinylpyridine, as claimed by Magnus and Levine;[2] the latter reaction yielded 1,3-di-4′-pyridylpropane. 1-(6-Methyl-2-pyridyl)-3-2′-pyridylpropane was obtained from 2-picoline with 2-methyl-6-vinylpyridine, but not from 2,6-lutidine with 2-vinylpyridine, which gave 1,3-di-(6-methyl-2-pyridyl)propane, identical with the product of the reaction between 2,6-lutidine and 2-methyl-6-vinylpyridine. Finally, reaction between 4-picoline and 2-methyl-6-vinylpyridine yielded 1-(6-methyl-2-pyridyl)-3,4′-pyridylpropane, whilst that between 2,6-lutidine and 4-vinylpyridine afforded 1,3-di-(6-methyl-2-pyridyl)propane. All the reactions also gave the corresponding 1,3,5-tripyridylpentanes as secondary products.

These reactions are undoubtedly of Michael type. In an effort to explain the "abnormal" course we have focused attention on two factors—the mass-action effect, and the formation and decomposition of isomeric anions,[3,4] derived from dipyridylpropanes. The following schemes, in which A and B represent activating (2- or 4-)pyridyl groups, are considered:



$$(a)\quad A\bar{C}H_2{-}CH_2{-}\bar{C}HB \rightleftharpoons ACH_2^- + CH_2{=}CHB \qquad (1)$$

$$(b)\quad A\bar{C}H{-}CH_2{-}CH_2B \rightleftharpoons ACH{=}CH_2 + {}^-CH_2B \qquad (2)$$

Carbanion (*a*) decomposes to starting materials. Carbanion (*b*) decomposes to a new vinylpyridine and the anion of a new alkylpyridine. Anions (*a*) and (*b*) are probably formed very rapidly.[5,6] The rates of their decomposition cannot be the same. If, of the ions ACH_2^- and BCH_2^-, the first is the more stable then the decomposition of carbanion

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[1] Part V, Godlewska-Zwierzak, Michalski, and Studniarski, *Roczniki Chem.*, 1959, **33**, 1215.
[2] Levine and Magnus, *J. Org. Chem.*, 1957, **22**, 270.
[3] Ingold and Powell, *J.*, 1921, **119**, 1976; Ingold and Perren, *ibid*, p. 1865.
[4] *Org. Reactions*, **10**, 185.
[5] de la Mare, Hughes, and Ingold, *J.*, 1948, 17.
[6] Schmidt and Kubitzek, *Chem. Ber.*, 1960, **93**, 866.

(*a*) is the favoured one; otherwise, the favoured decomposition is that of anion (*b*). Obviously the adduct $A{\cdot}[CH_2]_3{\cdot}B$ is the primary product in either of these two reactions:

$$ACH_3 + CH_2{=}CHB \longrightarrow A{\cdot}[CH_2]_3{\cdot}B \qquad (3)$$

$$BCH_3 + CH_2{=}CHA \longrightarrow A{\cdot}[CH_2]_3{\cdot}B \qquad (4)$$

Let us assume that the favoured decomposition is that of anion (*a*). Then reaction (3) is a simple reversal, but reaction (4) is a continuous exhaustion of the primary acceptor $ACH{=}CH_2$ and donor BCH_3 with formation of the secondary acceptor $BCH{=}CH_2$ and secondary donor ACH_3. However, since BCH_3 is invariably present in considerable excess, and its anion BCH_2^- is thermodynamically less stable, it is the anion of the primary donor BCH_2^- that attacks both the primary and the secondary vinylpyridines, yielding a mixture of $A{\cdot}[CH_2]_3{\cdot}B$ with $B{\cdot}[CH_2]_3{\cdot}B$. On decomposition of $A{\cdot}[CH_2]_3{\cdot}B$ a complex equilibrium is attained, in which there may exist simultaneously at least two donors, two acceptors, and three adducts. However, we have been unable to demonstrate the presence of adduct $A{\cdot}[CH_2]_3{\cdot}A$ and we attribute its absence to the relatively low chemical activity of the anion ACH_2^-.

The reactions of 2-picoline with 4-vinylpyridine and of 4-picoline with 2-vinylpyridine thus afforded 1-2′-pyridyl-3-4′-pyridyl- and 1,3-di-4′-pyridyl-propane, respectively. Therefore the 2-picoline anion is the thermodynamically more stable carbanion ACH_2^-, and the 4-picoline anion is BCH_2^-.

The greater stability of the 2-picoline anion is probably attributable to the fact that the carbon atom of the 2-methyl group can more readily accept a negative charge than can that of the 4-methyl group, owing to the $-I$ effect of the nitrogen atom operative in the former, but not in the latter. Considered in terms of the electron-density of the nucleophilic centre, the more pronounced nucleophilic properties of the 4-picoline anion agree with the electron-density distribution in 2- and 4-picoline anions.[7]

The products of the reactions of 2-picoline with 2-methyl-6-vinylpyridine, and 2,6-lutidine with 2-vinylpyridine, show that the 2-picoline anion is the thermodynamically more stable ACH_2^- and the 2,6-lutidine anion BCH_2^-. The lower stability and more pronounced nucleophilic character of the latter are due to the $+I$ effect of the 6-methyl group.

Similarly, in the reactions of 4-picoline with 2-methyl-6-vinylpyridine and of 2,6-lutidine with 4-vinylpyridine, the 4-picoline anion is the thermodynamically more stable ACH_2^-, and the less stable and more nucleophilic BCH_2^- is the 2,6-lutidine anion. The lower stability of the latter is explained as in the previous example.

To confirm the course of the reactions, we designed experiments: (i) to demonstrate the favoured direction of decomposition of the product $A{\cdot}[CH_2]_3{\cdot}B$, (ii) to permit isolation of the primary adduct $A{\cdot}[CH_2]_3{\cdot}B$, and (iii) to demonstrate that the less nucleophilic anion ACH_2^- can be displaced by the more nucleophilic anion BCH_2^- in reactions of the type:

$$2BCH_2 + A{\cdot}[CH_2]_3{\cdot}A \longrightarrow 2ACH_2 + B{\cdot}[CH_2]_3{\cdot}B \qquad (5)$$

When 1-2′-pyridyl-3,4′-pyridylpropane was treated under reflux with catalytic amounts of potassium the ratio of 2-picoline to 4-picoline produced was 4 : 1. This proves that the favoured direction of decomposition was as assumed.

The primary product $A{\cdot}[CH_2]_3{\cdot}B$ was isolated, though not without difficulty, when 4-picoline reacted with 2-vinylpyridine, 2,6-lutidine with 2-vinylpyridine, and 2,6-lutidine with 4-vinylpyridine for 5—15 minutes. The secondary reactions also occurred very rapidly, as was shown by appreciable yields of the secondary products.

To demonstrate the third point, we heated a considerable excess of 2,6-lutidine with 1,3-di-2′-pyridylpropane for about 8 hours in the presence of catalytic amounts of potassium; 1,3-di-(6-methyl-2-pyridyl)propane was obtained in 49% yield. Reaction

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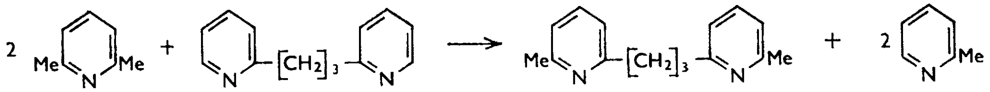
[7] Brown and Dewar, *J.*, 1953, 2406.

of 4-picoline with 1,3-di-2′-pyridylpropane led to 1,3-di-4′-pyridylpropane and some 4,4′-dimethyl-2,2′-bipyridyl, known to be formed readily by sustained heating of 4-picoline in the presence of sodium or potassium.



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These experiments suggest the following order of decreasing nucleophilic power for pyridylmethyl anions: 2,6-lutidine, 4-picoline, 2-picoline.

EXPERIMENTAL

M. p.s are uncorrected. Light petroleum refers to the fraction of b. p. 60—80°. Atmospheric moisture was excluded by drying tubes containing calcium chloride. Quinol was used in all reactions to prevent polymerisation of vinylpyridines. Alkyl- and vinyl-pyridines were freshly distilled from a little sodium or phosphoric oxide. All evaporations were at reduced pressure.

2-*Picoline and* 4-*Vinylpyridine*.—4-Vinylpyridine (50 g.), 2-picoline (253 g.), and sodium (1·5 g.) were heated under reflux for 4 hr. The catalyst was then removed and the remainder was washed with water, extracted with benzene, dried (K_2CO_3), and evaporated. Fractionation of the residual oil (85 g.) gave: (*a*) b. p. 100—103°/0·01 mm. (45·2 g.), (*b*) b. p. 135—142°/0·01 mm. (19 g.), and (*c*) b. p. 155—156°/0·01 mm. (18 g.). Repeated distillation of fraction (*a*) gave 1-2′-pyridyl-3-4′-pyridylpropane (42·2 g., 42·6%), b. p. 78—80°/0·01 mm., n_D^{20} 1·5569, d_4^{25} 1·0570 (Found: C, 78·5; H, 7·0; N, 13·9. Calc. for $C_{13}H_{14}N_2$: C, 78·75; H, 7·1; N, 14·1%). The *dipicrate* crystallised from water in yellow needles, m. p. 197—201° (Found: C, 46·0; H, 3·0; N, 16·7. $C_{25}H_{20}N_8O_{14}$ requires C, 45·7; H, 3·05; N, 17·1%). The *monoperchlorate* separated from aqueous methanol as needles, m. p. 212—215° (Found: C, 52·8; H, 5·2; N, 9·4. $C_{13}H_{14}N_2,HClO_4$ requires C, 52·3; H, 5·05; N, 9·5%). The *dimethiodide* crystallised from methanol as pale yellow needles, m. p. 232—235° not depressed on admixture with the dimethiodide (m. p. 232—234°) of the product of brief reaction between 4-picoline and 2-vinylpyridine.

Fractions (*b*) and (*c*) consisted largely of a tripyridylpentane [Found: *M* (Rast), 300. Calc.: *M*, 303]; tripicrate, m. p. 200—203° (from water) (Found: C, 46·1; H, 3·0; N, 17·1. Calc. for $C_{38}H_{30}N_{12}O_{21}$: C, 46·1; H, 3·0; N, 17·0%).

Isolation of 1,3-*Di*-4′-*pyridylpropane*.—Fractional crystallisation of dipicrates prepared from the crude dipyridylpropane gave a small quantity of 1,3-di-4′-pyridylpropane dipicrate, m. p. and mixed m. p. 180—182° (lit.,[2] reports m. p. 185—186°).

4-*Picoline and* 2-*Vinylpyridine*.—4-Picoline (180 g.), 2-vinylpyridine (41 g.), and sodium (2 g.) were refluxed for 2 hr. and worked up as described above. Two fractions were collected: (*a*) b. p. 77°/0·01 mm. (21·1 g., 27%), n_D^{25} 1·5578, d_4^{25} 1·0580, R_M 60·3 (59·79), and (*b*) b. p. 165—179°/0·01 mm. (24 g., 42%). Fraction (*a*) solidified and after crystallisation from light petroleum had m. p. 57—58·5°, undepressed on admixture of a sample of authentic 1,3-di-4′-pyridylpropane (lit., m. p. 62—65°,[2] 57—60°,[8] 60·5—61·5° [9] (Found: C, 78·6; H, 7·1; N, 14·05. Calc. for $C_{13}H_{14}N_2$: C, 78·75; H, 7·1; N, 14·1%). The *dipicrate* separated from ethanol in yellow needles, m. p. and mixed m. p. 182—184° (lit.,[4] 185—186°) (Found: C, 45·5; H, 3·3; N, 16·75. $C_{25}H_{20}N_8O_{14}$ requires C, 45·7; H, 3·05; N, 17·1%); the *diperchlorate* crystallised from methanol—ethanol as needles, m. p. and mixed m. p. 205—207° (Found: C, 39·2; H, 3·9; N, 7·2. $C_{13}H_{14}N_2,2HClO_4$ requires C, 39·1; H, 4·0; N, 7·0%); the *monomethiodide* (from ethanol) had m. p. and mixed m. p. 166—169° (Found: C, 37·4; H, 4·1; N, 5·5. $C_{14}H_{17}IN_2$ requires C, 37·35; H, 4·15; N, 5·8%). Throughout the purification of the dipicrate of the crude base small amounts of 1-2′-pyridyl-3-4′-pyridylpropane dipicrate, m. p. and mixed m. p. 196—200°, were isolated.

Fraction (*b*) solidified and after several crystallisations from benzene yielded a tripyridylpentane as needles, m. p. 215—218° [Found: C, 79·9; H, 6·6; N, 14·0%; *M* (Rast), 308.

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[8] Jampolsky *et al.*, *J. Amer. Chem. Soc.*, 1952, **74**, 5222.

[9] Lue-Yung Chow and Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 1095.

$C_{20}H_{21}N_3$ requires C, 79·2; H, 7·0; N, 13·8%; *M*, 303]. The tripicrate separated from water in yellow needles, m. p. 220—224° (Found: C, 46·3; H, 3·05; N, 17·0. $C_{38}H_{30}N_{12}O_{21}$ requires C, 46·6; H, 3·1; N, 17·0%).

Brief Reaction of 4-Picoline with 2-Vinylpyridine.—4-Picoline (30 g.), 2-vinylpyridine (30 g.), and potassium (1·5 g.) were refluxed for 5 min. and then rapidly cooled (ice-bath). Potassium was filtered off and the residue distilled; 1-2′-Pyridyl-3-4′-pyridylpropane (8 g.) had b. p. 90—94°/0·05 mm., n_D^{19} 1·5669; the dipicrate had m. p. and mixed m. p. 202—204°; the dimethiodide, m. p. and mixed m. p. 232—234°. The tripyridylpentane fraction was collected as an oil (11 g.), b. p. 106—165°/0·01 mm., n_D^{20} 1·5703.

2,6-Lutidine and 2-Vinylpyridine.—(*a*) *In the presence of sodium.* A mixture of 2,6-lutidine (315 g.), 2-vinylpyridine (70 g.), and sodium (3·5 g.) was heated under reflux for 2 hr. and worked up in the usual way. 1,3-*Di*-(6-*methyl*-2-*pyridyl*)*propane* distilled at 90—95°/0·01 mm. (81·1 g., 56%); it had n_D^{25} 1·5531, m. p. and mixed m. p. 38—40° (from light petroleum) (Found: C, 79·7; H, 7·75; N, 12·3. $C_{15}H_{18}N_2$ requires C, 79·6; H, 8·0; N, 12·4%); *dipicrate*, yellow needles (from methanol), m. p. and mixed m. p. 192—193° (Found: C, 47·5; H, 3·2; N, 16·4. $C_{27}H_{24}N_8O_{14}$ requires C, 47·4; H, 3·5; N, 16·35%); *diperchlorate* (from methanol), needles, m. p. and mixed m. p. 174—176° (Found: N, 6·6. $C_{15}H_{18}N_2,2HClO_4$ requires N, 6·55%); *monomethiodide* (from acetone), m. p. and mixed m. p. 171—172° (Found: C, 52·0; H, 5·9; N, 7·8. $C_{16}H_{21}IN_2$ requires C, 52·2; H, 5·7; N, 7·6%); *dimethiodide* (from ethanol), needles, m. p. and mixed m. p. 278—281° (Found: C, 38·4; H, 4·8; N, 5·4. $C_{17}H_{24}I_2N_2$ requires C, 39·7; H, 4·7; N, 5·4%).

The oily residue (40 g.) was set aside with perchloric acid; after two weeks crystalline material (25·7 g.), m. p. 215—220°, was collected and dissolved in water, the solution basified (Na_2CO_3), and the resulting base extracted with benzene, dried (K_2CO_3), and distilled to give 1,3,5-*tri*-(6-*methyl*-2-*pyridyl*)*pentane*, b. p. 165—167°/0·3 mm., n_D^{20} 1·5756, m. p. and mixed m. p. 76—78° (from benzene) (Found: C, 79·6; H, 7·8; N, 12·4. $C_{23}H_{27}N_3$ requires C, 80·0; H, 7·9; N, 12·2%); *tripicrate* (from acetone), yellow needles, m. p. and mixed m. p. 195—197° (Found: C, 48·0; H, 3·8; N, 16·3. $C_{41}H_{36}N_{12}O_{21}$ requires C, 47·7; H, 3·5; N, 16·3%).

(*b*) *In the presence of potassium.* Similar reaction of 2,6-lutidine (315 g.), 2-vinylpyridine (50 g.), and potassium (5 g.) for 5 hr. gave 1,3-di-(6-methyl-2-pyridyl)propane (51 g.), m. p. 38—40°, small quantities of 3-(6-methyl-2-pyridyl)-1-2′-pyridylpropane dipicrate, m. p. and mixed m. p. 200—202°, and 1,3,5-tri-(6-methyl-2-pyridyl)pentane, m. p. 76—78°.

6-Methyl-2-vinylpyridine and 2-Picoline.—6-Methyl-2-vinylpyridine (12 g.), 2-picoline (47 g.), and sodium (0·5 g.), heated under reflux for 2 hr., gave 1-(6-*methyl*-2-*pyridyl*)-3-2′-*pyridylpropane* (6 g., 29%), b. p. 124°/0·2 mm., n_D^{25} 1·5560, d_4^{25} 1·0469, R_M 64·52 (Found: C, 79·6; H, 7·5; N, 13·4. $C_{14}H_{16}N_2$ requires C, 79·2; H, 7·6; N, 13·2%; R_M 64·41); *dipicrate* (from acetone), yellow needles, m. p. 203—205° (Found: C, 46·5; H, 3·4; N, 16·3. $C_{26}H_{22}N_{16}O_{14}$ requires C, 46·4; H, 3·3; N, 16·7%); *diperchlorate* (from methanol), needles, m. p. 208—210° (Found: N, 6·9. $C_{14}H_{16}N_2,2HClO_4$ requires N, 6·8%); *dimethiodide* (from ethanol), needles, m. p. 231—233° (Found: N, 5·2. $C_{16}H_{22}I_2N_2$ requires N, 5·6%).

Throughout the purification of the dipicrate of the crude base, traces of 1,3-di-(6-methyl-2-pyridyl)propane dipicrate, m. p. and mixed m. p. 192—194°, were isolated.

Brief Reaction between 2,6-Lutidine and 2-Vinylpyridine.—2-Vinylpyridine (50 g.), 2,6-lutidine (60 g.), and potassium (15 g.) were refluxed for 10 min. and then rapidly cooled. Potassium was filtered off and the residue distilled. Two fractions were collected: (*a*) b. p. 73—79°/0·005 mm. (7 g., 7%), n_D^{21} 1·5541, and (*b*) b. p. 145—152°/0·005 mm. (3 g.), m. p. 50—60°. The latter is a mixture of tripyridylpentanes and was not investigated. Fraction (*a*) was redistilled to give 1-(6-methyl-2-pyridyl)-3-2′-pyridylpropane (3 g.), b. p. 75—80°/0·005 mm., n_D^{20} 1·5547 (Found: C, 79·2; H, 7·5; N, 13·2%) (dipicrate, m. p. and mixed m. p. 200—201°), and an oil (4 g.), whose picrate was fractionally crystallised to give mainly the above dipicrate, m. p. 200—201°, and a small amount of 1,3-di-(6-methyl-2-pyridyl)propane dipicrate, m. p. and mixed m. p. 190—192°.

6-Methyl-2-vinylpyridine and 4-Picoline.—6-Methyl-2-vinylpyridine (50 g.), 4-picoline (150 g.), and potassium (1·5 g.) were refluxed for 3 hr. and then worked up in the usual way. 1-(6-*Methyl*-2-*pyridyl*)-3-4′-*pyridylpropane* (23 g., 26%) had b. p. 106—112°/0·03 mm., n_D^{20} 1·5610, d_4^{20} 1·0483, R_M 64·8 (Found: C, 79·45; H, 7·7; N, 13·0. $C_{14}H_{16}N_2$ requires C, 79·2; H, 7·6; N, 13·2%; R_M 64·1); *dipicrate* (from ethanol), yellow needles, m. p. 161—163° (Found:

C, 46·3; H, 3·3; N, 17·2. $C_{16}H_{22}N_8O_{14}$ requires C, 46·4; H, 3·3; N, 16·7%); *dimethiodide* (from methanol), needles, m. p. 234—236° which did not depress the m. p. of the dimethiodide of the product of brief reaction between 2,6-lutidine and 4-vinylpyridine. Distillation of the residue gave a mixture (12 g.), b. p. 125—229°/0·03 mm., probably of tripyridylpentanes.

2,6-*Lutidine and* 4-*Vinylpyridine*.—2,6-Lutidine (315 g.), 4-vinylpyridine (30 g.), and potassium (5 g.), after 8 hr. gave, following the usual treatment, 1,3-di-(6-methyl-2-pyridyl)-propane (54 g., 50·5%), b. p. 78—92°/0·01 mm., n_D^{20} 1·5520, m. p. and mixed m. p. 38—40°. From the mother liquors a small amount of 1-(6-methyl-2-pyridyl)-3-4′-pyridylpropane was isolated as dipicrate (m. p. and mixed m. p. 160—162°).

Brief Reaction between 2,6-*Lutidine and* 4-*Vinylpyridine*.—2,6-Lutidine (120 g.), 4-vinylpyridine (30 g.), and potassium (1·5 g.) when refluxed for 15 min. gave 1-(6-methyl-2-pyridyl)-3-4′-pyridylpropane (6 g.), b. p. 88—89°/0·01 mm., n_D^{21} 1·5561 (Found: C, 78·7; H, 7·4; N, 13·3%); dimethiodide (from ethanol), needles, m. p. and mixed m. p. 234—236°; dipicrate (from ethanol), m. p. and mixed m. p. 160—162°. Fractional crystallisation of the crude picrate also gave traces of 1,3-di-(6-methyl-2-pyridyl)propane dipicrate, m. p. and mixed m. p. 193—195°.

Action of Potassium on 1,2′-*Pyridyl*-3-4′-*pyridylpropane*.—The base (10 g.) was refluxed with potassium (0·5 g.) for 5 hr. and the resultant mixture distilled to give a liquid (6 g.), b. p. 130—135°/740 mm. This, on fractional distillation through a short column, gave 2-picoline (4 g.), b. p. 129—130° (picrate, m. p. and mixed m. p. 162—163°), and 4-picoline (1 g.), b. p. 142—145° (picrate, m. p., and mixed m. p. 160—162°).

2,6-*Lutidine and* 1,3-*Di*-2′-*pyridylpropane*.—2,6-Lutidine (150 g.), 1,3-di-2′-pyridylpropane (50 g.), and potassium (2 g.) were heated under reflux for 8 hr. After removal of potassium the resultant mixture (140 g.) was fractionated to give 2-picoline (38 g.), b. p. 127—132°, n_D^{25} 1·5032 (picrate, m. p., and mixed m. p. 162—164°), 2,6-lutidine (90 g.), b. p. 140—143°, and then three fractions: (*a*) b. p. 79—85°/0·01 mm., n_D^{21} 1·5544 (11 g.), (*b*) b. p. 85—90°/0·01 mm., n_D^{21} 1·5549 (23 g.), and (*c*) b. p. 150—165°/0·01 mm. (7 g.). Fractions (*a*) and (*b*) were seeded and then furnished 1,3-di-(6-methyl-2-pyridyl)propane (27 g., 49%), m. p. and mixed m. p. 36—38° (dipicrate, m. p., and mixed m. p. 192—194°). Fraction (*c*) consisted of tripyridylpentanes.

4-*Picoline and* 1,3-*Di*-2′-*pyridylpropane*.—1,3-Di-2′-pyridylpropane (20 g.), 4-picoline (80 g.), and potassium (1 g.) were refluxed for 5 hr. and worked up in the usual way, giving a fraction, b. p. 125—135°/740 mm. (16 g., n_D^{20} 1·5020), consisting mainly of 2-picoline (picrate, m. p., and mixed m. p. 160—163°), unchanged 4-picoline (53 g.), b. p. 135—141°, and a residue (20 g.). From the residue crystals (0·2 g.) were obtained, m. p. 168—170° after recrystallisation from ethanol. These were recognised as 4,4′-dimethyl-2,2′-bipyridyl (lit.,[10] m. p. 169·5—170·5°) by comparison of m. p. and colour reaction with ferrous ions. Distillation of the residue did not afford pure material, but fractional crystallisation of the derived picrates gave some 1,3-di-4′-pyridylpropane dipicrate, m. p. and mixed m. p. 182—184°.

2,6-*Lutidine and* 6-*Methyl*-2-*vinylpyridine*.—2,6-Lutidine (40 g.), 6-methyl-2-vinylpyridine (8·5 g.), and sodium (0·5 g.) when refluxed for 2 hr. and processed as usual gave two fractions. The lower-boiling fraction gave 1,3-di-(6-methyl-2-pyridyl)propane (8 g., 49%), m. p. 40—42° (from light petroleum) (Found: C, 79·6; H, 7·8; N, 11·9%); dipicrate, yellow needles, m. p. 190—192°, from 1 : 1 acetone–methanol (Found: C, 47·1; H, 3·5; N, 15·85%); *diperchlorate* needles, m. p. 172—174°, from ethanol (Found: C, 42·3; H, 4·9; N, 6·7. $C_{15}H_{18}N_2,2HClO_4$ requires C, 42·6; H, 4·7; N, 6·55%); monomethiodide (from the base and methyl iodide in cold benzene), m. p. 168—171° (from methanol) (Found: C, 52·6; H, 5·9; N, 7·8%); dimethiodide (by refluxing excess of methyl iodide with the base in ethanol for 10 hr.), m. p. 283—284° (Found: N, 5·4%).

The higher-boiling fraction gave 1,3,5-tri-(6-methyl-2-pyridyl)pentane (3 g.), m. p. 76—78° (from benzene) (Found: C, 79·7; H, 7·7; N, 12·2%); tripicrate, yellow needles, m. p. 194—196°, from acetone (Found: C, 48·3; H, 3·6; N, 16·1%).

Department of Organic Chemistry,
Technical University (Politechnika),
Lodz, Poland.

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[10] Osuch and Levine, *J. Org. Chem.*, 1957, **22**, 939.