Electrochemical Reactions. Part X.[1] 4-Styrylpyridine: Polarography and Cyclic Voltammetry in Dimethylformamide and Reduction in Protic Solvents

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Polarography of 4-styrylpyridine in anhydrous dimethylformamide shows two separate one-electron waves with $E_{\frac{1}{2}}$ −1·88 and −2·22 V (*versus* s.c.e.). Cyclic voltammetry shows the first wave to be reversible and the 4-styrylpyridine anion radical produced has a half-life of *ca.* 10 s at 25 °C and longer at lower temperatures. In aqueous methanol 4-styrylpyridine shows one polarographic wave. The products from electroreduction in aqueous methanol are the dihydro-derivative and *meso*- and (±)-2,3-diphenyl-1,4-di-(4-pyridyl)butane. The (±)-isomer was resolved. Other substituted 4-styrylpyridines give analogus products on reduction.

THE polarography of 4-styrylpyridine (1) in protic solvents has been examined by a number of workers.[2,3] A single reduction wave was observed with a half-wave potential which was dependent on pH. Various techniques have been used to show that two electrons per molecule of 4-styrylpyridine are consumed in the process which gives rise to this wave and 4-(2-phenethyl)pyridine (2) was the presumed product. In contrast, one electron per molecule is taken up during the preparative electrochemical reduction of both 2- and 4-vinylpyridine to yield 1,4-di-(2-pyridyl)butane and the 4-pyridyl isomer respectively.[4] Concentrated solutions of the vinylpyridines were employed in the latter reactions and no mechanism for the dimerisation was suggested. Mixed reductive coupling between dibutyl maleate and 2-vinylpyridine and also between methyl vinyl ketone and 4-vinylpyridine was observed.[4]

Reduction of 4-styrylpyridine in anhydrous dimethyl formamide takes place in two successive stages at well separated cathode potentials to give two polarographic waves. From the ensuing data, each wave must be due to the consumption of one electron per molecule. Cyclic triangular wave voltammetry[5] over a voltage range which covers both polarographic waves shows two cathodic peaks each of approximately the same height (see Figure). There is an anodic peak to correspond with the first cathodic peak.

Cyclic voltammetry[5] over a range corresponding to the first polarographic wave shows the cathodic peak and a corresponding anodic peak. The ratio of anodic (i_{pa}) to cathodic (i_{pc}) peak heights varies with the scan rate (v) at 25 °C but becomes independent of scan rate when the solution is cooled to −46 °C. The function $i_{pc}/v_{\frac{1}{2}}$ is invariant with changing scan rate. The separation of anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}) at slow scan rates is 0·060, 0·050, and 0·045 V at 25, −46, and −64 °C respectively which corresponds closely to the values of 2·218 RT/F, 0·057, 0·043, and 0·040 V respectively,

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[1] Part IX, J. Grimshaw, J. T. Grimshaw, and E. J. F. Rea, *J. Chem. Soc.* (*C*), 1971, 683.

[2] J. Volke and J. Holubek, *Coll. Czech. Chem. Comm.*, 1962, **27**, 1777.

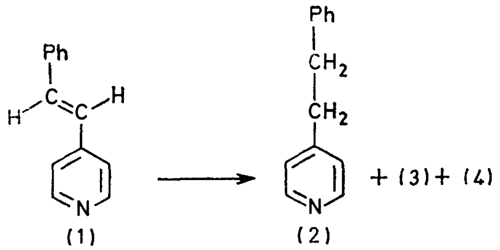
[3] J. Chodkowski and T. Giovanoli-Jakubczak, *Roczniki Chem.*, 1967, **41**, 373.

[4] J. D. Anderson, M. M. Baizer, and E. J. Prill, *J. Org. Chem.*, 1965, **30**, 1645.

[5] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706; J. L. Sadler and A. J. Bard, *J. Amer. Chem. Soc.*, 1968, **90**, 1979.

expected for a one-electron transfer without energy of activation.

Thus the process being observed is the redox reaction between 4-styrylpyridine and its anion radical. The anion radical has a half-life *ca.* 10 s at 25 °C, judged from the time required to sweep from E_{pc} to E_{pa} on the voltagram where $i_{pa}/i_{pc} = 0{\cdot}5$. At lower temperatures, the voltagrams appear more characteristic for a reversible process because the half-life of the anion-radical is now increased. However at lower temperatures E_{pc} and E_{pa} become dependent on v at relatively slow scan rates. The system 4-styrylpyridine and its anion-radical has $E_{\frac{1}{2}} = -1{\cdot}88$ V (*versus* s.c.e.) in dimethylformamide at the dropping mercury electrode. The anion-radical is analogous to the known[6] zwitterion radical (6) which is formally a cation radical, and we will discuss its reactivity in a later paper.



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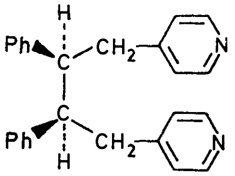

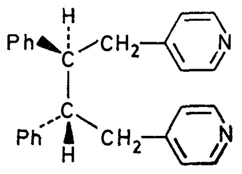
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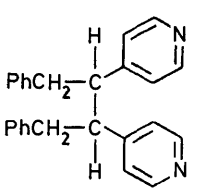
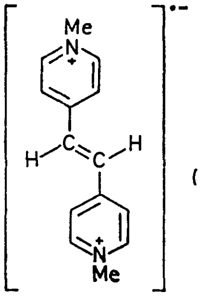
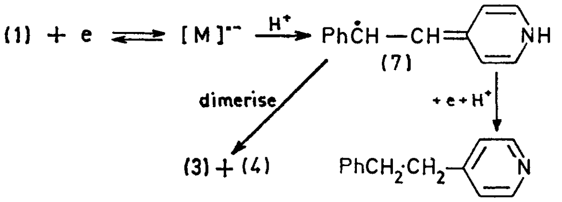


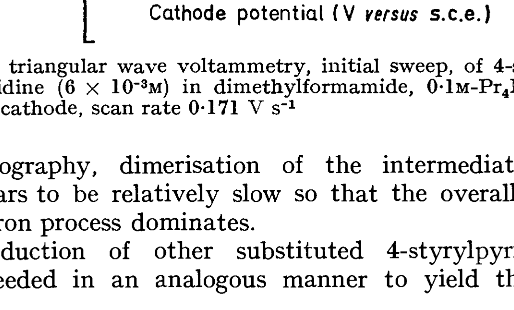

(6)

† No absolute stereochemistry intended

Preparative electrochemical reduction of 4-styrylpyridine as $5{\cdot}5 \times 10^{-2}$M solution in aqueous methanol, pH 3·7, afforded 4-(2-phenethyl)pyridine (2), and two further bases, $C_{26}H_{24}N_2$, both hydro-dimers of 4-styrylpyridine. One dimer was a solid, the other a gum. Each dimer has a ^{1}H n.m.r. spectrum which is consistent with the presence of two 4-pyridyl groups, two phenyl groups, and six aliphatic protons. Other pyridine derivatives have been shown to give europium-shifted ^{1}H n.m.r. spectra.[7] In the presence of a europium complex each dimer shows a ^{1}H n.m.r. spectrum in which the chemical shifts of the pyridyl and phenyl ring protons are altered downfield and the splitting patterns made more of the first order. Each dimer shows only one pattern of lines due to the two pyridyl and two phenyl rings which are present. Thus the pairs of pyridyl and phenyl rings must be arranged in a symmetrical manner along the aliphatic chain. The dimers therefore either have structures (3) and (4) or are the *meso*- and (±)-forms of (5). Resonance due to the aliphatic protons are not sufficiently well resolved to allow a distinction to be made between these two groups of structures.



In protic solvents the course of reduction of 4-styrylpyridine is probably addition of one electron to the lowest-energy antibonding molecular orbital to give the anion radical which is now protonated at the most basic centre, the nitrogen atom. This gives a radical of which (7) is one canonical form. The radical appears either to dimerise or to be reduced further at this potential to a carbanion which is protonated. On the basis of this interpretation the dimers must have structures (3) and (4), the pyridine rings being re-formed after tautomerism of some intermediate. Dimerisation by attack of the carbanion species on a molecule of 4-styrylpyridine seems most unlikely because, in the solvent used, protonation of the carbanion would be a much faster reaction. In the dilute solutions used for polarography, dimerisation of the intermediate (7) appears to be relatively slow so that the overall two-electron process dominates.



Cyclic triangular wave voltammetry, initial sweep, of 4-styrylpyridine (6×10^{-3}M) in dimethylformamide, 0·1M-Pr_4NClO_4, Hg cathode, scan rate 0·171 V s^{-1}

Reduction of other substituted 4-styrylpyridines proceeded in an analogous manner to yield the di-

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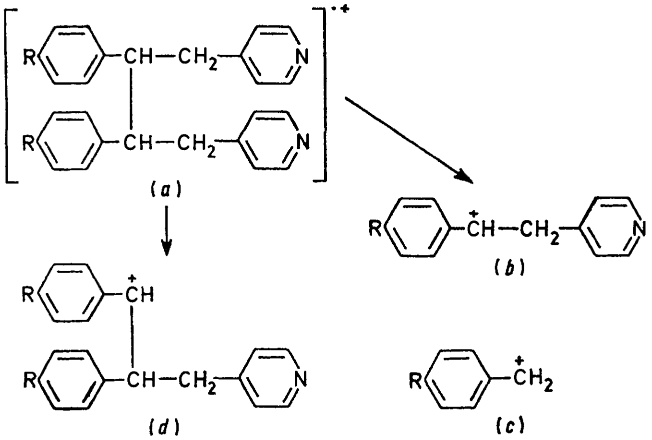
[6] J. E. Dickeson and L. A. Summers, *J. Chem. Soc.* (*C*), 1969, 1643.

[7] K. E. Stensio and U. Ahlin, *Tetrahedron Letters*, 1971, 4729.

hydro-derivative and two hydro-dimers, one solid and one gum. The most abundant fragments in the mass spectra of these dimers are (*b*) and (*c*) of the Scheme and Table 1. That the fragmentation (*a*) ⟶ (*d*) is due to loss of C_6H_6N, and not some combination which gives $PhCH_3$, is confirmed by examination of the mass shifts between the fragmentation patterns where R = H or Me. This supports structures of the type (**3**) and (**4**) for the hydro-dimers. The corresponding fragment (*d*) with R = OMe is of too low abundance for any further supporting conclusion to be drawn.



SCHEME Fragmentation pattern of derivatives of (**3**) and (**4**)

The liquid dimer from reduction of 4-styrylpyridine was resolved into enantiomers by crystallisation of the salt with camphor-10-sulphonic acid and the enantiomers were characterised as their crystalline methiodides. Thus the liquid dimer is the (±)-form (**4**) and the solid dimer must be the *meso*-form (**3**). On chromatography of a mixture over alumina the *meso*-form was more readily eluted. This order of elution was assumed to hold for the other stereoisomeric pairs of related dimers so that stereochemistry could be assigned to the individual isomers.

TABLE 1

m/*e* and % abundance of ion where dimer has R =

	H			Me			OMe		
Ion	*m*/*e*	*meso* (%)	(±) (%)	*m*/*e*	*meso* (%)	(±) (%)	*m*/*e*	*meso* (%)	(±) (%)
(*a*)	**364**	**36**	**52**	**392**	**30**	**31**	**424**	**65**	**36**
(*b*)	**182**	**100**	**100**	**196**	**100**	**100**	**212**	**100**	**100**
(*c*)	**91**	**27**	**24**	**105**	**24**	**18**	**121**	**19**	**26**
(*d*)	**272**	**6**	**4**	**300**	**4**	**6**	**332**	**0·8**	**0·1**

EXPERIMENTAL

All electrode potentials are measured with respect to an aqueous saturated calomel electrode |1·0M-NaNO$_3$| salt bridge containing the electrolysis solution so as to avoid the precipitation of $KClO_4$ at liquid junctions where the salt bridge contains ClO_4^- ions.[8] Liquid junctions were made through short 3 mm diameter plugs of porous Vycor glass attached to the glassware by polytetrafluorethylene tubes.[9] Electrochemical experiments were carried out under a nitrogen atmosphere deoxygenated with the BTS catalyst [10] and dried by molecular sieves. The polarography cell had saturated calomel (s.c.e.) reference electrode, Pt wire anode, and appropriate mercury cathode and was controlled by an operational amplifier potentiostat unit built in this Department. The potential waveform came from a Hewlett–Packard 3310A function generator and current–voltage curves were recorded on a Bryant 26000 series XY recorder. Large-scale electroreduction was carried out with a potentiostat [11] and a conventional H-type cell [12] with Ag anode and s.c.e. reference electrode.

^{1}H N.m.r. spectra were obtained in $CDCl_3$ with Me_4Si as internal lock with a Varian HA100 instrument and mass spectra on an AEI-MS904 instrument by direct insertion. Relative molecular masses in EtOH solution were determined with a Mechrolab vapour-pressure osmometer model 301A. Optical rotations were measured with a Perkin-Elmer polarimeter model 141.

4-*Styrylpyridines*.—These were prepared from the appropriate benzaldehyde by the method of Katritzky *et al.*[13] 4-Styrylpyridine had m.p. 130—131 °C (lit.,[14] m.p. 131 °C), 4-(4′-methylstyryl)pyridine had m.p. 150—151 °C (lit.,[13] m.p. 152 °C), and 4-(4′-methoxystyryl)pyridine had m.p. 134—135 °C (lit.,[15] m.p. 133 °C).

4-(2-*Phenethyl*)*pyridines*.—A methanolic solution of the corresponding 4-styrylpyridine was hydrogenated over Adams catalyst at room temperature and pressure. 4-(2-Phenethyl)pyridine had m.p. 69—70 °C (lit.,[16] m.p. 68 °C), 4-[2-(4-*methylphenyl*)*ethyl*]*pyridine*, needles from light petroleum (b.p. 40—60 °C), had m.p. 48—49 °C (Found: C, 85·8; H, 7·8; N, 7·2. $C_{14}H_{15}N$ requires C, 85·7; H, 7·6; N, 7·1%), and 4-[2-(4-*methoxyphenyl*)*ethyl*]*pyridine*, needles from light petroleum (b.p. 40—60 °C), had m.p. 53—54 °C (Found: C, 78·5; H, 7·2; N, 6·4. $C_{14}H_{15}NO$ requires C, 78·8; H, 7·0; N, 6·5%).

Polarography.—A dropping mercury electrode, mercury height 64·8 cm, flow-rate 1·52 × 10^{-3} g s^{-1}, drop time 4·9 s (aqueous 0·1M-KCl, open circuit) was used. To illustrate that change of solvent from aqueous EtOH to aqueous MeOH, and that introduction of Me and MeO substituents changes $E_{\frac{1}{2}}$ relatively little, $-E_{\frac{1}{2}}$ in McIlvaine buffer pH 8·0 with 0·1M-KCl (10 g) mixed with methanol (10 g), 4-styrylpyridine showed 1·31 V (lit. values in 50% EtOH, 1·02 V, pH 2·3; 1·34 V, pH 9·9;[2] 1·29 V,[3] pH 8·5), 4-(4′-methoxystyryl)pyridine showed 1·35 V, and 4-(4′-methylstyryl)pyridine showed 1·33 V.

Polarography of 4-styrylpyridine (1·0 × 10^{-3}M) in anhydrous dimethylformamide containing tetrapropylammonium perchlorate (0·1M) gave two waves, $E_{\frac{1}{2}}$ −1·88 and −2·22 V.

Cyclic Voltammetry.—The cathode was formed from a Pt sphere made by melting Pt wire (0·30 mm diam.) in a hydrogen–oxygen flame. It was supported in soda-glass

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[8] B. McDuffie, L. B. Anderson, and C. Reilley, *Analyt. Chem.*, 1966, **38**, 883.

[9] W. N. Carson, C. E. Michelson, and K. Koyama, *Analyt. Chem.*, 1955, **27**, 472.

[10] (*a*) M. Schütze, *Angew. Chem.*, 1958, **70**, 697; (*b*) Badische Anilin- and Soda-Fabrik AG, Technical Bulletin, ‘ BTS Catalyst.’

[11] J. Grimshaw and R. K. Quigg, *Analyst*, 1966, **91**, 667.

[12] L. Meites, *Analyt. Chem.*, 1955, **27**, 1116.

[13] A. R. Katritzky, D. J. Short, and A. J. Boulton, *J. Chem. Soc.*, 1960, 1516.

[14] B. D. Shaw and E. A. Wagstaff, *J. Chem. Soc.*, 1933, 77.

[15] E. R. Blout and V. W. Eager, *J. Amer. Chem. Soc.*, 1945, **67**, 1315.

[16] W. Herz and D. R. K. Murty, *J. Org. Chem.*, 1961, **26**, 418.

and coated with Hg before use. The cell contained 4-styrylpyridine (1·0 × 10^{-3}M) and tetrapropylammonium perchlorate (0·1M) in dimethylformamide dried over $CuSO_4$.[17] The initial scan cyclic triangular wave voltagram was recorded. A scan from −1·5 to −2·6 V is reproduced in the Figure, the results of scans from −1·6 to −2·15 V are recorded in Table 2.

TABLE 2

$\frac{v}{s^{-1}}$	$\frac{i_{pc}}{\mu A}$	$\frac{i_{cp}/v^{\frac{1}{2}}}{\mu A\ s^{-\frac{1}{2}}}$	$\frac{i_{pa}}{\mu A}$	$\frac{i_{pa}}{i_{pc}}$	$\frac{-E_{pc}}{V}$	$\frac{-E_{pa}}{V}$
Temperature 25 °C						
0·026	3·9	24	1·9	0·49	1·920	
0·040	5·0	25	2·6	0·52	1·920	1·860
0·080	6·8	24	3·9	0·57	1·920	1·860
0·19	11·1	25	7·2	0·65	1·925	1·855
0·38	14·0	21	10·0	0·71	1·930	1·855
Temperature −46 °C						
0·018	2·3	17	1·6	0·70	1·920	1·870
0·037	3·2	17	2·6	0·81	1·920	1·870
0·072	4·8	17	3·6	0·75	1·920	1·870
0·145	6·6	17	5·9	0·89	1·920	1·865
0·18	7·1	17	6·3	0·89	1·925	1·860
0·28	8·7	16	7·7	0·89	1·930	1·855
Temperature −64 °C						
0·018	1·6	12	1·2	0·75	1·915	1·870
0·036	2·0	10	1·6	0·80	1·915	1·870
0·072	3·1	11	2·5	0·80	1·920	1·865
0·144	4·1	11	3·6	0·88	1·925	1·860
0·180	4·6	11	3·9	0·85	1·930	1·855
0·288	5·6	10	5·0	0·89	1·938	1·850

Reduction of 4-*Styrylpyridine*.—A solution of lithium chloride (2M) and sodium acetate (0·2M) in acetic acid (0·2M) and aqueous methanol (50% w/w) was used as electrolyte (pH 3·7). The anode compartment contained this electrolyte and an Ag wire anode. 4-Styrylpyridine (1·7 g) in the electrolyte (170 ml) was reduced at a Hg pool cathode potential of 1·3—1·4 V (pool area 15 cm^2, initial current 0·21 A) for 24 h. The catholyte was then concentrated under reduced pressure, made strongly alkaline, and extracted with ether. The ether layer was washed with water and dried (Na_2SO_4) and the solvent removed to leave a resin which was chromatographed on alumina. Elution with ether yielded 4-(2-phenethyl)pyridine (0·27 g), m.p. and mixed m.p. 68—70 °C. Ether–methanol (1%) eluted meso-2,3-*diphenyl*-1,4-*di*-(4-*pyridyl*)*butane* (0·13 g), needles, m.p. 181—182 °C (from ether) (Found: C, 86·0; H, 6·2; N, 7·6%; *M*, 353. $C_{26}H_{24}N_2$ requires C, 85·7; H, 6·6; N, 7·7%; *M*, 364), τ 1·7 (d, 4H, *J* 6 Hz), 2·6—2·9 (m, 10H), 3·4 (d, 4H, *J* 6 Hz), 6·8—8·0 (m, 6H); τ [+Eu(tmhd)$_3$, 2·2 mol] −7·9br (s, 4H), −0·3br (s, 4H), 0·7 (d, 4H, *J* 7 Hz), 1·7 (t, 4H, J_{app} *ca.* 7 Hz), 2·1 (t, 2H, *J* 7 Hz), 3·9—4·6 (m, 6H). This diamine (0·3 g) was refluxed with iodomethane (1 ml) in methanol (10 ml) to yield the *di-dimethiodide*, needles, m.p. >300 °C (from ethanol) (Found: C, 52·0; H, 4·9; N, 4·3; I, 39·0. $C_{28}H_{30}I_2N_2$ requires C, 51·9; H, 4·7; N, 4·3; I, 39·1%), τ [$(CD_3)_2SO$] *inter alia*, pyridine protons 1·30 (d, area 2) 2·30 (d, area 2) *J* 6 Hz, benzene protons 2·5—2·8 (m, area 5).

Elution of the chromatogram with ether–methanol (5%) gave (±)-2,3-*diphenyl*-1,4-*di*-(4-*pyridyl*)*butane* (0·24 g) as a hygroscopic gum which refused to crystallise (Found: C, 85·1; H, 7·1; N, 7·2%; *M*, 335, 375, τ 1·6 (d, 4H, *J* 6 Hz), 2·5—5·3 (m, 14H), 6·5—7·3 (m, 6H); τ [+Eu(tmhd)$_3$, 2·2 mol] −7·35br (s, 4H), −0·5 (d, 4H, *J* 4 Hz), 1·3 (d, 4H, *J* 8 Hz), 2·1 (t, 4H, J_{app} *ca.* 8 Hz), 2·35 (t, 2H, *J* 7 Hz), 3·4—4·5 (m, 6H). The corresponding *dimethiodide* formed needles, m.p. 230—235° (decomp.), from methanol (Found: C, 51·9; H, 4·5; N, 4·5; I, 38·8%), τ [$(CD_3)_2SO$] *inter alia*, pyridine protons 1·22 (d, area 2) 2·08 (d, area 2) *J* 6 Hz, benzene protons 2·95 (s, area 5).

Resolution of (±)-2,3-*Diphenyl*-1,4-*di*-(4-*pyridyl*)*butane*.—The (±)-diamine (0·9 g) and (+)-camphor-10-sulphonic acid (1·15 g) were dissolved in dioxan (8 ml) and the solution cooled to 0 °C. The crystalline salt was collected and after recrystallisation from dioxan had m.p. 144—146 °C. It was then basified with aqueous sodium hydroxide and the amine recovered in ether. This afforded the (−)-diamine as a resin $[\alpha]_D^{25}$ −9·5°, $[\phi]_{589}$ −34·6°, $[\phi]_{578}$ −35·3°, $[\phi]_{546}$ −40·8°, $[\phi]_{436}$ −77·0 (*c*, 2 in $CHCl_3$). The mother-liquor from the first crystallisation was evaporated to dryness under reduced pressure and the amine isolated with ether, after basification. This afforded the partly resolved (+)-diamine as a resin $[\alpha]_D^{25}$ +4·8°, $[\phi]_{589}$ +17·6°, $[\phi]_{578}$ +19·6°, $[\phi]_{546}$ +22·4° (*c*, 2 in $CHCl_3$). The ^1H n.m.r. spectra ($CDCl_3$) of the enantiomers and the (±)-diamine were identical. Both enantiomers gave a dimethiodide, m.p. 230—235° (decomp).

The salt of the *meso*-isomer with (+)-camphorsulphonic acid was crystallised several times from dioxan. The recovered base, m.p. 182 °C, showed no optical activity.

Reduction of 4-(4′-*Methylstyryl*)*pyridine*.—McIlvaine buffer pH 3·0 containing potassium chloride (0·2M) was diluted with methanol (50% w/w) and used as electrolyte. 4-(4′-Methylstyryl)pyridine (1·7 g) in the electrolyte (150 ml) was reduced, as previously described, at a mercury cathode, −1·4 V (initial current 0·19 A). After 24 h the mixture was worked up and chromatographed on alumina. Elution with ether yielded 4-[2-(4-methylphenyl)ethyl]-pyridine (0·42 g), m.p. and mixed m.p. 48—49 °C. Ether–methanol (2%) eluted meso-2,3-*di*-(4-*methylphenyl*)-1,4-*di*-(4-*pyridyl*)*butane* (0·11 g), crystallised from light petroleum (b.p. 60—80 °C) as needles, m.p. 177—178 °C (Found: C, 85·9; H, 7·0; N, 7·2. $C_{28}H_{28}N_2$ requires C, 85·7; H, 7·2; N, 7·1%). Ether–methanol (5%) eluted (±)-2,3-*di*-(4-*methylphenyl*)-1,4-*di*-(4-*pyridyl*)*butane* (0·25 g), a gum (Found: N, 7·2%).

Reduction of 4-(4′-*Methoxystyryl*)*pyridine*.—This base (0·9 g) was reduced at pH 3·0 as for the previous example and the products chromatographed on alumina. Elution with ether yielded 4-[2-(4-methoxyphenyl)ethyl]pyridine (0·2 g), m.p. and mixed m.p. 53—54 °C. Elution with ether–methanol (3%) gave meso-2,3-*di*-(4-*methoxyphenyl*)-1,4-*di*-(4-*pyridyl*)*butane* (0·07 g), crystallised from light petroleum (b.p. 60—80 °C) as needles, m.p. 165—167 °C (Found: C, 79·1; H, 6·8; N, 6·4. $C_{28}H_{28}N_2O_2$ requires C, 79·2; H, 6·6; N, 6·6%). Ether–methanol (5%) eluted (±)-2,3-di-(4-methoxyphenyl)-1,4-di-(4-pyridyl)butane (0·16 g) as a gum (Found: C, 78·1; H, 7·3) which showed the expected mass spectrum but satisfactory analyses were not obtained.

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