Electrochemical Reactions. Part XIV.[1,2] Carbon–Halogen Bond Fragmentation in the Radical Anions from 4-(Chlorostyryl)pyridines. Factors which determine the Rate of Such Fragmentations

By **Khaled Alwair** and **James Grimshaw,*** Department of Chemistry, Queen's University, Belfast BT9 5AG

In dimethylformamide at 296 K the radical anion from 4-(3-chlorostyryl)pyridine is slowly destroyed by protonation. The radical anion from 4-(4-chlorostyryl)pyridine reacts at 296 K ($k = 1{\cdot}5 \pm 0{\cdot}4$ s^{-1}) to form 4-styrylpyridine but at 252 K fragmentation is not detected before the radical anion is destroyed by protonation. Other halogenated radical anions show different rates of fragmentation of the carbon–halogen bond depending on the position of substitution and these observations are explained by taking account of the free electron density distribution in the first antibonding molecular orbital. Reduction of 4-(4-chlorostyryl)pyridine in aqueous methanol parallels reduction of 4-styrylpyridine, and the chloro-substituent is not lost. The half-wave potentials for the two reduction waves of substituted 4-styrylpyridines have been correlated with the Hammett σ constant.

In a previous paper [2] we examined the reduction of 4-styrylpyridine in dimethylformamide and showed that each of the two polarographic waves which this compound exhibits corresponds to the uptake of one electron per molecule. For the first wave with $E_{\frac{1}{2}} = -1{\cdot}88$ V (*versus* s.c.e.), electron transfer proceeds without significant energy of activation and the radical anion formed has a half life of 10 s at room temperature. Under such circumstances, the half-wave potential is equal to the standard potential for the redox couple if activity coefficients are neglected and the diffusion coefficients of the reduced and oxidised species are assumed equal.[3] The half-wave potentials for styrylpyridine derivatives with substituents in the benzene ring would therefore be expected to show a linear correlation with the Hammett σ constant for the substituent. This Hammett correlation for a series of substituted 4-styrylpyridines is illustrated in Figure 1, and as anticipated the first reduction wave shows a good correlation, coefficient r 0·951. Nevertheless, further experiments show that some of the halogen substituted derivatives can undergo reactions which are different from that of the parent radical anion.

The Hammett correlation for the second reduction wave is poor, r 0·644. This is because, as is discussed below, addition of the first electron to the halogen substituted compounds in some cases initiates a series of reactions to produce 4-styrylpyridine radical anion. The radical anion being reduced in the second wave is then unrelated to the original substrate.

[1] Part XIII, J. Grimshaw and J. Trocha-Grimshaw, *J.C.S. Perkin I*, in the press.

4-(4-Chlorostyryl)pyridine.—Cyclic voltammetry at room temperature (Figure 2a) of 4-(4-chlorostyryl)-pyridine (1) in dimethylformamide at the potential

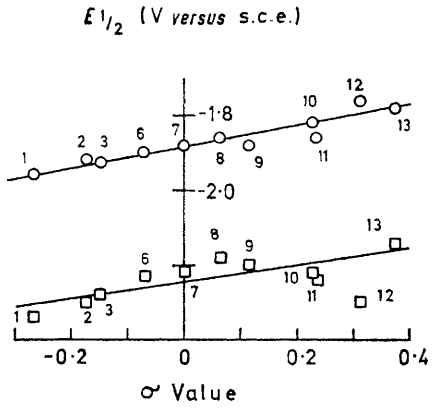


FIGURE 1 Hammett correlation for the two polarographic waves of substituted 4-styrylpyridines in solvent dimethylformamide (numbered compounds are identified in Table 3)

region of the first reduction wave showed this wave to be due to a series of electrochemical and chemical reactions. The first electron transfer which gives the cathodic peak 1 is followed by decomposition of the product to a substance which can take part in a reversible redox reaction of $E_0 = -1{\cdot}88$ V (*versus* s.c.e.) with cathodic peak 2 and anodic peak 3. This redox couple corresponds to 4-styrylpyridine and the derived radical

[2] This paper continues Part X, K. Alwair, J. F. Archer, and J. Grimshaw, *J.C.S. Perkin II*, 1972, 1663.

[3] J. Heyrovsky and J. Kuta, 'Principles of Polarography,' Academic Press, New York, 1966, ch. VII.

anion. Preparative scale electrolysis of 4-(4-chlorostyryl)pyridine in dimethylformamide at the half-peak potential of peak 1 was carried out using g.l.c. to monitor the progress of reduction (see Figure 3). 4-Styrylpyridine was formed and subsequently reduced further to yield 4-phenethylpyridine. Column chromatography and analysis of the products by mass spectrometry also revealed the presence of dimeric material but no pure dimer could be isolated.

Thus the voltagram can be explained as follows. The first electron transfer to 4-(4-chlorostyryl)pyridine (1) is followed by rapid fragmentation with eventual formation of chloride ion and 4-styrylpyridine (4) which undergoes its usual redox behaviour to give peaks 2 and 3. In the macro-scale electrolysis protonation of 4-styrylpyridine radical anion by extraneous moisture and reduction of

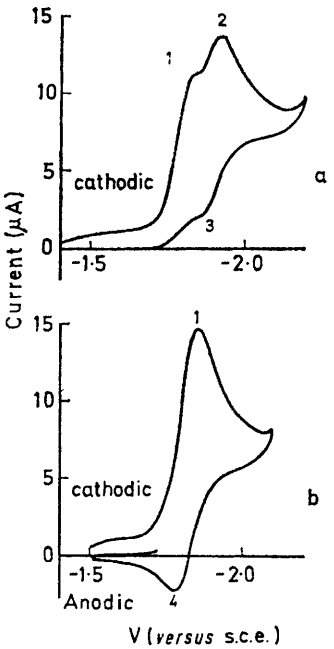


FIGURE 2 Cyclic voltammetry of 4-(4-chlorostyryl)pyridine in dimethylformamide: a, 296 K, v 0·032 V s^{-1}; b, 252 K, v 0·24 V s^{-1}

the resulting radical gives 4-phenethylpyridine as discussed previously [2] for reduction in aqueous methanol.

When the cyclic voltammetry experiments were carried out at progressively lower temperatures, the voltagram changed gradually from the situation of Figure 2a at room temperature to that of Figure 2b at 252 K. Peaks 2 and 3 disappeared and a new anodic peak 4 appeared. The peaks 1 and 4 are due to a new redox couple. This change can be interpreted as due to the effect of temperature on the rate constant for the fragmentation of the radical anion formed from 4-(4-chlorostyryl)pyridine at the potential range of peak 1. At lower temperatures this fragmentation becomes unimportant within the time period of a voltagram and the redox couple with peaks 1 and 4 is due to 4-(4-chlorostyryl)pyridine and the radical anion (2). At 252 K this

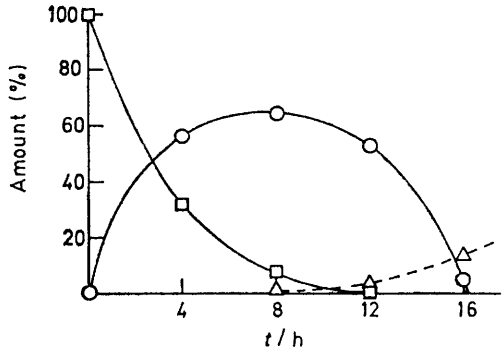
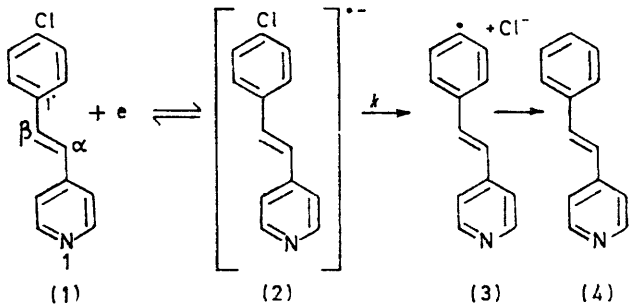


FIGURE 3 Products from the reduction of 4-(4-chlorostyryl)-pyridine in dimethylformamide at a Hg cathode with potential −1·4 V (*versus* s.c.e.): □, 4-(4-chlorostyryl)pyridine; ○, 4-styrylpyridine; △, 4-phenethylpyridine

radical anion has a half-life of 5 s and is destroyed either by protonation or by reaction with a molecule of the chlorostyrylpyridine to give a dimer as suggested by Baizer for some radical anions.[4]

At room temperature the radical anion (2) is formed and rapidly fragments. Fragmentation is assumed from electronegativity considerations to give the σ radical (3) and chloride ion, rather than a carbanion and a chlorine atom, and cleavage in the first sense is always assumed in the literature (*e.g.* refs. 4, 5 and others there cited). Further reaction of the σ radical (3) may be either by hydrogen abstraction from the solvent or by reduction to the carbanion and protonation.

In complete distinction to the above results in dimethylformamide, reduction of 4-(4-chlorostyryl)pyridine in aqueous methanol leads to the dihydro-compound (6) and two dimers with no formation of chloride ion. This is a parallel with the reduction of 4-styrylpyridine in protic solvents [2] and by analogy, the dimers are considered to be the *meso*- and (±)-forms of (7). Electroreduction in aqueous methanol is a useful route for



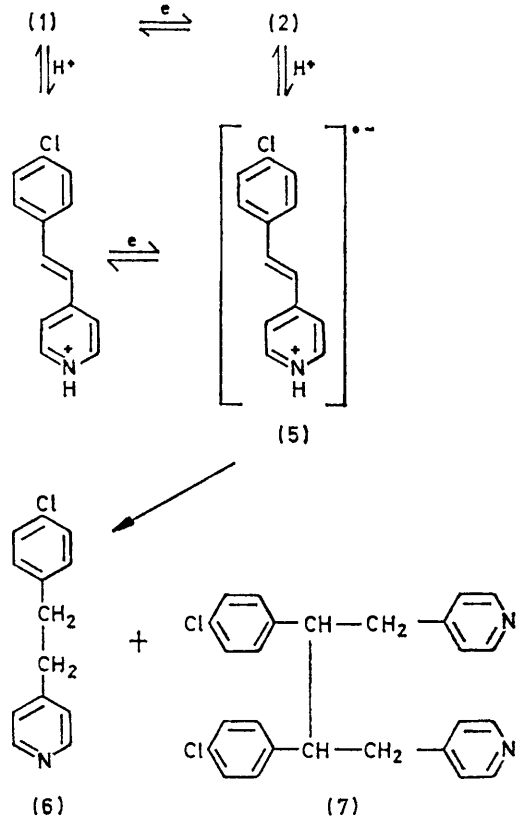
preparation of the dihydro-compound (6). Catalytic reduction over Pt or Pd under various conditions failed to give a dihydro-compound without some carbon–chlorine bond cleavage.

[4] J. P. Petrovich, M. M. Baizer, and M. R. Ort, *J. Electrochem. Soc.*, 1969, **116**, 743.

[5] R. P. Van Duyne and C. N. Reilley, *Analyt. Chem.*, 1972, **44**, 158.

The differing courses of reduction in protic and aprotic solvents can be accommodated in one reaction scheme by assuming that protonation of the initially formed radical anion is a very fast reaction. In aqueous methanol both the starting material and the radical anion are involved in rapid acid–base reactions and the radical anion is converted to products by rapid collapse of the protonated form (5) to a σ radical.

Van Duyne and Reilley[5] have also used voltammetry at low temperatures in aprotic solvents to demonstrate the formation and fragmentation of the radical anion from 4-iodonitrobenzene (8). The fragmentation



of 4-iodonitrobenzene radical anion to give a σ radical and iodide ion is considered to be reversible. The σ radical forms nitrobenzene by abstraction of a hydrogen atom from a molecule of the solvent. It has not been decided whether fragmentation or hydrogen abstraction is the rate-determining step.[5,6] The reduction of 4-iodonitrobenzene by dissolving metals in aqueous suspension is well known to give 4-iodophenylhydroxylamine and 4-iodoaniline.[7] Here the course of the reaction is parallel to the reduction of nitrobenzene and protonation of the formed radical ion in protic solvents must be faster than fragmentation.

The consequences to the appearance of cyclic voltagrams which result from variously coupled electrochemical and chemical reactions have been well explored.[8] The rate constant k for fragmentation of the radical anion (2) can be calculated using the results of these theoretical investigations. For the reaction sequence suggested the potential of peak 1, E_p, varies with the rate of voltage scan, v, according to the expression (1) where $a = Fv/RT$, $E_{\frac{1}{2}}$ is the half-wave potential

$$E_p - E_{\frac{1}{2}} = -RT(0{\cdot}780 - \ln k/a)/F \qquad (1)$$

at a dropping mercury electrode, and the other symbols have their usual significance. Application of this expression to each voltagram and then averaging the results (Table 4) gives $k = 1{\cdot}5 \pm 0{\cdot}4\ s^{-1}$ at 296 K. The large error arises because $E_p - E_{\frac{1}{2}}$ is a small quantity.

The cyclic voltagram for 4-(4-bromostyryl)pyridine in dimethylformamide resembles Figures 2a both at 296 and at 208 K. Even at the lower temperature fragmentation of this radical anion to give 4-styrylpyridine and bromide ion is extremely fast. The cyclic voltagram of 4-(4-fluorostyryl)pyridine at 296 K resembles the curve for 4-styrylpyridine. Thus the radical anion of the fluoro compound does not fragment under these conditions. However, it is more basic than the parent radical anion and shows a half life of *ca.* 0·8 s before it is destroyed by protonation or reaction with an unreduced molecule.

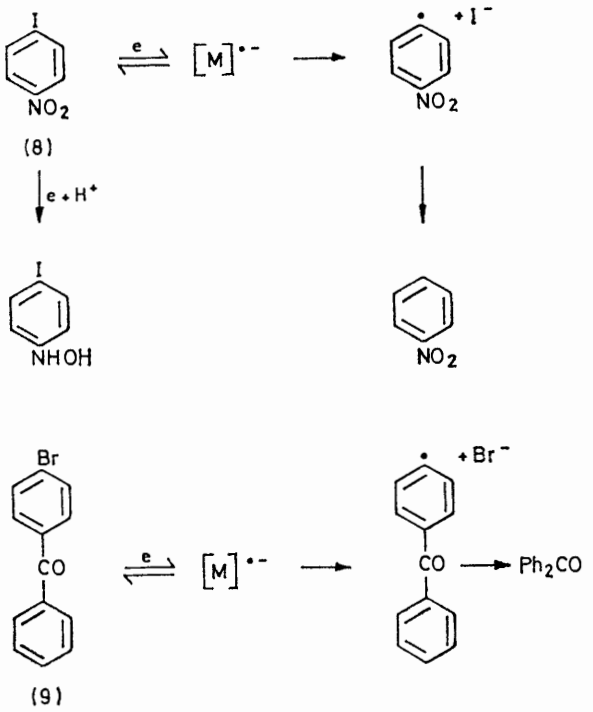
4-(3-*Chlorostyryl*)*pyridine*.—In contrast to the behaviour of its isomer discussed above, 4-(3-chlorostyryl)-pyridine and the formed radical anion show reversible redox behaviour on cyclic voltammetry in dimethylformamide. The voltammetric behaviour at 296 K exactly parallels the behaviour of 4-styrylpyridine. For the redox couple $E_0 = -1{\cdot}79$ V (*versus* s.c.e.) and the radical ion is slowly lost by protonation with extraneous moisture with a half-life of *ca.* 10 s.

DISCUSSION

This pathway for the cleavage of aromatic halogen bonds, where the radical anion is first formed in an aprotic solvent and fragments, has been established for a number of examples by cyclic voltammetry and e.s.r. techniques and the literature is summarised elsewhere.[6,9-11] Rate constants (see Table 2) have been measured for the cleavage of halogenonitrobenzenes [5,6] and for bromo- and chloro-benzophenones.[9] The ketones react in the manner illustrated, for example (9). Decomposition of the radical anion is the rate-determining step which may be reversible by itself but is followed by a fast and irreversible hydrogen abstraction from the solvent. These examples together with our styrylpyridine derivatives show that the rate of fragmentation of the carbon–halogen bond varies markedly with its

[6] J. G. Lawless and M. D. Hawley, *J. Electroanalyt. Chem.*, 1969, **21**, 365.
[7] E. Bamberger, *Ber.*, 1895, **28**, 249.
[8] R. S. Nicholson and I. Shain, *Analyt Chem.*, 1964, **36**, 706.
[9] L. Nadjo and J. M. Saveant, *J. Electroanalyt. Chem.*, 1971, **30**, 41.
[10] D. E. Bartak, T. M. Shields, and M. D. Hawley, *Electroanalyt. Chem.*, 1971, **30**, 289.
[11] D. E. Bartak, K. J. Houser, B. C. Rudy, M. O. Hawley, *J. Amer. Chem. Soc.*, 1972, **94**, 7526.

position of substitution in the radical ion. Hawley [12] has used an argument based on steric effects to explain the rapid decomposition of 2-iodonitrobenzene. The rate variation between *meta*- and *para*-isomers where the steric effects do not apply can be explained on the



hypothesis that the fragmentation rate is dependent on the free electron density in the radical anion at the carbon atom involved.

As a first approximation to this electron density in the styrylpyridine examples, the electron density distribution in the lowest energy antibonding molecular orbital of 4-styrylpyridine can be calculated by the HMO method.[13] The result taking $h_N = 0{\cdot}7$ and $k_{CN} = 1{\cdot}0$ is given in Table 1. Corresponding calculations for nitrobenzene and benzophenone are available (Table 2). These results do support the suggested dependence of the fragmentation rate of isomeric halogenated radical anions. Heterolytic cleavage of the carbon–chlorine bond in 4-(4-chlorostyryl)pyridine can be assisted by bond bending so that the free electron fractionally occupies the emptying carbon sp^2 orbital which has in this manner acquired some sp^3 character.

TABLE 1

Calculated free electron density distribution in the radical anion for 4-styrylpyridine

4-Styrylpyridine			
Position	HMO free electron density	Position	HMO free electron density
1	0·109	1′	0·031
2	0·035	2′	0·070
3	0·062	3′	0·004
4	0·086	4′	0·085
α	0·139		
β	0·206		

TABLE 2

Properties of the radical anions from nitrobenzene and benzophenone and the rate of fragmentation of their halogen derivatives

Position	HMO free electron density	$k_{relative}/s^{-1}$ for decomp. of the iodo-derivative [5,6]
For nitrobenzene radical ion [a,b]		
2	0·106	500
3	0·005	0·34
4	0·124	1

For benzophenone radical ion [c]	HMO free electron density	k/s^{-1} for decomp. of Chloro-derivative	Bromo-derivative
2	0·076	*d*	*d*
3	0·006	*e*	$(7{\cdot}4 \pm 2) \times 10^2$
4	0·097	10 ± 3	$(8{\cdot}0 \pm 2{\cdot}4) \times 10^4$

[a] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 609. [b] C. Ling and J. Gendell, *J. Chem. Phys.*, 1967, **47**, 3475. [c] S. V. Kulkani and C. Trapp, *J. Amer. Chem. Soc.*, 1970, **92**, 4809. [d] Not examined. [e] Fragmentation rate too slow to measure.

The free electron density distribution found for the 4-styrylpyridine radical anion is only an approximation to the density distribution in the chloro-substituted radical since the filled halogen *p* orbital can overlap with the aromatic π-orbitals, and similarly for the other examples. Such molecular orbital calculations are however already available for many aromatic systems and our aim is to show how these can be used as a guide to make qualitative predictions of the relative rates of fragmentation of carbon–halogen bonds which may be useful in designing electrochemical syntheses.

EXPERIMENTAL

For general directions and a description of the electrochemical apparatus see Part X.[2]

4-Styrylpyridines.—These were prepared from the appropriate benzaldehyde.[14] 4-(4-Isopropylstyryl)pyridine crystallised from light petroleum (b.p. 40—60°) as plates, m.p. 102—103° (lit.,[15] m.p. 66—68°) (Found: C, 85·9; H, 7·5; N, 6·0. Calc. for $C_{16}H_{17}N$: C, 86·1; H, 7·6; N, 6·3%). Previously unknown derivatives were *4-(3-methoxystyryl)pyridine*, needles, m.p. 60—61° [from light petroleum (b.p. 60—80°)] (Found: C, 79·4; H, 6·0; N, 6·5. $C_{14}H_{13}NO$ requires C, 79·6; H, 6·2; N, 6·6%); *4-(3,4-dimethoxystyryl)pyridine*, needles, m.p. 127—128° [from light petroleum (b.p. 60—80°)] (Found: C, 74·6; H, 6·2; N, 5·5. $C_{15}H_{15}NO_2$ requires C, 74·6; H, 6·2; N, 5·8%); *4-(3,4-methylenedioxystyryl)pyridine*, needles, m.p. 228—230° (from ethanol) (Found: C, 74·8; H, 5·0; N, 6·1. $C_{14}H_{11}NO_2$ requires C, 74·6; H, 4·9; N, 6·2%); *4-(4-fluorostyryl)pyridine*, m.p. 113—114° (from ethanol) (Found: C, 78·6; H, 5·3; N, 7·3. $C_{13}H_{10}FN$ requires C, 78·3; H, 5·0; N, 7·0%);

[12] W. C. Danen, T. T. Kensler, J. G. Lawless, M. F. Marcus, and M. D. Hawley, *J. Phys. Chem.*, 1969, **73**, 4389.

[13] A. Streitwieser, 'Molecular Orbital Theory,' Interscience, New York, 1963.

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

[15] A. K. Sheinkman and A. N. Rozenberg, *Zhur. obshchei Khim.*, 1964, **34**, 4046.

4-(3-*chlorostyryl*)*pyridine*, needles, m.p. 54—55° (from aqueous methanol) (Found: C, 72·3; H, 4·8; Cl, 16·4; N, 6·5. $C_{13}H_{10}ClN$ requires C, 72·3; H, 4·6; Cl, 16·3; N, 6·5%); and 4-(4-*bromostyryl*)*pyridine*, needles, m.p. 158—159° (from ethanol) (Found: C, 59·7; H, 3·9; N, 5·3. $C_{13}H_{10}BrN$ requires C, 60·0; H, 3·9; N, 5·4%).

Polarography.—The cell solution contained the 4-styrylpyridine (10^{-3}M) and tetrapropylammonium perchlorate (0·1M) in anhydrous dimethylformamide. Each derivative showed two waves with the half-wave potentials listed in Table 3. A Hammett correlation using the σ constants of McDaniel and Brown [16] gives for the first wave $\rho = 0{\cdot}28 \pm 0{\cdot}03$, $r = 0{\cdot}951$, and for the second wave $\rho = 0{\cdot}18 \pm 0{\cdot}06$, $r = 0{\cdot}644$.

TABLE 3

Half-wave potentials (V *versus* s.c.e.) for the polarography of substituted 4-styrylpyridines in dimethylformamide

No.	Substituent in phenyl ring	$-E_{\frac{1}{2}}$ Wave I	$-E_{\frac{1}{2}}$ Wave II	No.	Substituent in phenyl ring	$-E_{\frac{1}{2}}$ Wave I	$-E_{\frac{1}{2}}$ Wave II
1	4-OMe [a]	1·96	2·34	8	4-F	1·86	2·18
2	4-Me [a]	1·92	2·30	9	3-OMe	1·88	2·20
3	4-$CHMe_2$	1·93	2·28	10	4-Cl [a]	1·83	2·22
4	3,4-OMe_2	1·94	2·30	11	4-Br	1·86	2·24
5	3,4-O_2CH_2	1·92	2·28	12	4-OAc [c]	1·76	2·30
6	3-Me [b]	1·90	2·23	13	3-Cl	1·78	2·14
7	None [a]	1·88	2·22				

[a] Ref. 14. [b] G. Galtazzo, *Gazzetta*, 1965, **95**, 1322. [c] L. Horwitz, *J. Org. Chem.*, 1956, **21**, 1039.

Cyclic Voltammetry.—The cathode was a mercury coated platinum sphere, *ca.* 0·15 cm diameter. The cell solution was as for polarography and this could be immersed in ice and salt eutectic baths. The results of first scans from −1·6 to −2·15 V in the region where 4-styrylpyridine radical anion is formed are summarised below.

4-(4-*Chlorostyryl*)*pyridine*. Figure 2a shows a typical voltagram at 296 K where E_p^1, E_p^2, and E_p^3 are −1·84, −1·93, and −1·86 V respectively with v 0·032 V s^{-1}. When the scan is extended to more negative potentials a further cathodic wave with $E_p^5 = -2{\cdot}26$ V is seen. E_p^2, E_p^3, and E_p^5 are superimposable on the peaks in the voltagram of 4-styrylpyridine.[2] E_p^1 varies with v (Table 4) and writing

$$E_p^1 = E_{\frac{1}{2}} = 0{\cdot}030(A - \log v) \qquad (2)$$

equation (1) in the form (2) where $A = -1{\cdot}56/2{\cdot}303 + \log kRT/F$ enables the calculation of A and hence of k.

TABLE 4

Cyclic voltammetry of 4-(4-cholorostyryl)pyridine at 296 K. Calculation of the rate constant for fragmentation of the radical anion

$-E_p^1$/V	v/V s^{-1}	$A = \log v + (E_p - E_{\frac{1}{2}})/0{\cdot}03$
1·84	0·0320	−1·83 ± 0·4
1·85	0·0414	−2·05 ± 0·4
1·86	0·0690	−2·16 ± 0·3
1·87	0·138	−2·19 ± 0·3
1·85	0·0444	−2·12 ± 0·3

$A = -2{\cdot}1 \pm 0{\cdot}1$, hence $k = 1{\cdot}5 \pm 0{\cdot}4$ s^{-1}.

At 252 K (Figure 2b), peaks 1—3 are replaced by one reversible redox reaction with $E_p^1 = -1{\cdot}83$ and $E_p^4 = -1{\cdot}78$ V and the half-life of the radical anion formed is *ca.* 5 s. Continuous cyclic voltammetry at this temperature does not result in conversion of the voltagram from Figure 2b to 2a so the radical anion is not converted in significant amount to 4-styrylpyridine.

4-(3-*Chlorostyryl*)*pyridine*. At 296 K the first reduction wave shows the voltagram of a reversible redox reaction similar to Figure 2b with $E_p^1 = -1{\cdot}83$ and $E_p^4 = -1{\cdot}76$ V, half-life of the radical anion *ca.* 10 s.

4-(4-*Fluorostyryl*)*pyridine*. At 296 K the first reduction step shows a cathodic peak with $E_p = -1{\cdot}91$ V and on reverse scan the corresponding anodic peak is found only at rapid scan rates, half-life of the radical anion *ca.* 0·8 s.

4-(4-*Bromostyryl*)*pyridine*. At 208 K the voltagram around the potential of the first reduction wave has the appearance of Figure 2a with E_p^1, E_p^2, and E_p^3 −1·79, −1·92, and −1·87 V respectively which corresponds to very rapid decomposition of the radical anion to 4-styrylpyridine.

Reduction of 4-(4-*Chlorostyryl*)*pyridine*.—An H-type cell was used with mercury cathode, platinum anode, and anolyte containing the supporting electrolyte only.

(*a*) 4-(4-Chlorostyryl)pyridine (0·25 g) in anhydrous dimethylformamide (25 ml) containing tetrapropylammonium perchlorate (0·1M) was reduced under nitrogen at cathode potential −1·80 ± 0·02 V (*versus* s.c.e.) (cathode area 6·2 cm^2, initial current 0·012 A) for a fixed time after which the total catholyte was poured into water. 4-(4-Methylstyryl)pyridine was added as internal standard when the products were isolated in ether and washed with water and the volatile constituents were determined by g.l.c. using a Perkin-Elmer F11 instrument with flame ionisation detector and 2 m × 1/8 in column of 2-cyanoethylmethylsilicone (2·5%) at 195 °C. The results are given in Figure 3: retention times (min); 4-phenethylpyridine 3·2, 4-[2-(4-chlorophenyl)ethyl]pyridine 6·5 (not found as a product), 4-styrylpyridine 7·5, 4-(4-methylstyryl)pyridine 9·0, 4-(4-chlorostyryl)pyridine 15·0.

(*b*) McIlvaine buffer, pH 3·35, containing potassium chloride (0·2M) was diluted with methanol (50% w/w) and used as electrolyte. A solution of 4-(4-chlorostyryl)-pyridine (2·0 g) in the electrolyte (150 ml) was reduced at a mercury cathode (area 15 cm^2, initial current 0·21 A), potential −1·4 V, for 24 h when the catholyte was poured into water and made alkaline and the products were isolated in ether. Chromatography of the mixture over alumina afforded 4-[2-(4-*chlorophenyl*)*ethyl*]*pyridine* (0·14 g), eluted with ether and crystallised from methanol as needles, m.p. 74—75° (Found: C, 71·6; H, 5·7; Cl, 16·4; N, 6·7. $C_{13}H_{12}ClN$ requires C, 71·7; H, 5·6; Cl, 16·2; N, 6·4%), *m/e* 219 (26%) and 217 (74). Ether–methanol (3%) eluted *meso*-2,3-*bis*-(4-*chlorophenyl*)-1,4-*di*-(4-*pyridyl*)*butane* (0·40 g) which was crystallised from methanol, m.p. 224—226° (Found: C, 71·9; H, 5·1; Cl, 16·2; N, 6·4. $C_{26}H_{22}Cl_2N_2$ requires C, 71·8; H, 5·0; Cl, 16·3; N, 6·4%), *m/e* 436 (M^+, 7), 434 (M^+, 37), and 432 (M^+, 56). Ether–methanol (5%) eluted (±)-2,3-*bis*-(4-*chlorophenyl*)-1,4-*di*-(4-*pyridyl*)-*butane* (0·4 g) which was crystallised from ethanol, m.p. 55—56° (Found: C, 72·2; H, 4·7; Cl, 16·2; N, 6·5%), *m/e* 436 (M^+, 7%), 434 (M^+, 37), and 432 (M^+, 56). Stereochemistry is assigned by analogy with the dimers from reduction of 4-styrylpyridine where the *meso*-isomer is eluted first from alumina.[2]

We thank the S.R.C. for a grant for apparatus and the University of Aleppo, Syria, for a maintenance award (to K. A.) through the Ford Foundation.

[2/2825 *Received*, 15*th December*, 1972]

[16] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.