Electrochemical Reactions. Part XIII.[1] Reduction of Some Styrylpyrazole Derivatives

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5-Phenyl-3-styrylpyrazole ($E_{\frac{1}{2}}$ −2·16 and −2·60 V *versus* s.c.e.) and 1,5-diphenyl-3-styrylpyrazole ($E_{\frac{1}{2}}$ −2·27, −2·44, and −2·85 V) in dimethylformamide give rise to polarographic waves, but radical anions were not detected as intermediates by cyclic voltammetry. Reduction of 5-phenyl-3-styrylpyrazole at the potential of the first wave afforded 5-phenyl-3-(2-phenylethyl)pyrazole. Reduction of 1,5-diphenyl-3-styrylpyrazole at a potential near the diffusion plateau of the second wave (this is not completely separated from the first wave) gave 1,5-diphenyl-3-(2-phenylethyl)-Δ^2-pyrazoline.

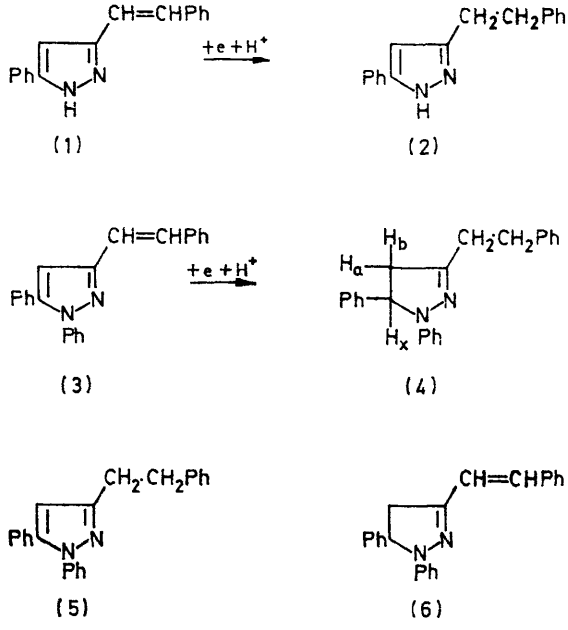
THE radical anions formed by reduction of stilbene [2] ($E_{\frac{1}{2}}$ −2·36 V) and 4-styrylpyridine [3] ($E_{\frac{1}{2}}$ −1·88 V) in anhydrous dimethylformamide are stable for short periods ($t_{\frac{1}{2}}$ *ca.* 10 s); introduction of a nitrogen atom in place of a CH group lowers the half-wave potential for reduction of the conjugated system. At more negative potentials each radical anion accepts a second electron. The polarography of 1,5-diphenyl- (3) and 5-phenyl-3-styrylpyrazole (1) has been examined in order to see the result of replacing a pyridine with a pyrazole ring.

5-Phenyl-3-styrylpyrazole (1) shows two polarographic waves (see Table). Cyclic voltammetry in the potential region of the first wave or of both waves indicated no reversible electron transfer, so any radical anion which is formed during the reduction has a half-life of less than 0·2 s. A small preparative-scale reduction of (1) in moist dimethylformamide at the potential of the first polarographic wave afforded the dihydro-derivative (2). No dimer was isolated although one could have resulted from coupling of radical intermediates from a stepwise addition of the two electrons and two protons. Thus the first polarographic wave corresponds to the process (1) ⟶ (2). The wave height is smaller than that for a similar process in the 1-phenylpyrazole series discussed later. This is probably because the NH group can hydrogen-bond to solvent molecules and in consequence pyrazoles diffuse more slowly than 1-phenylpyrazoles. The second polarographic wave of (1) corresponds to the reduction of 5-phenyl-3-(2-phenylethyl)pyrazole (2).

Polarography in dimethylformamide, 0·1M in Pr_4NClO_4, of pyrazole derivatives (1·0 × 10^{-3}M); the same capilliary and mercury height were used throughout

	$-E_{\frac{1}{2}}$ V *versus* s.c.e.	Wave ht. μA	$E_{\frac{1}{2}} - E_{\frac{1}{2}}$ V
5-Phenyl-3-styryl-pyrazole [a] (1)	2·16	2·1	0·08
	2·60	2·7	0·07
5-Phenyl-3-(2-phenylethyl) pyrazole (2)	2·55	2·5	0·17
1,5-Diphenyl-3-styrylpyrazole [b] (3)	2·27	total ht. 9·9	
	2·44		
	2·85	3·8	0·05
1,5-Diphenyl-3-(2-phenylethyl)-pyrazole (5)	2·50	4·7	0·08
	2·85	3·6	0·06
1,5-Diphenyl-3-(2-phenylethyl)-Δ^2-pyrazoline (4)	2·86	3·5	0·05

[a] A. Dornow and W. Bartsch, *Annalen*, 1957, **602**, 24. [b] W. A. F. Gladstone and R. O. C. Norman, *J. Chem. Soc.* (*C*), 1966, 1536.



1,5-Diphenyl-3-styrylpyrazole (3) shows three polarographic waves; the first two are not clearly separated. Cyclic voltammetry in the region of the first two waves indicated no reversible electron transfer, so any radical anion which is formed during the reduction has a half-life of less than 0·2 s. The third wave is close to the decomposition potential (−3·0 V) of the solvent plus supporting electrolyte and could not be examined satisfactorily by cyclic voltammetry. A small preparative scale reduction of (3) at a potential near the diffusion plateau of the first two waves afforded a tetrahydro-product, the ^{1}H n.m.r. spectrum of which indicated the presence of three aliphatic protons arranged as an ABX

[1] Part XII, Azizullah and J. Grimshaw, *J.C.S. Perkin I*, 1973, 425.

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

[3] K. Alwair, J. F. Archer, and J. Grimshaw, *J.C.S. Perkin II*, 1972, 1663.

system and isolated from coupling with four other aliphatic protons arranged as an A_2B_2 system. Thus the tetrahydro-product was thought to have structure (4) and this was confirmed by preparation of the same compound by catalytic hydrogenation of 1,5-diphenyl-3-styryl-Δ^2-pyrazoline (6). Catalytic hydrogenation of (3) afforded the previously unknown 1,5-diphenyl-3-(2-phenylethyl)pyrazole (5).

Comparison of the polarograms of compounds (3), (5), and (4) suggests that the first two polarographic waves for 1,5-diphenyl-3-styrylpyrazole are due to the steps (3) ⟶ (5) ⟶ (4), involving a total of four electrons. The first polarographic wave of (5) must be due to the process (5) ⟶ (4) involving two electrons. In accord with this, other workers [4] have shown that reduction of a 1-phenylpyrazole with sodium and ethanol gives the corresponding 1-phenyl-Δ^2-pyrazoline.

Electrolytic reduction of 3-styrylpyrazoles is an alternative route for the preparation of 3-(2-phenylethyl)pyrazoles. This route may be useful if other substituents interfere with catalytic hydrogenation of the styryl group.

EXPERIMENTAL

The apparatus for polarography and cyclic voltammetry has been described previously.[3] The dropping mercury electrode had drop time 6·3 s in 0·1M-KCl and flow rate of $1{\cdot}20 \times 10^{-3}$ g s^{-1}. A Heathkit variable voltage supply was used for the reductions. The cathode potential was measured (*versus* s.c.e.) with an F.E.T. voltmeter and controlled by manual adjustment of the applied voltage. Dimethylformamide was dried over $CuSO_4$.

Polarography and Cyclic Voltammetry.—The cell solution contained the pyrazole ($1{\cdot}0 \times 10^{-3}$M) and tetrapropylammonium perchlorate (0·1M) in anhydrous dimethylformamide. The results are given in the Table.

Reduction of 5-Phenyl-3-styrylpyrazole.—An H-type cell was used with a platinum anode and the electrolyte was 0·1M-tetrapropylammonium perchlorate in dimethylformamide containing water (5%). A solution of the pyrazole (0·20 g) in the electrolyte (20 ml) was reduced at a mercury cathode (area 6·2 cm^2; initial current 0·010 A), potential −2·1 to −2·5 V *versus* s.c.e., until 2 faraday per mol had been consumed (24 h). The catholyte was then concentrated to a small volume and diluted with water, and the products were isolated with ether. Evaporation of the ether left *5-phenyl-3-(2-phenylethyl)pyrazole* (0·15 g), which crystallised from light petroleum (b.p. 60—80°) as needles (0·12 g), m.p. 84—85° (Found: C, 82·4; H, 6·3; N, 11·6. $C_{17}H_{16}N_2$ requires C, 82·2; H, 6·5; N, 11·3%), τ ($CDCl_3$) 2·2—3·0 (11H, m), 3·71 (1H, s), and 7·12 (4H, s). On catalytic reduction over 5% palladium–charcoal in ethanol at room temperature and pressure 5-phenyl-3-styrylpyrazole took up 1 mol. equiv. of hydrogen to give the same dihydro-derivative, m.p. and mixed m.p. 84—85°.

Reduction of 1,5-Diphenyl-3-styrylpyrazole.—A solution of the pyrazole (0·20 g) in the electrolyte (15 ml) was reduced at a mercury cathode (initial current 0·006 A), potential −2·4 to −2·5 V. Isolation of the product with ether afforded a gum (0·18 g) which was chromatographed in light petroleum over alumina and crystallised from light petroleum (b.p. 60—80°) as needles, m.p. and mixed m.p. 94—95°, of *1,5-diphenyl-3-(2-phenylethyl)-Δ^2-pyrazoline* (Found: C, 84·6; H, 6·8; N, 8·6. $C_{23}H_{22}N_2$ requires C, 84·6; H, 6·9; N, 8·7%), τ ($CDCl_3$) 2·5—3·5 (15H, aromatic), 5·03 (H_x, q), 6·65 (H_b, q), 7·36 (H_a, q), 6·9—7·4 (4H, symmetrical m partly overlaying H_a), J_{ab} 17, J_{ax} 8, J_{bx} 12 Hz. This pyrazoline was also obtained by catalytic hydrogenation (uptake 1 mol. equiv.) of 1,5-diphenyl-3-styryl-Δ^2-pyrazoline over 5% palladium–charcoal in ethanol at room temperature and pressure.

1,5-Diphenyl-3-(2-phenylethyl)pyrazole.— Hydrogenation (uptake 1 mol. equiv.) of 1,5-diphenyl-3-styrylpyrazole over 5% palladium–charcoal in ethyl acetate at room temperature and pressure afforded *1,5-diphenyl-3-(2-phenylethyl)pyrazole*, which crystallised from aqueous methanol as needles, m.p. 45—46° (Found: C, 85·2; H, 6·2; N, 8·8. $C_{23}H_{18}N_2$ requires C, 85·2; H, 6·2; N, 8·5%), τ ($CDCl_3$) 2·6—2·9 (15H, m), 3·71 (1H, s), and 6·93 (4H, s).

[2/2666 *Received*, 27*th November*, 1972]

[4] K. Knorr and P. Duden, *Ber.*, 1893, **26**, 108; K. Knorr and H. Laubmann, *Ber.*, 1888, **21**, 1205; K. v. Auwers, *Ber.*, 1932, **65**, 832.