# Electrochemical Reactions. Part XVII.[1] Selective Dehalogenation of Styrylpyrazoline and Styrylpyrazole Derivatives

By **James Grimshaw** * and **Jadwiga Trocha-Grimshaw**, Department of Chemistry, Queen's University, Belfast BT9 5AG

Selective monodehalogenation of some dihalogeno-aromatic compounds has been achieved by controlled potential electrochemical reduction in dimethylformamide. 5-(4-Chlorophenyl)-3-(4-chlorostyryl)-1-phenyl-$\Delta^2$-pyrazoline and 3-(4-chlorophenyl)-5-(4-chlorostyryl)pyrazole were dehalogenated at the styryl 4-position, and the corresponding bromo-derivatives behaved in a similar manner. The selectivity of these reactions is discussed with respect to the correlation previously noted between the rate of carbon–halogen bond fragmentation and the free-electron density distribution in the first formed radical-anion. Only 1,5-diphenyl-3-styrylpyrazole could be isolated from reduction of 5-(4-chlorophenyl)-3-(4-chlorostyryl)-1-phenylpyrazole or the corresponding dibromo-derivative. Reduction in the presence of 1% deuterium oxide resulted in no deuterium being incorporated into the product, in accord with the mechanism previously proposed for the reaction.

REDUCTION of aryl halides involves first addition of one electron to the lowest-energy unoccupied $\pi$-orbital to form a radical-anion. This decomposes by fragmentation of the carbon–halogen bond to give a halide ion and a $\sigma$-radical, the latter abstracting a hydrogen atom from the solvent.[2] We have already demonstrated a

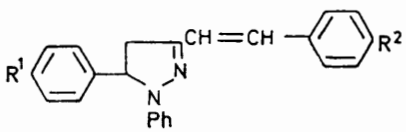
[1] Part XVI, J. Grimshaw and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1973, 2584.

[2] D. E. Bartak, K. J. Houser, B. C. Rudy, and M. D. Hawley, *J. Amer. Chem. Soc.*, 1972, **94**, 7526; J. G. Lawless and M. D. Hawley, *J. Electroanalyt. Chem.*, 1969, **21**, 365; and references cited therein.

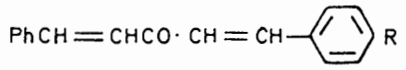
correlation between the rate of this fragmentation step and the free-electron density in the radical-anion on the carbon centre of reaction.[3] In the case of dihalogenated aromatic compounds where the radical-ion free-electron density differs greatly at the two positions of substitution, controlled electrochemical reduction offers the possibility of selective dehalogenation. Here we demonstrate such a selective reduction of some pyrazoline and pyrazole derivatives.

The pyrazoles and pyrazolines required were prepared by standard methods. Dornow and Bartsch [4] have described a route to pyrazoles involving conversion of the appropriate αβ-unsaturated ketone into its *p*-tolylsulphonylhydrazone and treatment of the latter with sodium methoxide in acetonitrile. We found during the preparation of pyrazoles of type (3) that the hydrazone intermediate must be prepared in concentrated solution in order to reduce the importance of side reactions, and dimethylformamide proved a suitable solvent. It was also found convenient to use powdered sodium hydroxide in acetonitrile as the base in the cyclisation step.

*Derivatives of* 1,5-*Diphenyl*-3-*styryl*-$\Delta^2$-*pyrazoline*.—Polarography and cyclic voltammetry of 1,5-diphenyl-3-styryl-$\Delta^2$-pyrazoline (1; $R^1 = R^2 = H$) show the generation of a redox couple ($E_0$ −2·06 V *vs.* s.c.e.) with the corresponding radical-anion, which is stable in dimethylformamide on the time-scale of these experiments. At more negative potentials ($E_{\frac{1}{2}}$ −2·38 V) the radical-anion is reduced in a further one-electron step to a dianion, and this is rapidly destroyed in a chemical reaction. In the radical-anion, the free electron is associated with the styrylimine system since this has an unoccupied π-orbital of much lower energy than is the case for the isolated 5-phenyl group. From our previous studies [5] of the correlation between the rate of carbon–halogen bond fragmentation in radical-anions and the $E_0$ value we expected the radical-anions from 3-(4-chlorostyryl)- and 3-(4-bromostyryl)-pyrazolines to undergo this fragmentation.



(1)

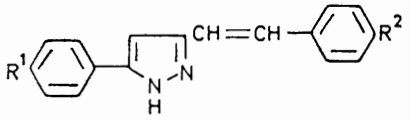


(2)

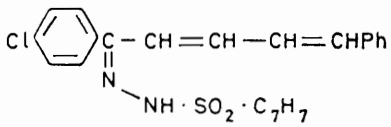
Each of the two pyrazolines (1; $R^1 = R^2 = Cl$ or Br) undergoes smooth electrochemical reduction in dimethylformamide at the potential of the first polarographic wave to give the corresponding monohalogeno-compound ($R^2 = H$). The $^1H$ n.m.r. spectra of these products show signals for the three protons of the pyrazoline ring, and the compounds are not identical with the isomeric pyrazolines (1; $R^1 = H$, $R^2 = Cl$ or Br) formed by reaction between phenylhydrazine and the appropriate halogeno-dibenzylideneacetone (2; R = Cl or Br). The orientation of the latter pyrazolines has been established by an oxidative degradation sequence.[6]

The two pyrazolines (1; $R^1 = R^2 = Cl$ or Br) are readily prepared from the corresponding dihalogeno-dibenzylideneacetones. The electrochemical reaction offers a simple route to pyrazolines which are not otherwise easily prepared.

*Derivatives of* 3-*Phenyl*-5-*styrylpyrazole*.—This pyrazole is reduced to 3-phenethyl-5-phenylpyrazole at the potential of the first polarographic wave.[7] The radical-anion is probably an intermediate in this process but its lifetime in dimethylformamide was too short for it to be detected by the techniques used. It was thought, however, that loss of halide ion from the halogeno-radical-anions derived from (3; $R^1 = R^2 = Cl$ or Br) would be sufficiently rapid to compete with the alternative mode of decomposition of the radical-ion which gives a dihydro-derivative of the substrate.



(3)



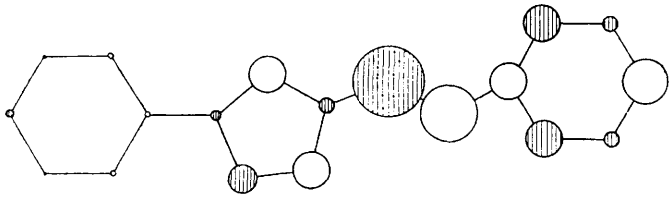
(4)

Reduction of each dihalogeno-derivative (3; $R^1 = R^2 = Cl$ or Br) in dimethylformamide at the potential of the first polarographic wave did indeed result in the replacement of one halogen atom in each case by a hydrogen atom. The products, isolated in good yield, showed the expected $^1H$ n.m.r. and mass spectral data for monohalogeno-derivatives. Oxidation of the chloro-compound with potassium permanganate gave 5-(4-chlorophenyl)pyrazole-3-carboxylic acid, thus confirming its structure as (3; $R^1 = Cl$, $R^2 = H$). In a similar manner, the bromo-compound was shown to be (3; $R^1 =$ Br, $R^2 = H$). The chloro-compound (3; $R^1 = Cl$, $R^2 = H$) was also obtained from the hydrazone (4) by the method of Dornow and Bartsch.[4] Conversion of the hydrazone of the ketone (2; R = Cl) into a pyrazole gave the expected mixture of (3; $R^1 = Cl$, $R^2 = H$) and (3; $R^1 = H$, $R^2 = Cl$).

If we consider 3-phenyl-5-styrylpyrazole as a fully

[3] K. Alwair and J. Grimshaw, *J.C.S. Perkin II*, 1973, 1150.
[4] A. Dornow and W. Bartsch, *Annalen*, 1957, **602**, 23.
[5] K. Alwair and J. Grimshaw, *J.C.S. Perkin II*, 1973, 1811.
[6] H. Ferres, M. S. Hamdam, and W. R. Jackson, *J. Chem. Soc.* (*B*), 1971, 1892.
[7] J. Grimshaw and J. Trocha-Grimshaw, *J.C.S. Perkin I*, 1973, 1275.

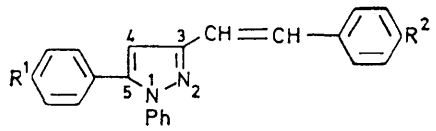
conjugated π-orbital system containing 20 electrons, the electron density distribution in the lowest-energy unoccupied orbital can be calculated as a first approximation to the free-electron density distribution in the radical-anions from the halogeno-derivatives. Then one can see if there is a big difference in free-electron density between the two possible sites for carbon–halogen bond fragmentation. Crystallographic studies on pyrazole have shown that the ring is planar and the bond lengths suggest a high degree of delocalisation for the ring π-electrons.[8,9] The result of an HMO calculation taking $h_N = 0{\cdot}5$ and $k_{CN} = 1{\cdot}0$ is shown in the Figure. There



Free-electron density distribution from HMO calculation for the radical anion from (3; $R^1 = R^2 = H$). The areas of the circles are proportional to the electron density. Radius and shading of the circles are characteristic of the size and sign of the coefficient in the LCAO

is a large difference in free-electron density between the two phenyl *para*-positions, which would lead us to expect that in the dihalogeno-derivatives the halogen function attached to the styryl group will be reduced first, as is observed.

*Derivatives of* 1,5-*Diphenyl*-3-*styrylpyrazole*.—Reduction of this pyrazole at the potential of the first polarographic wave has been shown to give 3-phenethyl-1,5-diphenyl-Δ²-pyrazoline.[7] The reaction probably proceeds in two stages but the reduction process cannot be halted



(5)

when only one double bond has been reduced. Reduction in dimethylformamide of the dihalogeno-derivatives (5; $R^1 = R^2 =$ Cl or Br) at a potential corresponding to the foot of the first polarographic wave afforded 1,5-diphenyl-3-styrylpyrazole (5; $R^1 = R^2 = H$) in good yield. A graph of coulombs passed against reaction time at a fixed cathode potential gave no indication that one halogen in a given molecule was reduced sufficiently faster than the other to make partial reduction a useful preparative procedure. No pure compound could be isolated from reactions which were stopped at a half-way stage, although mass spectra of the products indicated the presence of molecules with a mass number corresponding to (5; $R^1 =$ Cl or Br, $R^2 =$ H or *vice versa*).

[8] F. Krebs Larsen, M. S. Lehmann, L. Søtofle, and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 3248.

[9] J. Bertou, J. Elguero, and C. Rerat, *Acta Cryst.*, 1970, **B26**, 1880.

A crystal structure determination has been carried out on two derivatives of 1-phenylpyrazole [10,11] and the results (Table 1) enable us to offer an explanation for this difference in behaviour on reduction of the related pyrazole and 1-phenylpyrazole derivatives. In 1-phenylpyrazoles the bond between atoms 2 and 3 is shorter than that between atoms 1 and 5 and the bond between atoms 4 and 5 is shorter than that between

TABLE 1

Crystal structure data for pyrazole derivatives; atoms numbered as in structure (5)

| | Bond length (Å) between atoms | | | | |
|---|---|---|---|---|---|
| Pyrazole | 1,5 | 2,3 | 4,5 | 3,4 | 1,2 |
| Unsubst.[a] | 1·36 | 1·35 | 1·40 | 1·41 | 1·37 |
| Unsubst.[b] | 1·33 | 1·34 | 1·36 | 1·37 | 1·35 |
| 4-Cl-1-Dnp * [c] | 1·38 | 1·28 | 1·34 | 1·41 | 1·37 |
| 4-Br-1-Dnp * [d] | 1·41 | 1·33 | 1·33 | 1·41 | 1·38 |

* Dnp = 2,4-dinitrophenyl.

[a] Ref. 8. [b] Ref. 9. [c] Ref. 10. [d] Ref. 11.

atoms 3 and 4. In pyrazole itself these pairs of bonds have equal lengths. Thus there is evidence that in 1-phenylpyrazole the π-electrons are not so fully delocalised as in pyrazole. The extreme situation of bond localisation in 1,5-diphenyl-3-styrylpyrazole (5; $R^1 = R^2 = H$) is that in which the lone pair orbital of N-1 does not overlap with the remainder of the π-system, and in this case the free-electron densities in the radical-anion at the sites bearing $R^1$ and $R^2$ will be almost identical. A simple HMO calculation gives identical values. The other extreme of bond delocalisation is the situation in which no distinction in overlap is made between atoms 1 and 5 as compared to 2 and 3, and here the calculated free-electron densities show as large a difference as in the Figure. The true situation is probably intermediate between these extremes, such that significant free-electron density is found at both sites bearing $R^1$ and $R^2$. This would explain why in the case of the 1-phenylpyrazole derivatives (5; $R^1 = R^2 =$ Cl or Br) it is not possible to reduce selectively only one carbon–halogen bond.

*Reduction in the Presence of Deuterium Oxide*.—The hydrogen atom which replaces the halide during reduction of aryl halides is thought to be transferred from a solvent molecule by attack of the intermediate σ-radical. If this is the reaction course, no deuterium will be incorporated into the product when the reduction is carried out in the presence of deuterium oxide. On the other hand, if the intermediate σ-radical is reduced to a carbanion and protonated, reaction in the presence of deuterium oxide will result in the incorporation of deuterium into the product.

The pyrazole (5; $R^1 = R^2 =$ Cl) was reduced in dimethylformamide containing 1% deuterium oxide in apparatus which had previously been washed with deuterium oxide and dimethylformamide. Examination of the pyrazole produced (5; $R^1 = R^2 = H$) by mass

[10] J. L. Galigne and J. Falgueirettes, *Acta Cryst.*, 1970, **B26**, 380.

[11] J. L. Galigne and J. Falgueirettes, *Acta Cryst.*, 1969, **B25**, 1637.

spectrometry indicated no incorporation of deuterium. This confirms that in the last stage of the reduction sequence, the σ-radical abstracts hydrogen from the dimethylformamide solvent.

Coulometry carried out during the carbon–halogen bond reduction steps described in this paper indicated a requirement of 1·6—2·0 electrons for reduction of one carbon–halogen bond. One electron is required to form the initial radical-anion. In the final stage, abstraction of a hydrogen atom from the solvent leaves a solvent radical. This solvent radical may decompose in a number of ways but some radicals must be reduced at the cathode in order to account for the total coulometric requirement.

## EXPERIMENTAL

All electrode potentials were measured with respect to an aqueous saturated calomel electrode (s.c.e.) | 1·0M-sodium nitrate | salt bridge containing the electrolyte solution. The electrochemical apparatus and purification of nitrogen and dimethylformamide have been described in previous papers of this series.

N.m.r. spectra were determined for solutions in $CDCl_3$. *p*-Tolylsulphonylhydrazine was recrystallised from water before use. Optimum conditions for *p*-tolylsulphonylhydrazone formation were ascertained by t.l.c.[12] Silica plates were used and eluted with 4 : 1 light petroleum (b.p. 60—80°)–ethyl acetate; the order of increasing $R_F$ value was reagent ($R_F$ *ca.* 0·0), hydrazone, unchanged ketone.

1-(4-*Chlorophenyl*)-5-*phenylpenta*-2,4-*dien*-1-*one*.—Cinnamaldehyde (26 g) and *p*-chloroacetophenone (30 g) were dissolved in ethanol (150 ml) and aqueous sodium hydroxide (15 ml; 10%). After 12 h the precipitated 1-(4-chlorophenyl)-5-phenylpenta-2,4-dien-1-one was collected and crystallised from ethanol as needles (38 g), m.p. 142—143° (lit.,[13] 127°; 137°) (Found: C, 76·0; H, 4·7; Cl, 13·3. Calc. for $C_{17}H_{12}ClO$: C, 76·3; H, 4·5; Cl, 13·2%).

p-*Tolylsulphonylhydrazones*.—A solution of the ketone (2 g) and *p*-tolylsulphonylhydrazine (1·0 equiv.) in either anhydrous dimethylformamide (10 ml) or ethanol (10 ml) (depending on the ketone's solubility) was heated on a water-bath. In some cases addition of hydrochloric acid (10N; 4 drops) was necessary. The mixture was cooled, water was added, and the precipitated product was collected and chromatographed in ether over a short column of neutral alumina. 1,5-*Bis*-(4-*chlorophenyl*)*penta*-1,4-*dien*-3-*one* p-*tolylsulphonylhydrazone* (3 h heating in dimethylformamide) crystallised from ethanol as needles (2·0 g), m.p. 139—140° (Found: C, 61·1; H, 4·2; Cl, 15·0; N, 5·9; S, 6·8. $C_{24}H_{19}Cl_2N_2O_2S$ requires C, 60·9; H, 4·1; Cl, 15·2; N, 6·0; S, 6·9%). 1-(4-*Chlorophenyl*)-5-*phenylpenta*-2,4-*dien*-1-*one* p-*tolylsulphonylhydrazone* (4) (8 h heating in dimethylformamide–hydrochloric acid) gave needles (1·1 g), m.p. 170—171° (from ether) (Found: C, 65·9; H, 4·8; Cl, 8·1; N, 6·4; S, 7·3. $C_{24}H_{21}ClN_2O_2S$ requires C, 65·9; H, 4·8; Cl, 8·0; N, 6·3; S, 7·3%). 1,5-Bis-(4-bromophenyl)penta-1,5-dien-3-one *p*-tolylsulphonylhydrazone (5 min heating in ethanol–hydrochloric acid) was obtained as an unstable solid (1·5 g), m.p. 120—129°, which could not be crystallised without decomposition.

*Pyrazoles*.—The *p*-tolylsulphonylhydrazone (1·5 g) was dissolved in acetonitrile (5 ml), powdered sodium hydroxide (200 mg) was added, and the mixture was heated on a water-bath for 30 min. A white precipitate of sodium toluene-*p*-sulphinate was formed. The mixture was poured into water; the salt dissolved and the pyrazole which precipitated was collected. 5-(4-*Chlorophenyl*)-3-(4-*chlorostyryl*)*pyrazole* (3; $R^1 = R^2 = Cl$) crystallised from benzene as needles (0·83 g), m.p. 230—231° (Found: C, 64·8; H, 3·8; Cl, 22·5; N, 8·9. $C_{17}H_{12}Cl_2N_2$ requires C, 64·8; H, 3·9; Cl, 22·5; N, 8·6%). 5-(4-*Bromophenyl*)-3-(4-*bromostyryl*)*pyrazole* (3; $R^1 = R^2 = Br$) crystallised from chloroform as needles (0·60 g), m.p. 247—248° (Found: C, 50·5; H, 3·0; Br, 39·4; N, 6·9. $C_{17}H_{12}Br_2N_2$ requires C, 50·4; H, 3·0; Br, 39·6; N, 7·0%). 5-(4-*Chlorophenyl*)-3-*styrylpyrazole* (3; $R^1 = Cl$, $R^2 = H$) [prepared from the hydrazone (4)] crystallised from chloroform as needles, m.p. 211—212° (Found: C, 72·5; H, 4·6; Cl, 12·8; N, 9·8. $C_{17}H_{13}ClN_2$ requires C, 72·7; H, 4·7; Cl, 12·6; N, 9·9%).

*Pyrazoles from* 1-(4-*Chlorophenyl*)-5-*phenylpenta*-1,4-*dien*-3-*one*.—The ketone (2·0 g) and *p*-tolylsulphonyl hydrazine (1·4 g) were heated in ethanol (6 ml) and hydrochloric acid (10N; 4 drops) on a water-bath for 5 min. More ethanol (10 ml) was added and the solution was left at room temperature; the *hydrazone* (2·1 g) crystallised and was recrystallised from ethanol to give yellow needles (1·8 g), m.p. 150—151° (Found: C, 65·7; H, 4·8; Cl, 8·2; N, 6·4; S, 7·4. $C_{24}H_{21}ClN_2O_2S$ requires C, 65·9; H, 4·8; Cl, 8·1: N, 6·4; S, 7·3%).

This hydrazone (2·1 g) and sodium hydroxide (0·30 g) were refluxed in acetonitrile (6 ml) for 1 h. The hot solution was then poured into water and the precipitate (1·5 g) collected; m.p. 150—170°. The product was fractionally crystallised from chloroform to give (i) the pyrazole (3; $R^1 = Cl$, $R^2 = H$) (0·30 g), m.p. 209—210° [not depressed on admixture with the pyrazole from the hydrazone (4)]; (ii) a mixture (0·15 g), m.p. 175—180°; and (iii) 3-(4-*chlorostyryl*)-5-*phenylpyrazole* (3; $R^1 = H$, $R^2 = Cl$) as needles, m.p. 199—201° [depressed to 180—185° on admixture with the pyrazole from the hydrazone (4)] (Found: C, 72·5; H, 4·6; Cl, 12·6; N, 9·8%). The fractions (i) and (iii) showed different i.r. spectra (KBr disc).

5-(4-*Chlorophenyl*)-3-(4-*chlorostyryl*)-1-*phenylpyrazole*.—A suspension of 1,5-bis-(4-chlorophenyl)penta-1,4-dien-3-one (5·0 g) in acetic acid (100 ml) containing phenylhydrazine (1·8 g) was heated at 100° for 45 min; the ketone dissolved and on cooling the diphenylstyrylpyrazoline separated. Crystallisation from ethanol gave yellow needles, m.p. 219—220° (lit.,[14] 212°), τ 2·3—3·0 (m, aromatic and one olefinic H), 3·52 (d, *J* 16 Hz, one olefinic H, *trans* to the other), and 4·78 ($H_a$, q), 6·32 ($H_b$, q), and 7·08 ($H_c$, q) (pyrazoline ring protons, $J_{ab}$ 12, $J_{ac}$ 7, $J_{bc}$ 17 Hz).

A solution of the pyrazoline (3·7 g) in dichloromethane (100 ml) was mixed with lead(IV) acetate (7·0 g) in dichloromethane (50 ml) and left at room temperature for 24 h. The mixture was stirred with aqueous acetic acid and sufficient hydrazine to destroy the lead dioxide. The organic layer was then dried ($K_2CO_3$) and passed over alumina, and the solvent was removed. Crystallisation of the residue from ethanol afforded 5-(4-*chlorophenyl*)-3-(4-*chlorostyryl*)-1-*phenylpyrazole* (3·3 g) as needles, m.p. 145—146° (Found: C, 70·6; H, 4·0; Cl, 18·3; N, 7·3. $C_{23}H_{16}Cl_2N_2$ requires C, 70·6; H, 4·1; Cl, 18·1; N, 7·2%).

[12] F. Chang, *J. Org. Chem.*, 1965, **30**, 2053.
[13] A. A. Grigorenko, M. I. Shevchuk, and A. V. Dombrovskii, *Zhur. obshchei Khim.*, 1964, **34**, 2254; G. Pfister-Guillouzo and N. Lozach, *Bull. Soc. chim. France*, 1964, 3252.
[14] G.P. 1,060,714/1959 (*Chem. Abs.*, 1961, **55**, 20,736).

5-(4-*Bromophenyl*)-3-(4-*bromostyryl*)-1-*phenylpyrazole*.—Similar treatment of 1,5-bis-(4-bromophenyl)penta-1,4-dien-3-one (2·0 g) and phenylhydrazine (2·0 ml) in acetic acid (10 ml) afforded the pyrazoline, which crystallised from ethyl acetate as yellow needles (1·6 g), m.p. 227—228° (lit.,[15] 228°); n.m.r. spectrum similar to that of the dichloro-analogue. Oxidation of the pyrazoline (0·80 g) in dichloromethane (100 ml) with lead(IV) acetate as before gave 5-(4-*bromophenyl*)-3-(4-*bromostyryl*)-1-*phenylpyrazole*, which crystallised from ethanol as needles (0·50 g), m.p. 140—141° (Found: C, 57·3; H, 3·4; Br, 33·3; N, 6·0. $C_{23}H_{26}Br_2N_2$ requires C, 57·5; H, 3·4; Br, 33·3; N, 5·8%).

3-(4-*Chlorophenyl*)-1-*phenyl*-5-*styrylpyrazole*.—Phenylhydrazine hydrochloride (1·3 g) and sodium acetate (1·3 g) dissolved in the minimum of water were added to a refluxing solution of 1-(4-chlorophenyl)-5-phenylpenta-2,4-dien-1-one (1 g) in ethanol (50 ml). After 18 h, water was added and the precipitated phenylhydrazone was collected; m.p. 50—56°. This was heated at 100° in acetic acid (50 ml) for 4 h. On cooling, 3-(4-*chlorophenyl*)-1-*phenyl*-5-*styryl*-$\Delta^2$-*pyrazoline* separated; it crystallised from ethanol as yellow needles (0·60 g), m.p. 123—124° (Found: C, 77·0; H, 5·3; Cl, 9·9; N, 7·8. $C_{23}H_{19}ClN_2$ requires C, 76·7; H, 5·4; Cl, 9·9; N, 7·8%), τ 2·2—3·0 (aromatic) 3·34 (d, *J* 16 Hz) and 3·70 (q, *J* 16 and 7 Hz) (olefinic), and 5·03 ($H_a$, dt), 6·40 ($H_b$, q), and 6·92 ($H_c$, q) (pyrazoline ring, $J_{ab}$ 11, $J_{ac}$ 7, $J_{bc}$ 17 Hz; $H_a$ coupled to one olefinic proton with *J* 7 Hz).

Oxidation of the pyrazoline (3·0 g) in dichloromethane (100 ml) with lead(IV) acetate (6·0 g) afforded 3-(4-*chlorophenyl*)-1-*phenyl*-5-*styrylpyrazole*, crystallising from methanol as pale orange prisms (2·0 g), m.p. 133—134° (Found: C, 77·2; H, 4·8; Cl, 9·8; N, 7·8. $C_{23}H_{17}ClN_2$ requires C, 77·4; H, 4·8; Cl, 9·9; N, 7·9%).

1,3-*Diphenyl*-5-*styrylpyrazole*.—1,5-Diphenylpenta-2,4-dien-1-one (1·0 g), treated similarly, afforded the *phenylhydrazone* as needles (0·7 g), m.p. 136—137° (from ethanol) (Found: C, 85·6; H, 6·2; N, 8·8. $C_{23}H_{20}N_2$ requires C, 85·2; H, 6·2; N, 8·6%), showing no n.m.r. evidence for a pyrazoline. The hydrazone (0·7 g) was heated in acetic acid (10 ml) for 12 h at 100°. On cooling, 1,3-*diphenyl*-5-*styrylpyrazole* precipitated as needles, m.p. 145—146° (from ether) (Found: C, 85·6; H, 5·8; N, 8·6. $C_{23}H_{18}N_2$ requires C, 85·7; H, 5·6; N, 8·7%), τ 2·0—3·2 (m, aromatic and olefinic). The intermediate pyrazoline could not be isolated.

*Polarography and Cyclic Voltammetry*.—A three-electrode cell was used with a platinum wire anode and the s.c.e. reference electrode–salt bridge system already described. The cathode was either a dropping mercury electrode (flow rate $1·20 \times 10^{-3}$ g $s^{-1}$; drop time 6·3 s in 0·1M-KCl) or a mercury-coated platinum sphere. The cell solution contained tetra-n-propylammonium perchlorate (0·1M) and the substrate ($1·0 \times 10^{-3}$M) in anhydrous dimethylformamide. Only the pyrazolines were investigated by cyclic voltammetry since previous experience showed that pyrazole radical-anions cannot be detected with the apparatus used.[7]

Cyclic voltammetry of the pyrazoline (1; $R^1 = R^2 = H$) (sweep rate 0·044 V $s^{-1}$) in the region −1·7 to −2·3 V showed one cathodic peak ($E_p$ −2·12 V) and the corresponding anodic peak ($E_p$ −2·04 V) of equal height on reverse sweep. When the sweep range was extended to −2·7 V a second cathodic peak appeared ($E_p$ −2·44 V) but this had no corresponding anodic peak on reverse sweep. The first cathodic peak and first polarographic wave are due to formation of a radical-anion. Cyclic voltammetry of the pyrazolines (1; $R^1 = R^2 = Cl$ or Br) (sweep rate 0·044 V $s^{-1}$) in the region +1·7 to −2·3 V in each case showed one cathodic peak (Cl compound, $E_p$ −1·92; Br compound, $E_p$ −1·85 V), followed by a second cathodic peak and its corresponding anodic peak as for the parent pyrazoline (1; $R^1 = R^2 = H$). At the potential of the first cathodic peak each compound loses a halogen atom to give the pyrazoline (1; $R^1$ = Cl or Br, $R^2 = H$), which gives a stable radical ion like the unsubstituted compound.

TABLE 2

Polarographic behaviour of pyrazoline and pyrazole derivatives in dimethylformamide containing tetrapropylammonium perchlorate (0·1M)

| Compound | $-E_{\frac{1}{2}}$/V | Wave height (μA) | $(E_{\frac{1}{4}} - E_{\frac{3}{4}})$/V |
|---|---|---|---|
| (1; $R^1 = R^2 = H$) | 2·06 | 3·8 | 0·06 |
| | 2·38 | 5·2 | 0·11 |
| (1; $R^1 = R^2 = Cl$) [b] | 1·84 [a] | } total 8·0 | |
| | 2·04 | | |
| (1; $R^1 = R^2 = Br$) [b] | 1·80 [a] | } total 10·8 | |
| | 2·06 | | |
| (3; $R^1 = R^2 = Cl$) [b] | 1·98 | 5·2 | 0·10 |
| (3; $R^1 = R^2 = Br$) [b] | 1·86 | 4·4 | 0·09 |
| (5; $R^1 = R^2 = Cl$) | 2·02 | 9·4 | 0·07 |
| | 2·28 | } waves merge; | |
| | 2·46 | } total 10·0 | |
| | 2·87 | 2·2 | 0·05 |
| (5; $R^1 = R^2 = Br$) | 1·92 | 9·6 | |
| | 2·28 | } waves merge; | |
| | 2·45 | } total 9·6 | |
| | 2·85 | 2·2 | 0·05 |

[a] Pronounced maximum observed. [b] Beyond −2·3 V these show a series of ill-defined waves due to reduction of both the unsaturated system and the remaining halogen functions.

*Electrochemical Reduction*.—An H-type cell was used with mercury cathode (diam. 3·0 cm) and platinum anode separated by a sintered glass disc. The cathode potential was maintained constant with respect to a s.c.e.–salt bridge system. The anode compartment contained 0·1M-tetra-n-propylammonium perchlorate in dimethylformamide. The cathode compartment contained the substrate (0·4 g) in dimethylformamide (20 ml; containing 0·1M-tetrapropylammonium perchlorate). A hydrazine coulometer[16] was placed in series with the cell. Reduction was judged complete when the current through the cell fell to a very low value.

(a) *The pyrazoline* (1; $R^1 = R^2 = Cl$). Reduction was carried out at −1·9 to −1·98 V and required 1·73 Faraday $mol^{-1}$. The catholyte became green and finally dark turquoise. Dilution with water discharged this colour and precipitated 5-(4-*chlorophenyl*)-1-*phenyl*-$\Delta^2$-*pyrazoline*, which afforded yellow needles (0·20 g), m.p. 131—133° (from ethanol) (Found: C, 77·2; H, 5·5; Cl, 9·7; N, 7·8. $C_{23}H_{19}ClN_2$ requires C, 77·0; H, 5·3; Cl, 9·9; N, 7·8%), $M^+$ 358/360, τ ($CDCl_3$) 2·3—3·3 (aromatic and one olefinic proton), 3·52 (d, *J* 16 Hz, one olefinic proton), and 4·83 ($H_a$, q), 6·34 ($H_b$, q), and 7·09 ($H_c$, q) (pyrazoline ring protons, $J_{ab}$ 12, $J_{ac}$ 6, $J_{bc}$ 17 Hz).

(b) *The pyrazoline* (1; $R^1 = R^2 = Br$). Reduction was carried out at −1·7 to −1·8 V and required 1·85 Faraday $mol^{-1}$. At the end of the reaction the catholyte was deep turquoise. Dilution with water precipitated 5-(4-*bromophenyl*)-1-*phenyl*-3-*styryl*-$\Delta^2$-*pyrazoline*, which crystallised from methanol as yellow needles (0·28 g), m.p. 155—

[15] O. Neuhoeffer and D. Rosahl, *Chem. Ber.*, 1953, **86**, 226.
[16] J. A. Page and J. J. Lingane, *Analyt. Chim. Acta*, 1957, **16**, 175.

156° (Found: C, 69·2; H, 5·0; Br, 18·9; N, 7·1. $C_{23}H_{19}BrN_2$ requires C, 68·8; H, 4·7; Br, 19·6; N, 7·0%) $M^+$ 402/404, n.m.r. spectrum ($CDCl_3$) almost identical with that of the chloro-compound.

(c) *The pyrazole* (3; $R^1 = R^2 = Cl$). Reduction at −2·0 V required 2·0 Faraday $mol^{-1}$ and the catholyte remained colourless. The catholyte was acidified with a little acetic acid, concentrated under vacuum, and diluted with water; the product was isolated with ether. The ether solution was passed through a short column of alumina and evaporated. Crystallisation of the residue from ethanol afforded 5-(4-chlorophenyl)-3-styrylpyrazole as needles (0·20 g), m.p. 210—211°, not depressed on admixture with the sample prepared from the hydrazone (4).

(d) *The pyrazole* (3; $R^1 = R^2 = Br$). Reduction at −1·88 to −1·94 V required 1·6 Faraday $mol^{-1}$. Isolation of the product as described in (c) and crystallisation from chloroform afforded 5-(4-*bromophenyl*)-3-*styrylpyrazole* as needles (0·28 g), m.p. 209—210° (Found: C, 62·4; H, 4·0; Br, 24·8; N, 8·8. $C_{17}H_{13}BrN_2$ requires C, 62·7; H, 4·0; Br, 24·6; N, 8·6%), $M^+$ 324/326.

(e) *The pyrazole* (5; $R^1 = R^2 = Cl$). Reduction at −1·9 V required 3·2 Faraday $mol^{-1}$. Isolation of the product as described in (c) and crystallisation from ethanol afforded 1,3-diphenyl-5-styrylpyrazole (0·24 g), m.p. and mixed m.p. 137—139°. In another experiment, the apparatus had been washed with 10% deuterium oxide in dimethylformamide and the reaction was carried out with 1% deuterium oxide in dimethylformamide as solvent. The recovered 1,3-diphenyl-5-styrylpyrazole was analysed by mass spectrometry, using an ionising beam voltage of 12 eV so that the $M^+ - 1$ peak was negligible [Found: $(M^+ + 1)/M^+$, 25%. $C_{13}H_{18}N_2$ with natural isotopic abundance requires $(M^+ + 1)/M^+$, 25·9%]. Deuterium was not incorporated into the molecule.

(f) *The pyrazole* (5; $R^1 = R^2 = Br$). Reduction at −1·92 to −2·0 V required 3·3 Faraday $mol^{-1}$. Isolation as previously described afforded 1,3-diphenyl-5-styrylpyrazole (0·27 g), m.p. and mixed m.p. 138—139°.

5-(4-*Chlorophenyl*)*pyrazole*-3-*carboxylic Acid*.—5-(4-Chlorophenyl)-3-styrylpyrazole (0·20 g) was suspended in water (40 ml) containing potassium permanganate (0·30 g) and heated at 90° with stirring for 3 h. More potassium permanganate (0·05 g) was then added and heating was continued for 30 min. The excess of permanganate was destroyed with methanol, the hot solution was filtered, and the filtrate was acidified with sulphuric acid. The product was isolated with ether and crystallised from ethanol–water (3 : 2) as needles (0·11 g, 71%) of 5-(4-*chlorophenyl*)-*pyrazole*-3-*carboxylic acid*, m.p. 264—265° (Found: C, 54·0; H, 3·2; Cl, 15·9; N, 12·6. $C_{10}H_7ClN_2O_2$ requires C, 54·1; H, 3·3; Cl, 15·7; N, 12·5%), $M^+$ 222/224.

5-(4-*Bromophenyl*)*pyrazole*-3-*carboxylic Acid*.—5-(4-Bromophenyl)-3-styrylpyrazole was similarly oxidised with aqueous potassium permanganate; the product crystallised from ethanol–water (3 : 2) as needles of 5-(4-*bromophenyl*)-*pyrazole*-3-*carboxylic acid* (86%), m.p. 265—266° (Found: C, 45·2; H, 2·8; Br, 29·7; N, 10·3. $C_{10}H_7BrN_2O_2$ requires C, 45·0; H, 2·6; Br, 29·9; N, 10·5%), $M^+$ 266/268.

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