The Synthesis and Chemistry of Azolenines.† Part 3[1]. Some Reactions of 4*H*-Pyrazole Quaternary Salts

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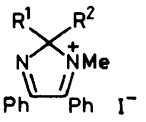
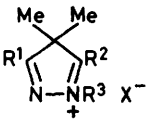
The preparation of some novel 4*H*-pyrazolium salts is described. Unlike the structurally related 2*H*-imidazolium salts (**1**), the metho-salts (**2**) of 4*H*-pyrazoles show no exchange with deuterium at the *N*-methyl protons. Exchange occurs readily at a 5-methyl group, anions formed at this site giving a cyanine dye (**10**) with triethoxymethane and benzylidene derivatives (**11**) and (**12**) with 1 mol equiv. of aromatic aldehyde. The activated benzylidene derivatives react further with an excess of aldehyde and base, apparently *via* an *N*-ylide intermediate, to give pyrazolo[5,1-*b*]oxazoles (**15**), which ring-open in the presence of acid forming *N*-(2-hydroxyethyl)-4*H*-pyrazolium salts (**13**). With sodium borohydride, the metho-salts (**2**) are reduced to 4,5-dihydropyrazoles (**16**), which with methyl iodide are quaternised at N-1 rather than N-2.

We recently reported the preparation and reactions of some novel 2*H*-imidazolium salts (**1**).[2] It was found that the *N*-methyl protons exchange readily with deuterium, and with base formed an ylide capable of undergoing cyclisation reactions. Further, reduction with sodium borohydride gave dihydroimidazoles, hydrolysable to α-amino ketones. It was of interest to establish whether the structurally related 4*H*-pyrazolium salts (**2**)—(**5**) would undergo similar reactions of potential synthetic use; as a class, the 4*H*-pyrazoles and their derivatives have received relatively little attention.[3]

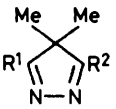
Structures



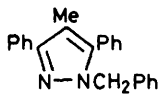
(**1**)



(**2**) R^3 = Me
(**3**) R^3 = Et
(**4**) R^3 = Pr^n
(**5**) R = $CH_2CH{=}CH_2$



(**6**)



(**7**)

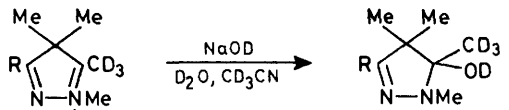
a; R^1 = R^2 = Me
b; R^1 = Ph; R^2 = Me
c; R^1 = R^2 = Ph

4*H*-Pyrazoles have largely been prepared from 2,2-disubstituted 1,3-diketones and hydrazine,[4] although a number of other methods are known, including addition of electrophiles to 1*H*-pyrazoles,[5] and alkylation of pyrazolone derivatives.[6] Base-catalysed H–D exchange has been observed at 3- and 5-methyl substituents.[4b,7] Quaternisation occurs readily at a ring nitrogen atom using alkyl iodides[8] or toluene-*p*-sulphonates[6b] to give the corresponding salts. Certain examples having a 5-methyl group have been shown to undergo aldol-type reactions at this site to yield photographic emulsion sensitisers[6b] and photo- and thermo-chromic substances.[9] Others have been reduced to dihydropyrazoles in high yields by lithium aluminium hydride,[8b] but reactions with sodium borohydride do not appear to have been studied.

Results and Discussion

The known[4b] 4*H*-pyrazoles (**6a**—**6c**) were prepared (65—80%) from the corresponding 1,3-diketones with hydrazine hydrate in ethanol; they were converted into salts (**2**)[8c] and (**3a**) in high yields by heating under reflux with an excess of the alkyl iodide. However, with 1-iodopropane, 3-bromopropene, and benzyl chloride this method did not give the expected products, and in the latter case the 1*H*-compound (**7**) was isolated. 1-Iodopropane gave a mixture of products, some probably resulting from loss of one of the 4-methyl groups. However, heating the pyrazole (**6a**) with 3-bromopropene in ethanol, or neat with 1-iodopropane at 60—70 °C gave the 4*H*-pyrazolium salts (**5a**) and (**4a**) respectively. New compounds are listed together with physical and analytical data in Table 1. ^{1}H N.m.r. chemical shifts for pyrazolium salts (Table 2) were in line with published data.[8b,8c]

With deuterium oxide in [$^2H_3$]acetonitrile, complete H–D exchange occurred at the 5-methyl group rapidly in the 3-phenyl compound (**2b**), and within 8 h for the pentamethyl analogue (**2a**). No exchange was observed at the *N*-methyl group in compounds (**2a**—**c**), either under these conditions, or in the presence of added pyridine at 20 °C and at 60 °C. Under the latter conditions, however, the 3-methyl protons of salt (**2a**) were exchanged completely within 24 h. Addition of 1 equivalent of sodium deuterioxide to the deuteriated salts (**8a**) and (**8b**) (Scheme 1) gave the dihydropyrazoles (**9a**) and (**9b**) *via*



(**8a**) R = Me
(**8b**) R = Ph

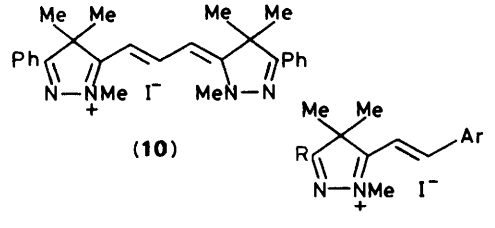
(**9a**) R = Me
(**9b**) R = Ph

Scheme 1.

† The term azolenines refers to non-aromatic isomers of azoles.

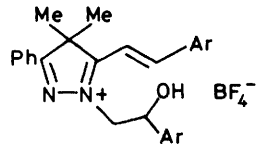
nucleophilic addition. The structures of the products were confirmed by a high-field shift for the *N*-methyl ^{1}H n.m.r. signal (respectively to δ 2.7 and 3.0), and by the non-equivalence of the methyl groups at C-4. The behaviour of the salts (**2**) towards H–D exchange is thus quite different from that of the 2*H*-imidazolium compounds (**1**), which exchange readily at the *N*-methyl group,[2] and similar to the pyridine series.[10]

Attention was thus turned to novel Knoevenagel-type reactions at the 5-methyl group. The salt (**2b**), when heated under reflux in pyridine with triethoxymethane, yielded a green crystalline product identified as the cyanine (**10**) from its ^{1}H n.m.r. spectrum. Specifically the *N*-methyl protons absorbed at δ 3.9, and the diene-bridge protons at δ 6.8 (2 H) and 8.2 (1 H); coupling (*J* 14 Hz) confirmed a *trans* configuration. Related compounds are reported to be silver bromide emulsion sensitisers.[6b]



(**10**)

(**11a**) R = Ph, Ar = *m*-$NO_2C_6H_4$
(**11b**) R = Ph, Ar = *p*-$NO_2C_6H_4$
(**11c**) R = Ph, Ar = *o*-ClC_6H_4
(**11d**) R = Ph, Ar = Ph
(**12a**) R = Me, Ar = *m*-$NO_2C_6H_4$

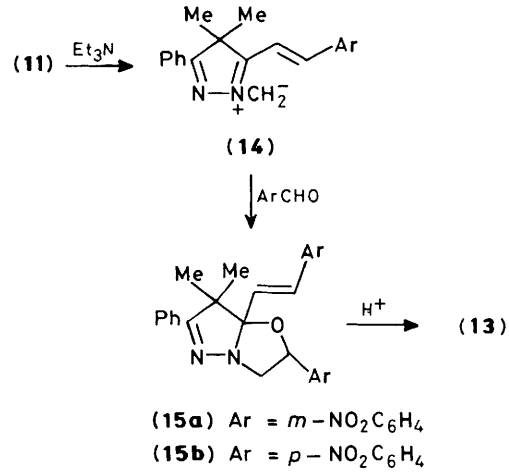


(**13a**) Ar = *m*-$NO_2C_6H_4$
(**13b**) Ar = *p*-$NO_2C_6H_4$

Reaction of the salt (**2b**) with an equimolar amount of *m*-nitrobenzaldehyde and a catalytic quantity of triethylamine in refluxing ethanol gave a high yield of the benzylidene derivative (**11a**) demonstrating further the acidity of the 5-methyl group. The analogues (**11b**—**d**) were isolated similarly using the appropriate aldehydes; the 3-methyl compound (**12a**) was prepared likewise from the salt (**2a**). All products were red to orange in colour; ^{1}H n.m.r. spectra are in Table 2.

In an initial experiment, equimolar amounts of triethylamine and the salt (**2b**) had been used, together with a 50% excess of *m*-nitrobenzaldehyde. Under these conditions, reaction occurred also at the *N*-methyl group giving the bis-adduct (**13a**) (45%), isolated as the tetrafluoroborate salt. When a 100% excess of *m*-nitrobenzaldehyde was used, the yield of the product (**13a**) was increased to 70%. The ^{1}H n.m.r. spectrum (300 MHz) showed non-equivalent methyl groups at C-4, an AMX pattern for the *N*-substituent alkyl protons (three double doublets at δ 5.0, 5.2, and 5.6 respectively), and a multiplet between δ 7.7 and 9.1 (15 H) for the aromatic and alkene protons. The OH group was observed as a broad signal at δ 4.5, and in the i.r. range at 3 530 cm^{-1}.

Since only the mono-adduct (**11a**) was formed when equimolar quantities of the salt (**2b**) and *m*-nitrobenzaldehyde were used, it appeared that (**11a**) was forming first, the conjugating substituent at C-5 rendering the *N*-methyl group now sufficiently acidic for further reaction to occur at this site. To confirm this, reaction with 2 mole equivalents of the potentially more-activating *p*-nitrobenzaldehyde was attempted; the reaction mixture on cooling deposited a dark solid identified as the pyrazolo[5,1-*b*]oxazole (**15b**), which was converted into the salt (**13b**) on treatment with tetrafluoroboric acid (Scheme 2). The i.r. spectrum of (**15b**) showed no OH

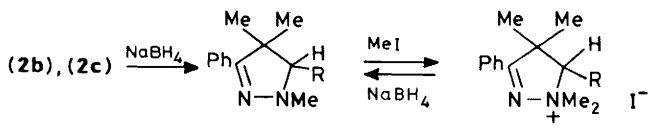


(**15a**) Ar = *m*-$NO_2C_6H_4$
(**15b**) Ar = *p*-$NO_2C_6H_4$

Scheme 2.

absorption, and its ^{1}H n.m.r. spectrum indicated only one isomer, although two diastereoisomeric forms are possible. The methyl groups at C-4 were non-equivalent, and there were multiplets at δ 3.9 (2 H, N–CH_2), 5.1 (1 H, O–CH), and between 6.9 and 7.4 (15 H). In the presence of trifluoroacetic acid, its ^{1}H n.m.r. spectrum became identical with that of the salt (**13b**) which, in turn, was similar to that of the isomer (**13a**). We thus believe that salts (**11a**) and (**11b**) in the presence of an excess of triethylamine can be converted into the ylides (**14**); these add to the extra mole of aldehyde, in a fashion analogous to that of the ylides derived from the salts (**1**),[2] to yield the bicycles (**15**) and, subsequently, on acid-treatment, the pyrazolium ethanols (**13**).[11] Interestingly, it had been suggested earlier that analogues of (**15**), formed by a different route, may have passed through intermediates structurally similar to the cations (**13**).[12] The less-activating benzaldehyde and *o*-chlorobenzaldehyde on reaction under similar conditions with the salt (**2b**) gave only complex mixtures of products.

The metho-salts (**1**) had been readily reduced by sodium borohydride to dihydroimidazoles;[2] similar reductions were attempted with compounds (**2**). The salts (**2b**) and (**2c**), in acetonitrile–methanol or ethanol (1 : 1) were converted into the dihydropyrazoles (**16**) in high yields (Scheme 3). In the ^{1}H n.m.r.



(**16a**) R = Me
(**16b**) R = Ph

(**17a**) R = Me
(**17b**) R = Ph

Scheme 3.

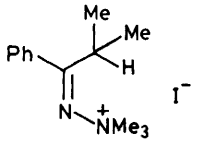
spectra, signals for the *N*-methyl group were found near δ 2.9, while those for the 5-methine proton in products (**16a**) and (**16b**) were at δ 2.65 and 3.7 respectively. The 4-methyl groups were diastereotopic. Treatment of the dihydropyrazoles (**16**) with

Table 1. Physical and analytical data for new compounds.

Compound	X	Yield (%)	M.p. (°C)	Recryst. solvent[a]	Found (%) C	H	N	Molecular formula	Requires (%) C	H	N
(**2b**)	I	76	176—178	A	47.6	5.25	8.5	$C_{13}H_{17}IN_2$	47.6	5.2	8.5
(**2c**)	I	71	148—151	A	55.4	4.9	7.15	$C_{18}H_{19}IN_2$	55.4	4.9	7.2
(**5a**)	BF_4	62	138—139	A	48.1	7.2	11.0	$C_{10}H_{17}BF_4N_2$	47.8	6.8	11.2
(**7**)	—	65	151—153	A	85.0	6.2	9.0	$C_{23}H_{20}N_2$	85.15	6.2	8.65
(**10**)	I	72	224—225	A	59.8	5.9	10.3	$C_{27}H_{31}IN_4$	60.2	5.8	10.4
(**11a**)	I	93[b]	186—188	A	51.95	4.4	9.1	$C_{20}H_{20}IN_3O_2$	52.1	4.35	9.1
(**11b**)	I	76	187—188	A	52.15	4.5	9.0	$C_{20}H_{20}IN_3O_2$	52.1	4.35	9.1
(**11c**)	I	48	168—169	A	53.1	4.4	5.9	$C_{20}H_{20}ClIN_2$	53.3	4.45	6.2
(**11d**)	I	60	172—174	A	57.95	5.1	6.7	$C_{20}H_{21}IN_2$	57.7	5.05	6.7
(**12a**)	I	74	178—179	A	45.0	4.4	10.25	$C_{15}H_{18}IN_3O_3$	45.1	4.5	10.5
(**13a**)	BF_4	70	153—157	A	56.7	4.4	9.8	$C_{27}H_{25}BF_4N_4O_5$	56.65	4.4	9.8
(**13b**)	BF_4	78	198—201	A	57.0	4.5	10.1	$C_{27}H_{25}BF_4N_4O_5$	56.65	4.4	9.8
(**15b**)	—	78	178—179	A	66.9	5.0	11.5	$C_{27}H_{24}N_4O_5$	66.9	5.0	11.55
(**16b**)	—	75	102—103	B	81.7	7.65	10.6	$C_{18}H_{20}N_2$	81.8	7.6	10.6
(**17a**)	I	81	230—231[c]	A	49.05	6.3	8.05	$C_{14}H_{21}IN_2$	48.85	6.15	8.1
(**17b**)	I	80	155—157	A	56.0	5.7	6.85	$C_{19}H_{23}IN_2$	56.2	5.7	6.9

[a] A = Ethanol; B = water. [b] Yield 35% when 0.5 mol equivalent Et_3N used. [c] With decomposition.

methyl iodide resulted in high yields of the salts (**17**) arising from quaternisation at N-1 rather than at N-2, in agreement with earlier observations.[13] The structures were confirmed by n.m.r. spectroscopy, ^1H signals for the 5-methine protons having moved to δ 4.55 and 5.25 respectively for products (**17a**) and (**17b**), suggesting that the positive charge was on the adjacent nitrogen atom, and the two (non-equivalent) *N*-methyl signals appearing near δ 3.5 and 4.0 in both compounds. Further, the ^{13}C n.m.r. spectrum of the salt (**17a**) showed strong similarities to that of the known[14] model compound (**18**). Signals for the *N*-methyl groups, C-3, and the 4-methyl groups appeared at δ 50.8 and 56.5, 180.0, and 9.6 and 21.6 respectively. Analogous signals for the hydrazonium salt (**18**) were



(**18**)

respectively at δ 57.1, 180.1, and 19.1. The large increase in chemical shift for C-3 in the dihydropyrazole (**16a**) on quaternisation at N-1 (from δ 157.7 to 180.0) is noteworthy, and suggests that the change in charge density plays a larger role in determining its magnitude than the loss of the paramagnetic contribution from the N-1 non-bonding electrons.

Attempts to reduce the C=N bond in the dihydropyrazolium salts (**17**) with sodium borohydride resulted in displacement of one *N*-methyl group and regeneration of the dihydropyrazoles (**16**) (Scheme 3).

Experimental

Melting points were measured on a Bristoline hot-stage microscope and are uncorrected. I.r. spectra were run as mulls in $CHBr_3$ on a Perkin-Elmer 283B spectrophotometer. ^1H N.m.r. spectra were recorded on JEOL-PMX 60, EM-360L, and Nicolet NT-300 (300 MHz) instruments with $SiMe_4$ as internal reference, and ^{13}C n.m.r. spectra on JEOL FX-100 and Nicolet NT-300 instruments, with $CDCl_3$ (77.0 p.p.m.) or $(CD_3)_2SO$ (39.5 p.p.m.) as internal references. The 4*H*-pyrazoles (**6a—c**)[4b,8b] and the hydrazonium salt (**18**)[14] were prepared by published procedures. The latter showed $\delta_H[(CD_3)_2SO]$ 1.10 (6 H, d, *J* 6.5 Hz), 2.84 (1 H, m, *J* 6.5 Hz), 3.38 (9 H, s), and 7.60 (5 H, s); $\delta_C[(CD_3)_2SO]$ 19.1 (C-*Me*$_2$), 40.0 (*C*-Me$_2$), 57.1 (N-Me), 126.8, 128.5, 129.9, and 131.9 (aryl-*C*), and 180.1 (*C*=N). Physical and analytical data for new compounds are given in Table 1.

Preparation of 1-*Alkyl*-4,4-*dimethyl*-4H-*pyrazolium Salts* (**2**)—(**5**).—*General procedure for salts* (**2**) *and* (**3**). The appropriate pyrazole (**6**) (10—20 mmol) was heated under reflux in an excess (30 ml) of alkyl iodide for 1—5 h. Anhydrous Et_2O (50 ml) was added, and the deposited solid was separated by filtration and recrystallised. For known compounds, physical data were: (**2a**), 87%, m.p. 178—180 °C (lit.,[8c] 180—183 °C) (**3a**), 75%, m.p. 174—175 °C (lit.,[8b] 167 °C).

3,4,4,5-*Tetramethyl*-1-*propyl*-4H-*pyrazolium Iodide* (**4a**).—The pyrazole (**6a**) (1.0 g, 8.1 mmol) and 1-iodopropane (1.5 g, 8.8 mmol) were heated on an oil-bath at 60—70 °C for 48 h. The residue was triturated repeatedly with Et_2O, dissolved in ethanol, and reprecipitated with Et_2O as an oil which subsequently solidified. Recrystallisation from ethanol gave the iodide (**4a**) (1.07 g, 45%), m.p. 134—136 °C (lit.,[8a] 142—142.5 °C).

3,4,4,5-*Tetramethyl*-1-*prop*-2-*enyl*-4H-*pyrazolium Tetrafluoroborate* (**5a**).—The pyrazole (**6a**) (2.0 g, 16.1 mmol) and 3-bromopropene (3.0 g, 25 mmol) were heated under reflux in ethanol for 10 h, and the solvent evaporated to give a brown oil (3.1 g, 75%). Treatment of the oil (1 g, 4.1 mmol) in ethanol (5 ml) with $NaBF_4$ (0.89 g, 8.1 mmol), followed by evaporation gave a solid, which on extraction into CH_2Cl_2 (15 ml) and reprecipitation with Et_2O yielded the *tetrafluoroborate* (**5a**) (0.84 g, 82%).

1-*Benzyl*-4-*methyl*-3,5-*diphenyl*-1H-*pyrazole* (**7**).—The pyrazole (**2c**) (1.0 g, 4.0 mmol) was refluxed in an excess of benzyl chloride for 9 h after which the solvent was removed. Et_2O (20 ml) and aqueous HI (57.4%; 2.0 ml) were then added and the resulting oil was dissolved in ethanol; on addition of Et_2O the

Table 2. ^{1}H N.m.r. spectra for 4*H*-pyrazolium salts.

Compound	X	Solvent[a]	R^1	R^2	R^3	δ[b] (C-4) Me_2[c]	R^{1d}			R^{2d}	R^{3d}
(2a)	I	A	Me	Me	Me	1.63	2.32			2.99	4.16
(2b)	I	A + B	Ph	Me	Me	1.82	7.77, 8.20 (3 H, m), (2 H, m)			2.85	4.23
(2c)	I	A	Ph	Ph	Me	1.92		7.83, 8.25 (6 H, m), (4 H, m)			4.23
(3a)	I	A	Me	Me	Et	1.66	2.43			3.10	1.66, 4.60 (3 H, t),[e] (2 H, q)[e]
(4a)	I	A	Me	Me	Pr^n	1.66	2.36			3.00	1.03, 2.10, 4.40 (3 H, t),[e] (2 H, m), (2 H, t)[e]
(5a)	BF_4	A + B	Me	Me	$CH_2CH{=}CH_2$	1.50	2.33			2.66	4.90, 5.20—6.30 (2 H, d),[f] (3 H, m)
(11a)	I	A + B	Ph	*m*-$NO_2C_6H_4CH{=}CH$	Me	2.15		7.40—8.60, 9.00 (10 H, m), (1 H, bs)			4.46
(11b)	I	A + B	Ph	*p*-$NO_2C_6H_4CH{=}CH$	Me	2.10		7.33—8.60 (11 H, m)			4.40
(11c)	I	A + B	Ph	*o*-$ClC_6H_4CH{=}CH$	Me	2.10	7.40, (1 H, d),[g]	7.66, 8.16, 8.77 (6 H, m), (3 H, m), (1 H, d)[g]			4.36
(11d)	I	A + B	Ph	$C_6H_5CH{=}CH$	Me	2.13		7.30—7.80, 7.93—8.65 (7 H, m), (5 H, m)			4.50
(12a)	I	A + B	Ph	*m*-$NO_2C_6H_4CH{=}CH$	Me	1.85	2.43		7.50, 7.80, 8.30 (1 H, d),[h] (1 H),[i] (1 H, d),[h] 8.36, 8.53, 8.80 (1 H, d), (1 H, d), (1 H, bs)		4.30

[a] A = $CDCl_3$; B = CF_3CO_2H. [b] Multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet. [c] 6 H, s. [d] 3 H, s unless otherwise indicated. [e] *J* 7 Hz. [f] *J* 6 Hz. [g] *J* 16 Hz, C*H*=. [h] *J* 17 Hz, C*H*=. [i] Apparent triplet.

pyrazole (**7**) (0.85 g, 65%) was deposited; $\delta_H(CDCl_3)$ 2.13 (3 H, s) 5.50 (2 H, s), and 7.0—7.9 (15 H, m).

Deuterium–Proton Exchange in Salts (**2a—c**).—*In absence of base.* The appropriate salt (**2**) (0.4—0.8 mmol) was dissolved in a mixture of D_2O and CD_3CN (3:1; 0.4 ml), and the methyl signals in the ^1H n.m.r. spectrum were monitored as a function of time.

With added pyridine. The experiment was carried out as above with the addition of pyridine (0.05 ml). The n.m.r. signals were monitored at 20 °C and at 60—70 °C.

With added sodium deuterioxide. The experiment was carried out as above, only NaOD (0.4—0.8 mmol) was added in place of pyridine; products were identified only by ^1H n.m.r. spectroscopy. The salt (**2a**) gave the dihydropyrazole (**9a**), δ_H 1.06 (3 H, s), 1.16 (3 H, s), 2.00 (3 H, s), and 2.72 (3 H, s); salt (**2b**) gave the dihydropyrazole (**9b**), δ_H 1.40 (3 H, s), 1.50 (3 H, s), 3.10 (3 H, s), and 7.6—8.1 (5 H, m).

Reaction between the Salt (**2b**) *and Triethoxymethane.*—The salt (**2b**) (1.0 g, 3.05 mmol) and triethoxymethane (0.9 g, 6.1 mmol) were heated under reflux in pyridine (9 ml) for 3 h. The solvent was evaporated and the residue was stirred with Et_2O (20 ml) for 2 h to give the *cyanine iodide* (**10**) (0.59 g, 72%), green needles from ethanol; $\nu_{max.}$ 1 570, 1 465, 1 400, 1 380, 1 235, 1 215, and 945 cm^{-1}; $\delta_H(CDCl_3)$ 1.91 (12 H, s), 3.93 (6 H, s), 6.81 (2 H, d, *J* 14 Hz), 7.60 (6 H, m), 7.92 (4 H, m), and 8.24 (1 H, t, *J* 14 Hz).

Reactions between the Salts (**2**) *and Aromatic Aldehydes.*—*With 1 mole of aldehyde: compounds* (**11**) *and* (**12**). The method for compound (**11a**) is described. The salt (**2b**) (1.0 g, 3.05 mmol), *m*-nitrobenzaldehyde (0.46 g, 3.05 mmol), and Et_3N (0.05 ml, 0.36 mmol) were refluxed together in EtOH (10 ml) for 3 h. On cooling, 1,4,4-*trimethyl*-5-[2-(m-*nitrophenyl*)*ethenyl*]-3-*phenyl*-4H-*pyrazolium iodide* (**11a**) (1.31 g, 93%) was deposited. Use of 1.52 mmol of Et_3N gave a lower (35%) yield. *Compounds* (**11b—d**) and (**12a**) were prepared similarly, a longer (12 h) reflux time being used for the latter.

With excess of m-*nitrobenzaldehyde and triethylamine: compound* (**13a**). The reaction was carried out as for (**11a**) above, only an excess of *m*-nitrobenzaldehyde (0.68 g, 4.5 mmol) and triethylamine (0.45 g, 4.5 mmol) were used, and the reflux time was increased to 48 h. The solvent was evaporated, the residue was triturated with Et_2O (25 ml), and the resulting mixture filtered to remove the triethylammonium iodide. The filtrate was treated with aqueous HBF_4 (2 ml; 48%) to give a green gummy precipitate which solidified on trituration with Et_2O to give 1-[2-*hydroxy*-2-m-*nitrophenyl*)*ethyl*]-4,4-*dimethyl*-5-[2-(m-*nitrophenyl*)*ethenyl*]-3-*phenyl*-4H-*pyrazolium tetrafluoroborate* (**13a**) (45%); $\nu_{max.}$ 3 530, 1 610, 1 550, 1 530, 1 300, and 1 070 cm^{-1}; $\delta_H[(CD_3)_2SO$, 300 MHz] 2.01 (3 H, s), 2.07 (3 H, s), 4.48 (1 H, br, OH), 5.00 (1 H, dd, *J* 4, 13 Hz), 5.18 (1 H, dd, *J* 7, 13 Hz), 5.56 (1 H, dd, *J* 4, 7 Hz), 7.7—8.7 (14 H, m), and 9.03 (1 H, bs). The yield of the product (**13a**) was increased to 70% on using 2 mol equiv. of *m*-nitrobenzaldehyde.

Compounds (**13b**) *and* (**15b**). The reaction was carried out as for compound (**13a**), only *p*-nitrobenzaldehyde (0.92 g, 6.1 mmol) and triethylamine (0.42 ml, 3.05 mmol) were used. The ethanol solution on cooling deposited a dark solid, 2,3,7,7a-*tetrahydro*-7,7-*dimethyl*-2-(p-*nitrophenyl*)-7a-[2-(p-*nitrophenyl*)*ethenyl*]-6-*phenylpyrazolo*[5,1-b]*oxazole* (**15b**) (1.15 g, 78%); $\nu_{max.}$ 1 595, 1 505, and 1 340 cm^{-1}; $\delta_H[(CD_3)_2SO]$ 1.33 (3 H, s), 1.50 (3 H, s), 3.8—4.0 (2 H, m), 5.2—5.5 (1 H, m), and 6.9—8.4 (15 H, m). When compound (**15b**) (0.4 g 0.82 mmol) was dissolved in CH_2Cl_2 (20 ml) and aqueous HBF_4 (0.3 ml; 48%) was added, followed by Et_2O (40 ml), 1-[2-*hydroxy*-2-(p-*nitrophenyl*)*ethyl*]-4,4-*dimethyl*-5-[2-(p-*nitrophenyl*)*ethenyl*]-3-*phenyl*-4H-*pyrazolium tetrafluoroborate* (**13b**) was deposited as a yellow-green solid (0.37 g, 78%); $\nu_{max.}$ 3 530, 1 620, 1 600, 1 550, 1 520, 1 450, 1 345, and 1 060 cm^{-1}; $\delta_H(CDCl_3$ with $CF_3CO_2H)$ 2.10 (3 H, s), 2.15 (3 H, s), 5.00 (2 H, m), 5.85 (1 H, m), and 7.3—8.6 (15 H, m).

Reduction of the Salts (**2**) *with Sodium Borohydride.*—The salt (**2c**) (1.0 g, 2.56 mmol) was dissolved in a mixture of CH_3CN and EtOH (1:1; 10 ml) and the solution was cooled in ice-water; to it was added slowly a solution of $NaBH_4$ (0.38 g, 10.3 mmol) in EtOH (2 ml). After the mixture had been stirred for 30 min, water (20 ml) was added to give 4,5-*dihydro*-1,4,4-*trimethyl*-3,5-*diphenylpyrazole* (**16b**) as a white solid (0.51 g, 75%); $\nu_{max.}$ 2 965, 2 790, 1 600, 1 580, 1 495, 1 460, 1 445, and 760 cm^{-1}; $\delta_H(CDCl_3)$ 0.88 (3 H, s), 1.40 (3 H, s), 2.85 (3 H, s), 3.70 (1 H, s), 7.40 (8 H, m), and 7.70 (2 H, m). For the salt (**2b**), MeOH was used in place of EtOH, and work-up was by evaporation of the solvent, trituration of the residue with Et_2O (15 ml), followed by filtration to remove inorganic salts, and evaporation of the filtrate to give 4,5-*dihydro*-1,4,4,5-*tetramethyl*-3-*phenylpyrazole* (**16a**) as a colourless oil (80%) (Found: M^+, *m/z* 202.1464. $C_{13}H_{18}N_2$ requires M^+, *m/z* 202.1470); $\nu_{max.}$ 2 960, 2 770, 1 590, 1 570, 1 490, 1 460, 1 440, and 760 cm^{-1}; $\delta_H(CDCl_3)$ 1.10 (3 H, s), 1.15 (3 H, d, *J* 7 Hz), 1.30 (3 H, s), 2.65 (1 H, q, *J* 7 Hz), 2.90 (3 H, s), 7.50 (3 H, m), and 7.80 (2 H, m); $\delta_C(CDCl_3)$ 10.5 and 17.5 (4-Me), 24.3 (5-Me), 40.6 (N-Me), 49.4 (C-4), 73.4 (C-5), 126.4, 128.0, 132.8 (aryl-C), and 157.7 (C-3).

Reaction of the Dihydropyrazoles (**16**) *with Methyl Iodide.*—The dihydropyrazole (1.5—2.0 mmol) was heated under reflux in methyl iodide (20 ml) for 60—72 h. Solvent was removed, the residue was triturated with Et_2O (20 ml), and the residue from the filtration recrystallised to give respectively 4,5-*dihydro*-1,1,4,4,5-*pentamethyl*-3-*phenylpyrazolium iodide* (**17a**); $\nu_{max.}$ 1 600, 1 565, 1 470, and 1 440 cm^{-1}; $\delta_H(CDCl_3)$ 1.53 (3 H, s), 1.63 (3 H, s), 1.80 (3 H, d, *J* 7 Hz), 3.50 (3 H, s), 3.95 (3 H, s), 4.55 (1 H, q, *J* 7 Hz), and 7.5—8.1 (5 H, m); $\delta_C(CDCl_3)$ 9.6 and 21.6 (4-Me), 24.75 (5-Me), 50.8 and 56.5 (N-Me), 53.75 (C-4), 76.8 (C-5), 126.5, 128.2, 128.6, 132.1 (aryl-C), and 180.0 (C-3); and 4,5-*dihydro*-1,1,4,4-*tetramethyl*-3,5-*diphenylpyrazolium iodide* (**17b**); $\nu_{max.}$ 2 920, 1 600, 1 495, 1 455, 1 440, 1 365, and 745 cm^{-1}; $\delta_H(CDCl_3)$ 1.00 (3 H, s), 1.53 (3 H, s), 3.38 (3 H, s), 3.90 (3 H, s), 5.25 (1 H, s), 7.3—7.8 (8 H, m), and 8.00 (2 H, m).

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