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Substituent effects in reductions of heteroaromatic cations

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epoc ABSTRACT: A set of 11 each of 2,4,6-triphenylpyrylium, -thiopyrylium and -*N*-methylpyridinium tetrafluoroborates carrying a range of substituents in the phenyl rings were prepared. First and second wave reduction potentials were determined. For the thiopyrylium series there are linear correlations between scaled potentials ($E°/0.05915$) and summed Hammett constants for substituents in the pendant phenyl groups ($\sigma = 2.29$ and 3.38 for first and second waves respectively). For the pyrylium series, a good linear relationship ($\sigma = 2.79$) is obtained for all substituent patterns for the first wave reduction potentials, but for the second wave there are separate correlations for salts carrying substituents in the 4-phenyl and for those carrying substituents in 2- and 6-phenyls. For the pyridinium series, the first wave potentials show separate correlations for salts carrying substituents in the 4-phenyl and for those carrying substituents in 2-and 6-phenyls, but a single linear relationship for the second wave potentials. These are related to particular structural features in the cations, radicals and anions in each series. Rates and products were determined for reductions of the pyrylium and thiopyrylium cations by sodium cyanoborohydride and of all cations by sodium borohydride in acetonitrile solution. Reactions are first order in reducing agent and cation. Primary kinetic isotope effects were determined for borohydride reduction of the least reactive of each of the series of cations. Plots of logarithms of second-order rate constants against summed Hammett constants for substituents in the pendant phenyl groups are linear for all combinations of reagent and cation with $0.91 < \sigma < 1.50$ across all substituent patterns. For parent pyrylium and thiopyryliums, $k\mathrm{BH_4}/k\mathrm{CNBH_3} = 8.4 \times 10^4$ and 1.5×10^4, respectively, and for reductions by borohydride the reactivities of the pyrylium, thiopyrylium and pyridinium, series decrease in the order $1.4 \times 10^5{:}8.8 \times 10^3{:}1$. Constant selectivities are not observed. Comparison of the correlations for electrochemical reduction and for hydride addition leads to the conclusion that charge neutralization in the hydride addition transition states runs ahead of bonding changes at the originating B—H bond. Copyright © 2002 John Wiley & Sons, Ltd.
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KEYWORDS: electrochemistry; heteroaromatic; cation; hydride; addition; substituent effect; LFER

INTRODUCTION

In this paper we complete[1] an examination of electronic effects in hydride transfers to electron-deficient carbon from borohydride and related anionic donors. These are synthetically useful reducing agents, especially for carbonyl or imine functionality, but the reactions with these groups are mechanistically complex, so that electronic effects are difficult to disentangle from those of steric demand and counterion coordination. In an earlier paper,[2] we described our experiments using the readily available heteroaromatic cations 2,4,6-triphenylpyrylium, 2,4,6-triphenylthiopyrylium and 2,4,6-triphenyl-*N*-methylpyridinium, **4** (X = O, S or NMe) in Fig. 1, as hydride acceptors in which variation of the heteroatom of the central aromatic ring provided a relatively coarse control of electron deficiency, and substituents on the phenyl groups a finer control within each series. Since these are charged acceptors, with extensive delocalization, forming neutral hydride adducts, the effects of counterion association were expected to be small. It was also hoped that steric effects would be comparable, but possible complications arising from the presence of the *N*-methyl group in the pyridinium series were noted.

In reductions of **4** (X = O, S and NMe), and sets of derivatives with substituents only on the pendant 4-phenyls, **3**, **5**, **6** and **8** (X = O, S, and NMe), by cyanoborohydride ion in acetonitrile solution all the *N*-methylpyridinium salts proved to be inert, but pyrylium and thiopyrylium salts gave good second-order kinetics [Eqn. (1)] in reductions with excess reagent. Sodium and tetrabutylammonium cyanoborohydride were equally reactive, confirming the anticipated absence of counterion involvement. Across a total reactivity range of just over 100-fold, logarithms of rate constants plotted against summed Hammett constants for substituents on the 4-phenyls showed linear relationships and reaction constants for both pyrylium and thiopyrylium series were determined.

$$\mathrm{CNBH_3}^- + \mathrm{Ar}^+ \xrightarrow{k} \mathrm{H{-}Ar} + (\mathrm{CNBH_2})$$

$$v = k[\mathrm{CNBH_3^-}][\mathrm{Ar}^+] \qquad (1)$$

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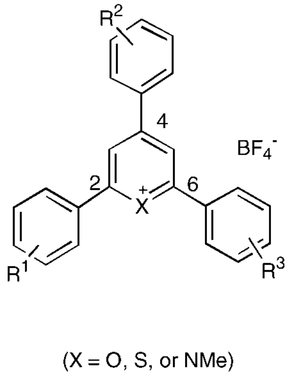


Compound	R^1	R^2	R^3	Σσ
1	*p*-CH_3	*p*-CH_3	*p*-CH_3	-0.51
2	*p*-CH_3	H	*p*-CH_3	-0.34
3	H	*p*-CH_3	H	-0.17
4	H	H	H	0.00
5	H	*m*-Cl	H	0.37
6	H	*p*-CF_3	H	0.54
7	*m*-Cl	H	*m*-Cl	0.74
8	H	*m,m'*-$(CF_3)_2$	H	0.86
9	*p*-CF_3	H	*p*-CF_3	1.08
10	H	*p*-CF_3	*m,m'*-$(CF_3)_2$	1.40
11	*m,m'*-$(CF_3)_2$	H	*m,m'*-$(CF_3)_2$	1.72

Figure 1. Structures, substituent patterns and summed substituent constants for the heterocyclic cations used in this work

Cyclic voltammetry of acetonitrile solutions of the salts showed two peaks for each cation, corresponding to sequential reversible one-electron reductions [Eqn. (2)] to radicals and then to anions which are, formally at least, anti-aromatic having eight π-electron arrays.[3] For the then available set, linear correlations were obtained in plots of $E_{1/2}$ against summed Hammett constants. Comparison of the reaction constants (ρ_{el}) for first wave reduction potentials, appropriately scaled to yield values of log K_{el} [Eqns (3) and (4)], with those for the hydride additions permitted the reasonable conclusion that transfer of hydride from cyanoborohydride was not initiated by rate limiting single electron transfer (SET).

$$\mathrm{Ar}^+ \overset{e^-}{\rightleftharpoons} \mathrm{Ar}^{\cdot} \overset{e^-}{\rightleftharpoons} \mathrm{Ar}^- \tag{2}$$

$$e^- + \mathrm{Ar}^+ \overset{K_{el(1)}}{\rightleftharpoons} \mathrm{Ar}^{\cdot}$$

$$\log K_{el(1)} = FE^\circ_{(1)}/2.303RT \tag{3}$$

$$e^- + \mathrm{Ar}^{\cdot} \overset{K_{el(2)}}{\rightleftharpoons} \mathrm{Ar}^-$$

$$\log K_{el(2)} = FE^\circ_{(2)}/2.303RT \tag{4}$$

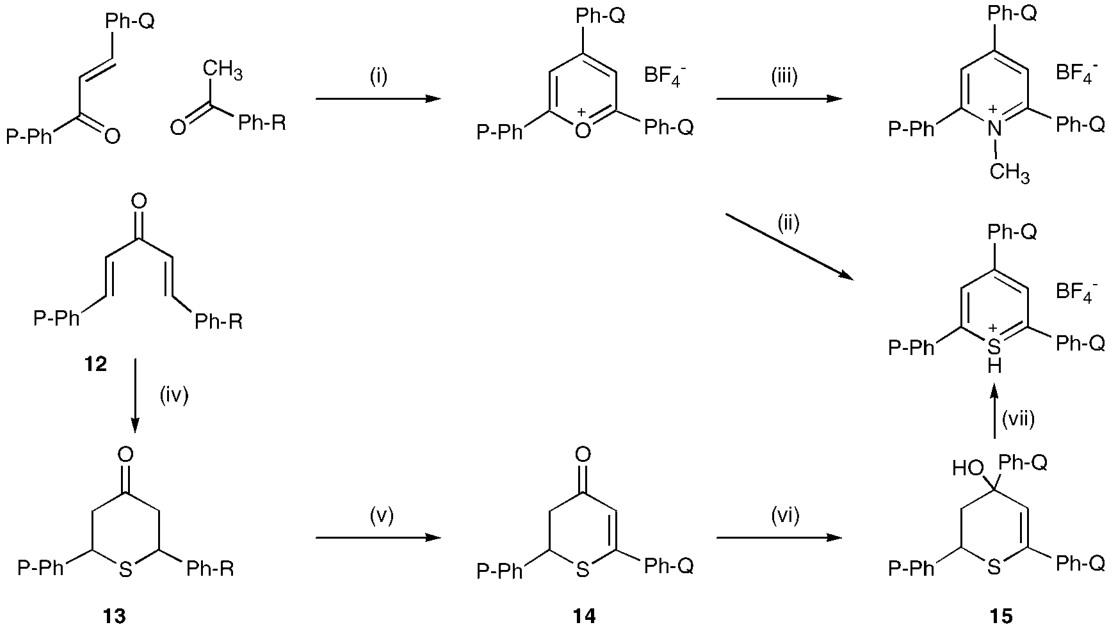
In this work, we extended the range of reactivities and report here the preparation and reduction of heteroaromatic salts which carry substituents also on phenyls at the 2- and 6-positions. We now compare the behaviour of cyanoborohydride, $NCBH_3^-$, with the more reactive hydride donor, borohydride, BH_4^-. Figure 1 shows the compounds used in this and earlier work and collects values for summed Hammett constants of their phenyl substituents (values of σ are taken from Ref. 4). For the most part, the new compounds, **1**, **2**, **7**, **9** and **11** (X = O, S and NMe), retain the symmetry of the parent cations but the set includes one asymmetrically substituted group, **10** (X = O, S and NMe). As with the earlier work, the substituents and their placing were selected to maximize the range of electronic character while excluding interaction of substituent with the heteroaromatic ring by through-conjugation.

PREPARATION, STRUCTURE, AND ELECTROCHEMISTRY OF CATIONS

Pyrylium salts were prepared conventionally by acid-catalysed condensations of appropriately substituted chalcones and acetophenones, and served as precursors for substituted *N*-methylpyridinium salts and some of the thiopyryliums (Scheme 1). As noted in our earlier work, electron-withdrawing phenyl substituents inhibit conversion of pyryliums to thiopyryliums by reaction with hydrogen sulphide, and the alternative approach, also shown in Scheme 1, via substituted dihydro-4*H*-thiopyrones, **14**, was then used to obtain **10** and **11** (X = S)

Acetonitrile, as a robust aprotic dipolar solvent,[5] was retained as solvent for the measurements. Solutions of all cations in this solvent were indefinitely stable, and cyclic voltammetry of the new compounds again showed two peaks corresponding to two reversible one-electron reductions (radical dimerizations giving rise to irreversible behaviour are associated with cations having H, CH_2Ph or styryl substituents at 2- or 4-positions[6]). First and second wave potentials for the new compounds are presented in Table 1. Values of log *K* for the reversible electrode processes were plotted against summed Hammett constants for the phenyl substituents (Fig. 2) and tested for the existence of linear free energy relationships across these extended series.

Thiopyrylium salts are most easily reduced, and the



Scheme 1. Preparation of heterocyclic cations. Reagents: - (i) see text; (ii) Na_2S then HBF_4; (iii) $MeNH_3$ then HBF_4; (iv) H_2S/NaOAc; (v) NCS/pyridine; (vi) Q-PhLi in THF; (vii) HBF4, Ph_3COH

Hammett plots for the thiopyrylium series shows the simplest behaviour. Both first and second wave potentials show good linear correlations [Eqns (5) and (6)] with the reaction constant for formation of the anion from the radical ($\rho_2 = 3.28$) being significantly larger than that for radical formation from the cation ($\rho_1 = 2.29$). These values do not differ significantly from those obtained in the earlier work with the compounds having only substituents on the 4-phenyls, so that there is no detectable differential stabilisation of cation, radical, or anion by substituents at either pendant 4- or 2- and 6-phenyls.

For X = S:

$$E^\circ_{(1)}/0.05915 = 2.29\ (\pm 0.04)\quad \Sigma\sigma - 3.70\ (\pm 0.04)\quad (r^2 = 0.997,\ 11\ \text{points}) \tag{5}$$

For X = S:

$$E^\circ_{(2)}/0.05915 = 3.28\ (\pm 0.04)\quad \Sigma\sigma - 19.85\ (\pm 0.08)\quad (r^2 = 0.992,\ 11\ \text{points}) \tag{6}$$

Reaction constants for Hammett correlations of radical formation at benzylic positions are usually small[7,8] so that the major contribution to the reaction constants is expected to arise from the interaction of substituents with the charge on the heteroaromatic cation or anion, and relative values of ρ_1 and ρ_2 suggests a greater demand on the substituents when negative charge is developed. For each wave, the change in charge type differs, and the ability of the central ring to accommodate positive and negative charge is expected to differ and the demand on the substituents in the pendant rings should vary correspondingly. Thiopyrylium cations are well characterized,[9] with x-ray crystal structures showing planar heterocyclic rings with little restriction as to torsion angles about bonds to pendant phenyls. The structure of thiopyranyl anions remains a matter of debate, but the corresponding 2*H*-dihydrothiopyran is reported to have $pK_a = 19.5$ and, on deprotonation, to yield a stable red 2,4,6-triphenylthiopyranyl anion.[10] The availability of d-orbitals on the sulphur allows an anti-Hückel[11] topology in the cyclic π-orbital array, so that a fully conjugated and planar thiopyranyl anion may be aromatic.[12]

For the pyrylium series, a good linear relationship extends across the complete series [Eqn. (7)] with the first wave potentials. Again, we associate this with interaction of the substituents with the positive charge on the heteroaromatic cation, and again, there is no detectable differential stabilization from substituents at pendant 4- or 2- and 6-phenyls. The value of $\rho_1 = 2.79$ is larger than that in the thiopyrylium series, indicating a larger electron demand on the substituents, in turn reflecting the relative abilities of trivalent oxygen and sulphur to accommodate positive charge.

For X = O:

$$E^\circ_{(1)}/0.05915 = 2.79\ (\pm 0.05)\quad \Sigma\sigma - 5.36\ (\pm 0.04)\quad (r^2 = 0.997,\ 11\ \text{points}) \tag{7}$$

For the second wave potentials, the linear correlation including all substitution patterns (not shown) is poor ($r^2 = 0.943$) and the value of $\rho_2 = 3.59$ differs significantly from that obtained earlier with the reduced set of

Table 1. UV–VIS absorption spectroscopic data and first and second wave reduction potentials from cyclic voltammetry of new phenyl-substituted 2,4,6-triphenylthiopyrylium and 2,4,6-triphenyl-*N*-methylpyridinium salts

Compound		UV absorption, λ_{max} (nm) (log ε)			$E°$ (V)	
					1st wave	2nd wave
X = 0	**1**	424 (4.46)	376 (4.61)	288 (4.26)	−0.40	−1.53
	2	428 (4.42)	360 (4.51)	288 (4.17)	−0.38	−1.48
	7	390s (4.43)	364 (4.53)	276 (4.21)	−0.19	−1.31
	9		368 (4.58)	268 (4.31)	−0.15	−1.21
	10	402 (4.30)	388 (4.36)	274 (4.13)	−0.08	−1.09
	11		372 (4.72)	266 (4.36)	−0.03	−1.10
X = S	**1**	394 (4.42)	278 (4.10)	258 (4.04)	−0.29	−1.26
	2	430 (4.35)	370 (4.38)	278 (4.26)	−0.27	−1.24
	7	380 (4.45)	276 (4.10)		−0.13	−1.05
	9	378 (4.56)	244 (4.36)		−0.07	−0.97
	10	400 (4.14)	346 (4.25)	268 (4.09)	−0.03	−0.88
	11	378 (4.53)	244 (4.35)		0.01	−0.85
X = NMe	**1**	318 (4.55)			−1.07	−1.52
	2	306 (4.41)			−1.05	−1.51
	7	304 (4.44)			−0.93	−1.30
	9	302 (4.44)			−0.89	−1.22
	10	292 (4.45)			−0.81	−1.15
	11	304 (4.48)			−0.81	−1.07

compounds. Better separate linear relationships are found for compounds **3**, **4**, **5**, **6** and **8**, having substituent only on the 4-phenyl ($\rho_2 = 5.31$, $r^2 = 0.993$, five points) and for compounds **2**, **4**, **7**, **9** and **11**, having substituents on pendant phenyls at 2- and 6-positions ($\rho_2 = 3.25$, $r^2 = 0.990$, five points). Equivalently, a multiple linear regression analysis using contributions from 4- and (2 + 6)-phenyl substituents as separate independent variables, including compounds **1** and **10** (X = O), which yields the relationship shown in Eqn. (8) for the reduction of the pyranyl radical to the anion.

For X = O:

$$E^{\circ}_{(2)}/0.05915 = 3.22\ (\pm 0.13)\sigma_{(2,6)} + 5.14\ (\pm 0.24)\sigma_{(4)} - 24.16\ (\pm 0.10) \quad (r^2 = 0.992,\ 11\ \text{points}) \tag{8}$$

By either treatment, phenyl substituents at each 2- or 6-position of the central heterocycle are only ca 30% as effective as when at a 4-position, consistent with either significant charge localization at the 4-position of the anion and/or shape changes in the transformation which restrict torsional angles between pendant phenyls and the central ring. Crystal structures of pyrylium cations show that the heteroaromatic arrays are planar, and that there is little steric hindrance to small dihedral angles between the heterocyclic ring and its pendant phenyls. Indeed, these angles have been related to the electronics of the substituents on the pendant phenyls.[13] A fully delocalized anion, however, would have eight electrons formally occupying the π-array on the heteroaromatic ring, but for the oxygen heteroatom d-orbital participation is not possible. Distortions of the molecular framework to minimize anti-aromatic destabilisation are therefore expected (Fig. 3). For example, a conformation with 4-phenyl placed axially on a boat conformation ring would no longer have a fully conjugated cyclic array, and the negative charge would be concentrated at that position, placing a higher demand on substituents on the 4-phenyl, experimentally shown in their higher value of ρ. Valence isomerization to a bicyclic array has been proposed[3] to account for the products of decomposition of putative transient 2,4,6-triphenylpyranyl anions generated by deprotonation of the corresponding 4*H*-dihydropyran ($pK_a \approx 37$),[10] and might also account for the observed second wave electrochemical behaviour.

The pyridinium series exhibits yet a third pattern of behaviour. First wave potentials now show a poor correlation across the complete series ($r^2 = 0.943$, 11 points) with the slope of the line ($\rho_1 = 2.16$) deviating significantly from that obtained earlier ($\rho = 3.10$) with the reduced set. Compounds having substituent only on the 4-phenyl ($\rho_1 = 3.03$, $r^2 = 0.993$, five points) and those with substituents on pendant phenyls at 2- and 6-positions ($\rho_1 = 1.95$, $r^2 = 0.999$, five points) now show good separate correlations with the first wave data. Treatment of the full data set by multiple linear regression using contributions from 4- and (2 + 6)-phenyl substituents as separate independent variables, including compounds **1** and **10** (X = NMe) now yields a relationship [Eqn. (9)] which is consistent with the separation of effects with individual 2- or 6-substituents being ca 30% as effective as a 4-substituent.

For X = NMe :

$$E^{\circ}_{(1)}/0.05915 = 1.96\ (\pm 0.06)\sigma_{(2,6)} + 2.95\ (\pm 0.11)\sigma_{(4)} - 17.12\ (\pm 0.05) \quad (r^2 = 0.995, 11\ \text{points}) \tag{9}$$

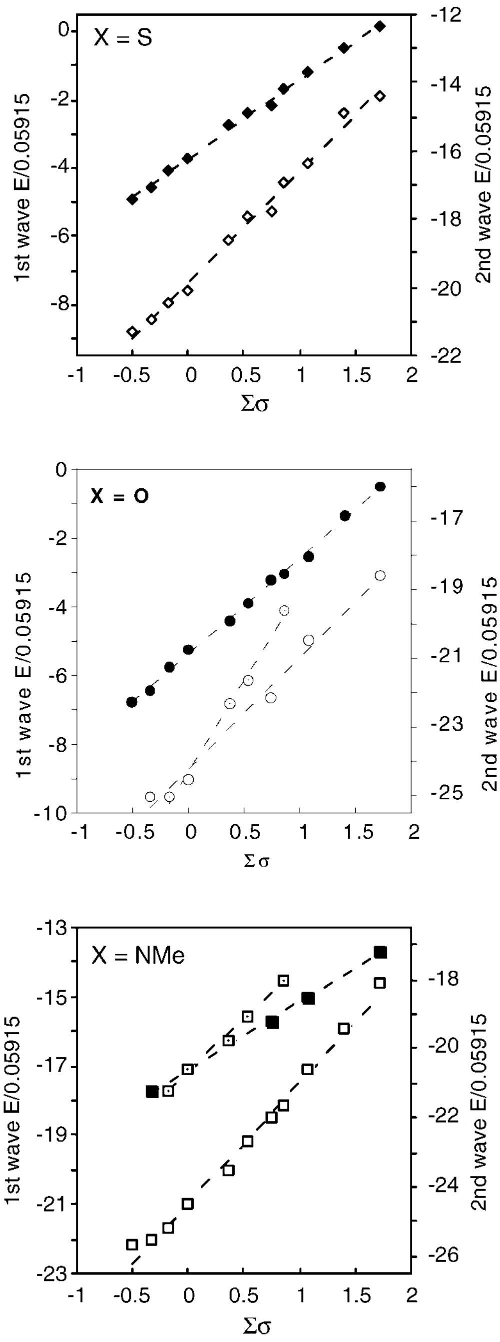


Figure 2. Plots of scaled reduction potentials [0.05915 = (2.303 *R T*)/*F*, where *T* = 298 K] against summed Hammett substituent constants for the heteroaromatic cations with X = S, O or N. Upper sets of data points are for first wave potentials, referred to the LH scale, and the lower sets are second wave potentials, referred to the RH scale. For X = O and X = S, 4-substituted sets are dotted centrally

The second wave potentials yield a good linear relationship [Eqn. (10)] across the complete series.

For X = NMe :

$$E^\circ_{(2)}/0.05915 = 3.49\ (\pm 0.12)\quad \Sigma\sigma - 24.43\ (\pm 0.10)$$
$$(r^2 = 0.990, 11\ \text{points}) \qquad (10)$$

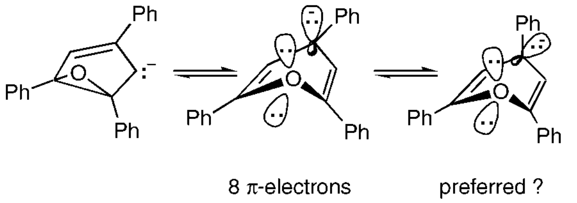


Figure 3. Possible conformations and valence isomerization of a pyranyl anion

We suggest that the differing electrochemical responses of the pyridinium and pyrylium salts reflect the presence of the *N*-methyl group in the pyridinium series, which introduces additional steric compressions and leaves only one lone pair on the heteroatom. In contrast to the structural patterns of pyryliums noted above, structural studies on monocyclic *N*-benzylpyridiniums[14] suggest unavoidable steric compressions between the *N*-benzyl group and substituents and pendant 2-and 6-phenyls. The crystal structures of 2,4,6-triphenyl-*N*-methylpyridinium tetrafluoroborate[2] and of 1-methyl-4-(4-methoxyphenyl)-2,6-diphenylpyridinium perchlorate[15] showed the heterocyclic ring to adopt a flattened boat conformation, and that while the dihedral angle between the heterocyclic ring and pendant phenyl on the 4-position were small (ca 25°), those at the 2- and 6-positions were much larger (ca 55°), reducing nonbonded interaction between *o*-hydrogens on these phenyls and the *N*-methyl at the expense of reduced overlap between the π-arrays of the pendant phenyls and the heteroaromatic central ring. We argue that these differences are reflected in ρ_1 because the radical places little demand on the substituents. A dependence of reaction constant on dihedral angle, despite our initial selection of the phenyl substituents for their inability to interact by resonance (*R*) with the central ring[16] highlights the complex interaction of π-electron transfer effects in systems with varying electron demand. These have been subject to a range of computational studies,[17] but qualitatively, the dependence arises because effects based on electronegativity differences between atoms, whether transmitted as induced dipoles through bonds or through space as an electrostatic field (*F* or χ), are short range, and the interaction of substituents at 3′-or 4′-positions of pendant phenyls with a charge on the central heteroaromatic by these mechanisms would be small. For significant interaction, the charges must be delocalized into the pendant phenyl by another longer range mechanism which is resonance, and dependent on the dihedral angle between the two rings.

The absence of separation in ρ_2 shows that there is neither charge localization nor differing restrictions on torsions to 4- or 2- and 6-phenyl groups in the anion (Fig. 4). An indication of the preferred conformation of the triphenylpyridyl anion is seen in the crystal structure of an isoelectronic 1,2,4,6-tetraarylated-1,4-dihydropyra-

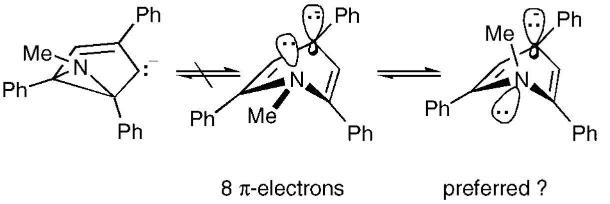


Figure 4. Possible conformations and valence isomerisation of a pyridyl anion

zine[18] which adopts a flattened boat conformation with nitrogen atoms at prow and stern positions. One of the nitrogen atoms has a planar arrangement of ligands, and contributes an electron pair to the conjugated array; the other is pyramidal with an axial substituent so that the cyclic conjugation is interrupted. Figure 4 shows a possible structure for the anion, with the methyl group in an axial position, which would permit delocalization of the negative charge to all phenylated positions. Semi-empirical MO calculations (AM1) on the corresponding *N*-benzyl anion[19] support this picture. Unlike the pyranyl series, there is no indication of valence isomerization.

We briefly compare the electrochemical behaviour of this set of cations with those of substituted acetophenones, for which Loufty and Loufty[20] have measured half-wave reduction potentials (also for acetonitrile solutions). Their series included *p*-MeO and *p*-NO_2 groups, and correlations with simple Hammett constants were very poor but notably improved by exclusion of the data for *p*-nitroacetophenone. Hammett plots, using potentials scaled as above, then gave $\rho = 11.75$ ($r^2 = 0.945$), reflecting a much greater demand on the substituents.

REACTION OF CATIONS WITH CYANOBOROHYDRIDE AND BOROHYDRIDE

Solutions of sodium cyanoborohydride and sodium borohydride (ca 0.05 M) in acetonitrile could be prepared. The borohydride solutions were notably sensitive to traces of moisture but, provided that oxygen and moisture were rigorously excluded, showed no sign of decomposition or loss of reducing power on storage.

Product characterization and stability

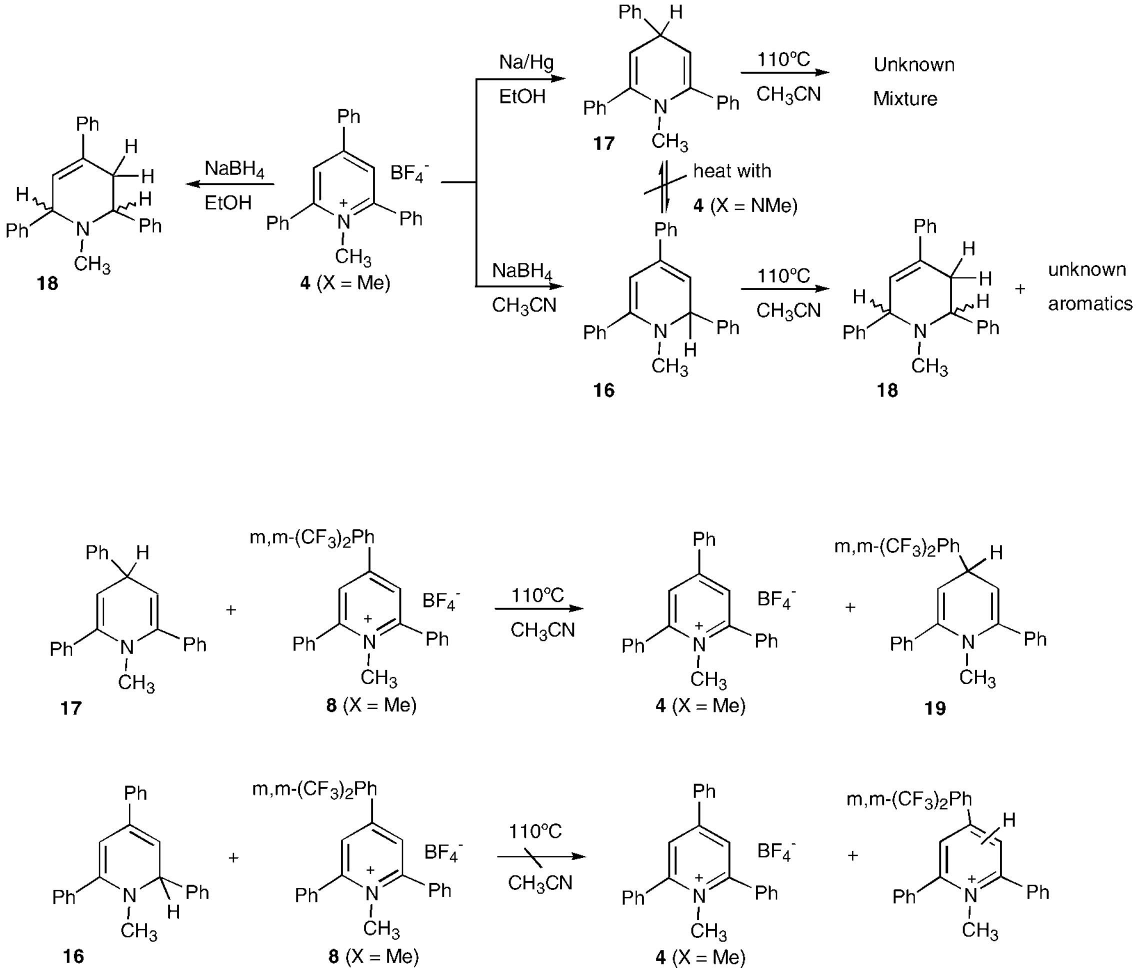
The immediate products of reduction were determined by ^{1}H NMR spectroscopy of solutions of the cations in CD_3CN to which excess reducing agent had been added.

As noted earlier, 2,4,6-triphenylpyrylium, **4** (X = O), is reduced by cyanoborohydride in acetonitrile to the corresponding 4*H*- and 2*H*-pyrans in a 25:74 ratio, with the 2*H*-pyran suffering ring opening to 1,3,5-triphenylpentadienone.[2] Substituents at the 4-phenyl have a relatively small effect on product distribution with electron-withdrawing groups favouring the 2*H*-pyran. For the new compounds, with substituents at the 2- and 6-phenyls, the effect on product distribution is similarly small, and over the whole series ranges only from 11:89 for **8** (X = O) to 29:71 for **1** (X = O), a small shift in favour of the 2*H*-pyran induced by electron-withdrawing groups at either of the phenyls. For the asymmetrically substituted pyrylium, **10** (X = O), the 4*H*-pyran: 2*H*-pyran ratio is 16:84 with the 84% of 2*H*-pyran addition being divided 38:36 between the possible isomers.

For reactions of the pyryliums with borohydride, the 1,3,5-triphenylcyclopentadienone from ring opening of the 2*H*-pyran is further reduced to the corresponding dienol. This is a slow process compared with the initial reduction of the cation and did not interfere with rate measurements. It did, however, complicate measurements of product ratios, especially for the more reactive salts. For the least reactive pyrylium, **1** (X = O), the 4*H*-pyran: 2*H*-pyran ratio is 3:97. As for the cyanoborohydride reductions, phenyl substituents had only minor effects on the product ratio, and in all cases the fraction of 4*H*-pyran is less than 7% (probably considerably less), so that the more reactive borohydride shows a higher selectivity for reaction *via* the 2-position of the cations.

With excess cyanoborohydride in acetonitrile, 2,4,6-triphenylthiopyrylium, **4** (X = S), itself yields 2*H*- and 4*H*-thiopyrans in a 55:45 ratio. There is a similar muted response of product ratio to substitution in the 4-phenyls, but electron-withdrawing groups in the 2- and 6-phenyls induce a more significant shift in favour of the 4*H*-thiopyran with **11** (X = S) showing a 4*H*-pyran: 2*H*-pyran ratio of 71:29. With the more reactive borohydride, the product ratio for **4** (X = S) is unchanged, and the spread across the whole series is slightly attenuated. Both 4*H*- and 2*H*-thiopyrans are stable to the reaction conditions with either of the two reagents but may be isolated and equilibrated by heating in presence of the corresponding thiopyrylium salt.[21] Doddi and Ercolani[22] reported $K = 7.1$ favouring the 2*H*-thiopyran (25 °C in $CHCl_3$); we repeated the equilibration and found $K = 32$ for reaction in acetonitrile-d_3 at 25 °C.

The pyridinium salts, all inert to cyanoborohydride, all reacted with excess borohydride to yield single dihydropyridines, identified from their ^{1}H NMR spectra as the 2*H*-isomers. For 2,4,6-triphenyl-*N*-methylpyridinium, **4** (X = NMe), for example, the product shows one-hydrogen signals at δ 5.62 (dd, $J = 6$ and 2 Hz), δ 5.40 (d, $J = 2$ Hz) and δ 5.14 (d, $J = 6$ Hz), readily assigned to hydrogens at the 5-, 3- and 6-positions of the 1,2-dihydropyridine **16**;[23] In the absence of a proton source, further reduction by borohydride does not occur.[24] An authentic sample of the isomeric 1,4-dihydropyridine **17** was prepared quantitatively by reduction of the salt in ethanol solution by sodium–mercury amalgam; its symmetry and structure were confirmed by a two-



Scheme 2. Reductions of 1,2,3-triphenyl-*N*-methylpyridinium tetrafluoroborate and reactions of reduced species

hydrogen doublet at δ 5.10 (J = 5 Hz) and a one-hydrogen triplet δ 4.45 (J = 5 Hz) in its ^{1}H NMR spectrum, associated with hydrogens at 3- and 4-positions of the heteroaromatic ring (Scheme 2).

Solutions of the isomeric dihydropyridines in degassed acetonitrile-d_3 were stable indefinitely at 25 °C, and experiments to establish the relative stabilities of the isomeric dihydropyridines by equilibration in the presence of their parent cation in a similar manner to the dihydrothiopyrans were attempted. In the case of the 4*H*-isomer **17**, prolonged heating at 110 °C, with or without added cation, yielded coloured high molecular weight products, which have not been identified. In the case of the 2*H*-isomer **16**, similar treatment yielded new aromatic material, again unidentified, and $\Delta^{3,4}$-2,4,6-triphenyl-*N*-methyltetrahydropyridine, **18**, identified by comparison with an authentic sample prepared by reduction of **4** (X = NMe) by sodium borohydride in ethanol.[24] We have not established the stereochemical relationship between 2- and 6-phenyls, but the coupling constants are consistent with a *cis* relationship. In the absence of a structure for the aromatic product, the mechanism of formation of **18** must remain speculative, but the net process seems to be a disproportionation, and different from the homolytic pathways discovered by Katritzky *et al.* in the thermolyses (neat at 210 °C) of *N*-benzyl- and *N*-octyl-2,4,6-triphenylpyrydinium salts.[25] We can only note that a 1,5-methyl migration would convert **16** into 2,3-dihydro-3-methyl-2,4,6-triphenylpyridine, capable of directly regenerating 3-methyl-2,4,6-triphenylpyridine by H_2 transfer to **16**.

The failure of cation **4** (X = NMe) to catalyse the equilibration of **17** and **18** indicates a high barrier to hydride transfers to 2-positions of the cation or from the 2*H*-isomer, probably reflecting the steric crowding at that position discussed earlier. The relative ease of hydride transfer between **4**-positions was demonstrated by heating **16** and **17** separately with the more electron-deficient pyridinium salt **8** (X = NMe). Compound **16** did not reduce this salt, but with **17** there was rapid formation of the substituted 1,4-dihydropyridine **19** (showing a doublet and triplet at δ 5.11 and 4.52, respectively). That this reactivity pattern is a feature of the *N*-methylpyridinium series was also shown by rapid reaction of **17**, but

Table 2. Rates and activation parameters for reductions of phenyl-substituted heteroaromatic cations by sodium cyanoborohydride in anhydrous acetonitrile

Compound		k (25 °C) ($dm^3 mol^{-1} s^{-1}$)	E_a ($kJ mol^{-1}$)	Log A
X = O	**1**	5.44 (±0.03)	79.20 (±0.34)	14.61 (±0.06)
	2	1.17 (±0.02) × 10^1	76.28 (±0.29)	14.43 (±0.05)
	3	2.73 (±0.04) × 10^1	71.96 (±1.17)	14.42 (±0.20)
	4	6.37 (±0.03) × 10^1	71.96 (±0.29)	14.41 (±0.05)
	5	1.96 (±0.03) × 10^2	71.62 (±0.75)	14.84 (±0.06)
	6	4.89 (±0.17) × 10^2	67.02 (±0.71)	14.43 (±0.14)
	7	5.34 (±0.21) × 10^2	65.26 (±0.81)	14.16 (±0.14)
	8	9.64 (±0.13) × 10^2	68.99 (±0.77)	15.07 (±0.13)
	9	1.87 (±0.09) × 10^2	61.93 (±0.10)	14.12 (±0.02)
	10	6.52 (±0.21) × 10^2	64.65 (±0.30)	15.14 (±0.21)
	11	1.27 (±0.03) × 10^4	62.77 (±0.68)	15.1 (±0.11)
X = S	**1**	5.27 (±0.02)	74.94 (±0.34)	13.85 (±0.06)
	2	9.31 (±0.01)	72.73 (±0.17)	13.71 (±0.03)
	3	1.22 (±0.02) × 10	73.57 (±0.02)	14.00 (±0.03)
	4	2.26 (±0.08) × 10	72.55 (±0.25)	14.08 (±0.06)
	5	3.77 (±0.07) × 10	66.31 (±0.29)	13.20 (±0.06)
	6	8.82 (±0.14) × 10	69.08 (±0.21)	14.04 (±0.03)
	7	1.12 (±0.02) × 10^2	67.84 (±0.08)	13.93 (±0.01)
	8	1.45 (±0.07) × 10^2	68.50 (±0.24)	14.16 (±0.04)
	9	2.71 (±0.02) × 10^2	67.71 (±0.31)	14.29 (±0.05)
	10	6.02 (±0.02) × 10^2	66.34 (±0.35)	14.40 (±0.06)
	11	1.17 (±0.09) × 10^3	64.50 (±0.15)	14.37 (±0.03)

not **16**, with 2,4,6-triphenylthiopyrylium, **4** (X = S), to yield a 56:44 mixture of 4*H*- and 2*H*-dihydrothiopyrans.

Reaction kinetics

For reactions of pyryliums and thiopyryliums with cyanoborohydride and most cations with borohydride, progress was conveniently monitored by UV spectrophotometry using appropriate absorptions of the cations (see Table 1). Cation concentrations were usually less than 2×10^{-5} M and reducing agent at least 10-fold higher. Under these conditions, good first-order decays were observed. Reactions of the more electron-deficient pyryliums with borohydride were inconveniently fast under these conditions and all concentrations were reduced ca 10-fold to bring the rates within measurable ranges. Reaction progress was then monitored by spectrofluorimetry, providing rate data for **5**–**9** (X = O).

First-order rate constants for reactions with both cyanoborohydride and borohydride were shown to be accurately proportional to reducing agent concentration up to 10^{-3} M, and second-order rate constants and Arrhenius parameters for all combinations of cation and reducing agent are presented in Tables 2 and 3.

For cyanoborohydride, only reductions of the pyrylium and thiopyrylium series were observed, the parent pyrylium **4** (X = O) being three times more reactive than the parent thiopyrylium **4** (X = S). Activation parameters are presented in Table 2 and are for the production of mixtures, so that detailed interpretations are difficult. It is clear, however, that activation at 25 °C is mainly enthalpic ($62 < \Delta H^{\ddagger} < 72$ kJ mol^{-1} for X = S and $60 < \Delta H^{\ddagger} < 76$ kJ mol^{-1} for X = O), with entropies of activation being small and positive ($0.5 < \Delta S^{\ddagger} < 22.5$ J K^{-1} mol^{-1} for X = S and $16 < \Delta S^{\ddagger} < 36$ J K^{-1} mol^{-1} for X = O).

With sodium borohydride, all cations were reactive, and heats were determined for reactions of the parent cations, **4** (X = S or NMe), with sodium borohydride in acetonitrile. These were exothermic, with $\Delta H = -390.6$ and -315.2 kJ mol^{-1}, respectively, and we note, as we did earlier, that these values probably contain a substantial element from reaction of the borane produced with the acetonitrile. A value was also determined for reaction of **4** (X = O) giving $\Delta H = -484.2$ kJ mol^{-1} but, as noted above, this measurement will include contributions for the electrocyclic ring opening of the 1,2-dihydropyran product, and further reduction of the resulting dienone.

Rates of reaction with borohydride for the separate series increase in order *N*-methylpyridinium < thiopyrylium < pyrylium with a rate ratio of $1{:}8.8 \times 10^3{:}1.4 \times 10^5$ for the parent cations, **4** (X = O, S, or NMe), but even with the most reactive of the cations studied, **9** (X = O), the rate ($k = 7.91 \times 10^7$ dm^3 mol^{-1} s^{-1}) does not approach the diffusion limit for a simple anion–cation combination ($k_{diff} > 10^{10}$ dm^3 mol^{-1} s^{-1}) in this solvent.[26] The parent pyrylium **4** (X = O) is 16 times more reactive than the thiopyrylium **4** (X = S), so that for this pair of cations, the more reactive hydride donor, borohydride, is the more selective reagent. As for the

Table 3. Rates and activation parameters for reductions of phenyl-substituted heteroaromatic cartions by sodium borohydride in anhydrous acetonitrile

Compound		k (25 °C) (dm^3 mol^{-1} s^{-1})	E_a (kJ mol^{-1})	Log A
X = O	**1**	8.79 (±0.03) × 10^5	37.48 (±0.18)	12.51 (±0.03)
	2	2.22 (±0.31) × 10^6	37.30 (±0.53)	12.88 (±0.03)
	3	2.26 (±0.22) × 10^6	36.33 (±2.39)	12.72 (±0.46)
	4	5.34 (±0.61) × 10^6	37.00 (±3.31)	13.21 (±0.63)
	5	1.16 (±0.03) × 10^7	35.83 (±1.26)	13.34 (±0.23)
	6	2.22 (±0.08) × 10^2	34.62 (±0.71)	13.41 (±0.14)
	7	2.73 (±0.04) × 10^7	36.67 (±0.68)	13.86 (±0.12)
	9	7.91 (±0.09) × 10^7	35.23 (±0.29)	14.07 (±0.05)
X = S	**1**	1.00 (±0.02) × 10^5	53.76 (±0.93)	14.42 (±0.17)
	2	1.63 (±0.03) × 10^5	49.93 (±0.91)	13.96 (±0.17)
	3	1.97 (±1.49) × 10^5	53.92 (±0.27)	14.74 (±0.35)
	4	3.48 (±0.16) × 10^5	45.66 (±0.34)	13.54 (±0.08)
	5	5.31 (±0.20) × 10^5	44.66 (±3.56)	13.55 (±0.64)
	6	9.40 (±0.02) × 10^5	43.08 (±0.45)	13.52 (±0.08)
	7	1.34 (±0.04) × 10^6	47.23 (±0.79)	14.40 (±0.15)
	8	2.16 (±0.02) × 10^6	45.75 (±0.44)	14.35 (±0.08)
	9	2.92 (±0.07) × 10^6	46.32 (±0.85)	14.58 (±0.16)
	10	5.12 (±0.08) × 10^6	39.56 (±0.36)	13.64 (±0.07)
	11	1.17 (±0.02) × 10^7	48.88 (±0.70)	15.63 (±0.13)
X = NMe	**1**	9.96 (±0.01)	82.95 (±0.06)	15.53 (±0.01)
	2	1.79 (±0.08) × 10^1	82.36 (±0.24)	15.68 (±0.04)
	3	2.15 (±0.03) × 10^1	77.96 (±0.46)	14.99 (±0.08)
	4	3.93 (±0.03) × 10^1	77.32 (±0.21)	15.14 (±0.03)
	5	9.93 (±0.08) × 10^1	77.02 (±0.42)	15.49 (±0.07)
	6	1.71 (±0.04) × 10^2	75.22 (±1.31)	15.41 (±0.24)
	7	2.84 (±0.02) × 10^2	75.16 (±1.38)	15.62 (±0.06)
	8	4.58 (±0.03) × 10^2	74.09 (±0.32)	15.64 (±0.08)
	9	6.22 (±0.04) × 10^2	72.13 (±0.59)	15.43 (±0.10)
	10	1.92 (±0.06) × 10^2	72.93 (±0.91)	16.06 (±0.15)
	11	4.14 (±0.13) × 10^3	68.80 (±1.16)	15.67 (±0.19)

cyanoborohydride reductions, activation energies are dominated by enthalpic contributions (for X = O, 32.1 < $\Delta H^\ddagger$ <35.0 kJ mol^{-1}, for X = S, 37.1 < $\Delta H^\ddagger$ <51.3 kJ mol^{-1} and for X = NMe, 66.3 < $\Delta H^\ddagger$ <80.5 kJ mol^{-1}). The entropies of activation range from relatively small for the pyrylium series (−13 < $\Delta S^\ddagger$ <16 J K^{-1} mol^{-1}), through moderate for the thiopyryliums (6 < $\Delta S^\ddagger$ <46 J K^{-1} mol^{-1}) to distinctly positive for the *N*-methylpyridiniums (33.4 < $\Delta S^\ddagger$ <54.2 J K^{-1} mol^{-1}), but again show no obvious trend within the separate series.

For both reductants, the positive entropies of activation are consistent with loss of solvent electrostriction as charge neutralization occurs, the relatively small values reflecting large size and extensive delocalization in the cations. They contrast notably with the entropy-dominated activations in reductions of ketones by borohydride in alcoholic medium ($\Delta H^\ddagger \approx$ 12 kJ mol^{-1}, and $\Delta S^\ddagger \approx$ −160 kJ mol^{-1})[27,28] or of carbenium ions by silanes ($\Delta H^\ddagger \approx$ 20 kJ mol^{-1} and $\Delta S^\ddagger \approx$ −100 kJ mol^{-1})[29] or, to a lesser extent, of carbenium ions by amine boranes ($\Delta H^\ddagger \approx$ 50 kJ mol^{-1} and $\Delta S^\ddagger \approx$ −50 kJ mol^{-1}).[30]

The data for the pyrylium and thiopyrylium series also permit a direct comparison of the ability of borohydride and cyanoborohydride to donate hydride to these cations in this particular medium. For the parent cations, **4** (X = O) and **4** (X = S), $k_{\mathrm{BH_4}}/k_{\mathrm{CNBH_3}}$ = 8.4 × 10^4 and 1.5 × 10^4, respectively, corresponding to $\Delta\Delta G^\ddagger$ = 28.1 and 23.8 kJ mol^{-1}, respectively, notably less than the difference (92.5 kJ mol^{-1}) in the gas-phase hydride affinities of borane and cyanoborane.[31] Differential solvation of these compounds or of their hydride adducts[32] would contribute to the attenuation but the few data available[33] suggest that this would not be a large effect. The attenuation would also be consistent with hydride transfer transition states with only small degrees of transfer of hydride from boron to carbon. Kinetic hydrogen isotope effects for reductions by cyanoborohydride have been reported previously and were small, and believed to be consistent with early transition states. In this work we determined kinetic isotope effects for the borohydride reductions of the least reactive cation in each of the series **1** (X = O, S and NMe) and found $k_{\mathrm{BH_4}}/k_{\mathrm{BD_4}}$ (25 °C) = 1.25, 1.63 and 0.94, respectively. These values are similar to those found for other borohydride reductions[34] and are also believed to be consistent with early transition states.

Plots of logarithms of the second-order rate constants against summed Hammett constants for the phenyl substituents are shown in Fig. 5. For the five available combinations of reducing agent and cation series, good linear relationships [Eqns (11)–(15)] are found with no indication of distinct behaviour for groups with 4- and 2,6-substituents. Neither is there any indication in the reductions of the pyrylium series by borohydride of a break in the correlation, which might indicate the onset of diffusion control for the most reactive of the series.

For X = O by $NaBH_3CN$:

$$E^\circ/0.05915 = 1.50(\pm0.05)\Sigma\sigma + 1.67(\pm0.04)$$
$$(r^2 = 0.989, 11 \text{ points}) \qquad (11)$$

For X = O by $NaBH_4$:

$$E^\circ/0.05915 = 1.17(\pm0.06)\Sigma\sigma + 6.64(\pm0.04)$$
$$(r^2 = 0.985, 8 \text{ points}) \qquad (12)$$

For X = S by $NaBH_3CN$:

$$E^\circ/0.05915 = 1.05(\pm0.02)\Sigma\sigma + 1.29(\pm0.02)$$
$$(r^2 = 0.995, 11 \text{ points}) \qquad (13)$$

For X = S by $NaBH_4$:

$$E^\circ/0.05915 = 0.91(\pm0.02)\Sigma\sigma + 5.48(\pm0.02)$$
$$(r^2 = 0.995, 11 \text{ points}) \qquad (14)$$

For X = NMe by $NaBH_4$:

$$E^\circ/0.05915 = 1.18(\pm0.02)\Sigma\sigma + 1.58(\pm0.02)$$
$$(r^2 = 0.998, 11 \text{ points}) \qquad (15)$$

Reaction constants are smaller than those reported ($3.2 > \rho > 2.5$) for reductions of substituted acetophenones or benzophenones[28] by sodium borohydride in alcoholic solution, and the range of ρ values ($0.91 > \rho > 1.50$) seems small considering the total span of reactivities. However, for the pyrylium and thiopyrylium series, where both reagents are active, differences between the behaviour of borohydride and cyanoborohydride are significant. In both cases, and especially for the pyrylium series, the reactions with the less reactive hydride donor ($NaBH_3CN$) have larger reaction constants so that the selectivities of the hydride donors are not independent of the nature of the cationic acceptor. This contrasts with the constant selectivities[35] found by Mayr *et al.*[29] in reductions by some silanes, germanes and stannanes of benzhydryl cations. Remarkably, there is a constant selectivity between the pyrylium and *N*-methylpyridinium series in their reactivities towards sodium borohydride. The reaction constants are indistinguishable (1.17 ± 0.06 and 1.18 ± 0.02), so that the rate ratio for similarly substituted pairs of cations (1.4×10^5) do not vary with absolute reactivity of the cations. The behaviour of the thiopyrylium series does not conform to this pattern.

Table 4 compares reaction constants for hydride additions with those for the corresponding electrochemical reductions. For the pyrylium and thiopyrylium series, the existence of linear Hammett relationships for both hydride additions and for the first wave reduction potentials demands a proportionality between the free energies of activation of the former and the free energy change for formation of the radical from the cation. Values of $\rho_{(BH_3R)}/\rho_{(electrochem)}$ for the pyrylium series are

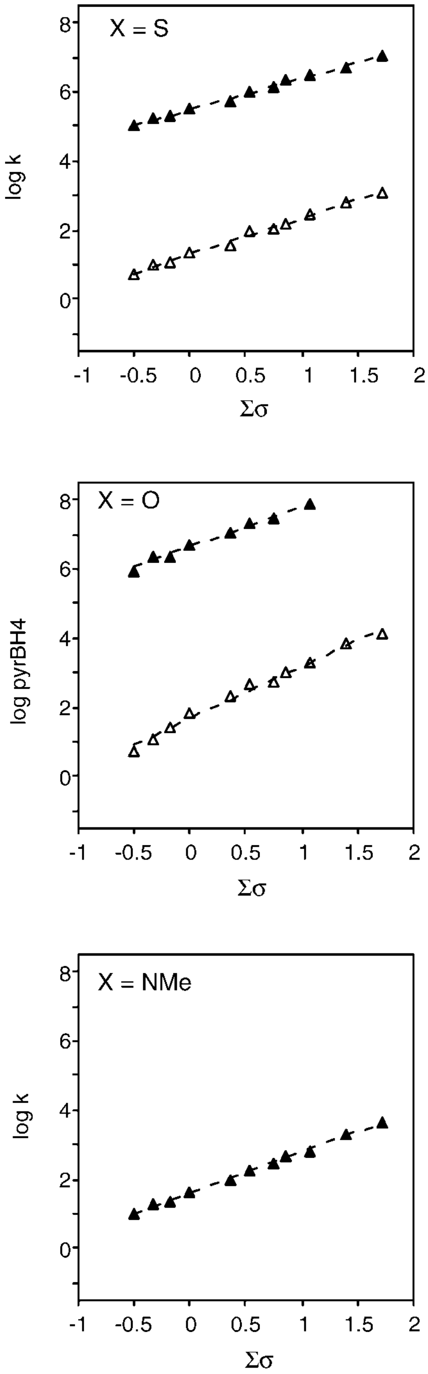


Figure 5. Plots of logarithms of second-order rate constants for reduction by sodium cyanoborohydride (△) or sodium borohydride (▲) against Hammett substituent constants of heteroaromatic cations with X = S, O, or NMe

Table 4. Reaction constants for electrochemical and borohydride reductions of phenyl-substituted 2,4,6-triphenylpyrylium, -thiopyrylium and -*N*-methyltriphenylpyridinium salts

Reaction	Cation series	Points	ρ	r^2
Scaled C.V. first wave potentials (Fig. 2):	X = O	11	2.79 (±0.05)	0.997
	X = S	11	2.29 (±0.04)	0.997
	X = NMe (all)	11	2.16 (±0.15)	0.958
	X = NMe (2,6)	5	1.95 (±0.04)	0.999
	X = NMe (4)	5	3.03 (±0.14)	0.993
Scaled C.V. second wave reductions	X = O (all)	11	3.59 (±0.30)	0.943
	X = O (2,6)	5	3.25 (±0.20)	0.990
	X = O (4)	5	5.31 (±0.25)	0.993
	X = S	11	3.38 (±0.10)	0.992
	X = NMe (all)	11	3.49 (±0.12)	0.990
Second order rate constants for hydride reductions (Fig. 5)	X = O (by Na BH_3CN)	11	1.50 (±0.05)	0.989
	X = O (by Na BH_4)	8	1.17 (±0.06)	0.985
	X = S (by Na BH_3CN)	11	1.05 (±0.02)	0.995
	X = S (by Na BH_4)	11	0.91 (±0.02)	0.995
	X = NMe (by Na BH_4)	11	1.18 (±0.02)	0.998

0.54 and 0.42 for cyanoborohydride and borohydride reductions, respectively and 0.45 and 0.40 for the thiopyrylium series. We note that Handoo *et al.*[36] found a linear relationship with near unity slope in a plot of free energies for hydride affinities of substituted benzyl cations against electron affinities, also in acetonitrile solution, and similar, but less good correlations have also been noted by Arnett *et al.*[37] in comparison of heats of transfer of hydride from cyanoborohydride to substituted trityl cations in sulfolane solution with their reduction potentials. These correlations between thermodynamic parameters are consistent with the view that the substituents affect mainly the stabilities of the common precursors, i.e. the cations, in the changes involved. Following Bunting,[38] who interpreted related linear relationships in reductions of cationic hydride acceptors by 1,4-dihydropyridines, we have argued before that the ratios $\rho_{(BH_3R)}/\rho_{(\text{electrochem})}$ give an indication of the extent of charge destruction at the cation in the hydride addition transition structures. On this basis, charge reorganization in the additions to pyryliums and thiopyryliums is less advanced in the transition states with the more reactive hydride donor, but the actual values ($0.54 < \rho_{(BH_3R)}/\rho_{(\text{electrochem})} < 0.40$), are difficult to reconcile with the primary kinetic isotope effects found in this and our earlier work. These are uniformly small compared with the estimated Westheimer maximum ($k_H/k_D = 4.56$ at 25 °C) (estimate based on the difference in zero-point energies for a B–H stretching vibration with $v = 2340\ \text{cm}^{-1}$)[39] for a B···H···C transfer and within the formalism which links primary kinetic isotope effects to bond order changes[40] at the hydron, indicative of either very early or very late transition states. As indicated above, we prefer the former, and must conclude that charge transfer runs ahead of the bonding changes in these reductions, but without the formation of discrete radical intermediates. Similar observations and conclusions have also been made for formal transfers of hydride from 1,4-dihydropyridines to some cationic acceptors[38] and for reactions of arylmethanes with 9-arylfluorenyl cations,[41] and Bunting presented a rationale in terms of the valence-bond configuration mixing theory.

For the pyridinium series, because there is differing electrochemical behaviour of compounds having substituents at 2- and 6-phenyls as opposed to 4-phenyls, the reasoning demands that the extents of charge neutralization in the hydride additions also differ for the two substitution patterns, which show values of $\rho_{(BH_4)}/\rho_{(\text{electrochem})} = 0.61$ and 0.39, respectively. It does not seem unreasonable that a larger extent of charge neutralization would occur in the transition states of the series where the substituents are less effective at stabilizing the ground-state charge of the cation. Again, the primary isotope effect and reaction energetics point to early transition states in terms of bonding changes at the B—H bond, so that there must be some uncoupling of electron and nuclear motion.

EXPERIMENT

Full experimental details, including descriptions of the preparation and characterization of the compounds used or encountered in this study, can be found as supplementary material at the epoc website at http://www.wiley.com/epoc.

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