

# Substituent effects in cyanoborohydride reductions of heterocyclic aromatic cations



Roy Beddoes (in part), David Heyes, Ramesh S. Menon and C. Ian. F. Watt\*

Department of Chemistry, University of Manchester, Manchester, UK M13 9PL

First and second wave  $E_{1/2}^{\text{redn}}$  potentials have been measured by cyclic voltammetry for a set of fifteen 2,6-diphenyl-4-(X-phenyl)-pyrylium, -thiopyrylium and -*N*-methylpyridinium tetrafluoroborates, with X = *p*-CH<sub>3</sub>, -H, *m*-Cl, *p*-CF<sub>3</sub> and *m,m'*-(CF<sub>3</sub>)<sub>2</sub>. There are linear correlations between Hammett substituent constants and scaled potentials ( $E/0.05915$ ) giving slopes of  $\rho = 2.59 \pm 0.06$  ( $r^2 = 0.9984$ ),  $2.38 \pm 0.07$  ( $r^2 = 0.9973$ ) and  $3.10 \pm 0.16$  ( $r^2 = 0.9918$ ), respectively, for the first wave potentials.

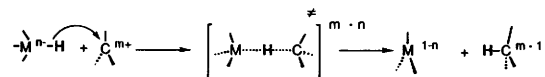
Products, rates and kinetic hydrogen isotope effects for reductions of the cations with sodium and tetrabutylammonium cyanoborohydride in acetonitrile solution have been determined. Reaction of the thiopyrylium 2 (X = H) yields kinetically controlled 54:46 mixture of the 4*H*- and 2*H*-thiopyrans. With the pyrylium ion 1 (X = H) the 4*H*- to 2*H*- ratio is 24:76 with the 2*H*-pyran suffering electrocyclic ring opening to 1,3,5-triphenylpentadienal. Product ratios are weakly sensitive to substituents on the 4-phenyl, with electron withdrawing groups increasing the amount of 2*H*-product for both thiopyryliums and pyrylium cations. Reductions are first order in cation and cyanoborohydride. For sodium cyanoborohydride and 2,4,6-triphenylpyrylium,  $k(25^\circ\text{C}) = 65.6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and for 2,4,6-triphenylthiopyrylium,  $k(25^\circ\text{C}) = 16.7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , with kinetic isotope effects ( $k_{\text{BH}_3\text{CN}}/k_{\text{BD}_3\text{CN}}$ ) of 1.17 and 1.68, respectively. Logarithms of rate constants correlate with Hammett constants giving  $\rho = 1.46 \pm 0.06$  ( $r^2 = 0.9951$ ) for the pyrylium series and  $\rho = 1.12 \pm 0.08$  ( $r^2 = 0.9831$ ) for the thiopyryliums. The *N*-methylpyridinium ions do not react with cyanoborohydride.

The X-ray crystal structure of 2,4,6-triphenyl-*N*-methylpyridinium tetrafluoroborate has been determined. Dihedral angles about bonds from the pyridinium ring to the 2- and 6-phenyls are larger than corresponding angles in 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiopyryliums and are ascribed to relief of non-bonded interactions between the 2- and 6-phenyls and the *N*-methyl group.

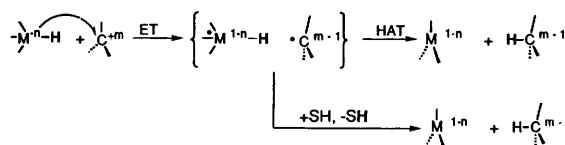
## Introduction

This work continues an interest in the mechanisms of addition of hydrogen to organic molecules, particularly in polar reactions formally initiated by delivery of hydride to the organic acceptor. In earlier work we have examined transfers of hydride between carbonyl groups in saturated aliphatic arrays, focusing on stereochemical requirements, and on the effects of metallic counterions on reactivity.<sup>1</sup> We now examine electronic effects in some hydride transfers from borohydride and related reagents to electron deficient carbon. Net transfer may occur *via* a concerted process with a three-centre transition structure having two electrons delocalised over that array (A in Scheme 1), but non-concerted processes initiated by an electron transfer (ET) yielding a transient radical pair can yield the same result (B in Scheme 1). The experiments in this work are designed to probe this mechanistic dichotomy and to discover what combinations of structural and electronic features in the donor and acceptor favour one mechanism rather than the other.

Borohydride itself, BH<sub>4</sub><sup>-</sup>, and the related ions, cyanoborohydride, NCBH<sub>3</sub><sup>-</sup>, and triethylborohydride, Et<sub>3</sub>BH<sup>-</sup>, are commonly used in synthetic organic chemistry for reductions of polar double bonds, especially those of carbonyls or imines.† Gas phase hydride affinity measurements<sup>2</sup> for borane (74.2 kcal mol<sup>-1</sup>) (1 cal = 4.184 J), cyanoborane (96.3 kcal mol<sup>-1</sup>) and triethylborane (69.5 kcal mol<sup>-1</sup>) give a good indication of the relative powers of the ions as hydride donors in the absence of solvent or counterion, and the reactivity ordering, EtBH<sub>3</sub><sup>-</sup> > BH<sub>4</sub><sup>-</sup> > NCBH<sub>3</sub><sup>-</sup>, is also found in solution



A Concerted hydride transfer



B Hydride transfer initiated by electron transfer

Scheme 1 Possible mechanisms for addition of hydride

reactions, although the gas phase energy differences are far from fully expressed.

The effects of varying electron demand in hydride acceptors have been examined by measurement of reaction constants ( $\rho$ ) for sodium borohydride reductions of substituted aryltrifluoromethyl,<sup>3</sup> and aryl methyl or *tert*-butyl ketones.<sup>4</sup> In protic media, these are  $3.12 > \rho > 2.3$ , but correlations are not particularly good with any of the available substituent parameter sets. The  $\rho$ -values have been taken to be consistent with a product-like transition state, but interpretation of these substrate substituent effects is complicated by the importance of co-ordination of a proton, or an other electrophile, at the carbonyl oxygen in such reductions.<sup>5</sup> Variation of metallic counterion, particularly in aprotic solvents, has been used to control reactivities and selectivities, but these effects, although valuable synthetically, should be quantified, or eliminated, in experiments designed to probe electronic effects.

Borohydrides also react with some electron deficient aromatics and related species. Neutral species such as 1,3,5-trinitrobenzene yield ionic Jackson–Meisenheimer hydride

† Recent IUPAC recommendations (1993) recommend that the BH<sub>4</sub><sup>-</sup> anion be denoted as boranuide, however, the traditional borohydride names have been retained throughout this paper.

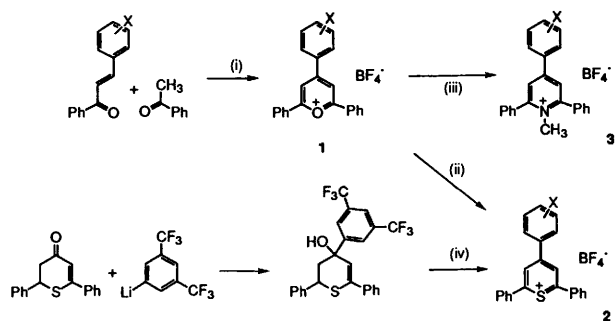
adducts.<sup>6</sup> Indications of ET initiated processes have been found in reactions of dinitrobenzenes in benzene with tetrabutylammonium borohydride, where, while the 1,3-dinitrobenzene forms an adduct, 1,4-dinitrobenzene yields a paramagnetic species identified as the radical anion.<sup>7</sup> A number of quinones, polycyanoaromatics and heteroaromatic bases with reduction potentials less negative than  $-1.5$  V (*vs.* SCE) have also been shown to yield radical anions under these conditions,<sup>8</sup> and reactions of electronically excited arenes with sodium borohydride in acetonitrile are believed to involve an initial electron transfer.<sup>9</sup>

We describe here an examination of the reactions of the weakest of the three hydride donors, cyanoborohydride, with the heteroaromatic cations **1**, **2** and **3**, in which charge is extensively delocalised and which are known to react with hydride donors by attachment of hydride at either the 2- or 4-position to yield neutral primary products. Counterion effects are therefore unlikely to dominate reactivity patterns as they do in carbonyl reductions, and these heterocyclic cations may thus comprise a useful series of acceptors in which electronic effects may be adjusted, measured and compared with reactivities in hydride reductions. Variation of the heteroatom (O, S or N-alkyl) affords a relatively coarse control of electron deficiency in the cation; finer tuning may be provided by introduction of substituents on the pendant phenyls, and for each heteroaromatic cation the local slope of any global structure–reactivity relationship may thus be obtained. In this initial study we have placed substituents on the 4-phenyl group, retaining the symmetry of the reacting system. Substituents in this initial study were *p*-CH<sub>3</sub>, H, *m*-Cl, *p*-CF<sub>3</sub> and *m,m'*-(CF<sub>3</sub>)<sub>2</sub>, selected to provide a reasonable range of electronic character, with neither structures nor positions of attachment allowing for conjugative interaction of the substituent with the heteroaromatic ring.

## Results

### Preparation, structure and properties of cations and reducing agents

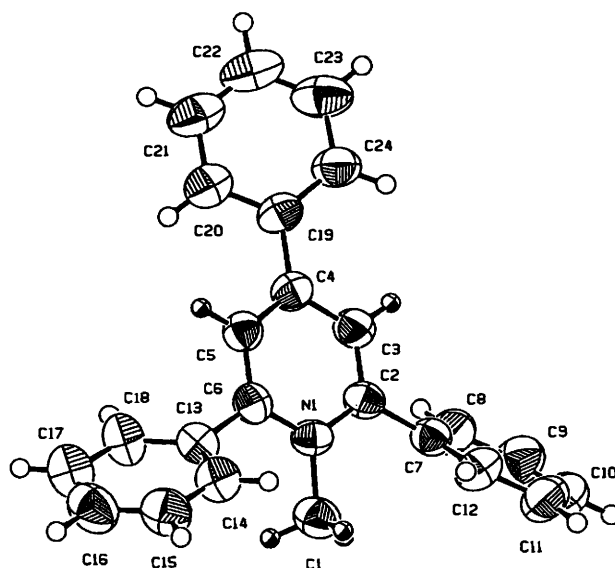
The synthetic chemistry of such cations is relatively well worked out,<sup>10</sup> and pyrylium salts were prepared by acid-catalysed condensation of acetophenone with substituted chalcones as shown in Scheme 2. Use of fluoroboric acid in acetic acid



**Scheme 2** Preparation and structure of heterocyclic cations **1**, **2** and **3**. Reagents: i, see text; ii, Na<sub>2</sub>S then HBF<sub>4</sub>; iii, MeNH<sub>3</sub> then HBF<sub>4</sub>; iv, HBF<sub>4</sub>, Ph<sub>3</sub>COH

effected cyclisation for all but the *p*-trifluoromethyl-substituted compound. For production of this salt, the medium was changed to trifluoroacetic acid, and prolonged reflux then provided an acceptable yield of the salt **1** ( $X = p\text{-CF}_3$ ). The pyrylium salts then serve as precursors of the corresponding thiopyrylium and *N*-methylpyridinium salts.

With the more electron-withdrawing 4-phenyl substituents, the conversions of the pyryliums to thiopyryliums became more difficult. From UV spectrometric studies, it was clear that reaction of the pyryliums with sodium sulfide yielded the



**Fig. 1** X-Ray crystal structure of **3** ( $X = \text{H}$ ) showing thermal ellipsoids and atomic numbering system. Dihedral angles between the mean plane of the pyridinium ring and those of the phenyls at C2, C4 and C6 are 55°, 25° and 55°, respectively.

expected anionic product of addition and ring opening, but acidification regenerated the pyrylium rather than thiopyrylium salts. For the preparation of **2** [ $X = m,m'-(\text{CF}_3)_2$ ], the general route was abandoned in favour of the alternative also shown in Scheme 2, involving addition of the substituted phenyllithium to the 2,6-diphenyldihydro-4*H*-thiopyrone<sup>11</sup> followed by dehydration of and hydride abstraction from the resulting alcohol.

In an ideal series of reactants for comparison of electronic effects, steric effects would be constant, or simply related to electronic effects. X-Ray crystal structures have been reported for a 2,4,6-triphenylpyrylium<sup>12</sup> and for some phenyl-substituted 2,4,6-triphenyl-pyryliums and -thiopyryliums,<sup>13</sup> **1** and **2**, but surprisingly, not for *N*-methyl-2,4,6-triphenylpyridinium,<sup>14</sup> and we have therefore determined the crystal structure of **3** ( $X = \text{H}$ ), details of which are presented in Fig. 1. The pyridinium shows a small distortion towards a boat conformation with N1 and C4 being displaced above the ring mean plane by 0.02 Å, while the other ring atoms show a smaller displacement in the opposite sense. Internal angles at N1, C2 and C6 are 120°, within experimental error. Those at C5 and C3 are slightly expanded to 122° and that at C4 contracted correspondingly to 116°.

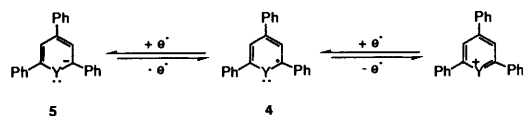
The local geometries at the carbons of the heterocyclic ring of the structure of **3** ( $X = \text{H}$ ) are remarkably similar to those reported for pyryliums and thiopyryliums. All are near planar, and even the larger size of the heteroatom in the thiopyryliums [ $d(\text{C}-\text{S}) = 1.72$ ,  $d(\text{C}-\text{N}) = 1.36$  and  $d(\text{C}-\text{O}) = 1.36$  Å] is compensated for by a closing of the interatomic angle at the heteroatom from 121° in pyryliums or pyridiniums to 103° in thiopyryliums. Torsions about bonds to the pendant 2-, 4- and 6-phenyls also affect steric requirements at the reactive sites, and are linked to electronic interaction between these phenyls and the cationic centres in the ring, an extreme case arising in the structures of 4-(4-nitrophenyl)-2,6-diphenylpyrylium and of 4-(4-dimethylaminophenyl)-2,6-diphenylpyrylium<sup>13</sup> where the dihedral angles to the substituted 4-phenyls are 30.5° and 3.0°, respectively. In the absence of strongly interacting substituents on the phenyl rings, dihedral angles to pyrylium and thiopyrylium rings range from 2.3° to 37.7° and appear to reflect crystal packing forces as much as intramolecular interactions. This is not the case, however, with the 2- and 6-phenyls of the *N*-methylpyridinium **3** ( $X = \text{H}$ ). Dihedral angles here are 55°, which can be regarded as a structural response

**Table 1** First and second wave reduction potentials from cyclic voltammetry of 2,6-diphenyl-4-(X-phenyl)-pyrylium, -thiopyrylium and -N-methylpyridinium tetrafluoroborate salts, UV-VIS absorption and fluorescence spectroscopic data

X	$E_{1/2}^{\text{redn}}/\text{V}$		UV	
	1st	2nd	Absorption $\lambda_{\text{max}}(\log \epsilon)/\text{nm}$	Emission $\lambda_{\text{max}}/\text{nm}$
<b>Pyrylium salts 1</b>				
<i>p</i> -CH <sub>3</sub>	-0.34	-1.48	376 (4.68), 276 (4.32), 222 (4.31)	465
H	-0.31	-1.45	406 (4.46), 356 (4.56), 276 (4.29)	476
<i>m</i> -Cl	-0.26	-1.32	412 (4.43), 348 (4.45), 278 (4.31)	480
<i>p</i> -CF <sub>3</sub>	-0.23	-1.28	414 (4.51), 435 (4.57), 280 (4.46)	487
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	-0.18	-1.16	418 (4.41), 334 (4.38), 286 (4.37)	482
<b>Thiopyrylium salts 2</b>				
<i>p</i> -CH <sub>3</sub>	-0.24	-1.21	396 (4.54), 250 (4.22), 226 (4.16)	487
H	-0.22	-1.19	402 (4.29), 370 (4.36), 272 (4.46)	490
<i>m</i> -Cl	-0.16	-1.10	408 (4.39), 356 (4.39), 274 (4.28)	495
<i>p</i> -CF <sub>3</sub>	-0.14	-1.06	412 (4.32), 362 (4.35), 272 (4.28)	500
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	-0.10	-1.00	416 (4.29), 326 (4.28), 272 (4.30)	508
<b>N-Methylpyridinium salts 3</b>				
<i>p</i> -CH <sub>3</sub>	-1.05	-1.49	316 (4.45)	426
H	-1.01	-1.45	302 (4.44)	436
<i>m</i> -Cl	-0.96	-1.39	296 (4.48)	435
<i>p</i> -CF <sub>3</sub>	-0.92	-1.34	288 (4.46)	432
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	-0.86	-1.28	280 (4.33)	439

relieving otherwise impossibly close non-bonded contacts between *o*-hydrogens on these phenyls and those of the *N*-methyl group. A sizeable displacement (0.213 Å) of the methyl group from the mean plane of the atoms of the pyridinium while the carbons of the phenyls [C7 and C13] are displaced by 0.08 Å in the opposite sense, reflects the same compression. In contrast, the dihedral angle between the plane of the heteroaromatic ring and the 4-phenyl is only 25°, and C19 is only 0.09 Å from the ring mean plane. The available structural data thus suggests that the steric demand of *N*-methylpyridiniums, especially at the 2- and 6-positions, will differ from that of pyryliums or thiopyryliums with the same substitution patterns. It is also to be expected that these differences in molecular geometry will be linked to electronic differences since there will be steric inhibition of orbital overlap between the  $\pi$ -arrays of the 2- and 6-phenyls and that of the central heteroaromatic array of the *N*-methylpyridiniums.

Provided they are protected from oxygen and moisture, solutions of the cations in acetonitrile are indefinitely stable and were used for all our measurements.<sup>15</sup> Some physical properties of the salts possibly relevant to their behaviour in reactions with hydride donors are listed in Table 1. In particular, the electrochemical behaviour of the salts was examined by cyclic voltammetry (CV). All showed two peaks corresponding to reversible,<sup>16</sup> one-electron reductions to radicals **4** and then to anions **5** (Scheme 3). No peaks corresponding to oxidations



**Scheme 3** Electrochemical reductions of heteroaromatic cations **2**, **1** and **3** (X = H)

were found. The half-wave potentials (*vs.* SCE) for the first and second waves are presented in Table 1.

For the unsubstituted cations **1**, **2** and **3** (X = H), the difficulty of reduction increases in the order  $2 < 1 \ll 3$  for first waves, and the very marked difference between the *N*-methylpyridinium on the one hand and the pyryliums and thiopyryliums on the other could be a reflection of the steric inhibition of overlap at the 2- and 6-phenyls in the *N*-

methylpyridinium indicated in the structural study. For second waves, thiopyryl radical **4** (Y = S) is the most easily reduced, and notably, the pyryl and *N*-methylpyridyl radicals **4** (Y = O and Y = NMe) have  $E_{1/2}^{\text{redn}}$  values which are the same, within experimental error. The data for **1** and **2** (X = H) are in good agreement with literature values.<sup>17,18</sup> Reduction potentials have been related<sup>19</sup> to the energies of lowest unoccupied molecular orbitals ( $E_{\text{LUMO}}$ ), with correction for differential solvation of reduced and oxidised species, and not unexpectedly, trends in  $E_{1/2}^{\text{redn}}$  are paralleled, qualitatively at least, by trends in  $\lambda_{\text{max}}$  of absorption and emission maxima in the spectra of the salts. These relationships have been discussed extensively elsewhere,<sup>17,20</sup> as has the use of redox potentials in comparing structural effects on reactivity.<sup>21</sup>

Within each series, there are clear but lesser changes associated with variation of substituent, X, in the 4-phenyl. With the relationship shown in eqn. (1), values for log *K* for the

$$\log K = nFE_{1/2}/2.303 RT \quad (1)$$

reversible electrode processes shown in Scheme 3 can be extracted and correlations of log *K* with various substituent parameter sets examined. With Hammett constants [values of  $\sigma$  used<sup>22</sup> are *p*-CH<sub>3</sub>: -0.17, *m*-Cl: 0.37, *p*-CF<sub>3</sub>: 0.54 and *m,m'*-(CF<sub>3</sub>)<sub>2</sub>: 0.86], reasonable linear correlations are obtained with the first wave potentials, with the pyrylium, thiopyrylium and *N*-methylpyridinium series giving slopes  $\rho = 2.59 \pm 0.06$  ( $r^2 = 0.9984$ ),  $2.38 \pm 0.07$  ( $r^2 = 0.9973$ ) and  $3.10 \pm 0.16$  ( $r^2 = 0.9918$ ), respectively, showing that the pyridinium cations, which are most difficult to reduce, are also most sensitive to substituent effects. Plots for first wave potentials for pyryliums and thiopyryliums are shown later in Fig. 2. Interestingly, Hammett correlations for the second wave potentials give  $\rho = 5.31 \pm 0.26$  ( $r^2 = 0.9931$ ),  $3.66 \pm 0.15$  ( $r^2 = 0.9950$ ) and  $3.49 \pm 0.16$  ( $r^2 = 0.9900$ ), respectively, showing a reversal in the selectivities. Use of other substituent constants sets gives qualitatively similar results, but the substituent set is too small for significant comparisons of either goodness-of-fit or resultant  $\rho$ -values.

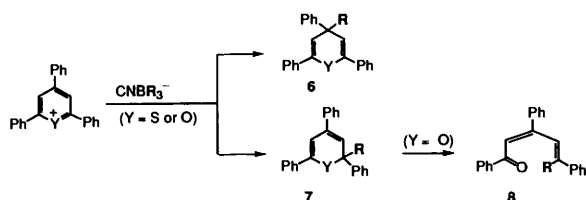
Solutions of sodium cyanoborohydride in acetonitrile of concentration up to 0.05 mol dm<sup>-3</sup> could be prepared, and showed no loss of reducing power over a period of at least one week. These were also examined by cyclic voltammetry, but

while they showed a broad oxidation wave ( $E_p \approx 1.2$  V vs. SCE at a scan rate of  $50$  mV s<sup>-1</sup>), a coupled reduction peak could not be detected, even at low temperature and the fastest available scan rate. Peak positions varied with scan rate, and a plot of  $E_p$  vs.  $\log \nu$  gave a slope of approximately  $99$  mV per decade, significantly larger than that expected for a reversible process, as were the peak widths ( $E_p - E_p/2 \approx 220$  mV). This behaviour is indicative of an irreversible electrode process,<sup>23</sup> with the cyanoborohydride radical, like those derived from other borohydrides<sup>24</sup> being insufficiently stable to permit measurement of a one-electron potential for the  $\text{NCBH}_3^-/\text{NCBH}_3\cdot$  couple in this way.

#### Reaction of cations with cyanoborohydride

**Product characterisation.** Sodium cyanoborohydride in acetonitrile solution at  $25^\circ\text{C}$  reduced all the pyryliums **1** and thiopyryliums **2**. None of the *N*-methylpyridinium salts reacted, even at high temperature.

In the case of **2** ( $X = \text{H}$ ), a mixture of the *4H*- and *2H*-thiopyrans **6** ( $X = \text{H}$ ,  $Y = \text{S}$ ) and **7** ( $X = \text{H}$ ,  $Y = \text{S}$ ) was produced (Scheme 4). These were readily identified by proton



**Scheme 4** Products from cyanoborohydride or cyanoborodeuteride reduction of heterocyclic cations ( $R = \text{H}$  or  $\text{D}$ )

NMR spectroscopy with **6** ( $X = \text{H}$ ,  $Y = \text{S}$ ) showing signals from heterocyclic ring hydrogens at  $\delta$  6.14 (d) and 4.62 (t) and **7** ( $X = \text{H}$ ,  $Y = \text{S}$ ) showing signals at  $\delta$  7.01 (s), 6.28 (d) and 5.05 (d). Integration of signals gave a ratio 55:45 for hydride attack at 4- and 2-positions of the heterocyclic ring. The separated products are stable to the reduction conditions, and this product ratio is kinetically determined. Equilibration of **6** ( $X = \text{H}$ ,  $Y = \text{S}$ ) and **7** ( $X = \text{H}$ ,  $Y = \text{S}$ ) is known to give near complete conversion to **7** ( $X = \text{H}$ ,  $Y = \text{S}$ )<sup>25</sup> with  $K_{\text{eq}} = 7.1$  ( $25^\circ\text{C}$ ). With tetrabutylammonium cyanoborohydride, the same products were formed in the same ratio. With the deuteriated reagent, proton NMR spectra of the reaction products showed high (>95%) incorporation of deuterium at their 2- and 4-positions and that the ratio of 1,4- to 1,2- addition was, within experimental uncertainty, the same as for the hydride reagent.

The proton NMR spectra of the product mixtures from sodium cyanoborohydride reduction of the pyrylium, **1** ( $X = \text{H}$ ) again showed signals (doublet at  $\delta$  5.62 and triplet at  $\delta$  4.40) characteristic of the *4H*-pyran **6** ( $X = \text{H}$ ,  $Y = \text{O}$ ), but those expected from the *2H*-pyran **7** ( $X = \text{H}$ ,  $Y = \text{S}$ ) were replaced by doublets at  $\delta$  8.39 and 6.71 with splitting of 16 Hz, and a singlet at  $\delta$  6.97; these are assigned to the hydrogens on the *trans*-4,5-double bond in 1,3,5-triphenylpentadienone **8**, known to arise from **6** ( $X = \text{H}$ ,  $Y = \text{O}$ ) by electrocyclic ring opening.<sup>26</sup> Experiments with an authentic sample of **8** showed that it is not reduced under the reaction conditions. Integration of appropriate signals gave a ratio of 24:76 for hydride attack at the 4- and 2- positions of the 2,4,6-triphenylpyrylium. Again, changing from sodium to tetrabutylammonium cyanoborohydride did not alter this ratio. With the deuteriated reducing agent, the spectra indicated incorporation of deuterium at the expected positions, again with no detectable variation of the [1,4]:[1,2] ratio (Scheme 4).

Corresponding observations were made for reductions of the available 4-phenyl substituted pyryliums and thiopyryliums. In all cases, the products were those of competing 1,4- and 1,2-

hydride attack on the cations. Product ratios are summarised later in Table 7.

We have not been able to determine the fate of the cyanoborohydride in these reactions, but the immediate formal product of hydride loss would be cyanoborane, expected to be a powerful Lewis acid.<sup>2</sup> Complex formation with acetonitrile is possible, and indeed, further reactions of such a complex cannot be excluded. Despite these uncertainties, heats of reactions of **1** ( $X = \text{H}$ ) and **2** ( $X = \text{H}$ ) with sodium cyanoborohydride in acetonitrile were determined. These were exothermic, giving  $\Delta H = -15.53 (\pm 0.45)$  and  $-17.01 (\pm 0.88)$  kcal mol<sup>-1</sup>, respectively. Arnett<sup>27</sup> has noted correlations between first reduction potentials of carbonium ions and their heats of reaction with cyanoborohydride, but any relationship here would be complicated both by the product mix and by an unquantified contribution, possibly endothermic, from the electrocyclic ring opening of **6** ( $X = \text{H}$ ,  $Y = \text{O}$ ) to **8** in the pyrylium reaction. Both values will contain equal but unknown contributions from any cyanoborane-solvent reaction.

**Rate measurements.** The progress of cyanoborohydride reductions of the cations was monitored by UV spectroscopy. Superimposed spectra of reacting solutions of the 2,4,6-triphenylthiopyryliums gave no indication of accumulation of reactive intermediates. Reduction of the parent compound **2** ( $X = \text{H}$ ), for example, showed a tight isosbestic point at 275 nm, and with excess reducing agent, the change in absorption at 371 nm showed good first order behaviour, with pseudo-first order rate constants thus obtained being directly proportional to the concentrations of added cyanoborohydride.

The pyrylium salts were considerably more reactive, and superimposed spectra showed complex behaviour consistent with the formation of the 1,2-addition product [ $\lambda_{\text{max}} = 359$  nm,  $\epsilon_{\text{max}} = 15\,000$ , for **7** ( $X = \text{H}$ )] and its further conversion to the pentadienal [ $\lambda_{\text{max}} = 349$  nm,  $\epsilon_{\text{max}} = 24\,000$ , for **8** ( $X = \text{H}$ )]. All the pyryliums show a strong long wave absorption where there is no significant absorption by the corresponding substituted **7** or **8**, and with excess cyanoborohydride, disappearance of the cation monitored at these longest wavelength maxima (see Table 1) showed good first order behaviour over many half-lives. The pseudo-first order rate constants thus obtained were again directly proportional to the concentrations of added cyanoborohydride. Second order rate constants for all the cations and reducing agents are presented in Tables 2 to 6, together with Arrhenius parameters and constants extrapolated or interpolated to  $25^\circ\text{C}$ .

## Discussion

Table 7 summarises the relative rates and product data for the reductions of the cations by cyanoborohydride in acetonitrile. We first draw attention to the effect of change of counterion in the reducing agent from sodium to tetrabutylammonium. At the concentrations used ( $< 5 \times 10^{-3}$  mol dm<sup>-3</sup>), it is likely that sodium cyanoborohydride is more than 90% dissociated in acetonitrile solution (for  $\text{NaBF}_4$  in acetonitrile  $K_d = 2.2 \times 10^{-2}$ )<sup>28</sup> and the tetrabutylammonium salt even more so.<sup>29</sup> Because of difficulties in measuring cyanoborohydride concentrations in tetrabutylammonium cyanoborohydride (see Experimental section), uncertainties in the tabulated second order rate constants for these reductions are much larger than for the sodium cyanoborohydride reactions, but even so, with  $k_{(\text{Bu}_4\text{N})}/k_{(\text{Na})} = 0.95 (\pm 0.24)$  for the pyrylium, and  $k_{(\text{Bu}_4\text{N})}/k_{(\text{Na})} = 1.52 (\pm 0.38)$  for thiopyrylium, it is clear that the effects are very much smaller than those found for variation of cation in borohydride-carbonyl reductions ( $k_{\text{Na}}/k_{\text{Bu}_4} \approx 10^2$ )<sup>5</sup> and indeed in the opposite sense in the latter case. We take this as support for the anticipated absence of complication from electrophilic catalysis by metal ions in these reductions, and associate differences in reactivity in the pyrylium and

**Table 2** Rate data for reductions of 2,6-diphenyl-4-(X-phenyl)pyrylium tetrafluoroborate salts by sodium cyanoborohydride in acetonitrile

X + reagent	T/°C	$k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Activation parameters
<i>p</i> -CH <sub>3</sub> + NaBH <sub>3</sub> CN	20.56	$1.76 \times 10^1$	$E_a = 17.20 (\pm 0.28) \text{ kcal mol}^{-1}$ $\log A = 14.04 (\pm 0.20)$
	25.21	$2.84 \times 10^1$	
	29.99	$4.38 \times 10^1$	
	34.65	$6.59 \times 10^1$	
	40.29	$1.15 \times 10^2$	
25.00 (calc.)	$2.93 \times 10^1$		
H + NaBH <sub>3</sub> CN	20.64	$4.24 \times 10^1$	$E_a = 17.19 (\pm 0.07) \text{ kcal mol}^{-1}$ $\log A = 14.41 (\pm 0.05)$
	25.33	$6.80 \times 10^1$	
	30.30	$1.10 \times 10^2$	
	35.37	$1.73 \times 10^2$	
	40.02	$2.63 \times 10^2$	
25.00 (calc.)	$6.46 \times 10^1$		
<i>m</i> -Cl + NaBH <sub>3</sub> CN	20.48	$1.26 \times 10^2$	$E_a = 17.11 (\pm 0.18) \text{ kcal mol}^{-1}$ $\log A = 14.84 (\pm 0.13)$
	25.17	$2.05 \times 10^2$	
	29.99	$3.25 \times 10^2$	
	35.00	$5.02 \times 10^2$	
	39.67	$7.70 \times 10^2$	
25.00 (calc.)	$1.96 \times 10^2$		
<i>p</i> -CH <sub>3</sub> + NaBH <sub>3</sub> CN	20.29	$2.63 \times 10^2$	$E_a = 16.31 (\pm 0.18) \text{ kcal mol}^{-1}$ $\log A = 14.55 (\pm 0.13)$
	24.98	$4.00 \times 10^2$	
	29.63	$6.04 \times 10^2$	
	34.48	$9.09 \times 10^2$	
	39.12	$1.38 \times 10^3$	
25.00 (calc.)	$3.89 \times 10^2$		
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub> + NaBH <sub>3</sub> CN	30.5	$1.61 \times 10^3$	$E_a = 16.49 (\pm 0.19) \text{ kcal mol}^{-1}$ $\log A = 15.17 (\pm 0.14)$
	33.9	$2.15 \times 10^3$	
	37.8	$3.12 \times 10^3$	
	43.5	$4.98 \times 10^3$	
	49.2	$7.79 \times 10^3$	
25.00 (calc.)	$9.59 \times 10^2$		

**Table 3** Rate data for reductions of 2,6-diphenyl-4-(X-phenyl)pyrylium tetrafluoroborate salts by sodium cyanoborodeuteride in acetonitrile

X + reagent	T/°C	$k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Activation parameters
<i>p</i> -CH <sub>3</sub> + NaBD <sub>3</sub> CN	20.57	$1.56 \times 10$	$E_a = 17.28 (\pm 0.24) \text{ kcal mol}^{-1}$ $\log A = 14.31 (\pm 0.15)$
	25.30	$2.47 \times 10$	
	30.14	$4.15 \times 10$	
	34.85	$6.34 \times 10$	
	40.48	$1.05 \times 10^2$	
25.00 (calc.)	$2.34 \times 10$		
H + NaBD <sub>3</sub> CN	20.61	$3.64 \times 10$	$E_a = 17.08 (\pm 0.12) \text{ kcal mol}^{-1}$ $\log A = 14.27 (\pm 0.09)$
	25.23	$5.74 \times 10$	
	30.13	$8.96 \times 10$	
	34.97	$1.42 \times 10^2$	
	39.46	$2.13 \times 10^2$	
25.00 (calc.)	$5.59 \times 10$		
<i>m</i> -Cl + NaBD <sub>3</sub> CN	20.20	$1.04 \times 10^2$	$E_a = 16.61 (\pm 0.12) \text{ kcal mol}^{-1}$ $\log A = 14.40 (\pm 0.09)$
	25.19	$1.72 \times 10^2$	
	30.04	$2.67 \times 10^2$	
	34.77	$4.06 \times 10^2$	
	40.18	$6.47 \times 10^2$	
25.00 (calc.)	$1.67 \times 10^2$		
<i>p</i> -CF <sub>3</sub> + NaBD <sub>3</sub> CN	20.23	$2.00 \times 10^2$	$E_a = 16.30 (\pm 0.10) \text{ kcal mol}^{-1}$ $\log A = 14.44 (\pm 0.07)$
	24.92	$3.10 \times 10^2$	
	29.84	$4.82 \times 10^2$	
	34.47	$7.21 \times 10^2$	
	39.87	$1.16 \times 10^3$	
25.00 (calc.)	$3.12 \times 10^2$		
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub> + NaBD <sub>3</sub> CN	29.9	$1.16 \times 10^3$	$E_a = 16.18 (\pm 0.25) \text{ kcal mol}^{-1}$ $\log A = 14.74 (\pm 0.17)$
	34.7	$1.83 \times 10^3$	
	39.5	$2.73 \times 10^3$	
	44.3	$4.03 \times 10^3$	
	49.1	$5.77 \times 10^3$	
25.00 (calc.)	$7.52 \times 10^2$		

**Table 4** Rate data for reductions of 2,6-diphenyl-4-(X-phenyl)thiopyrylium tetrafluoroborate salts by sodium cyanoborohydride in acetonitrile

X + reagent	$T/^\circ\text{C}$	$k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Activation parameters
<i>p</i> -CH <sub>3</sub> + NaBH <sub>3</sub> CN	16.20	3.34	$E_a = 17.92 (\pm 0.23) \text{ kcal mol}^{-1}$ $\log A = 14.06 (\pm 0.17)$
	20.31	5.25	
	25.57	8.96	
	30.14	1.45	
	34.85	2.20	
	25.00 (calc.)	8.46	
H + NaBH <sub>3</sub> CN	16.40	7.68	$E_a = 15.43 (\pm 0.15) \text{ kcal mol}^{-1}$ $\log A = 12.53 (\pm 0.11)$
	19.70	$1.05 \times 10$	
	24.50	$1.61 \times 10$	
	29.25	$2.37 \times 10$	
	35.08	$3.95 \times 10$	
	25.00 (calc.)	$1.67 \times 10$	
<i>m</i> -Cl + NaBH <sub>3</sub> CN	9.43	9.08	$E_a = 15.84 (\pm 0.07) \text{ kcal mol}^{-1}$ $\log A = 13.20 (\pm 0.06)$
	14.71	$1.52 \times 10$	
	19.87	$2.45 \times 10$	
	24.48	$3.76 \times 10$	
	29.99	$6.16 \times 10$	
	25.00 (calc.)	$3.95 \times 10$	
<i>p</i> -CF <sub>3</sub> + NaBH <sub>3</sub> CN	2.32	5.74	$E_a = 15.33 (\pm 0.19) \text{ kcal mol}^{-1}$ $\log A = 12.92 (\pm 0.15)$
	5.85	7.93	
	10.30	$1.26 \times 10$	
	14.03	$1.77 \times 10$	
	17.94	$2.56 \times 10$	
	25.00 (calc.)	$4.78 \times 10$	
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub> + NaBH <sub>3</sub> CN	29.9	$2.27 \times 10^2$	$E_a = 16.39 (\pm 0.04) \text{ kcal mol}^{-1}$ $\log A = 14.18 (\pm 0.12)$
	34.6	$3.46 \times 10^2$	
	39.5	$5.25 \times 10^2$	
	44.2	$7.77 \times 10^2$	
	49.1	$1.15 \times 10^3$	
	25.00 (calc.)	$1.46 \times 10^2$	

**Table 5** Rate data for reductions of 2,6-diphenyl-4-(X-phenyl)thiopyrylium tetrafluoroborate salts by sodium cyanoborodeuteride in acetonitrile

X + reagent	$T/^\circ\text{C}$	$k_2/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	Activation parameters
<i>p</i> -CH <sub>3</sub> + NaBD <sub>3</sub> CN	34.77	$1.54 \times 10$	$E_a = 18.92 (\pm 0.54) \text{ kcal mol}^{-1}$ $\log A = 14.63 (\pm 0.40)$
	30.00	$1.01 \times 10$	
	25.47	6.25	
	20.85	3.84	
	16.23	2.17	
	25.00 (calc.)	5.80	
H + NaBD <sub>3</sub> CN	16.94	4.81	$E_a = 16.24 (\pm 0.40) \text{ kcal mol}^{-1}$ $\log A = 12.90 (\pm 0.29)$
	19.70	5.80	
	24.61	9.62	
	29.31	$1.49 \times 10$	
	34.85	$2.39 \times 10$	
	25.00 (calc.)	9.96	
<i>m</i> -Cl + NaBD <sub>3</sub> CN	16.34	$1.03 \times 10$	$E_a = 16.23 (\pm 0.21) \text{ kcal mol}^{-1}$ $\log A = 13.27 (\pm 0.15)$
	20.91	$1.62 \times 10$	
	25.25	$2.37 \times 10$	
	29.91	$3.74 \times 10$	
	34.77	$5.55 \times 10$	
	25.00 (calc.)	$2.35 \times 10$	
<i>p</i> -CF <sub>3</sub> + NaBD <sub>3</sub> CN	-0.63	2.39	$E_a = 15.92 (\pm 0.55) \text{ kcal mol}^{-1}$ $\log A = 13.12 (\pm 0.42)$
	5.61	4.23	
	9.25	6.26	
	14.53	$1.03 \times 10$	
	19.91	$1.89 \times 10$	
	25.00 (calc.)	$2.85 \times 10$	
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub> + NaBD <sub>3</sub> CN	30.0	$1.36 \times 10^2$	$E_a = 16.64 (\pm 0.09) \text{ kcal mol}^{-1}$ $\log A = 14.13 (\pm 0.07)$
	34.7	$2.05 \times 10^2$	
	39.4	$3.07 \times 10^2$	
	44.3	$4.67 \times 10^2$	
	49.1	$6.97 \times 10^2$	
	25.00 (calc.)	$8.35 \times 10$	

**Table 6** Rate data for reductions of 2,4,6-triphenylpyrylium tetrafluoroborate and 2,4,6-triphenylthiopyrylium tetrafluoroborate by tetrabutylammonium cyanoborohydride in acetonitrile

Salt	$T/^\circ\text{C}$	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	Activation parameters
Pyrylium	10.81	$1.53 \times 10$	$E_a = 16.90 (\pm 0.22) \text{ kcal mol}^{-1}$ $\log A = 14.18 (\pm 0.18)$
	15.21	$2.36 \times 10$	
	20.65	$4.00 \times 10$	
	25.24	$6.42 \times 10$	
	29.77	$9.94 \times 10$	
	25.00 (calc.)	$6.25 \times 10$	
Thiopyrylium	16.02	$1.08 \times 10$	$E_a = 16.31 (\pm 0.13) \text{ kcal mol}^{-1}$ $\log A = 13.36 (\pm 0.08)$
	20.62	$1.71 \times 10$	
	25.26	$2.59 \times 10$	
	30.86	$4.29 \times 10$	
	35.51	$6.55 \times 10$	
	25.00 (calc.)	$2.55 \times 10$	

**Table 7** Product ratios, relative rates and kinetic hydrogen isotope effects for reductions of 2,6-diphenyl-4-(X-phenyl)-pyrylium and -thiopyrylium tetrafluoroborate salts by sodium and tetrabutylammonium cyanoborohydrides ( $\text{MBH}_3\text{CN}$ ) in acetonitriles

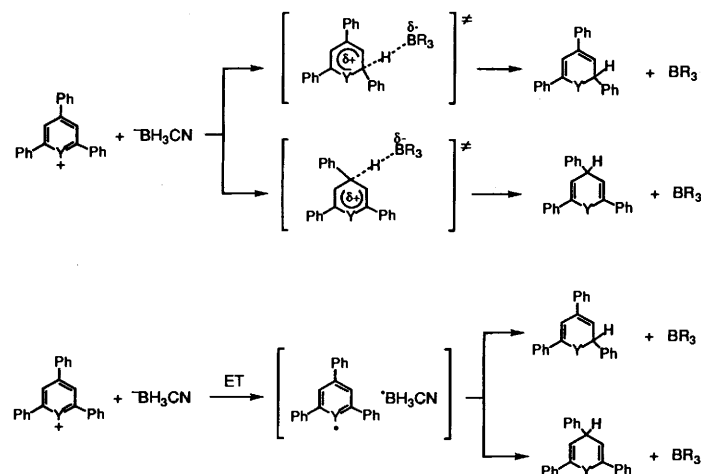
X	M	Product ratio [6]:([7] or [8])	$k_{\text{BH}_3\text{CN}}$ (rel) at $25^\circ\text{C}$	$k_{\text{BH}_3\text{CN}}/k_{\text{BD}_3\text{CN}}$ at $25^\circ\text{C}$
Pyrylium salts				
<i>p</i> -CH <sub>3</sub>	Na	25:75	3.21	1.12
H	Na	24:76	7.72	1.17
H	Bu <sub>4</sub> N	24:76	8.52	
<i>m</i> -Cl	Na	17:83	23.4	1.19
<i>p</i> -CF <sub>3</sub>	Na	19:81	47.3	1.29
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	Na	11:89	113.4	1.28
Thiopyrylium salts				
<i>p</i> -CH <sub>3</sub>	Na	58:42	1.00	1.45
H	Na	55:45	1.96	1.68
H	Bu <sub>4</sub> N	54:46	3.47	
<i>m</i> -Cl	Na	52:48	4.65	1.68
<i>p</i> -CF <sub>3</sub>	Na	52:48	5.65	1.68
<i>m,m'</i> -(CF <sub>3</sub> ) <sub>2</sub>	Na	42:58	17.26	1.75

thiopyryliums series with variation of electronic effects in the cations.

The selectivity of <90% in formation of 1,2- and 1,4-addition products requires that activation energies of the pathways for their formation differ by less than 1 kcal mol<sup>-1</sup>. Distributions may be the result of competing concerted processes, or possibly arise from partition in a hydrogen atom transfer step following a rate limiting ET from the cyanoborohydride to the heteroaromatic cation (Scheme 5). Increasing reactivity in both series is associated with a small increase in the proportion of the 1,2-addition product (see Table 7). For the pyryliums **1**, the fraction of 1,2-addition ranges from 75% (X = *p*-CH<sub>3</sub>) to 81% (X = *p*-CF<sub>3</sub>), and for the thiopyryliums from 42% (X =

*p*-CH<sub>3</sub>) to 48% (X = *p*-CF<sub>3</sub>), closely resembling ratios found in kinetically controlled additions of alkoxide<sup>30</sup> or amine<sup>31</sup> nucleophiles to **1** and **2** (X = H).

The dependences are not strong, but their sense indicates that the effects from substituents (chosen for their inability to interact conjugatively) in the phenyl attached at the 4-position of the heteroaromatic are actually larger at the 2-position of the array. Introduction of an electron withdrawing substituent at the 4-position of the heteroaromatic ring, represented (Fig. 2) by an added dipole at that position, shifts relative stabilities, and thus also the weighting of the canonical forms in the resonance hybrid describing the cation structures. The substituent destabilises form **11** more than either **9** or **10**, and



**Scheme 5** Mechanisms for formation of 1,2- and 1,4-addition products

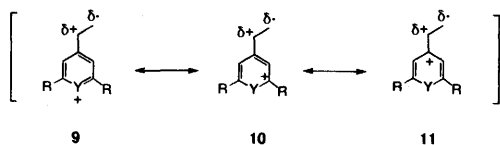


Fig. 2 Canonical forms and the effects of 4-substitution on charge distribution in the heteroaromatic cations

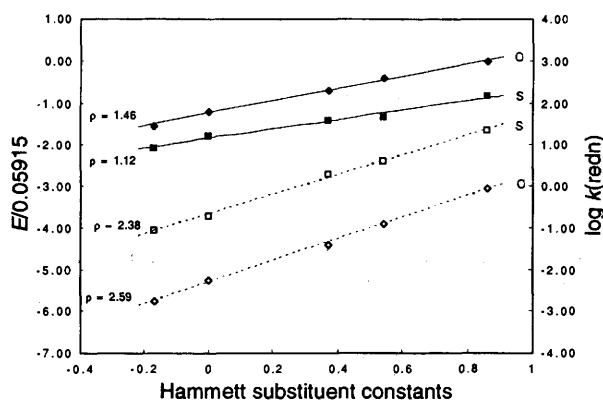
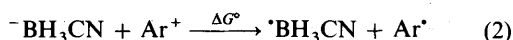


Fig. 3 Hammett plots of scaled first wave reduction potentials (open symbols and dashed lines, left axis) and for rate of cyanoborohydride reductions of pyrylium and thiopyrylium salts (closed symbols and full lines, right axis)

reduces its contribution to the hybrid so that while the total charge on the heteroaromatic array increases with the electron-withdrawing ability of the substituent, there is also a shift in charge from the 4- to the 2-position of the array. In competing polar concerted mechanisms, a corresponding increase in 1,2-addition product is expected. The effects of substituents on 2- or 4-position reactivities in the hypothetical radical intermediate in the ET initiated mechanism is not obvious.

In the case of ET initiated reductions, the activation parameters in Tables 2 to 6 would be associated with that first ET step. Temperature dependences for the sodium cyanoborohydride reductions of **1** ( $X = H$ ) and **2** ( $X = H$ ) yield free energies of activation,  $\Delta G^\ddagger = 15.0$  and  $15.8$  kcal mol<sup>-1</sup>, respectively, and for an initial electron transfer from cyanoborohydride anion, these cannot be less than the free energy changes ( $\Delta G^\circ$ ) for the redox reaction (2).



where

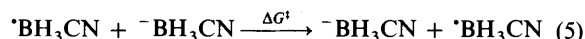
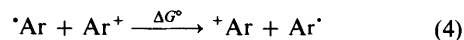
$$\Delta G^\circ = -23.06 (E^\circ_{\text{Ar}^{\cdot}/\text{Ar}^+} - E^\circ_{\text{BH}_3\text{CN}^{\cdot}/\text{BH}_3\text{CN}^-}) \text{ kcal mol}^{-1}$$

The tabulated experimental values of  $E_{\frac{1}{2}}^{\text{redn}}$  for **1** ( $X = H$ ) and **2** ( $X = H$ ) then require that  $E^\circ(\text{BH}_3\text{CN}^{\cdot}/\text{BH}_3\text{CN}^-)$  not exceed 0.34 V (*vs.* SCE) in the case of **1** ( $X = H$ ) or 0.46 V (*vs.* SCE) in the case of **2** ( $X = H$ ) for this electron transfer to be an energetically feasible process. As noted earlier, we have not been able to measure the potential for the  $\text{BH}_3\text{CN}^{\cdot}/\text{BH}_3\text{CN}^-$  couple, although the value of  $E_p = 1.2$  V *vs.* SCE found in the cyclic voltammetry of  $\text{BH}_3\text{CN}^-$  probably means that its  $E^\circ$  is higher than this because of very rapid follow-on reactions,<sup>24</sup> and it is unlikely in the extreme that these reactions can be ET initiated.

This conclusion is further supported by estimates of activation energies,  $\Delta G^\ddagger$ , for outer sphere ET reactions using the Marcus expression<sup>32</sup> which relates these to  $\Delta G^\circ$ , the free energy change associated with the electron transfer<sup>33</sup> [eqn. (3)]. The work term in the equation,  $W$ , is associated with

$$\Delta G^\ddagger = W + \Delta G_{\text{int}}^\ddagger [1 + (\Delta G^\circ/4\Delta G_{\text{int}}^\ddagger)]^2 \quad (3)$$

bringing together oxidant and reductant to form the complex in which ET occurs, and with oppositely charged ions in a polar reaction medium is expected to be small and negative (*ca.* -1.5 kcal mol<sup>-1</sup> for a contact distance of 6 Å). The remaining parameter,  $\Delta G_{\text{int}}^\ddagger$ , the intrinsic barrier, in the Marcus treatment is the average of those for the self-exchange reactions (4) and (5). These are not known for either of the cations, or for the



cyanoborohydride, but analogies can be drawn. Those for the organic cation-radical exchanges involving highly conjugated structures are expected to be small. The trityl radical-trityl cation exchange,<sup>34</sup> for example, has  $\Delta G^\ddagger \approx 4$  kcal mol<sup>-1</sup>. Because of their more localised structures,  $\Delta G^\ddagger$  for the cyanoborohydride anion-radical exchanges are expected to be much larger. The largest recorded identity barrier, for example, is 35 kcal mol<sup>-1</sup> for the  $\text{NO}_2^{\cdot}/\text{NO}_2$  exchange<sup>35</sup> in acetonitrile.

If  $\Delta G_{\text{int}}^\ddagger$  is assigned a value of 18 kcal mol<sup>-1</sup> (less than the average of the two examples cited above), and  $E^\circ(\text{BH}_3\text{CN}^{\cdot}/\text{BH}_3\text{CN}^-)$  an unlikely low value of 0.35 V (*vs.* SCE), then Marcus activation energies for electron transfer from  $\text{BH}_3\text{CN}^-$  to 2,4,6-triphenylpyrylium and 2,4,6-triphenylthiopyrylium are 24.10 and 22.79 kcal mol<sup>-1</sup>, respectively, more than 7 kcal mol<sup>-1</sup> higher than the experimentally determined barriers for the reductions.

Plots of  $\log k$  for the cyanoborohydride reductions against Hammett substituent constants are shown in Fig. 3, and compared with those for the first wave potentials of the electrochemical reductions. Over the range of substituents, correlations are moderate with electron withdrawing substituents enhancing reactivity. The reaction constants are  $\rho = 1.46 \pm 0.06$  ( $r^2 = 0.9951$ ) for the pyrylium series and  $\rho = 1.12 \pm 0.08$  ( $r^2 = 0.9831$ ) for the thiopyryliums.

The Hammett plot of the appropriately scaled electrochemical measurements of first wave  $E_{\frac{1}{2}}^{\text{redn}}$  of the pyrylium and thiopyrylium series are also shown in Fig. 3, and even with the limited substituent set, it is clear that  $\rho_{(\text{electrochem})} > \rho_{(\text{BH}_3\text{CN}^-)}$  for both the pyrylium and thiopyrylium series, further indicating that neither react with cyanoborohydride by initial ET. The potentials are for reversible formation of the neutral radical from the cation (Scheme 3); since reaction constants from Hammett correlations for radical formation at benzylic positions *via* non-polar transition states are small,<sup>36</sup> especially with non-conjugating substituents, values of  $\rho_{(\text{electrochem})}$  can be crudely associated with full neutralization of positive charge on the cations. The ratios,  $\rho_{(\text{BH}_3\text{CN}^-)}/\rho_{(\text{electrochem})} = 0.56 \pm 0.04$  (pyryliums) and  $\rho_{(\text{BH}_3\text{CN}^-)}/\rho_{(\text{electrochem})} = 0.47 \pm 0.05$  (thiopyryliums) then give a measure of the extent of charge neutralisation on the cation in the transition states of the cyanoborohydride reductions, and also perhaps the position of their transition states along the hydride transfer reaction coordinate.

Kinetic isotope effect (KIE) data is also collected in Table 7. At 25 °C,  $k_{(\text{BH}_3\text{CN}^-)}/k_{(\text{BD}_3\text{CN}^-)}$  for reduction of 2,4,6-triphenylpyrylium **1** ( $X = H$ ) is 1.17, and that for the less reactive 2,4,6-triphenylthiopyrylium **2** ( $X = H$ ), is 1.68. Changes associated with variation of the 4-phenyl substituent ( $X$ ) within each cation series are small, and lie within the experimental uncertainties ( $\pm$  *ca.* 10%) for the rate ratios. Computational studies of this reaction are in progress with the aim of finding transition state models consistent with the observed kinetic isotope effects. These will be reported separately, but we can make some qualitative comments here.

Because the evidence from the substituent effects is not consistent with rate limiting ET, we discuss the isotope effects



within the framework of competing concerted processes, in which case, rates would be composites of those for the 1,2- and 1,4-additions. Unfortunately, in the absence of the temperature dependence of product ratios, no significance can be attached to the values for  $(E_{\text{aD}} - E_{\text{aH}})$  and  $A_{\text{H}}/A_{\text{D}}$  as indicators of a tunnelling contribution to the effects.<sup>37</sup>

Like those in many other borohydride reductions,<sup>38</sup> the effects are only a small fraction of the maximum expected for a primary effect in breaking of a B–H bond. IR spectra of sodium cyanoborohydride and cyanoborodeuteride show bands associated with B–H or B–D stretching at 2340 and at 1770  $\text{cm}^{-1}$ , respectively.<sup>39</sup> A full expression of the zero-point energy differences in this single vibration,<sup>40</sup> occurring in a hypothetical linear symmetric transition state with equal B–H and C–H bond-stretching force constants would give the Westheimer maximum<sup>41</sup> for the primary kinetic isotope effect with  $k_{\text{H}}/k_{\text{D}} = 4.56$  at 25 °C.

Within the bond energy–bond order (BEBO) formalism, the force constant ( $f_n$ ) for a bond of a particular order ( $n$ ) is equated to the single bond force constants ( $f_0$ ) multiplied by the bond order.<sup>42</sup> With the frequency of a saturated C–H stretching vibration (*ca.* 3000  $\text{cm}^{-1}$ ) being larger than that for a B–H bond,  $f_0(\text{C–H}) > f_0(\text{B–H})$ , and the symmetric transition state, in terms of force constants behaviour, must occur when  $n(\text{B–H}) > n(\text{C–H})$ ; that is, relatively early on a reaction coordinate defined in terms of bond order changes. Actual values of  $n$  will depend on how the sum of these bond orders change in the transition state, but if, as is commonly assumed, bond orders at the migrating hydrogen are conserved with  $n(\text{B–H}) + n(\text{C–H}) = 1$ , then  $n(\text{B–H}) = 0.63$  and  $n(\text{C–H}) = 0.37$ . Transition states occurring earlier or later than this give rise to smaller isotope effects. With  $n(\text{B–H}) = n(\text{C–H}) = 0.5$ , the same treatment gives  $k_{\text{H}}/k_{\text{D}} = 1.83$  at 25 °C, and for very late transition states with  $n(\text{C–H}) > 0.73$  or  $n(\text{B–H}) < 0.27$ , inverse kinetic isotope effects are expected. In the extreme, the calculated equilibrium isotope effect for the hydride transfer is  $k_{\text{H}}/k_{\text{D}} = 0.62$  using the frequencies cited above.

With this simple model the observed effects are reproduced for pre-Westheimer maximum transition states with  $n(\text{C–H}) = 0.07$  for the pyryliums and  $n(\text{C–H}) = 0.21$  for the thiopyryliums. Very early transition states, with that of the more reactive pyrylium being earlier than that of the thiopyrylium, would be in accord with the Bell–Evans–Polanyi principle<sup>43</sup> with very strongly exoergic hydride transfers. Exotherms were indeed found in the solution calorimetry, but we repeat that the exotherms may have a large contribution from events occurring after hydride transfer from boron to carbon, and cannot be taken as measures of the exothermicity of that process. For post-Westheimer maximum transition states, the corresponding values are  $n(\text{C–H}) = 0.66$  and 0.53, in quite reasonable agreement with the indicators of transition state position obtained from the analysis of the substituent effects which assumed that charge development and bonding changes occurred synchronously.

Better agreement, but possibly not better understanding, may come from consideration of more detailed models. Reduced isotope effects could also arise in tight transition states where  $n(\text{B–H}) + n(\text{C–H}) > 1$ , or from the development of stiff B–H–C bending modes in the transition state. Secondary  $\alpha$ -deuterium effects from the two formally non-participating hydrogens of the cyanoborohydride must also be considered. In displacements at saturated carbon in which hybridization changes from  $\text{sp}^3$  to  $\text{sp}^2$ ,  $\alpha$ -D KIE are usually greater than one and have been explained<sup>44</sup> in terms of transformation of a C–H bending vibration in the tetra-coordinate ground state to a lower frequency out-of-plane bending vibration in the transition state. If hybridisation at boron similarly changes from  $\text{sp}^3$  to  $\text{sp}^2$  in the transfer of hydride to the cation, a B–H bending vibration in the tetra-coordinate cyanoborohydride would be

transformed to an out-of-plane bending vibration in the putative cyanoborane product. We have no IR spectroscopic data on cyanoborane to permit a quantitative estimate of this contribution, but the analogy between reaction at boron and at carbon suggests that secondary effects will be greater than one. As noted earlier, however, cyanoborane is expected to be a powerful Lewis acid, and if tight nitrile co-ordination at the boron accompanies hydride transfer, then the secondary isotope effects are expected to be much smaller. Almost certainly, additional measurements with heavy atom isotopic substitutions will be required to define a TS model for even these simple reactions.

## Experimental

IR spectra were recorded on a Perkin-Elmer 1710-FT spectrometer, routinely on thin films deposited on KBr discs. Routine UV spectra were recorded on a Hewlett Packard 8452A Diode-array spectrophotometer on solutions in acetonitrile.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were run on a Bruker AC 300E spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts are reported in ppm ( $\delta$ ) relative to internal TMS. Signal splittings are reported as singlet (s), doublet (d) or triplet (t), complex multiplet (cm) and  $J$  values are given in Hz. Mass spectra were run on a Kratos Concept LS1, using fast atom bombardment (FAB) to generate ions from the organic salts. Fluorescence spectra were recorded using a Perkin-Elmer LS-5 luminescence spectrometer using acetonitrile as the solvent. Melting points were determined on a Kofler hot stage microscope and are uncorrected. Elemental analyses were carried out at the micro-analytical laboratories of the University of Manchester under the direction of Mr M. Hart. Ether refers to diethyl ether.

### 2,4,6-Triphenylpyrylium tetrafluoroborate, 1 (X = H)

Compound 1 (X = H) was prepared by the method of Gabrielsen *et al.*<sup>45</sup> The salt was recrystallised using absolute ethanol (7.0 g, 31%), mp 241–242 °C (lit., 250–251 °C) (Found: C, 69.5; H, 4.6; B, 2.3.  $\text{C}_{23}\text{H}_{12}\text{OBF}_4$  requires C, 69.7; H, 4.3; B, 2.7%).

### 4-(4-Methylphenyl)-2,6-diphenylpyrylium tetrafluoroborate, 1 (X = *p*-Me)

Compound 1 (X = *p*-Me) was prepared by the method of Reichardt and Muller,<sup>46</sup> mp 256–257 °C (lit., 261–265 °C) (Found C, 70.5; H, 4.8;  $\text{C}_{24}\text{H}_{16}\text{OBF}_4$  requires C, 70.2; H, 4.6%);  $\delta_{\text{H}}(\text{CD}_3\text{CN})$  8.70 (2 H, s, pyrylium ring), 8.45 (4 H, d,  $J$  7.5, aromatic), 8.27 (2 H, d,  $J$  9, aromatic), 7.80 (6 H, cm, aromatic), 7.59 (2 H, d,  $J$  7.5, aromatic) and 2.54 (3 H, s,  $\text{Ph-CH}_3$ );  $m/z$  (FAB) 323 ( $\text{M}^+$ , 100%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1626, 1602, 1493, 1258 and 1084.

### 4-(3-Chlorophenyl)-2,6-diphenylpyrylium tetrafluoroborate, 1 (X = *m*-Cl)

3-(3-Chlorophenyl)-1-phenylprop-2-enone (6.8 g, 0.03 mol), acetophenone (1.8 g, 0.015 mol) and chloroform (10  $\text{cm}^3$ ) were heated to 70 °C in a round bottom flask. A solution of fluoroboric acid, prepared by cautious addition of acetic anhydride (8 g) to aqueous fluoroboric acid (2.2 g of 40% w/w solution) was then added. The mixture was then refluxed for 30 min before concentration at reduced pressure, and trituration of the resulting red oil to give yellow crystals which were filtered, washed with cold ether and recrystallised from absolute ethanol (2.0 g, 31%), mp 225–226.5 °C (Found C, 63.9; H, 3.6; Cl, 8.2.  $\text{C}_{23}\text{H}_{16}\text{ClBF}_4$  requires C, 64.2, H, 3.7; Cl, 8.3%);  $\delta_{\text{H}}(\text{CD}_3\text{CN})$  8.70 (2 H, s, pyrylium ring), 8.43 (4 H, d,  $J$  7.5, aromatic), 8.33 (1 H, t, aromatic), 8.23 (1 H, d,  $J$  7.5, aromatic) and 7.80 (8 H, cm, aromatic);  $m/z$  (FAB) 343 ( $\text{M}^+$ , 100%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1624, 1580, 1496, 1468 and 1084.

**2,6-Diphenyl-4-(4-trifluoromethylphenyl)pyrylium tetrafluoroborate, 1 (X = *p*-CF<sub>3</sub>)**

Compound 1 (X = *p*-CF<sub>3</sub>) was prepared by the method of Reichardt and Muller,<sup>47</sup> mp 244–246 °C (lit., 248–249 °C) (Found C, 61.9; H, 3.5. C<sub>24</sub>H<sub>16</sub>OBF<sub>7</sub> requires C, 62.1; H, 3.5%).

**2,6-Diphenyl-4-[3,5-bis(trifluoromethyl)phenyl]pyrylium tetrafluoroborate, 1 [X = *m,m'*-(CF<sub>3</sub>)<sub>2</sub>]**

Reaction of 3,5-bis(trifluoromethyl)benzaldehyde (1.0 g, 4.13 mmol) and acetophenone (0.496 g, 4.13 mmol) in a mixture of water (3 cm<sup>3</sup>) and ethanol (1 cm<sup>3</sup>) in which sodium hydroxide (0.22 g) had been dissolved yielded the substituted chalcone in 88% yield as pale green needles after recrystallisation from light petroleum, mp 110–111 °C (Found C, 59.25; H, 2.7. C<sub>17</sub>H<sub>10</sub>F<sub>6</sub>O requires C 59.3; H, 2.9%). This chalcone (0.72 g, 2.09 mmol) and acetophenone (0.125 g, 1.04 mmol) were heated in refluxing ethylene chloride while fluoroboric acid (0.6 cm<sup>3</sup> of a 54% w/w solution in ether) was added dropwise over a period of a few minutes. Refluxing was continued for 5 h before cooling and diluted with ether (25 cm<sup>3</sup>) to give a yellow precipitate, which was collected, washed with fresh ether, and recrystallised from ethylene chloride (0.19 g, 36%), mp 264–70 °C (Found C, 56.7; H, 2.9. C<sub>25</sub>H<sub>15</sub>F<sub>6</sub>OBF<sub>4</sub> requires C, 56.42; H, 2.84%); δ<sub>H</sub>(CD<sub>3</sub>CN) 8.84 (4 H, s), 8.58 (5 H, cm, aromatic) and 7.75 (6 H, cm, aromatic); *m/z* (FAB) 445 (M<sup>+</sup>); ν<sub>max</sub>/cm<sup>-1</sup> 1627, 1513, 1470, 1281, 1137 and 1053.

**2,4,6-Triphenylthiopyrylium tetrafluoroborate, 2 (X = H)**

Compound 2 (X = H) was prepared by the method of Saeva and Olin.<sup>17</sup> The product was then recrystallised from absolute ethanol (0.24 g, 80%), mp 197–198 °C (lit., 195–196 °C) (Found C, 66.8; H, 4.4; S, 7.3. C<sub>23</sub>H<sub>17</sub>SBF<sub>4</sub> requires C, 67.0; H, 4.1; S, 7.8%).

**4-(4-Methylphenyl)-2,6-diphenylthiopyrylium tetrafluoroborate, 2 (X = *p*-Me)**

4-(4-Methylphenyl)-2,6-diphenylpyrylium tetrafluoroborate (0.3 g) was dissolved in 20 cm<sup>3</sup> of acetone and slowly added to a solution of sodium sulfide (0.4 g in 4 cm<sup>3</sup> of water). The mixture was left to stand for 40 min with occasional shaking. To the resulting red mixture, fluoroboric acid (4 cm<sup>3</sup> of 40% w/w solution) was added to give a yellow solution. The mixture was stirred for a further 2 h, after which a yellow precipitate formed. Half of the solvent was removed *in vacuo* and the yellow precipitate filtered, dried and recrystallised from absolute ethanol (0.29 g, 93%), mp 179.5–180.5 °C (Found C, 67.5; H, 4.6. C<sub>24</sub>H<sub>19</sub>SBF<sub>4</sub> requires C, 67.6; H, 4.5%); δ<sub>H</sub>(CD<sub>3</sub>CN) 9.00 (2 H, s, thiopyrylium ring), 8.20 (6 H, cm, aromatic), 7.78 (6 H, cm, aromatic), 7.57 (2 H, d, *J* 7.5, aromatic) and 2.50 (3 H, s, CH<sub>3</sub>); *m/z* (FAB) 339 (M<sup>+</sup>, 100%); ν<sub>max</sub>/cm<sup>-1</sup> 1626, 1573, 1494, 1470, 1450, 1423 and 1084.

**4-(3-Chlorophenyl)-2,6-diphenylthiopyrylium tetrafluoroborate, 2 (X = *m*-Cl)**

Treatment of 4-(3-chlorophenyl)-2,6-diphenylpyrylium tetrafluoroborate (0.1 g, 0.22 mmol) with sodium sulfide (0.25 g) as described above gave a yellow precipitate which was filtered, dried and recrystallised from absolute ethanol (0.046 g, 44%), mp 188–190 °C (Found C, 61.4; H, 3.8; Cl, 7.6. C<sub>23</sub>H<sub>16</sub>ClSBF<sub>4</sub> requires C, 61.8; H, 3.6; Cl, 7.9%); δ<sub>H</sub>(CD<sub>3</sub>CN) 9.00 (2 H, s, thiopyrylium ring), 8.23 (1 H, s, aromatic), 8.09 (4 H, m, aromatic) and 7.79 (9 H, cm, aromatic); *m/z* (FAB) 359 (M<sup>+</sup>, 100%); ν<sub>max</sub>/cm<sup>-1</sup> 1706, 1688, 1583, 1469, 1448, 1400 and 1084.

**2,6-Diphenyl-4-(4-trifluoromethylphenyl)thiopyrylium tetrafluoroborate, 2 (X = *p*-CF<sub>3</sub>)**

Treatment of 2,6-diphenyl-4-(4-trifluoromethylphenyl)pyrylium tetrafluoroborate (0.4 g) with sodium sulfide (0.45 g) as described above yielded a yellow precipitate which was

filtered, dried and recrystallised from absolute ethanol (0.120 g, 29%), mp 97–98 °C (Found C, 60.2; H, 3.1; S, 6.3. C<sub>24</sub>H<sub>16</sub>SBF<sub>7</sub> requires C, 60.0; H, 3.3; S, 6.7%); δ<sub>H</sub>(CD<sub>3</sub>CN) 9.05 (2 H, s, thiopyrylium ring), 8.32 (2 H, d, *J* 7.5, aromatic), 8.13 (4 H, d, *J* 7.5, aromatic), 8.05 (2 H, d, *J* 7.5, aromatic) and 7.80 (6 H, cm, aromatic); *m/z* (FAB) 393 (M<sup>+</sup>, 100%); ν<sub>max</sub>/cm<sup>-1</sup> 1620, 1586, 1473, 1449, 1421, 1394, 1325 and 1072.

**2,6-Diphenyl-4-[(3,5-bistrifluoromethyl)phenyl]thiopyrylium tetrafluoroborate, 2 [X = *m,m'*-(CF<sub>3</sub>)<sub>2</sub>]**

Butyllithium in benzene (2.4 cm<sup>3</sup> of 1.58 mol dm<sup>-3</sup>) was added to a stirred cooled solution (–78 °C) of 3,5-bis(trifluoromethyl)bromobenzene (1.14 g) in THF (3.0 cm<sup>3</sup>). After 1.25 h, the resulting dark mixture was transferred by cannula to a flask containing a cooled (–78 °C) stirred solution of 2,6-diphenyldihydro-4*H*-thiopyran-4-one (2.5 mmol)<sup>11</sup> in THF (5 cm<sup>3</sup>). The mixture was stirred at –78 °C for 1.5 h then allowed to warm to room temperature before quenching with saturated aqueous ammonium chloride. The mixture was then extracted with dichloromethane, the combined extracts dried over anhydrous sodium sulfate and evaporated to yield a dark brown oil. NMR examination and TLC showed this to contain two major components, one of which (*ca.* 44%) was recovered 2,6-diphenyldihydro-4*H*-thiopyran-4-one. The crude material was taken up in dichloroethane (10 cm<sup>3</sup>) and refluxed with fluoroboric acid in ether (0.5 cm<sup>3</sup> of 7.32 mol dm<sup>-3</sup>) for 3 h. The solvent was then replaced with trifluoroacetic acid and triphenylmethanol (0.651 g, 2.5 mmol) added before further reflux for 3 h. Evaporation of solvent yielded crude product which was taken up in a mixture of ether and 95% ethanol to which excess fluoroboric acid had been added. A crystalline mass formed slowly (425 mg, 31% from the dihydrothiopyranone) and recrystallization from a mixture of benzene and dichloroethane yielded bright yellow crystals, mp 230–236 °C (Found C, 55.1; H, 2.6; S, 6.2. C<sub>25</sub>H<sub>15</sub>F<sub>6</sub>SBF<sub>4</sub> requires C, 54.77; H, 2.76; S, 5.85%); δ<sub>H</sub>(CD<sub>3</sub>CN) 9.10 (2 H, s, thiopyrylium ring), 8.7 (2 H, s, aromatic), 8.41 (1 H, s, aromatic), 8.21 (4 H, d, *J* 7.5, aromatic) and 7.80 (6 H, cm, aromatic); *m/z* (FAB) 461 (M<sup>+</sup>, 100%); ν<sub>max</sub>/cm<sup>-1</sup> 1587, 1436, 1281, 1137 and 1056.

**1-Methyl-2,4,6-triphenylpyridinium tetrafluoroborate, 3 (X = H)**

Compound 3 (X = H) was prepared by the method of Katritzky *et al.*<sup>47</sup> The crystals were washed with absolute ethanol and then redissolved in acetone and precipitated with cold ether (0.68 g, 74%), mp 222–223 °C (Found C, 70.3; H, 5.1; N, 3.5; B, 2.4. C<sub>24</sub>H<sub>20</sub>NBF<sub>4</sub> requires C, 70.4; H, 4.9; N, 3.4; B, 2.6%).

**Methyl-4-(4-methylphenyl)-2,6-diphenylpyridinium tetrafluoroborate, 3 (X = *p*-Me)**

4-(4-Methylphenyl)-2,6-diphenylpyrylium tetrafluoroborate (0.2 g), methylamine (0.075 g as 33% w/w methylated spirit solution) and 5 cm<sup>3</sup> of absolute ethanol were added to a 100 cm<sup>3</sup> round bottom flask and the solution was stirred for 2 h. Ether (20 cm<sup>3</sup>) was then added to give a white precipitate which was isolated and recrystallised from absolute ethanol (0.187 g, 91%), mp 185–186 °C (Found C, 71.1; H, 5.5; N, 3.4. C<sub>25</sub>H<sub>17</sub>NBF<sub>4</sub> requires C, 71.0; H, 5.2; N, 3.3%); δ<sub>H</sub>(CD<sub>3</sub>CN) 8.17 (2 H, s, pyridinium ring), 7.91 (2 H, d, *J* 9, aromatic), 7.69 (10 H, cm, aromatic), 7.42 (2 H, d, *J* 9, aromatic), 3.73 (3 H, s, NCH<sub>3</sub>) and 2.44 (3 H, s, *p*-CH<sub>3</sub>); *m/z* (FAB) 336 (M<sup>+</sup>, 100%); ν<sub>max</sub>/cm<sup>-1</sup> 1620, 1400, 1259, 1169 and 1084.

**4-(3-Chlorophenyl)-1-methyl-2,6-diphenylpyridinium tetrafluoroborate, 3 (X = *m*-Cl)**

Treatment of 4-(3-chlorophenyl)-2,6-diphenylpyrylium tetrafluoroborate (0.5 g) with methylamine (0.275 g as 33% w/w solu-

tion) as described above produced a white precipitate which was filtered and recrystallised from absolute ethanol (0.286 g, 56%), mp 213–214 °C (Found C, 65.0; H, 4.8; N, 3.0. C<sub>24</sub>H<sub>19</sub>NCIBF<sub>4</sub> requires C, 65.0; H, 4.4; N, 3.2%);  $\delta_{\text{H}}(\text{CD}_3\text{CN})$  8.20 (2 H, s, pyridinium ring), 8.08 (1 H, t, aromatic), 7.94 (1 H, d, *J* 6, aromatic), 7.70 (12 H, cm, aromatic) and 3.80 (3 H, s, NCH<sub>3</sub>); *m/z* (FAB) 356 (M<sup>+</sup>, 100%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1626, 1577, 1561, 1494 and 1084.

#### 1-Methyl-2,6-diphenyl-4-(4-trifluoromethylphenyl)pyridinium tetrafluoroborate, 3 (X = *p*-CF<sub>3</sub>)

Treatment of 2,6-diphenyl-4-(4-trifluoromethylphenyl)pyrylium tetrafluoroborate (0.20 g) with methylamine (0.10 g as 33% w/w methylated spirit solution) produced a white precipitate which was filtered and recrystallised from absolute ethanol (0.120 g, 58%), mp 246–247 °C, (Found C, 62.8; H, 4.1; N, 2.9. C<sub>25</sub>H<sub>19</sub>NBF<sub>7</sub> requires C, 62.9; H, 4.0; N, 2.9%);  $\delta_{\text{H}}(\text{CD}_3\text{CN})$  8.26 (2 H, s, pyridinium ring), 8.19 (2 H, d, *J* 7.5, aromatic), 7.94 (2 H, d, *J* 7.5, aromatic), 7.71 (10 H, cm, aromatic) and 3.80 (3 H, s, NCH<sub>3</sub>); *m/z* (FAB) 390 (M<sup>+</sup>, 100%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1626, 1568, 1326 and 1070.

#### 1-Methyl-2,6-diphenyl-4-[3,5-bis(trifluoromethyl)phenyl]-pyridinium tetrafluoroborate, 3 [X = *m,m'*-(CF<sub>3</sub>)<sub>2</sub>]

The pyrylium salt 3 [X = *m,m'*-(CF<sub>3</sub>)<sub>2</sub>] (0.133 g 0.25 mmol) was stirred in absolute ethanol (0.6 cm<sup>3</sup>) and methylamine (0.10 g as 33% w/w methylated spirit solution) added to yield a red solution. After 24 h, ether was added to yield a precipitate (0.84 g, 62%) which was recrystallised from a mixture of ether and dichloromethane, mp 236–240 °C (Found C, 57.5; H, 3.0; N, 2.7. C<sub>26</sub>H<sub>18</sub>F<sub>6</sub>NBF<sub>4</sub> requires C, 57.28; H, 3.33; N, 2.57%);  $\delta_{\text{H}}(\text{CD}_3\text{CN})$  8.58 (2 H, s, pyridinium ring), 8.35 (2 H, s, aromatic), 8.27 (1 H, s, aromatic), 7.74 (10 H, unresolved aromatic) and 3.83 (3 H, s, NCH<sub>3</sub>); *m/z* (FAB) 458 (M<sup>+</sup>, 100%);  $\nu_{\text{max}}/\text{cm}^{-1}$  1630, 1572, 1342, 1282, 1175, 1137 and 1056.

#### Cyclic voltammetry

Measurements were carried out with an EG & G Parc model 175 Universal programmer and an EG & G parc model 173 potentiostat or a BAS 100. Experiments were performed at 25 °C in a 10 cm<sup>3</sup> volume three electrode cell using glassy carbon and a platinum wire as working and auxiliary electrodes. Potentials were measured against a calomel reference electrode. Acetonitrile was refluxed over P<sub>2</sub>O<sub>5</sub> under nitrogen and distilled from P<sub>2</sub>O<sub>5</sub> before use. A test solution containing supporting electrolyte (tetrabutylammonium tetrafluoroborate, 0.2 mol dm<sup>-3</sup>) in 10 cm<sup>3</sup> of oxygen-free acetonitrile was placed in the cell, and nitrogen was bubbled through the solution to remove any residual oxygen. A background scan of the quiet test solution was made over the potential range of  $\pm 2.0$  V. The test compounds were weighed out to give a 10<sup>-3</sup> mol dm<sup>-3</sup> solution when added to 10 cm<sup>3</sup> of solvent in the cell, and nitrogen was passed through the solutions for 2 min to stir and ensure they were oxygen free. A single scan was made to determine the current response for the electron transfer over the range of  $\pm 2.0$  V and the chart recorder adjusted to appropriate values. Each current peak was then investigated separately using four different scan rates, *viz.* 50, 100, 200 and 500 mV s<sup>-1</sup>. Half-wave potentials are reported as the mean ( $\pm 0.07$  V) of the peak voltages for the forward and reverse sweeps, and were not dependent on scan rate.

#### Reductions with sodium cyanoborohydride for product analysis

The heterocyclic cation (0.005 g) was dissolved in 0.5 cm<sup>3</sup> CD<sub>3</sub>CN in a standard NMR tube. The proton NMR spectrum of the sample was then run before addition of an equal volume of a saturated solution of sodium cyanoborohydride in CD<sub>3</sub>CN. The NMR spectrum was then re-run within 5 min of mixing. For all salts except the pyridinium derivatives, the

spectroscopy showed complete reaction in this time. For details of the spectra, see text.

#### Spectrofluorimetry

The sample (0.005 g) was dissolved in 500 cm<sup>3</sup> of acetonitrile to give an approximate concentration of 2.5 mmol dm<sup>-3</sup>. For the spectrofluorimetry, the stock solution was further diluted to give solutions with final concentrations ranging from 2.5  $\times$  10<sup>-5</sup> to 2.5  $\times$  10<sup>-7</sup> mol dm<sup>-3</sup>. The sample was then irradiated at a wavelength  $\lambda_{\text{ex}}$ , where  $\lambda_{\text{ex}}$  is one of the  $\lambda_{\text{max}}$  in the UV–VIS spectrum of the sample.

#### Rate Measurements

All operations were conducted under nitrogen atmosphere. Sodium cyanoborohydride or cyanoborodeuteride (*ca.* 0.32 g) was stirred with acetonitrile (50 cm<sup>3</sup>) which had been freshly distilled from phosphorus pentoxide. The cloudy mixture was filtered and the resulting clear solution evaporated *in vacuo*. The resulting crystalline sodium cyanoborohydride was placed under high vacuum until it reached constant weight, then redissolved in acetonitrile (100 cm<sup>3</sup>) yielding a clear solution approximately 0.05 mol dm<sup>-3</sup> in NaBH<sub>4</sub>CN. The exact concentration was determined by treatment of aliquots of the solutions with iodine solution and back titration with standard thiosulfate.<sup>48</sup> The sodium cyanoborohydride solution was 0.049 mol dm<sup>-3</sup> and the borodeuteride was 0.046 mol dm<sup>-3</sup> with uncertainties of  $\pm 2\%$ . This analytical method fails with the tetrabutylammonium cyanoborohydride; addition of the cyanoborohydride solution to the iodide solution gave a brown oil which soon yielded a brown solid, which did not titrate to an observable endpoint with thiosulfate. Clear filtered solutions were therefore prepared and concentrations calculated from the weighed amounts of the salt (Aldrich) recovered after the evaporation of aliquots to constant mass. Uncertainties are probably  $\pm 15\%$ .

In a typical kinetic experiment, solutions of the thiopyrylium salts (5  $\times$  10<sup>-5</sup> mol dm<sup>-3</sup>) in dry acetonitrile were prepared and 3 cm<sup>3</sup> pipetted into a 1 cm stoppered quartz UV cell which was placed in the thermostatted block of a Cary 2000 UV spectrometer. The cell was allowed to equilibrate to the set temperature for at least 15 min before the addition of reducing agent solution by micropipette to make final concentrations of <sup>-</sup>BH<sub>3</sub>CN in the cell at least 5  $\times$  10<sup>-4</sup> mol dm<sup>-3</sup>. The cell was stoppered, shaken quickly, and the decrease in absorbance at  $\lambda = 406$  nm recorded. A least 30 measurements were taken over at least three half-lives.

The more reactive thiopyrylium ions and the pyryliums were studied using a Hi-Tech SF-61 stop-flow apparatus. All reactions were monitored at the longest wavelength absorption maximum of the cation (see Table 2)

First order rate constants were extracted by non-linear least-squares regression of an exponential decay to the data, using the decay constant, and both initial and infinity values as adjustable parameters. Calculated and experimental values of the latter two were in good agreement, and the standard deviation of the fitted rate constant was less than 1% of its value. For each temperature, the experiment was repeated three times. Rate constants thus obtained agreed to within 5% and were averaged. Second order rate constants were obtained by dividing the pseudo-first order constants by the cyanoborohydride concentrations. With the combined uncertainties in the concentration and rate measurements, uncertainties in the tabulated second order rate constants are  $\pm 5\%$  for the sodium cyanoborohydride reductions and  $\pm 20\%$  for the tetrabutylammonium cyanoborohydride reductions.

#### Reduction of 2,4,6-triphenylthiopyrylium tetrafluoroborate to 2,4,6-triphenyl-4H-thiopyran

Sodium borohydride (0.036 g) was gradually added over 30 min, with stirring, to a solution of 2,4,6-triphenylthiopyrylium

tetrafluoroborate (0.1 g in 30 cm<sup>3</sup> of dry acetonitrile). The reaction mixture was then concentrated and ether (10 cm<sup>3</sup>) added. The solution was then filtered and the ethereal solution washed with water before drying over magnesium sulfate and evaporation of the solvent. Recrystallisation of the oily residue from methanol gave yellow crystals (0.044 g, 31%) which were examined spectroscopically (see text).

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An authentic sample was prepared by the method of Kostanecki and Rossbach.<sup>49</sup>

### X-Ray crystal structure determination of 3 (X = H)

A colourless tabular crystal of C<sub>24</sub>H<sub>20</sub>BF<sub>4</sub>N having approximate dimensions of 0.15 × 0.45 × 0.47 mm was mounted on a glass fibre. All measurements were made on a Rigaku AFC5R X-ray diffractometer with graphite-monochromated Cu-K $\alpha$  radiation and a 12 kW rotating anode generator.

Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 22 carefully centred reflections in the range 29.25 < 2 $\theta$  < 32.97° corresponded to an orthorhombic cell with dimensions  $a = 15.420(1)$ ,  $b = 17.909(4)$ ,  $c = 15.173(6)$  Å with  $V = 4190(2)$  Å<sup>3</sup>. For  $Z = 8$  and  $F_w = 409.23$ , the calculated density is 1.297 g cm<sup>-3</sup>. Based on the systematic absences of  $0kl$ :  $k \neq 2n$ ;  $h0l$ :  $l \neq 2n$ ;  $hk0$ :  $h \neq 2n$ , and the successful solution and refinement of the structure, the space group was determined to be *Pbca* (#61).

The data were collected at a temperature of 21 ± 1 °C, using the  $\omega$ -2 $\theta$  scanning technique to a maximum 2 $\theta$  value of 120.2°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.21° with a take-off angle of 6.0°. Scans of (1.10 + 0.30 tan  $\theta$ )° were made at a speed of 32.0° min<sup>-1</sup> (in omega). The weak reflections [ $I < 10.0\sigma(I)$ ] were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

A total of 3502 reflections was collected. The intensities of three representative reflections which were measured after every 150 reflections declined by 9.22%. A linear correction factor was applied to the data to account for this phenomenon. The linear absorption coefficient for Cu-K $\alpha$  is 8.1 cm<sup>-1</sup>. An empirical absorption correction, using the program DIFABS,<sup>50</sup> was applied which resulted in transmission factors ranging from 0.79 to 1.22. The data were corrected for Lorentz and polarization effects.

The structure was solved by direct methods.<sup>51</sup> The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealised positions (C-H = 0.95 Å), and were assigned isotropic thermal parameters which were 20% greater than the equivalent  $B$  value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 1777 observed reflections [ $I > 3.00\sigma(I)$ ] and 299 variable parameters and converged (largest parameter shift was < 0.07 times its esd) with unweighted and weighted agreement factors of  $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.056$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0.066$ . The standard deviation of an observation of unit weight was 2.11. The weighting scheme was based on counting statistics and included a factor ( $p = 0.03$ ) to downweight the intense reflections. Plots of  $\sum w(|F_o| - |F_c|)^2$  versus  $|F_o|$ , reflection order in data collection,  $\sin \theta/\lambda$  and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.17 and -0.16 e Å<sup>-3</sup>, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.<sup>52</sup> Anomalous dispersion effects were included in

$F_{\text{calc}}$ ,<sup>53</sup> the values for  $\Delta f'$  and  $\Delta f''$  were those of Cromer. All calculations were performed using the TEXSAN crystallographic software package<sup>54</sup> of Molecular Structure Corporation.

Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.‡

### Solution calorimetry

The apparatus and experimental method has been fully described elsewhere.<sup>55</sup> An accurately measured amount of the salt (ca. 100 mg) was dissolved in acetonitrile (100 cm<sup>3</sup>) in the calorimeter vessel. The NaBH<sub>3</sub>CN samples were sealed in teflon ampoules, which were broken under the acetonitrile solution at the appropriate time by means of an ampoule breaker.

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‡ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.

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