Electrogeneration of Cyanomethyl Anion from Phenylsulphonylacetonitrile and Cyanomethyltrimesitylphosphonium Iodide and the Relative Acidities of XCH$_2$CN (X = Ph$_3$P$^+$, Ph$_3$As$^+$, Mes$_3$P$^+$, or PhSO$_2$) *versus* Acetic Acid in Acetonitrile

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Contrary to a previous report, PhSO$_2$CH$_2$CN has been shown to exhibit a one-electron reduction (two-electron reductive cleavage followed by deprotonation of PhSO$_2$CH$_2$CN by $^-$CH$_2$CN). Mes$_3\overset{+}{P}$CH$_2$CN I$^-$ behaves similarly. The relative acidities of XCH$_2$CN (X = Ph$_3$P$^+$, Ph$_3$As$^+$, Mes$_3$P$^+$, or PhSO$_2$) *versus* acetic acid in acetonitrile has been studied both voltammetrically and spectrophotometrically. Ph$_3\overset{+}{P}$CH$_2$CN is a stronger acid than CH$_3$CO$_2$H; Ph$_3\overset{+}{As}$CH$_2$CN, Mes$_3\overset{+}{P}$CH$_2$CN, and PhSO$_2$CH$_2$CN are weaker acids than CH$_3$CO$_2$H. PhSO$_2$CH$_2$CN and Mes$_3$-$\overset{+}{P}$CH$_2$CN I$^-$ have been used in an electroanalytical method for studying the addition of $^-$CH$_2$CN to various electrophiles.

In an earlier paper[1] we demonstrated the use of linear sweep voltammetry in studying the addition of electrogenerated $^-$CH$_2$CN to aromatic carbonyl compounds. Various azo-compounds in acetonitrile, and Ph$_3\overset{+}{P}$CH$_2$CN Br$^-$ and Ph$_3\overset{+}{As}$CH$_2$CN Br$^-$ in DMF, were used as sources of $^-$CH$_2$CN. Due to the side reactions which these latter two precursors exhibit, *viz.* deprotonation of the precursor by the electrogenerated $^-$CH$_2$CN, we have been looking for other systems for use in DMF. We now report on a study of PhSO$_2$CH$_2$CN and Mes$_3\overset{+}{P}$CH$_2$CN I$^-$, and further work on Ph$_3\overset{+}{P}$CH$_2$CN Br$^-$ and Ph$_3\overset{+}{As}$CH$_2$CN Br$^-$.

RESULTS AND DISCUSSION

Phenylsulphonylacetonitrile.—The paper by Lamm and Ankner,[2] which described the polarographic and preparative electrolytic behaviour of PhSO$_2$CH$_2$CN, reported that it gave a chemically irreversible two-electron reduction (0.5mM in 0.4M-Bu$_4$NClO$_4$–DMF) at $E_{\frac{1}{2}}$ −1.42 V (*versus* Ag–AgI in 0.1M-Bu$_4$NI–DMF), and that the polarographic wave was unchanged in the presence of phenol. Preparative electrolysis showed that the reduction products, in the presence of phenol, were benzenesulphinate ion and acetonitrile [reaction (1)]. It thus

$$\mathrm{PhSO_2CH_2CN} \xrightarrow{2e} \mathrm{PhSO_2}^- + {}^-\mathrm{CH_2CN} \xrightarrow{\mathrm{PhOH}} \mathrm{CH_3CN} \quad (1)$$

appeared that PhSO$_2$CH$_2$CN might be a useful source of electrogenerated $^-$CH$_2$CN, which did not suffer from the limitation exhibited by the previously examined substrates,[1] namely deprotonation of the substrate by $^-$CH$_2$CN. However, on examination by cyclic voltammetry at a hanging mercury drop electrode (2mM in 0.1M-Et$_4$NBF$_4$–DMF, v 172 mV s^{-1}) we observed an irreversible peak at −2.38 V (*versus* Ag–0.1M-AgNO$_3$–DMF ‡), with $E_p - E_{p/2}$ *ca.* 80 mV, and an i_p approximately equal to that of the first electron transfer of benzophenone. Since the assignment of a two-electron wave by Lamm and Ankner[2] was based on a comparison with the reduction wave of PhSO$_2$CH$_3$, which is known[3] to give an irreversible two-electron wave, and on the absence of any change on addition of phenol, we have also compared the behaviour of PhSO$_2$CH$_2$CN with that of PhSO$_2$CH$_3$. Cyclic voltammetry of 2mM-PhSO$_2$CH$_3$ in 0.1M-Et$_4$NBF$_4$–DMF (172 mV s^{-1}) showed an irreversible peak at −2.87 V (*versus* Ag–0.1M-AgNO$_3$), $E_p - E_{p/2}$ *ca.* 60 mV, with i_p almost exactly twice the height of that of PhSO$_2$CH$_2$CN. When the solution was 2mM in both PhSO$_2$CH$_3$ and PhSO$_2$CH$_2$CN the ratio of the i_p values was 2.0 : 1.1. Polarographic analysis (forced drop mercury electrode) of 0.5mM-PhSO$_2$CH$_2$CN in 0.4M-Et$_4$NBF$_4$–DMF showed a reduction wave at $E_{\frac{1}{2}}$ −2.25 V, while that of 0.5mM-PhSO$_2$CH$_3$ showed $E_{\frac{1}{2}}$ −2.73 V. Although it was not possible to measure accurately the i_d for PhSO$_2$CH$_3$ owing to the proximity of the solvent–electrolyte cut-off, it was *ca.* 1.7 times the i_d of PhSO$_2$CH$_2$CN, which in turn was 0.95 times the i_d for the first electron transfer of 0.5mM-benzophenone under the same conditions When the solution was 0.5mM in both PhSO$_2$CH$_3$ and PhSO$_2$CH$_2$CN the ratio of the i_d values was almost 1, with the i_d value for PhSO$_2$CH$_3$ being about half its value in the absence of PhSO$_2$CH$_2$CN.

We therefore conclude that PhSO$_2$CH$_2$CN gives a one-electron reduction peak–wave, and not a two-electron wave as originally reported.[2] A possible source for this error lies in the use of PhSO$_2$CH$_3$ as an internal standard; as we have shown above, when PhSO$_2$CH$_2$CN and

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‡ The $E_{\frac{1}{2}}$ of PhSO$_2$CH$_3$ is reported to be −1.93 V (*versus* Ag–AgI–0.1M-Bu$_4$NI–DMF)[2] and −2.355 V (*versus* s.c.e.).[3] The Ag–AgI reference is therefore *ca.* −0.425 V *versus* s.c.e. We found the $E_{\frac{1}{2}}$ of PhSO$_2$CH$_3$ to be −2.73 V (*versus* Ag–0.1M-AgNO$_3$–DMF). The Ag–0.1M-AgNO$_3$ reference is therefore *ca.* +0.375 V *versus* s.c.e., and *ca.* +0.80 V *versus* Ag–AgI.

$PhSO_2CH_3$ are present together the wave for the latter is smaller than when $PhSO_2CH_2CN$ is absent. Presumably in this situation the reduction products from $PhSO_2CH_2CN$ render some of the $PhSO_2CH_3$ electroinactive. The one-electron peak–wave for $PhSO_2CH_2CN$ can be accounted for by a similar process to that reported[4] for the cyanomethyltriphenylphosphonium cations in which half the molecules of $PhSO_2CH_2CN$ reaching the electrode surface undergo a two-electron reduction while the other half is rendered electroinactive through deprotonation by the generated $^-CH_2CN$.* This is supported by the observation that for 1mM solutions of $PhSO_2CH_2CN$ in 0.1M-Et_4NBF_4–acetonitrile, whose cyclic voltammetric and polarographic behaviour is directly comparable with those in DMF, the i_p and i_d values are doubled by making the solution 2mM in acetic acid. Thus, in the presence of acetic acid $PhSO_2CH_2CN$ gives a two-electron peak–wave, with the electrogenerated $^-CH_2CN$ and/or $PhSO_2\overset{-}{C}HCN$ being protonated by the acid. The failure of Lamm and Ankner[2] to observe any change on adding phenol to solutions of $PhSO_2CH_2CN$ in DMF parallels our own observations with $Ph_3\overset{+}{P}CH_2CN$, with phenol and acetic acid producing only small changes in DMF, but doubling the height of the peak–wave in acetonitrile (see below). We attribute this difference to the greater basicity of the solvent, or an impurity, in the case of DMF.

Cyanomethyltrimesitylphosphonium Iodide.—Since the use of $Ph_3\overset{+}{P}CH_2CN$ as a source of electrogenerated $^-CH_2CN$ is complicated by the deprotonation of the cation by $^-CH_2CN$,[1,4] we anticipated that by making the methylene group more sterically crowded the rate of deprotonation would be considerably reduced. We therefore prepared and tested cyanomethyltrimesitylphosphonium iodide. Cyclic voltammetry of the latter (2mM in 0.1M-Et_4NBF_4–DMF, v 172 mV s^{-1}) gave two irreversible peaks at −1.99 V ($E_p - E_{p/2}$ *ca.* 80 mV) and −2.75 V ($E_p - E_{p/2}$ *ca.* 50 mV) with peak currents in the ratio 1 : 1.30. The addition of trimesitylphosphine (2mM) had no effect upon the voltammogram. Under the same conditions $Ph_3\overset{+}{P}CH_2CN$ Br^- gave two irreversible peaks at −1.95 V ($E_p - F_{p/2}$ *ca.* 65 mV) and −2.85 V ($E_p - E_{p/2}$ *ca.* 90 mV, very close to solvent–electrolyte cut-off) with peak currents in the ratio 1 : 1.5; the second peak has been attributed[4] to reduction of the ylide formed during the first reduction process. The i_p of the first peak for the reduction of $Mes_3\overset{+}{P}CH_2CN$ was 0.81 times that for the corresponding peak of $Ph_3\overset{+}{P}CH_2CN$, and 0.59 times that for the first electron transfer of benzophenone. The i_p of the first peak of $Ph_3\overset{+}{P}CH_2CN$ was 0.67 times that for the first electron transfer of benzophenone.

From these data we conclude that the reduction of $Mes_3\overset{+}{P}CH_2CN$ follows the same course as $Ph_3\overset{+}{P}CH_2CN$. The first peak corresponds to a one-electron reduction (bearing in mind the larger $E_p - E_{p/2}$ value, and the greater size of the molecule), which arises *via* a two-electron reduction of half the molecules reaching the electrode surface and deactivation of the other half through deprotonation by the generated $^-CH_2CN$. The second peak presumably corresponds to reduction of the ylide formed during the first reduction process. This interpretation is further supported by the observation that the first reduction peak for 1mM-$Mes_3\overset{+}{P}CH_2CN$ in 0.1M-Et_4NBF_4–acetonitrile doubled in height when the solution was made 2.0—3.0mM in acetic acid, and the second peak disappeared. $Ph_3\overset{+}{P}CH_2CN$ behaved similarly (see below), except that a higher concentration of acetic acid was required in this case.

Effect of Acetic Acid on the Linear Sweep Voltammograms and Polarograms of XCH_2CN ($X = Ph_3P^+$, Ph_3As^+, Mes_3P^+, *or* $PhSO_2$), *and on the Absorption Spectra of* $X\overset{-}{C}HCN$.—The effect of acetic acid on the voltammograms of $PhSO_2CH_2CN$ and $Mes_3\overset{+}{P}CH_2CN$ I^- has already been described briefly. The behaviour of $Ph_3\overset{+}{As}CH_2CN$ Br^- (1mM) in acetonitrile was very similar to that of $Mes_3\overset{+}{P}CH_2CN$ I^-, in that the first reduction peak (E_p − 1.49 V, irreversible, $E_p - E_{p/2}$ *ca.* 100 mV) was doubled in height on making the solution 2.0—3.0mM in acetic acid. The peak also moved to −1.55 V ($E_p - E_{p/2}$ *ca.* 90 mV), a cathodic shift of 60 mV. The polarographic wave also doubled in height. The second reduction peak (E_p − 2.52 V, irreversible, $E_p - E_{p/2}$ *ca.* 40 mV), which was 2.83 times the height of the first peak, disappeared in the presence of acetic acid. In the case of $Mes_3\overset{+}{P}CH_2CN$ the increase in the peak height was accompanied by a cathodic shift of *ca.* 30 mV, but in the case of $PhSO_2CH_2CN$ there was no cathodic shift. (The polarographic wave for $PhSO_2CH_2CN$ was shifted cathodically by *ca.* 40 mV.)

The behaviour of $Ph_3\overset{+}{P}CH_2CN$ Br^- appeared to be more complex than that of the other members of the series, and was studied in more detail. The original 1mM solution of $Ph_3\overset{+}{P}CH_2CN$ Br^- (v 214 mV s^{-1}) had E_p − 1.81 V ($E_p - E_{p/2}$ *ca.* 55 mV), with the second reduction peak as a shoulder at *ca.* −2.9 V. The addition of acetic acid at increasing concentrations caused the following changes: 1mM-CH_3CO_2H, a new peak appeared at −2.59 V; 2—5mM-CH_3CO_2H, a new peak appeared at −1.95 V, increasing in height with increasing acetic acid concentration, and the peak at −2.59 V decreased and became obscured by the acetic acid cut-off; 10—60mM-CH_3CO_2H, the peaks at −1.81 and −1.95 V merged and became a single peak at E_p − 1.84 V ($E_p - E_{p/2}$ *ca.* 70 mV), with the final peak being 2.1 times the height of the original peak at −1.81 V. The changes in the peaks between −1.5 and −2.2 V are shown in Figure 1. The behaviour of $Ph_3\overset{+}{P}CD_2CN$ Br^- was identical. The polarograms of 1mM-$Ph_3\overset{+}{P}CH_2CN$ Br^- changed as follows:

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* From the acidifying effects of the SO_2 and CN groups on an adjacent C–H bond,[5] we estimate that $PhSO_2CH_2CN$ would have a pK_a of 14—16.

initial solution, $E_{\frac{1}{2}}$ — 1.73 and —2.75 V (i_d values equal); 1mM-CH_3CO_2H, new waves at —1.9 and —2.52 V; 2—5mM-CH_3CO_2H, wave at —1.9 V increasing in height, and wave at —2.52 V decreasing and becoming lost in the acetic acid cut-off; 10—40mM-CH_3CO_2H, the waves at —1.73 and —1.9 V merged to give a single wave at —1.77 V, with an i_d 2.0 times that of the original peak at —1.73 V. The changes are shown in Figure 2. The behaviour of $Ph_3\overset{+}{P}CH_2COPh$ Br^-, which had been studied previously [6] although not in such detail, was very similar to that of $Ph_3\overset{+}{P}CH_2CN$ Br^- except that slightly more acetic acid was required to produce the same effects, and the voltammograms were more complex due to one of the cleavage products ($PhCOCH_3$) being electroactive.

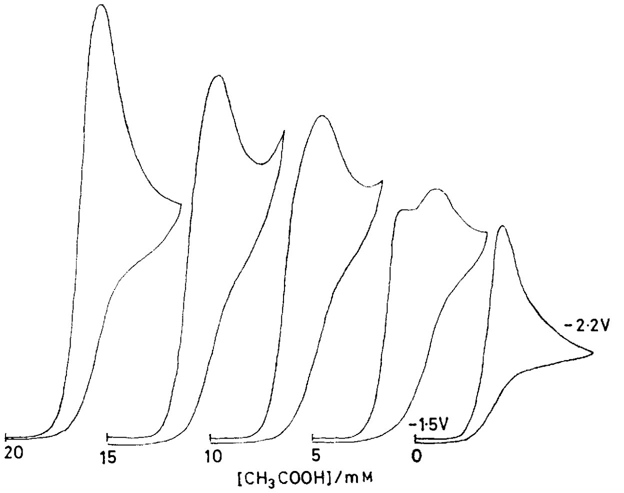

FIGURE 1 Changes in the linear sweep voltammogram of $Ph_3\overset{+}{P}CH_2CN$ Br^- (1mM) in CH_3CN–0.1M-Et_4NBF_4 during the addition of acetic acid

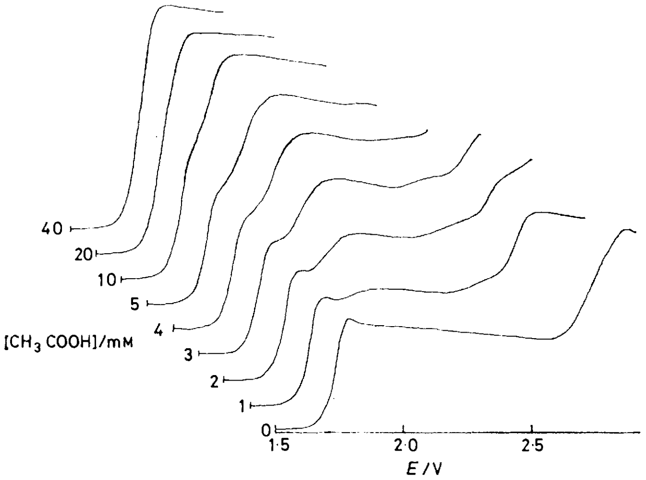

FIGURE 2 Changes in the polarogram of $Ph_3\overset{+}{P}CH_2CN$ Br^- (1mM) in CH_3CN–0.1M-Et_4NBF_4 during the addition of acetic acid

The ylide, Ph_3PCHCN, was studied in a similar manner and the following changes were observed: initial solution (1mM), E_p — 2.83 V with a shoulder at —2.74 V; 1mM-CH_3CO_2H, new peaks appeared at —2.05 and —2.64 V; 2—5mM-CH_3CO_2H, the first peak shifted to —2.01 V and increased in height, while the second peak shifted to —2.61 V, decreased, and was finally lost in the acetic acid cut-off; 10—40mM-CH_3CO_2H, the first peak stopped increasing when it was about the same height as that obtained from 1mM-$Ph_3\overset{+}{P}CH_2CN$ Br^- under the same conditions, and the final E_p was —1.88 V. At no stage was there a double peak in this region, *cf.* $Ph_3\overset{+}{P}CH_2CN$ Br^-. Changes in the polarograms followed a similar pattern giving a final $E_{\frac{1}{2}}$ of —1.80 V, with an i_d comparable with that for 1mM-$Ph_3\overset{+}{P}CH_2CN$ Br^- under the same conditions. The original $E_{\frac{1}{2}}$ was *ca.* —2.72 V, and at no stage was there a double wave in the region —1.8 to —1.9 V, *cf.* $Ph_3\overset{+}{P}CH_2CN$ Br^-.

These data may be interpreted on the assumption that $Ph_3\overset{+}{P}CH_2CN$ Br^- (and $Ph_3\overset{+}{P}CH_2COPh$ Br^-) is a stronger acid than CH_3CO_2H in acetonitrile.*

$$Ph_3\overset{+}{P}CH_2CN + 2e \rightleftharpoons Ph_3P + {}^-CH_2CN \qquad (2)$$

$$Ph_3\overset{+}{P}CH_2CN + {}^-CH_2CN \rightleftharpoons Ph_3PCHCN + CH_3CN \qquad (3)$$

$$CH_3CO_2H + {}^-CH_2CN \rightleftharpoons CH_3CO_2{}^- + CH_3CN \qquad (4)$$

$$Ph_3PCHCN + CH_3CO_2H \overset{K}{\rightleftharpoons} Ph_3\overset{+}{P}CH_2CN + CH_3CO_2{}^- \qquad (5)$$

Reduction *via* reactions (2) and (3) would be the path followed in the absence of acetic acid, giving E_p — 1.81 V and $E_{\frac{1}{2}}$ — 1.73 V, with the second reduction peak–wave corresponding to reduction of the ylide generated in (3). In the presence of acetic acid, if the phosphonium cation is a stronger acid than CH_3CO_2H, reaction (3) will be more important than reaction (4). However, in the presence of an excess of CH_3CO_2H, $Ph_3\overset{+}{P}CH_2CN$ will be made available for reduction by reaction (5), and the position of the reduction peak–wave will depend upon the equilibrium constant (K) for reaction (5).[7] For small values of K ($\ll 1$, assumed), the ratio $K/1 + K \longrightarrow K$ and there will be a cathodic shift in the reduction peak–wave of $(RT/nF)\ln K$. Thus the reduction of $Ph_3\overset{+}{P}CH_2CN$ derived from Ph_3PCHCN will occur at a more negative potential than that at which direct reduction of $Ph_3\overset{+}{P}CH_2CN$ occurs, giving rise to a double peak–wave. This is supported by the data for the reduction of Ph_3PCHCN in the presence of CH_3CO_2H, for which no double peak–wave was observed and the reduction peak–wave was cathodic of that for $Ph_3\overset{+}{P}CH_2CN$ in the absence of CH_3CO_2H.

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* In aqueous media $Ph_3\overset{+}{P}CH_2COPh$ is a weaker acid than acetic acid, and this is probably also true for $Ph_3\overset{+}{P}CH_2CN$ (see G. Aksnes and J. Songstad, *Acta Chem. Scand.*, 1964, **18**, 655; A. Thiel and D. Greig, *Z. Phys. Chem.*, 1935, **172**, 245).

TABLE 1

Absorbance measurements of solutions of Ph_3PCHCN (1mM) in CH_3CN during titration with acetic acid

	$[Et_4NBF_4]$/M					
$[CH_3CO_2H]$/ mM	0 Absorbance	K	0.1 Absorbance	K	1.0 Absorbance	K
0	1.55		1.62		1.48	
5	1.49	3.14×10^{-4}	1.51	1.00×10^{-3}	1.28	4.34×10^{-3}
10	1.41	9.05×10^{-4}	1.34	3.68×10^{-3}	1.06	1.16×10^{-2}
15			1.16	7.65×10^{-3}	0.86	2.07×10^{-2}
20	1.21	3.12×10^{-3}	0.99	1.26×10^{-2}	0.69	3.14×10^{-2}
25			0.83	1.89×10^{-2}	0.55	4.36×10^{-2}
30			0.68	2.73×10^{-2}	0.45	5.44×10^{-2}
35			0.56	3.61×10^{-2}		
40	0.81	1.10×10^{-2}	0.46	4.60×10^{-2}	0.32	7.25×10^{-2}
50			0.31	6.95×10^{-2}	0.25	8.32×10^{-2}
60			0.21	9.88×10^{-2}	0.21	8.77×10^{-2}

In order to study the relative acidities of the various XCH_2CN systems and acetic acid in acetonitrile further, the titration of the conjugate bases $X\bar{C}HCN$ against acetic acid was followed spectrophotometrically. In the case of $Ph_3\overset{+}{P}CH_2CN$, the ylide Ph_3PCHCN was readily prepared,[8] and had $\lambda_{max.}$ (CH_3CN) 298 (ε 1 600), 273 (2 240), 266 (2 820), and 260 nm (2 740), with a shoulder at 255 nm (ε 2 440). $Ph_3\overset{+}{P}CH_2CN$ had $\lambda_{max.}$ (CH_3CN) 277 (ε 3 060) and 270 nm (3 560), with a shoulder at 254 nm (ε 2 760), and no absorption above 290 nm. The titration of 1mM-Ph_3PCHCN in acetonitrile containing 0, 0.1, and 1.0M-Et_4NBF_4 with acetic acid was followed by monitoring the absorbance at 298 nm. The results are given in Table 1. The equilibrium constant K for reaction (5) was calculated from equation (6), taking $[Ph_3PCHCN] =$

$$K = [Ph_3\overset{+}{P}CH_2CN][CH_3CO_2^-]/[Ph_3PCHCN][CH_3CO_2H] \quad (6)$$

A/A_0, $[Ph_3\overset{+}{P}CH_2CN] = [CH_3CO_2^-] = (A_0 - A)/A_0$, and $[CH_3CO_2H] = c - (A_0 - A)/A_0$, where A_0 and A are the absorbances initially and at any stage during the titration, respectively, and c is the ratio of the concention of acetic acid added to the initial concentration of Ph_3PCHCN. It was assumed that CH_3CO_2H was undissociated. Under all three sets of conditions the value of K is not constant but increases with the concentration of acetic acid. It was found that a plot of log K *versus* log c gave a straight line with slope 1.72 (r 0.9992) for no Et_4NBF_4 present, 1.84 (r 0.999) for 0.1M-Et_4NBF_4, and 1.42 (r 0.9999, first six points only) and 1.25 (r 0.991, all

$$\log K = m\log c + \text{const.} = \log c^m + \text{const.} \quad (7)$$

nine points) for 1.0M-Et_4NBF_4. Thus, equation (7) is obtained. Therefore log (K/c^m) and K/c^m are constants. This suggests the empirical equation (8) as the equilibrium

$$K' = K/c^m = \frac{[(A_0 - A)/A_0]^2}{(A/A_0)[c - (A_0 - A)/A_0]c^m} \quad (8)$$

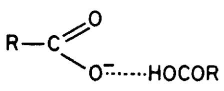
constant for the reaction between Ph_3PCHCN and CH_3CO_2H. However such an equation has no physical basis, and a similar equation (9) based on the chemical equation (10) in which m molecules of acetic acid are bound up with the products of the reaction, seems more realistic. Calculation of K'' for the data obtained with

$$K'' = \frac{[(A_0 - A)/A_0]^2}{(A/A_0)[c - (m + 1)(A_0 - A)/A_0]^{m+1}} \quad (9)$$

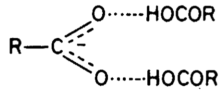
$$Ph_3PCHCN + (m + 1)CH_3CO_2H \overset{K''}{\rightleftharpoons} Ph_3\overset{+}{P}CH_2CN + CH_3CO_2^- + mCH_3CO_2H \quad (10)$$

0.1M-Et_4NBF_4 gave K'' $5.91 \pm 0.10 \times 10^{-5}$ with the observed m value of 1.84, K'' $6.68 \pm 0.24 \times 10^{-5}$ with m 1.8, and K'' $4.93 \pm 0.23 \times 10^{-5}$ with m 1.9. Thus the value of K'' calculated using the observed slope from the log K *versus* log c plot represents the situation in which the standard deviation is minimized. The calculated value of K' using m 1.84 was $5.20 \pm 0.08 \times 10^{-5}$. K'' for 1.0M-Et_4NBF_4 was $5.06 \pm 0.09 \times 10^{-5}$ (using m 1.42, from six points), and for no Et_4NBF_4 present was $1.98 \pm 0.12 \times 10^{-5}$.

The fact that m lies between 1 and 2 suggests that the ' extra ' molecules of CH_3CO_2H are bound to the acetate ion in equation (10), in a similar manner to that suggested by Gordon [9] to account for the behaviour of substituted benzoic acids in acetonitrile during neutralisation, *viz.* the existence of dimeric (A) and trimeric (B) anions with



(A)



(B)

their relative importance varying with the the concentration of other species in solution.

The acidity of $Ph_3\overset{+}{P}CH_2CN$ relative to CH_3CO_2H was also estimated by generating the ylide from a 1mM solution of $Ph_3\overset{+}{P}CH_2CN$ in acetonitrile (no Et_4NBF_4 present) with sodium hydride, and then titrating with acetic acid. The sodium hydride treatment (0.5—1.0 h) produced the characteristic absorption at 297 nm, which decreased on adding acetic acid; 85 equivalents of acetic acid were required to reduce the absorbance to 25% of its original value. The relative acidities of $Ph_3\overset{+}{As}CH_2CN$, $Mes_3\overset{+}{P}CH_2CN$, and $PhSO_2CH_2CN$ were also estimated by this method:

(i) A solution of $Ph_3\overset{+}{As}CH_2CN\ Br^-$ in acetonitrile had $\lambda_{max.}$ (CH_3CN) 271 (ε 2 440), 264 (2 980), and 258 nm (2 320), with no absorption at 297 nm. After treatment with sodium hydride (1 h) an absorption characteristic of the ylide, $\lambda_{max.}$ 297 nm (ε *ca.* 2 000) had developed, and addition of acetic acid restored the original spectrum. The absorption at 297 nm was reduced to 25% of its initial absorbance by the addition of 0.75 equivalents of acetic acid.

(ii) A solution of $Mes_3\overset{+}{P}CH_2CN\ I^-$ in acetonitrile had $\lambda_{max.}$ (CH_3CN) 326 (ε 940), 288 (6 250), and 248 nm (43 500). After treatment with sodium hydride, the absorption at 326 nm had become a more intense shoulder at 320 nm (ε 1 850). The addition of 0.75 equivalents of acetic acid reduced the absorbance at 320 nm to 30% of its initial value (corrected for original absorbance at 326 nm). An excess of acetic acid (30 equivalents) caused the absorbance at 320 nm to fall below that exhibited by the original solution.

(iii) A solution of $PhSO_2CH_2CN$ in acetonitrile had $\lambda_{max.}$ (CH_3CN) 272 (ε 1 110), 265 (1 310), and 259 nm (940), with no absorption at 296 nm. After treatment with sodium hydride (1—1.5 h) an absorption at $\lambda_{max.}$ 296 nm (ε 3 900) had developed, and addition of acetic acid restored the original spectrum. The absorption at 296 nm was reduced to 13% of its initial absorbance by the addition of 0.88 equivalents of acetic acid. Samples of $PhSO_2\bar{C}HCN\ K^+$ and $PhSO_2\bar{C}HCN\ Et_4N^+$, prepared by treating solid $PhSO_2CH_2CN$ with aqueous KOH and Et_4NOH respectively, also gave $\lambda_{max.}$ (CH_3CN) 296 nm, and the spectrum of $PhSO_2CH_2CN$ was restored on adding acetic acid.

The above spectrophotometric measurements indicate that $Ph_3\overset{+}{As}CH_2CN$, $Mes_3\overset{+}{P}CH_2CN$, and $PhSO_2CH_2CN$ are all less acidic than acetic acid in acetonitrile, their conjugate bases being neutralised by equivalent amounts of CH_3CO_2H. $Ph_3\overset{+}{P}CH_2CN$, however, is somewhat more acidic than CH_3CO_2H in acetonitrile, the ylide being only about 75% neutralised by 85 equivalents of CH_3CO_2H. This supports the voltammetric measurements in which only small amounts (2—3 equivalents) of acetic acid were required to double the i_p and i_d values for $Ph_3\overset{+}{As}CH_2CN\ Br^-$, $Mes_3\overset{+}{P}CH_2CN\ I^-$, and $PhSO_2CH_2CN$, whereas $Ph_3\overset{+}{P}CH_2CN\ Br^-$ required 30—40 equivalents. Furthermore, the original assumption that $Ph_3\overset{+}{P}CH_2CN$ is much more acidic than CH_3CO_2H in acetonitrile, which was made to explain the double peak–wave observed during the addition of CH_3CO_2H to solutions of $Ph_3\overset{+}{P}CH_2CN\ Br^-$, is now shown to be valid, and it is now apparent why the other systems did not produce a double peak–wave.

Linear Sweep Voltammetry of Various Electrophiles in DMF in the Presence of $PhSO_2CH_2CN$ *and* $Mes_3\overset{+}{P}CH_2CN\ I^-$.—The effect of $Ph_3\overset{+}{P}CH_2CN\ Br^-$ and $Ph_3\overset{+}{As}CH_2CN\ Br^-$ on the linear sweep voltammetry of benzophenone and indan-1-one in DMF has already been reported.[1] Both cations are non-ideal sources for electrogenerated $^-CH_2CN$, since they both react with $^-CH_2CN$ to produce the corresponding ylides. There is therefore a competition between the precursor and the carbonyl compound for the available $^-CH_2CN$, and this complicates the study of the addition of $^-CH_2CN$ to the carbonyl group. It was originally hoped that $PhSO_2CH_2CN$ and $Mes_3\overset{+}{P}CH_2CN\ I^-$ would be more ideal, since the former was reported [2] to exhibit a simple two-electron reductive cleavage and the latter might have sufficient steric crowding around the methylene group to inhibit deprotonation. However, as demonstrated above, both are rapidly deprotonated by the liberated $^-CH_2CN$.

Nevertheless we have studied the effect of adding these precursors to solutions of various electrophiles in DMF, and the results are given in Table 2. The results with benzophenone and $Mes_3\overset{+}{P}CH_2CN\ I^-$ are almost identical to those with benzophenone and $Ph_3\overset{+}{As}CH_2CN\ Br^-$,[1] with the effect being only half that observed using $Ph_3\overset{+}{P}CH_2CN\ Br^-$. A comparison of the effect of 2mM-$PhSO_2CH_2CN$ on the voltammogram of indan-1-one with that using $Ph_3\overset{+}{P}CH_2CN\ Br^-$ (23% decrease) shows that $PhSO_2CH_2CN$ is probably the most successful precursor so far discovered, presumably due to its lower acidity, *cf.* $Ph_3\overset{+}{P}CH_2CN$. (The kinetic acidity may be more important than the thermodynamic acidity in these experiments.) A direct comparison between the effect of $PhSO_2CH_2CN$ and $Ph_3\overset{+}{P}CH_2CN\ Br^-$ on the voltammogram of benzophenone was not possible due to the E_p of the former being so close to that of benzophenone.

TABLE 2

% Decrease in $i_{p,c}$ of substrate (2mM) on addition of precursors of $^-CH_2CN$

Substrate ($E_{p,c}$/V *versus* Ag–Ag+)	Precursor			
	$PhSO_2CH_2CN$		$Mes_3\overset{+}{P}CH_2CN$	
	2mM	4mM	2mM	4mM
Acetophenone (−2.52)	41	78		
Propiophenone (−2.51)		67		
Isopropyl phenyl ketone (−2.52)		57		
Phenyl t-butyl ketone (−2.57)		49		
Acetylmesitylene (−2.87)		14		
Indan-1-one (−2.57)	42 [a]	75 [a]	5 [b]	14 [b]
Acrylonitrile (−2.55)	29	61		
Benzophenone (−2.28)			16	34

Substrate (2mM) + precursor (2 or 4mM) in 0.1M-Et_4NBF_4–DMF; hanging mercury drop, sweep rate 250 mV s^{-1}.

[a] The addition of $Et_4\overset{+}{N}\ PhSO_2^-$ (2 and 4 mM) had no effect.

[b] Second peak of $Mes_3\overset{+}{P}CH_2CN$ at −2.76 V may contribute to total current at −2.57 V and hence affect calculated % decrease in $i_{p,c}$ at −2.57 V.

The effect of $PhSO_2CH_2CN$ on the voltammograms of the other ketones in Table 2 shows a trend similar to that observed using azobenzene in acetonitrile as the precursor for $^-CH_2CN$ (see Table 1, ref. 1), *viz.* a fall-off in the percentage decrease in the i_p of the ketone as the carbonyl group becomes more crowded. The present results are not complicated by the $^-CH_2CN$ regeneration process which occurs in acetonitrile. A full account of the behaviour of acrylonitrile will be given in a subsequent paper.

EXPERIMENTAL

Phenylsulphonylacetonitrile was prepared as previously described,[2] m.p. 114—115 °C (lit.,[2] 112 °C). Phenylsulphonylmethane was prepared by a modification of the method of Baldwin and Robinson,[10] m.p. 86.5—88 °C (from water) (lit.,[10] 87—88 °C), δ ($CDCl_3$) 3.52 (s, CH_3). Phenacyltriphenylphosphonium bromide was prepared by reacting phenacyl bromide and triphenylphosphine in ethyl acetate, m.p. 285—288.5 °C (from ethanol) (lit.,[11] 284—286 °C).

Tetraethylammonium Benzenesulphinate.—A concentrated aqueous solution of sodium benzenesulphinate was acidified (to pH 1) with 4M-hydrochloric acid and the solid was filtered off and washed twice with water. The acid was then dissolved in water and neutralised with 20% aqueous tetraethylammonium hydroxide. The water was evaporated *in vacuo* to give a semi-crystalline residue which was soluble in chloroform, ethanol, and acetone, but insoluble in benzene. The residue was successively mixed with the following solvents and evaporated: ethanol, benzene, DMF, and finally pumped under high vacuum. The crystalline solid (m.p. < 100 °C) was highly deliquescent, δ ($CDCl_3$) 7.5 (m, 5 H), 3.2 (q, 8 H), and 1.3 (t, further split, 12 H).

Cyanomethyltrimesitylphosphonium Iodide.—Trimesitylphosphine was prepared from bromomesitylene by the method of Stepanov *et al.*[12] It had m.p. 195—199 °C (lit.,[12] 192—193 °C), and its i.r. spectrum was identical to that reported.[12] The phosphine (0.5 g) was alkylated with iodoacetonitrile (2.5 ml; Aldrich) at 110 °C during 4.5 h. The product, cyanomethyltrimesitylphosphonium iodide (0.50 g), was an off-white powder, m.p. 253.5—254.5 °C (Found: C, 59.45, 59.55; H, 5.95, 6.15; N, 2.5, 2.55. Calc. for $C_{29}H_{35}INP$: C, 62.7; H, 6.35; N, 2.5%). It was subsequently shown that the I^- salt was contaminated by the HgI_4^{2-} salt (82.5 : 17.5, respectively), the contaminant coming from HgI_2 (0.20% Hg) in the iodoacetonitrile. This will be fully reported in a paper on the spectroscopic properties of $Mes_3\overset{+}{P}CH_2CN\ I^-$ and $Mes_3\overset{+}{P}CH_3\ I^-$. Attempts to purify the iodide only increased the proportion of the contaminant, and the mixture was therefore converted to the fluoroborate salt by treatment in ethanol with 40% aqueous fluoroboric acid, m.p. 284—286.5 °C (crystals from nitromethane) (Found: C, 67.85; H, 6.9; N, 2.65. $C_{29}H_{35}BF_4NP$ requires C, 67.6; H, 6.85; N, 2.7%).

Voltammetric Measurements.—Acetonitrile and DMF were purified as previously described.[1] The reference electrode was Ag–0.1M–$AgNO_3$ in the appropriate solvent. The hanging mercury drop electrode of constant surface area has been described.[13] For the experiments in which acetic acid was added, a solution of acetic acid (0.300 g) in acetonitrile (5.00 ml) was used, the additions being in 10—100 μl. Before acetic acid was added, the current for the 0.1M–Et_4NBF_4–CH_3CN solution did not exceed 1 μA until beyond −3.0 V. As the concentration of acetic acid increased, the potential at which the background current exceeded 1 μA became more anodic, *viz.* 1mM, −2.68 V; 2mM, −2.49 V; 5mM, −2.32 V; 10mM, −2.25 V; 20mM, −2.17 V; 30mM, −2.10 V; 40mM, −2.07 V; *cf.* 2mM-benzophenone has i_p *ca.* 3 μA using the same hanging mercury drop electrode (240 mV s^{-1}).

The procedure for measuring the percentage decrease in the i_p of various substrates on adding XCH_2CN has been described.[1]

Spectrophotometric Measurements.—A solution of acetic acid (0.45 g) in acetonitrile (5.0 ml) was used for the additions (0.5—10 μl).

We thank Professor J. M. Saveant, Dr. B. Lamm, and Dr. B. M. Lowe for helpful discussions, and the University of Edinburgh for a demonstratorship (to I. S. M.).

[0/1790 *Received, 20th November,* 1980]

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