# Nucleophilic Attacks on Carbon–Nitrogen Double Bonds. Part 4.[1] Substitution of *N*-Arylbenzimidoyl Cyanides by Amines in Acetonitrile and by Alkoxides in Alcohols

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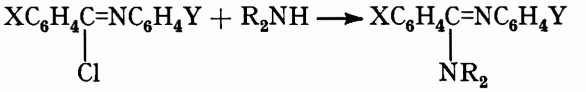
The substitution of the cyano-group of *N*-arylbenzimidoyl cyanides $PhC(CN)=NC_6H_4Y$ by nucleophiles was studied. With amines in acetonitrile several reactions had showed first- ($k'$) and second-order ($k''$) terms in the amine. With $EtO^-$ in EtOH, both zero- ($k^0$) and first-order ($k'$) terms in the nucleophile were found, while with $Bu^tO^-$ in $Bu^tOH$ the reaction is of first order in the base. It is suggested that a common initial step in these reactions is nucleophilic attack of the amine, an alkoxide ion, or ethanol on the imidoyl cyanide. The subsequent expulsion of the leaving group may be uncatalysed or amine-catalysed in acetonitrile, and solvent-assisted in the alcohols. The reactions were compared with those of the corresponding *N*-arylbenzimidoyl chlorides.

THE mechanism of displacement of chloride ion from simple imidoyl chlorides was studied recently in some detail. In solvolytic media, such as aqueous acetone [2] or aqueous dioxan,[3] the reactions proceed *via* cationoid intermediates, and the appearance of common ion rate depression suggests that products are formed from the free cations.[4] The reaction of diarylimidoyl chlorides (1) with amines [equation (1)] was studied recently in benzene [5,6] and in acetonitrile,[1] and diversity of reaction routes was found. Both first- and second-order terms in the amine, and Hammett plots with minima were found in benzene.[5,6] These were ascribed to a combination of a mechanism involving a rate-determining capture of intermediate ion pair by the nucleophile [7] for electron-donating substituents, and a nucleophilic addition–elimination for electron-attracting substituents. Both processes were either non-catalysed or amine-catalysed.[6] In acetonitrile, a solvent with higher dielectric constant, the amine-catalysed routes disappeared. Instead, both zero- and first-order processes in the amine characterise the reactions with non-hindered nucleophiles, while with a hindered nucleophile some systems showed common ion rate depression.[1] The operation of bimolecular nucleophilic addition–elimination route together with reactions *via* ion pairs or *via* free nitrilium ions was suggested.[1]



$$\underset{\textstyle (1)}{XC_6H_4\underset{\textstyle Cl}{C}=NC_6H_4Y} + R_2NH \longrightarrow \underset{\textstyle (2)}{XC_6H_4\underset{\textstyle NR_2}{C}=NC_6H_4Y} \qquad (1)$$

A unified picture of substituent and solvent effects emerges from these studies. The reaction *via* more dissociated cationoid intermediates gains importance with the increase in the electron donation by the substituents on the aryl groups or by increasing the solvent polarity.

Another parameter which can change the mechanism of the reaction is the change of the leaving group. However, except for the $k_{Br}/k_{Cl}$ ratio of 440 in the reaction of $PhC(X)=NPh$ with piperidine in benzene, which argues for an initial ionisation step,[6] this change was not yet investigated for simple $C(X)=N$ systems. A change to a system carrying a sluggish leaving group compared with chloride, in a good solvent, is expected to reverse the change caused by increasing the solvent polarity. Reactions *via* cationoid intermediates should contribute less to the overall reaction, while amine-catalysed routes may reappear. Moreover, the reactions with much more reactive nucleophiles, such as alkoxide ions, could then be studied by the usual spectrophotometric techniques. Since the change of the leaving group from chloro to cyano was studied in the analogous substitutions at activated $C=C$ systems,[8-10] we have studied the reactions of *N*-arylbenzimidoyl cyanides with amines in acetonitrile and with alkoxides in alcohols, for comparison with the corresponding reactions of the imidoyl chlorides and the reactions at the $C(X)=C$ bond. The acid catalysed hydrolysis of *N*-arylbenzimidoyl cyanides was previously studied.[11]

## RESULTS

*Reactions with Amines.*—The substitution of the diarylimidoyl cyanides (3d and e) with piperidine and morpholine gives the amidines (2d and e) [equation (2)]. Products from attack on the cyano-group were not formed. These reactions were followed spectrophotometrically in the presence of excess ($10^2$—$10^4$) of amine. The reactions of the imidoyl cyanides (3a—c) were too

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[1] Part 3, R. Ta-Shma and Z. Rappoport, *J. Amer. Chem. Soc.*, in the press.

[2] I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, 1962, **95**, 126.

[3] A. F. Hegarty, J. D. Cronin, and F. L. Scott, *J.C.S. Perkin II*, 1975, 429.

[4] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and G. C. Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328.

[5] Z. Rappoport and R. Ta-Shma, *Tetrahedron Letters*, 1971, 3813.

[6] R. Ta-Shma and Z. Rappoport, *J. Amer. Chem. Soc.*, in the press.

[7] R. A. Sneen, *Accounts Chem. Res.*, 1973, **6**, 46.

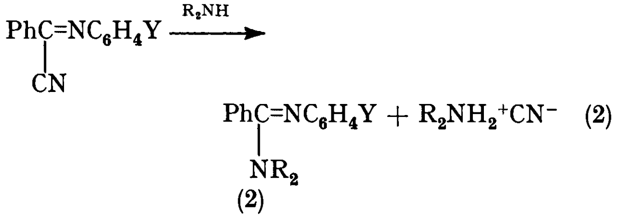
[8] (*a*) Z. Rappoport, *J. Chem. Soc.*, 1963, 4498; (*b*) Z. Rappoport, P. Greenzaid, and A. Horowitz, *ibid.*, 1964, 1334.

[9] Z. Rappoport and R. Ta-Shma, *J. Chem. Soc.* (*B*), 1971, (*a*) 871; (*b*) 1461.

[10] Z. Rappoport and P. Peled, *J.C.S. Perkin II*, 1973, 616.

[11] M. Masui, H. Ohmori, C. Ueda, and M. Yamauchi, *J.C.S. Perkin II*, 1974, 1448.

slow to follow under convenient reaction conditions, *e.g.*, (3b) was stable to one mole of piperidine at room temperature for two weeks. The reactions were pseudo-first-order in (3d and e) up to >90% reaction, and by



$$\mathrm{PhC(CN){=}NC_6H_4Y \xrightarrow{R_2NH} PhC(NR_2){=}NC_6H_4Y + R_2NH_2{}^+CN^-} \quad (2)$$

(2)

a; $Y = p$-MeO
b; $Y = H$
c; $Y = p$-Cl
d; $Y = m$-Cl
e; $Y = p$-NO$_2$

dividing the first-order constants ($k^1_{obs}$) by the amine concentration, the second-order constants $k^2_{obs}$ of Table 1 were obtained. Third-order constants, $k^3_{obs} = k^2_{obs}/$[Amine] are also given in Table 1.*

When the reaction was conducted in ethanol, the u.v. spectra of the products formed during the reaction

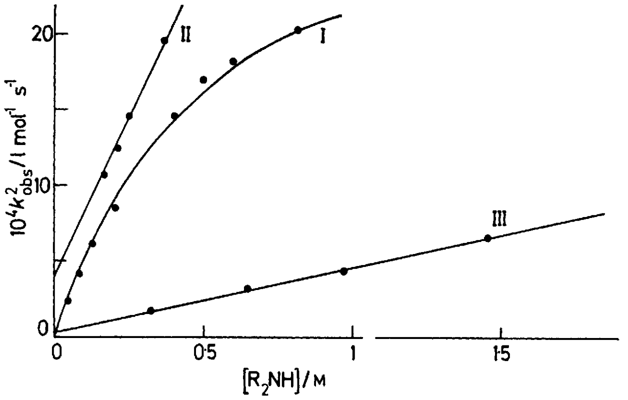


FIGURE 1 Dependence of $k^2_{obs}$ for (3e) on the amine concentration in acetonitrile: I, reaction with piperidine at 30°; II, reaction with piperidine at 45°; III, reaction with morpholine at 30°

showed that even in the presence of 0.1—0.6M piperidine or of 1M morpholine the imidates (4) were the only products formed. These were formed from the reaction with the equilibrium concentrations of ethoxide ion according to equations (4) and (5).

TABLE 1

Second- ($k^2_{obs}$) and third-order ($k^3_{obs}$) rate constants for the reaction of diarylimidoyl cyanides [a] with amines in acetonitrile

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| [Piperidine]/M | 1.98 | 2.97 | 3.97 | | | | | |
| $10^6k^2_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3d) at 45° | 2.51 | 2.48 | 2.84 | | | | | |
| $10^6k^3_{obs}$/l$^2$ mol$^{-2}$ s$^{-2}$ for (3d) at 45° | 1.27 | 0.84 | 0.71 | | | | | |
| 10[Morpholine]/M | 3.23 | 6.46 | 9.69 | 14.54 | | | | |
| $10^5k^2_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3e) at 30° | 1.68 | 3.24 | 4.43 | 6.64 | | | | |
| $10^5k^3_{obs}$/l$^2$ mol$^{-2}$ s$^{-1}$ for (3e) at 30° | 5.20 | 5.02 | 4.58 | 4.57 | | | | |
| 10[Piperidine]/M | 0.42 | 0.84 | 1.25 | 1.98 | 3.97 | 4.96 | 5.96 | 7.96 |
| $10^4k^2_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3e) at 30° | 2.40 | 4.21 | 6.22 | 8.54 | 14.6 | 17.1 | 18.2 | 18.5 |
| $10^4k^3_{obs}$/l$^2$ mol$^{-2}$ s$^{-1}$ for (3e) at 30° | 57.1 | 50.2 | 49.7 | 43.0 | 36.8 | 34.4 | 30.5 | 23.3 |
| 10[Piperidine]/M | 1.63 | 2.04 | 2.44 | 3.66 | | | | |
| $10^3k^2_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3e) at 45° | 1.07 | 1.24 | 1.46 | 1.96 | | | | |
| $10^3k^3_{obs}$/l$^2$ mol$^{-2}$ s$^{-1}$ for (3e) at 45° | 6.57 | 6.08 | 5.98 | 5.35 | | | | |

[a] [RCN] = (7—9) × $10^{-5}$ M.

The dependence of $k^2_{obs}$ values on the amine concentration differs for the different systems. The $k^2_{obs}$ values for (3d) with piperidine at 45° are relatively constant. Those for the reaction of (3e) with piperidine at 30° showed a convex dependence on the [Amine]. For the reactions of (3e) with morpholine at 30° or with piperidine at 45° the $k^2_{obs}$ *versus* [Amine] plots were linear according to equation (3), and the $k'$ and $k''$ values are summarized in Table 2. The possibility that these lines are linear only at the concentration range studied, and that at a wider concentration range a convex dependence is obtained cannot be unequivocally excluded. The $k^3_{obs}$ values for all the systems decrease with the increase in the

$$k^2_{obs} = k' + k''[\text{Amine}] \quad (3)$$

amine concentration. The different kinetic behaviours are shown in Figure 1.

$$\mathrm{R_2NH + EtOH \rightleftharpoons R_2NH_2{}^+ + EtO^-} \quad (4)$$

$$\underset{}{\mathrm{EtO^-}} + \underset{(3)}{\mathrm{Ar^1C(CN){=}NAr^2}} \longrightarrow \underset{(4)}{\mathrm{Ar^1C(OEt){=}NAr^2}} \quad (5)$$

Assuming that a change from water to ethanol reduces the p$K_a$ value of an ammonium ion by 0.8 p$K_a$ units,[12] $K_a$(piperidine) = 4.8 × $10^{-11}$ in EtOH. Taken together with the autoprotolysis constant of EtOH (1.32 × $10^{-19}$ at 25°),[13] 0.1—0.6M-piperidine in EtOH will give (1.7—4.0) × $10^{-5}$M-ethoxide ions. The substitutions of (1d and e) are *ca.* 2 × $10^5$ times slower with amines in acetonitrile than with ethoxide ions in ethanol (Table 2). A factor of 10 for the solvent change acetonitrile ⟶ ethanol is a reasonable estimate based on the

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* Rate constants $k^1_{obs}$, $k^2_{obs}$ *etc.* are experimentally observed rate constants where the superscript is related to the kinetic order of the process; $k'$ and $k''$ are derived rate constants from plots of $k_{obs}$ against [Amine]; $k_1$, $k_{-1}$, $k_2$, *etc.* are rate constants for the steps in the Schemes.

[12] H. C. Brown, D. H. McDaniel, and O. Höflinger in ' Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, 1955, vol. 1, p. 619.

[13] K. Bowden, *Canad. J. Chem.*, 1965, **43**, 2624.

similar value found for the reaction of compound (5; X = OEt) with piperidine.[10] By using these data we calculate that 3—7% of (3) will react with piperidine in

$$p\text{-Me}_2\text{NC}_6\text{H}_4\text{C(X)=C(CN)}_2 \quad (5)$$

ethanol, while most of the compound will react with the ethoxide ions formed in equilibrium (4), as was indeed observed.

*Reactions in Ethanol and in t-Butyl Alcohol.*—The reactions of the imidoyl cyanides (3a—e) with sodium ethoxide in ethanol gave only the imidates (4) [equation (6)]. Pseudo-first-order rate constants in the imidoyl

$$\text{Ar}^1\text{C(CN)=NAr}^2 + \text{EtO}^- \longrightarrow \text{Ar}^1\text{C(OEt)=NAr}^2 \qquad (6)$$

cyanide were obtained with high molar excess of ethoxide ions. The $k^1_{\text{obs}}$ values (Table 3) increase linearly with the ethoxide ion concentration according to equation (7),

$$k^1_{\text{obs}} = k^0 + k'[\text{EtO}^-] \qquad (7)$$

and the $k^0$ and $k'$ values are given in Table 2. Due to the high reactivity of compound (3e) only two base concentrations were used, and at this range overall second-order kinetics were observed.

A Hammett plot of log $k'$ *versus* $\sigma$[14] is linear for four of the five compounds studied. The point for Y = $p$-NO$_2$ showed a positive deviation from the best line defined by the other substituents. This point will be on the line if a $\sigma$ (or a $\sigma^-$) value of 1.00 is used for $p$-NO$_2$ instead of 0.78. The $\rho$ value for all five points is 4.5 ±0.3, and when the value for the deviating point is neglected, 3.8 ±0.06 (Figure 2).

TABLE 2

First- ($k^0$), second- ($k'$), and third-order ($k''$) rate constants for the reactions of PhC(X)=NC$_6$H$_4$Y with nucleophiles[a]

| Y | X | Solvent | Nucleophile | $T$/°C | $10^5k^0$/s$^{-1}$ | $10^5k'$/l mol$^{-1}$ s$^{-1}$ | $10^5k''$/l$^2$ mol$^{-2}$ s$^{-1}$ | $(k''/k')$/l mol$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| $p$-NO$_2$ | CN | CH$_3$CN | Piperidine | 30 | | 350 ± 40[b] | 610 ± 10 | |
| $p$-NO$_2$ | CN | CH$_3$CN | Piperidine | 45 | | 40 ± 16 | 440 ± 60 | 11 ± 7 |
| $p$-NO$_2$ | CN | CH$_3$CN | Morpholine | 30 | | 0.33 ± 0.1 | 4.3 ± 0.1[c] | 13 ± 6 |
| $m$-Cl | CN | CH$_3$CN | Piperidine | 45 | | 0.26 ± 0.015 | | |
| $p$-MeO | CN | EtOH | EtO$^-$ | 30 | 4.5 ± 0.2 | 66 ± 2 | | |
| $p$-MeO | CN | EtOH | EtO$^-$ | 45 | 13.6 ± 0.9 | 360 ± 10 | | |
| H | CN | EtOH | EtO$^-$ | 30 | 7.4 ± 0.2 | 447 ± 5 | | |
| $p$-Cl | CN | EtOH | EtO$^-$ | 30 | 9.0 ± 1.5 | 6 430 ± 150 | | |
| $m$-Cl | CN | EtOH | EtO$^-$ | 30 | 14.0 ± 3 | 17 000 ± 350 | | |
| $m$-Cl | CN | EtOH | EtO$^-$ | 45 | 57.0 ± 10 | 51 700 ± 1 600 | | |
| $p$-NO$_2$ | CN | EtOH | EtO$^-$ | 30 | | $3.23 \times 10^6 \pm 9 \times 10^4$ | | |
| $p$-NO$_2$ | CN | Pr$^i$OH | Pr$^i$O$^-$ | 22 | | $\sim 1.90 \times 10^6$ | | |
| H | CN | Bu$^t$OH | Bu$^t$O$^-$ | 30 | | 5 730 ± 20[d] | | |
| $p$-Cl | CN | Bu$^t$OH | Bu$^t$O$^-$ | 30 | | 31 400 ± 10 000[d] | | |
| $p$-NO$_2$ | CN | Bu$^t$OH | Bu$^t$O$^-$ | 30 | | $2.5 \times 10^6 \pm 2.5 \times 10^5$[d] | | |
| $p$-NO$_2$ | Cl | CH$_3$CN | Piperidine | 30 | | 5 900 ± 130[e] | | |
| $p$-NO$_2$ | Cl | CH$_3$CN | Morpholine | 30 | | 410 ± 20[e] | | |
| $p$-NO$_2$ | Cl | C$_6$H$_6$ | Piperidine | 30 | | 132 ± 3[f] | 128 ± 8[f] | 0.97[f] |
| $p$-NO$_2$ | Cl | C$_6$H$_6$ | Morpholine | 30 | | 6.2 ± 0.4[f] | 11.1 ± 0.6[f] | 1.8[f] |

[a] For all the linear relationships used for calculating the $k$ values, $r > 0.996$. [b] $k_1$ Value (see Discussion section). [c] Average $k^3_{\text{obs}} = 4.8 \times 10^{-5}$ l$^2$ mol$^{-2}$ s$^{-1}$. [d] $k^2_{\text{obs}}$ Value. [e] From ref. 1. [f] From ref. 6.

TABLE 3

Pseudo-first order constants ($k^1_{\text{obs}}$) for the reaction of diarylimidoyl cyanides[a] with sodium ethoxide in ethanol

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $10^2$[EtO$^-$]/M | 1.93 | 3.86 | 5.79 | 7.72 | 9.65 | 11.58 | | | |
| $10^5k^1_{\text{obs}}$/s$^{-1}$ for (3a) at 30° | 5.70 | 7.08 | 8.72 | 9.69 | 10.9 | 12.2 | | | |
| $10^2$[EtO$^-$]/M | 2.05 | 4.10 | 6.15 | 8.20 | 10.25 | 12.3 | | | |
| $10^4k^1_{\text{obs}}$/s$^{-1}$ for (3a) at 45° | 2.12 | 2.75 | 3.50 | 4.42 | 5.05 | 5.67 | | | |
| $10^3$[EtO$^-$]/M | 1.68 | 2.52 | 4.20 | 10.2 | 20.4 | 30.6 | 40.6 | 60.9 | 81.2 |
| $10^5k^1_{\text{obs}}$/s$^{-1}$ for (3b) at 30° | 6.85 | 7.60 | 8.51 | 11.7 | 16.7 | 21.4 | 25.1 | 34.6 | 43.4 |
| $10^3$[EtO$^-$]/M | 3.63 | 4.53 | 5.43 | 6.34 | 8.16 | 12.10 | | | |
| $10^4k^1_{\text{obs}}$/s$^{-1}$ for (3c) at 30° | 3.19 | 3.73 | 4.33 | 4.87 | 5.87 | 8.72 | | | |
| $10^3$[EtO$^-$]/M | 1.37 | 2.74 | 4.11 | 5.48 | 6.85 | 8.22 | 12.33 | | |
| $10^4k^1_{\text{obs}}$/s$^{-1}$ for (3d) at 30° | 3.68 | 5.78 | 8.32 | 10.85 | 13.25 | 15.90 | 21.85 | | |
| $10^3$[EtO$^-$]/M | 1.35 | 2.70 | 4.05 | 5.40 | | | | | |
| $10^3k^1_{\text{obs}}$/s$^{-1}$ for (3d) at 45° | 1.25 | 2.05 | 2.58 | 3.40 | | | | | |
| $10^3$[EtO$^-$]/M | 0.654 | 1.44 | | | | | | | |
| $10^2k^1_{\text{obs}}$/s$^{-1}$ for (3e) at 30° | 2.1[b] | 4.65[b] | | | | | | | |

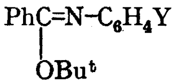
[a] [RCN] = (3—40) × $10^{-5}$M. [b] ±0·1 from triplicate experiments.

The activation parameters for the two processes, that based on $k^0$ and that based on $k'$, are given in Table 4. Since $k^0$ is low compared with $k'$ and is obtained as an intercept of equation (7), the values based on it are less accurate.

The reactions of (3b, c, and e) with potassium t-butoxide in t-butyl alcohol were also followed. In the

[14] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

reactions of (3b and e) the only products isolated were the benzanilides, while in the reaction of (3c) the corresponding imidate (6; Y = *p*-Cl) was obtained, admixed



$PhC(OBu^t)=N-C_6H_4Y$

(6)

with the corresponding benzanilide. We believe that the benzanilides are formed by decomposition of the initially formed (6), since it is known that *O*-alkyl imidates eliminate the alkyl group as olefin on heating.[15] Moreover, heating of *O*-alkyl diphenylbenzimidates in alkyl halide as the solvent gives benzanilide and olefin.[16] We followed the reaction in t-butyl alcohol by monitoring the disappearance of the absorptions of compounds (3).

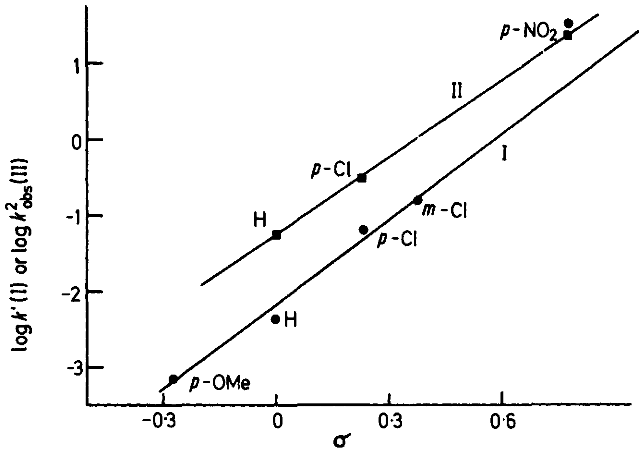


FIGURE 2 Hammett plots for the reaction of $PhC(CN)=NC_6H_4Y$ with alkoxides: I, log *k'* for the reactions with NaOEt in EtOH *versus* σ; II, log $k^2_{obs}$ for the reactions of $Bu^tOK$ in $Bu^tOH$ *versus* σ

TABLE 4

Activation parameters for the reaction of $PhC(CN)=NC_6H_4Y$ with $EtO^-$ in EtOH

| Y | Rate constant | $\Delta H^‡$/ kcal mol$^{-1}$ [a] | $\Delta S^‡$/ cal mol$^{-1}$ K$^{-1}$ [a] |
|---|---|---|---|
| *p*-MeO | $k^0$ | 13 ± 1 | −36 ± 5 |
| *p*-MeO | $k'$ | 21 ± 0.7 | −6 ± 2 |
| *m*-Cl | $k^0$ | 17 ± 2 | −21 ± 8 |
| *m*-Cl | $k'$ | 13.4 ± 0.3 | −19 ± 2 |

[a] The errors in $\Delta H^‡$ and $\Delta S^‡$ were calculated according to R. C. Petersen, J. H. Markgraf, and S. D. Ross, *J. Amer. Chem. Soc.*, 1961, **83**, 3819.

With excess of potassium t-butoxide the reaction was first-order in (3), but the order in $Bu^tOK$ was dependent on the base concentration.

The $k^2_{obs}$ values (Table 5) at 0.000 5—0.008M-$Bu^tOK$ are relatively constant, but they decrease on increasing the base concentration. This is probably due to the incomplete dissociation of the base in the low dielectric t-butyl alcohol (ε 10.9 at 30°).[17] Complete dissociation at low base concentrations probably takes place, as judged by the constant rate constants observed for the reaction of 0.000 1—0.007M of $Bu^tOK$ and $Bu^tONa$ with 2,4,6-trinitrobenzene in t-butyl alcohol.[18]

TABLE 5

Second-order rate constants ($k^2_{obs}$) for the reaction of diarylimidoyl cyanides [a] with potassium t-butoxide in t-butyl alcohol at 30°

| | | | | | | |
|---|---|---|---|---|---|---|
| $10^3[Bu^tO^-]$/M | 3.47 | 4.73 | 5.36 | 9.55 [b] | 38.2 [b] | 57.3 |
| $10^2k^2_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3b) | 5.77 | 5.70 | 5.73 | 4.42 | 3.93 | 3.22 |
| $10^3[Bu^tO^-]$/M | 2.10 | 2.88 | 4.20 | 5.30 | 6.29 | 7.42 |
| $10k^2k_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3c) | 3.01 | 3.41 | 3.16 | 3.11 | 2.99 | 3.05 |
| $10^4[Bu^tO^-]$/M | 5.03 | 6.78 | 7.07 | 7.57 | 10.1 | 10.3 |
| $10k^2_{obs}$/l mol$^{-1}$ s$^{-1}$ for (3e) | 25.8 | 23.6 | 21.8 | 25.6 | 29.4 | 22.5 |

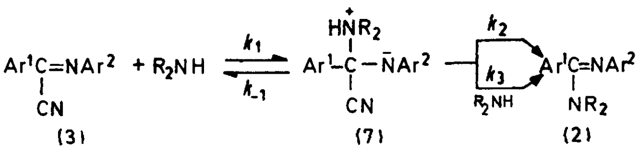
[a] [RCN] = (4—10) × $10^{-5}$M. [b] When $[Bu^tOK] > 8 \times 10^{-3}$M $k^2_{obs}$ decreases regularly.

A Hammett plot of log $k^2_{obs}$ *versus* σ for the three compounds is linear (Figure 2) with ρ 3.3 ± 0.1.

## DISCUSSION

*Reaction with Amines in Acetonitrile.*—The reactions of the imidoyl cyanides (3) with amines in acetonitrile may be compared with the reactions of the corresponding imidoyl chlorides (1).[1,5,6] The reactions of (3) with piperidine and morpholine in acetonitrile resemble those of (1) in benzene [6] both in the absolute values of the rate constants (Table 2) and in the appearance of both first- and second-order terms in the amine [equation (3)]. On the other hand, they differ from the reactions of (1) in acetonitrile in two respects: compounds (1) are 2—3 orders of magnitude more reactive than compounds (3), and for them the reaction order in the amine is either zero, or zero plus one.[1]

A similar decrease in the reactivity and increase in the reaction order in the amine in the same solvent were previously found when the nucleophilic substitution of activated vinyl cyanides [8a,10] was compared with that of the corresponding chlorides.[8b,9] A nucleophilic addition–elimination mechanism (*Ad*$_N$-*E*, Scheme 1) with a different rate-determining step for different leaving groups



SCHEME 1

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[15] J. W. Schulenberg and S. Archer, *Org. Reactions*, 1965, **14**, 27.

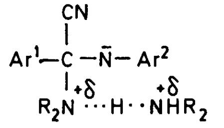
[16] A. E. Arbuzov and V. E. Shishkin, *Doklady Akad. Nauk S.S.S.R.*, 1961, **141**, 349 (*Chem. Abs.*, 1962, **56**, 11,491).

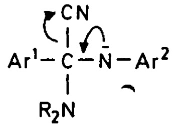
[17] 'Techniques of Organic Chemistry, Vol. VII: Organic Solvents,' ed. A. Weissberger, Interscience, New York, 1955, 2nd edn., p. 97.

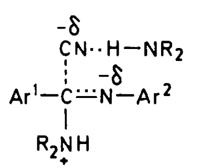
[18] L. H. Gan and A. R. Norris, *Canad. J. Chem.*, 1971, **49**, 2490.

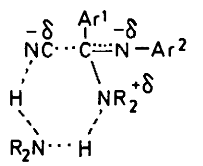
accounts for these results for both the C=C [8-10] and the C=N systems. The addition step is rate determining with good leaving groups, *i.e.*, for the chlorides (1), although a rate-determining elimination is possible. For sluggish leaving groups such as cyanide, the elimination step becomes slow and rate determining, and it then may be acid-, base-, or bifunctional-catalysed.[6] The bell-shaped *k versus* pH profile for the acid-catalysed hydrolysis of diarylimidoyl cyanides [11] and for the hydrolysis of benzoyl cyanides [19] also indicate a multi-step substitution *via* addition–elimination. We note that as the dielectric constant is lowered, a rate-determining addition can be replaced by a rate-determining elimination as suggested for the reactions of the chlorides (1) in benzene.[6]

In Scheme 1 $k_2$ and $k_3$ are the uncatalysed and the catalysed elimination steps. The transition state for the catalysed elimination may be base-catalysed [(8)] when proton expulsion from the zwitterion (7) gives the anion (9), or (9) can be formed in a pre-equilibrium followed by an electrophilically assisted expulsion of the $CN^-$ by the formed $R_2NH_2^+$, as suggested earlier.[6,10,20] It may be also electrophilically assisted by the amine [transition state (10)] or bifunctional-catalysed [transition state (11)]. Since cyano is a sluggish leaving group compared with chloro, as judged by the stability of organic nitriles to $S_N1$ and $S_N2$ reactions, the 300—1 200-fold lower reactivity of (3) compared with (1) is mainly due to lower values of $k_2$ and $k_3$, although the difference in $k_1$ may also contribute (see below).


(8)


(9)


(10)


(11)

The pseudo-first-order constant $k^1_{obs}$ which corresponds to Scheme 1 is given by equation (8), and when $k_{-1} \gg k_2 + k_3[R_2NH]$ as suggested for the analogous scheme in benzene,[6] the second-order constant $k^2_{obs}$ is linear in $[R_2NH]$ [equation (9)]. Since equations (3) and (9) have the same form, the ratio of the second-order term to the first-order term in the amine is given by the ratio of the rate constants for the amine-catalysed *versus* the non-catalysed elimination of Scheme 1, *i.e.*, $k''/k' = k_3/k_2$.

$$k^1_{obs} = \frac{k_1(k_2 + k_3[R_2NH])[R_2NH]}{k_{-1} + k_2 + k_3[R_2NH]} \qquad (8)$$

$$k^2_{obs} = k_1k_2/k_{-1} + k_1k_3[R_2NH]/k_{-1} \qquad (9)$$

The $k''/k'$ values for the reactions which obey equation (3) are 11—13 (Table 2), and at our amine concentrations of 0.2—1.4M the contribution of the $k''[R_2NH]$ term to $k^2_{obs}$ is dominant. Under these conditions it is not easy to decide whether $k'$ reflects a non-catalysed reaction, or whether the reaction is of second order in the amine, and $k^3_{obs}$ decreases due to the lowering of the dielectric constant of the medium by the added amine.

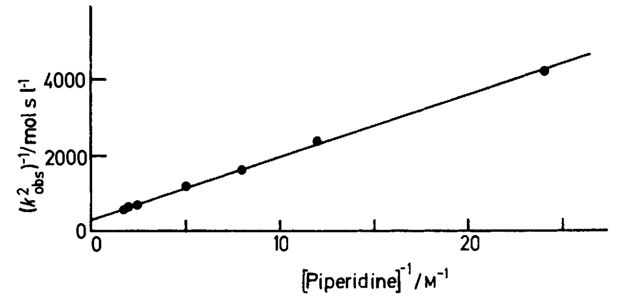


FIGURE 3 Dependence of $1/k^2_{obs}$ on 1/[Piperidine] for the reaction of (3e) with piperidine in acetonitrile

When $k_{-1} \sim k_2 + k_3[R_2NH]$ equation (8) predicts a convex $k^2_{obs}$ *versus* $[R_2NH]$ plot with a plateau where $k^2_{obs} = k_1$ when $k_{-1} \ll k_2 + k_3[R_2NH]$. The $k''/k'$ ratios for compound (3e) justify an additional assumption that $k_3[R_2NH] \gg k_2$, and inversion of equation (8) would then predict linearity between $1/k^2_{obs}$ and $1/[R_2NH]$ [equation (10)].

$$1/k^2_{obs} = 1/k_1 + (k_{-1}/k_1k_3) \cdot 1/[R_2NH] \qquad (10)$$

Indeed, the convex plot of $k^2_{obs}$ at 30° for (3e) *versus* [Piperidine] (Figure 1) is transformed to a linear $1/k^2_{obs}$ *versus* 1/[Piperidine] plot (Figure 3) with $r$ 0.999. The intercept of 290 ± 40 s and the slope of 164 ± 4 mol s l$^{-1}$ yield $k_1 = (3.5 \pm 0.4) \times 10^{-3}$ s$^{-1}$, $k'' = (6.1 \pm 0.1) \times 10^{-3}$ l mol$^{-1}$ s$^{-1}$ and $k_3/k_{-1} = 1.8$ l mol$^{-1}$. Hence, the catalysed expulsion of cyanide ion and the expulsion of the ammonium ion from (7) proceed with similar rates.

Comparison of the $k''$ values gives $k''$(piperidine)/$k''$(morpholine) = 140. The $K_a$(piperidine)/$K_a$(morpholine) ratio is 230 in acetonitrile [21] and if the carbon basicities of the amines (*i.e.*, $k_1/k_{-1}$) towards the imidoyl cyanides follow their hydrogen basicities the $k_3$(piperidine)/$k_3$(morpholine) ratios will be close to unity. The curved $k^2_{obs}$ *versus* $[R_2NH]$ relationship for piperidine but not for morpholine seems therefore to be due to the higher $k_{-1}$ value rather than from a lower $k_3$ value for morpholine.

The $k''$ values for (3e) with piperidine at 30 and 45° lead to $\Delta H^\ddagger = -4 \pm 3$ kcal mol$^{-1}$ and $\Delta S^\ddagger = -85 \pm 12$ cal mol$^{-1}$ K$^{-1}$. Although these values which are based on $k''$ values which were obtained by a different method at each temperature contain a large error, it is clear that the barrier for the catalysed route is mainly entropic, as observed for catalysed processes in vinylic systems.[8-10]

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[19] F. Hibbert and D. P. N. Satchell, *J. Chem. Soc.* (*B*), 1967, 653.

[20] Z. Rappoport and D. Ladkani, *J.C.S. Perkin II*, 1973, 1045.

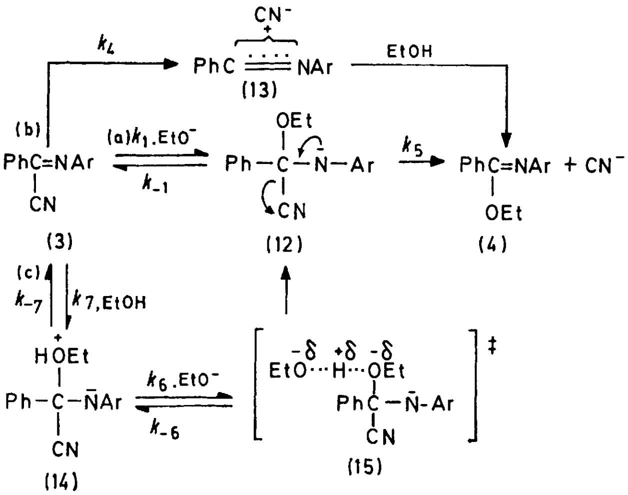
[21] J. F. Coetzee and G. R. Padmanabhan, *J. Amer. Chem. Soc.*, 1965, **87**, 5005.

Comparison of $k_1$ for (3e) with piperidine [1] with $k'$ for the reaction of the corresponding imidoyl chloride (1; $X = H, Y = p\text{-NO}_2$) with piperidine gives $k'(1;\ X = H,\ Y = p\text{-NO}_2)/k_1\ (3e) = 17 \pm 4$. Whether the $k'$ value for the imidoyl chloride is identical with $k_1$ for the nucleophilic attack or with $k_1k_2/k_{-1}$ (when $k_{-1} > k_2$) for the corresponding reaction scheme with (1), the attack on the imidoyl chloride is much faster than the attack on the imidoyl cyanide. This is reminiscent of the higher reactivity of tricyanovinyl chloride than that of tetracyanoethylene towards nucleophilic reagents.[8,22] We have no satifactory explanation to this behaviour since from the $\sigma_p$ values [23] cyano is more electron withdrawing than chloro, and the α-carbon of (3) should be correspondingly more electrophilic than that of the analogous compounds (1).

The absence of a second-order term in the amine for the reaction of (3d) with piperidine is surprising since $k^2_{\text{obs}}$ increases strongly with $[R_2NH]$ for (3e). Even if the lowering of the dielectric constant by the amine masks some of the rate enhancement, any catalysis by the amine is rather small. If the zwitterion (7; $Y = m\text{-Cl}$) is much less stable than (7; $Y = p\text{-NO}_2$) the uncatalysed cyanide ion expulsion from the former will be relatively enhanced and $k_3/k_2$ will be so much reduced that catalysis will not be observed. This explanation demands high response of $k_2$ to the change in the substituent, and fits the Hammett ρ value of 5.4 obtained by comparing the rates of (3d and e). This high value also explains the relative inertness of the imidoyl cyanides with $\sigma_Y < 0.3$ towards piperidine.

*Reaction with* $EtO^-$ *in* EtOH.—The change of the nucleophile–solvent system from $R_2NH$–acetonitrile to $EtO^-$–EtOH resulted in the same kinetic changes observed when system (3) was replaced by system (1) in acetonitrile.[1] The substitution rate increases by 3—5 orders of magnitude, and the second-order term in the nucleophile was replaced by a zero-order term in the nucleophile.[1] Although the contribution of the $k^0$ term is small we believe that neither the $k^0$ values nor their relative order are accidental, although they may include a relatively high experimental error. The justification for this belief is that the correlation coefficients of equation (7) are high, and that when second-order rate constants $k^2_{\text{obs}} = k^1_{\text{obs}}/[EtO^-]$ were calculated they remained constant only for compound (3d) where the $k'/k^0$ ratio at 30° is the highest. In the other cases the values decrease strongly with $EtO^-$, and this cannot be due to incomplete dissociation of NaOEt since the base concentrations are low.

The kinetics could be *a priori* accounted for by two routes for the formation of the imidates (4), as shown in Scheme 2. These routes are analogous to those suggested for compounds (1) in acetonitrile: [1] (a) a second-order formation of the anion (12) which is followed by a solvent-assisted expulsion of $CN^-$ [(3) $\longrightarrow$ (12) $\longrightarrow$ (4)], where either step ($k_1$ or $k_5$) may be rate determining and (b) a slow first-order solvent-assisted C–CN bond cleavage which forms the ion pair (13) (or the free nitrilium ion) followed by a fast capture of the intermediate by the solvent or ethoxide ion [(3) $\longrightarrow$ (13) $\longrightarrow$ (4)]. However, while there is little doubt concerning the nature of the bimolecular route (a), the ionisation route (b) should be excluded for three reasons. First, substitution *via* an initial C–CN bond cleavage is very rare, and the only example known to us is for the photolysis of aryldiphenylmethyl cyanides ($YC_6H_4CPh_2CN$) which carry electron-donating Y groups.[24] Secondly, route (b) should be observed even in the absence of ethoxide ion, but solutions of (3) are stable for a long time in neutral ethanol. Thirdly, the change of the substituent Y leads to a Hammett ρ value of *ca.* 0.7 which has the wrong sign and a low magnitude for an ionisation mechanism.



Scheme 2

These difficulties disappear if we ascribe the first-order route to nucleophilic reaction with the solvent [Scheme 2, route (c)]. A rate-determining formation of the zwitterion (14), which is then deprotonated by $EtO^-$ [*cf.* transition state (15)] gives the anion (12), which is mainly formed by the bimolecular route (a). In route (c) no C–CN bond cleavage takes place prior to carbon–nucleophile bond formation. Moreover, since the proton transfer between oxygens is fast,[25] $k_6[EtO^-] > k_{-7}$ and either $k_7$ or $k_5$ can be rate determining. In either case a positive ρ value is predicted for both, since the substituent effects on $k_1$ and $k_7$ will be in the same direction. Finally, in the absence of added base $k_{-7} \gg k_6[EtO^-]$, *i.e.*, expulsion of the cyanide ion from the zwitterion does not take place, and substitution does not occur.

The main substitution route with all the substituents is *via* attack by $EtO^-$. The importance of this route increases with the increase in $\sigma_Y$, and the $k'/k^0$ values

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[22] C. L. Dickinson, D. W. Wiley, and B. C. McKusick, *J. Amer. Chem. Soc.*, 1960, **82**, 6132; C. W. Rigby, E. Lord, M. P. Naan, and C. D. Hall, *J. Chem. Soc.* (*B*), 1971, 1192.

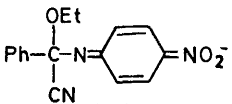
[23] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420.

[24] V. B. Ivanov and V. L. Ivanov, *Zhur. org. Khim.*, 1972, **8**, 621.

[25] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

increase from 15 for Y = $p$-MeO to 910 when Y = $p$-NO$_2$ where the reaction with the solvent is negligible. This is reflected in the $\rho$ values of 4.5 for the reaction with the ethoxide ion and of *ca.* 0.7 for the reaction with ethanol. It is an example of a reaction when attack by the weaker nucleophile shows lower response to the substituent effect than the attack by the stronger nucleophile, in contrast with the prediction of the selectivity–reactivity principle.[26]

The positive deviation of the point for Y = $p$-NO$_2$ from the log $k'$ *versus* $\sigma$ line is understood in terms of an extensive resonative negative charge dispersal in the ion (16) and in the transition state leading to it. The better fit with the suggested[27] $\sigma_{p\text{-NO}_2}$ value of 1.00 is reminiscent of the nucleophilic addition of thiolate ions to aryl vinyl sulphones,[28] which proceeds *via* an analogous tetrahedral intermediate.

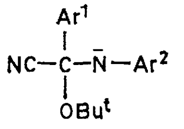

(16)

It should be emphasized that in routes (a) and (c) an assisted C–N bond cleavage ($k_5$) may be the slowest step in the overall reaction, since the solvent assists even in the expulsion of a better leaving group than cyano, *e.g.*, in the substitution of compound (5; X = F) in alcohols.[9b] The present data connot distinguish between a rate-determining nucleophilic attack ($k_1$,$k_7$) and a rate-determining elimination ($k_5$).

As expected, the activation enthalpy for the bimolecular route is higher when Y = $p$-MeO than when Y = $m$-Cl (Table 4). Both values, as well as the activation entropies are consistent with a rate-determining nucleophilic attack, as judged by the activation parameters for nucleophilic vinylic substitutions.[29] The values for the reaction with ethanol are not sufficiently accurate to warrant further discussion.

*Reaction with* Bu$^t$O$^-$ *in* Bu$^t$OH.—Changing the solvent-base system from EtO$^-$–EtOH to Bu$^t$O$^-$–Bu$^t$OH reduces the polarity of the solvent (EtOH $\varepsilon$ 24.3; Bu$^t$OH $\varepsilon$ 10.9).[17] Simultaneously, the base (Bu$^t$O$^-$) is more basic than EtO$^-$ (EtOH p$K_a$ 18; Bu$^t$OH p$K_a$ $\sim$ 22)[13] and more sterically hindered. It is therefore not surprising that $k_1$ of Scheme 2 is larger than $k_7$ and that the zero-order process in the nucleophile completely disappears. A reaction *via* the intermediate anion (17) is supported by the positive $\rho$ value.

It is difficult to predict whether the change of the nucleophile from EtO$^-$ to Bu$^t$O$^-$ will increase or decrease the overall rate, since the inductive and the steric effects in the nucleophile affect $k_1$ in opposite directions. Analogy with nucleophilic aromatic substitution may be useful although it is not clear whether the different steric effects in the two reactions will make the comparison valid.


$$\mathrm{NC{-}}\overset{\displaystyle \mathrm{Ar^1}}{\underset{\displaystyle \mathrm{OBu^t}}{\mathrm{C}}}\mathrm{{-}\bar{N}{-}Ar^2}$$
(17)

In the addition of alkoxide ions to 1,3,5-trinitrobenzene, a change from ethoxide to t-butoxide resulted in a 0.9- or 1.3-fold change in the addition rate constant,[18,30] and in a 16- or 28-fold decrease in the rate constant for the reverse reaction.[18,30] This was mainly ascribed to a lower solvation of the bulkier RO$^-$.[18] In the attack of CN$^-$ on 1,3,5-trinitrobenzene the equilibrium constant for formation of the anionic adduct is 400 times higher in Bu$^t$OH than in EtOH,[31] and this was ascribed to a reduced solvation of CN$^-$ in Bu$^t$OH.

The hypothetical reaction of 1-cyano-2,4,6-trinitrobenzene with alkoxide ions to give the 1-alkoxy-derivative *via* the $\sigma$-complex can be constructed as a model for our reaction. From the above data its rate decreases 40-fold on changing EtO$^-$–EtOH to Bu$^t$O$^-$–Bu$^t$OH. In our system, the rate in Bu$^t$O$^-$–Bu$^t$OH is 1.3-times slower for (3e), but it is 5 and 13 times faster for compounds (3c and b), respectively. If analogy with our reaction is applicable, the higher ratio for the less reactive compounds is more in agreement with a rate-determining C–CN bond cleavage of (17) which is assisted by electron-donating Y groups, than with a rate-determining $k_1$ with a tighter transition state for the less reactive compound. However, it should be realized that it is not at all clear that the rate-determining step is identical in the two alcoholic solvents.

## EXPERIMENTAL

M.p.s were determined with a Beckman apparatus and are uncorrected. U.v. spectra were recorded with a Perkin-Elmer 450 spectrophotometer, i.r. spectra with a Perkin-Elmer 337 spectrophotometer, and n.m.r. spectra with a Varian T-60 instrument. The signal positions are given in p.p.m. downfield from internal tetramethylsilane.

*Solvents*.—Dry acetonitrile was prepared from an analytical grade solvent (Baker) by drying over phosphorus pentaoxide and over calcium hydride.[32] The solvent was distilled and kept under argon. Ethanol was dried according to Vogel,[33] and t-butyl alcohol was dried according to Bethell and Cockerill.[34]

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[26] A. Pross, *Adv. Phys. Org. Chem.*, in the press. See however, C. D. Johnson, *Chem. Rev.*, 1975, **75**, 753.

[27] F. G. Bordwell and H. M. Andersen, *J. Amer. Chem. Soc.*, 1953, **75**, 6019.

[28] P. DeMaria and A. Fini, *J. Chem. Soc.* (*B*), 1971, 2335.

[29] Z. Rappoport, *Adv. Phys. Org. Chem.*, 1969, **7**, 1.

[30] C. F. Bernasconi, *J. Amer. Chem. Soc.*, 1970, **92**, 4682.

[31] E. Buncel, A. R. Norris, W. Proudlock, and K. E. Russell, *Canad. J. Chem.*, 1969, **47**, 4129.

[32] J. F. Coetzee, *Progr. Phys. Org. Chem.*, 1967, **4**, 56.

[33] A. I. Vogel, 'Practical Organic Chemistry,' Longman, London, 1948, p. 161.

[34] D. Bethell and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1966, 913.

*N*-Arylbenzimidoyl cyanides (3) were prepared from the corresponding chlorides by a method similar to that reported in the literature.[35] The solution of the imidoyl chloride in ether was shaken for a few hours with an excess of aqueous potassium cyanide. The organic layer was separated, dried, and evaporated, and the imidoyl cyanide was separated from the by-product benzanilide by several crystallizations from light petroleum (b.p. 40—60°). The analytical data are in Table 6. The imidoyl cyanides are yellow solids and they are stable for long periods both in the solid state and in solution.

TABLE 6

Analytical data for the new diarylimidoyl cyanides and imidates $PhC(Z)=NC_6H_4Y$

| | | | | Found (%) | | | | | Calc. (%) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Y | Z | M.p. (°C) | Crystalline form, colour | C | H | N | Cl | Formula | C | H | N | Cl |
| *m*-Cl | CN | 80 | Yellow needles | 69.95 | 3.65 | 11.15 | 15.25 | $C_{14}H_9ClN_2$ | 69.85 | 3.75 | 11.65 | 14.75 |
| *p*-$NO_2$ | CN | 139 | Yellow needles | 67.25 | 3.8 | 16.95 | | $C_{14}H_9N_3O_2$ | 66·95 | 3.6 | 16.75 | |
| *p*-MeO | OEt | | Yellow oil | 74.95 | 6.3 | 5.9 | | $C_{16}H_{17}NO_2$ | 75.3 | 6.65 | 5.5 | |
| *p*-Cl | OEt | 41 | Yellow solid | 69.35 | 5.5 | 5.65 | 13.35 | $C_{15}H_{14}ClNO$ | 69.35 | 5.4 | 5.4 | 13.7 |
| *m*-Cl | OEt | | Yellow oil | 69.6 | 5.3 | 5.2 | 13.35 | $C_{15}H_{14}ClNO$ | 69.35 | 5.4 | 5.4 | 13.7 |
| *p*-$NO_2$ | OEt | 91 | Yellow needles | 66.75 | 5.2 | 10.75 | | $C_{15}H_{14}N_2O_3$ | 66.65 | 5.8 | 10.35 | |

TABLE 7

U.v. data for *N*-arylbenzimidoyl cyanides $PhC(CN)=NC_6H_4Y$ in EtOH

| Y | $\lambda_{max.}$/nm (ε) |
|---|---|
| *p*-MeO | 231 (11 000), 284 (11 900), 389 (9 500) |
| H | 222 (10 700), 277 (13 400), 358 (4 700) |
| *p*-Cl | 230 (13 000), 281 (12 600), 365 (5 100) |
| *m*-Cl | 215sh (16 500), 279 (14 400), 352 (3 900) |
| *p*-$NO_2$ | 222sh (15 000), 295 (17 300), 350sh (7 700) |
| *p*-$NO_2$ [a] | 294 (19 000), 345sh (8 200) |

[a] In MeCN.

TABLE 8

U.v. and n.m.r. data for the imidates $PhC(OEt)=NC_6H_4Y$

| | | δ($CDCl_3$) | | | | |
|---|---|---|---|---|---|---|
| Y | $\lambda_{max}$/EtOH (ε) | $CH_2$ [a] | Me [b] | ArC | ArN | OMe |
| *p*-MeO | 233 (13 000), 297 (3 200) | 4.35 | 1.42 | 7.18 (5 H, m) | 6.63 (4 H, m) | 3.67 (3 H, s) |
| H | 230 (21 200), 272 (3 600) | 4.35 | 1.37 | 6.70—7.13 (10 H, m) | | |
| *p*-Cl | 237 (17 800), 275 (3 800) | 4.35 | 1.36 | 7.20 (5 H, m) | 6.82 (4 H, q) | |
| *m*-Cl | 228sh (16 000), 273 (2 700) | 4.35 | 1.36 | 6.45—7.20 (9 H, m) | | |
| *p*-$NO_2$ | 225sh (15 000), 325 (12 000) | | | | | |

[a] 2 H, q. [b] 3 H, t.

The u.v. data for the imidoyl cyanides are given in Table 7. The substitution of the chlorine of imidoyl chlorides by a cyano-group results in a bathochromic change of the two longer wavelength maxima, while the high intensity short wavelength absorption was not found for the imidoyl chlorides. The characteristic features of the i.r. spectra are strong absorption at 1 600—1 615 cm$^{-1}$ for the C(CN)=N bond, and the low intensity of the C≡N absorption at 2 225—2 240 cm$^{-1}$.

Diarylbenzamidines were prepared as described previously.[6]

*O*-Ethyl *N*-arylbenzimidates were prepared by Lander's method [36] from the instantaneous reaction of the imidoyl chlorides in ether with small excess of sodium ethoxide in ethanol. After filtering the salt and washing with water the products were separated from the benzanilides by dissolving in light petroleum (b.p. 40—60°), filtering, and evaporating the solvent. The analytical and spectral data are in Tables 6 and 8.

Attempts to prepare *O*-t-butyl N-arylimidates failed. Reaction of the imidoyl chlorides in ether with potassium t-butoxide in t-butyl alcohol gave potassium chloride immediately, but only the benzanilides were isolated, except in the reaction of (3c) where the analysis and the mass spectra showed that a mixture of the imidate and the benzanilide was formed. The imidates were not observed even when anhydrous conditions were applied during the work-up.

The initial spectra of the reaction mixture of (3) with potassium t-butoxide are analogous to those of the *O*-ethyl imidates and they remain stable for a day or longer. However, spectral changes take place on standing, and the final spectra are those of the corresponding benzanilides. Addi-

TABLE 9

Spectral changes following the formation of the imidates (6) in $Bu^tOH$ [a]

| Y | $\lambda_{max.}$/nm (ε) initial [b] | $\lambda_{max.}$/nm (ε) final [c] | $\lambda_{max.}$/nm (ε) of $PhCONHC_6H_4Y$ |
|---|---|---|---|
| H | 242 (12 000) | 266 (13 000) | 267 (13 200) |
| *p*-Cl | 258 (13 800),<br>320 (1 000) [d] | 272 (12 000) | 224 (10 800),<br>272 (14 000) |
| *p*-$NO_2$ | 233 (34 000),<br>410 (15 500) | 323 (17 000) | 235 (12 600),<br>323 (18 000) |

[a] Due to the low solubility of the imidoyl cyanides, benzimidates, and benzanilides in $Bu^tOH$ the errors in the ε values are ±5%. [b] Spectra of (6) formed during the kinetic study. [c] Spectra after several days or after addition of water. [d] Spectrum of the partially purified imidate (6).

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[35] O. Mumm, *Ber.*, 1910, **43**, 892; A. H. Lamberton and A. E. Standage, *J. Chem. Soc.*, 1960, 2964.

[36] G. D. Lander, *J. Chem. Soc.*, 1902, 591.

tion of a drop of water or of an acid to a solution which has the spectrum of the *O*-t-butyl imidate resulted in an immediate appearance of the spectrum of the benzanilide. These changes are described in Table 9.

*Kinetic Measurements*.—The reactions were followed in the thermostatted chamber of a Gilford 2 400 S spectrophotometer, at a wavelength where the difference between the absorption of the starting material and of the product has its highest value.

[6/1128 *Received, 14th June, 1976*]