Addition of Hydrogen Cyanide to Benzylideneanilines. Oxidation Products

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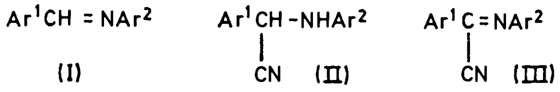
Substituted *p*-nitrobenzylideneanilines (I) react with hydrogen cyanide in methanol by consuming an equivalent amount of oxygen to give the corresponding α-phenylimino-*p*-nitrobenzyl cyanides (III) in *ca.* 50% yields *via* α-anilino-*p*-nitrobenzyl cyanides (II). The other substituted benzylideneanilines give α-anilinobenzyl cyanides, but no dehydrogenation product was obtained. The reaction proceeds by consecutive pseudo-first-order steps (I) + HCN $\longrightarrow$ (II); (II) + O_2 $\longrightarrow$ (III). For the first step the polar effect is expressed as a ρ value of −1·60. The second step involves base-catalysed dehydrogenation by atmospheric oxygen with a ρ^+ value of −0·36. These results suggest a mechanism involving a hydrogen abstraction or an electron transfer from the conjugate base of (II).

Hydrogen cyanide adds in alcoholic solutions to substituted benzylideneanilines (I) to give generally the corresponding α-arylaminobenzyl cyanide (α-cyanobenzylanilines) (II), but the reaction with *p*-nitrobenzylideneaniline (I; $Ar^1 = p\text{-}NO_2{\cdot}C_6H_4$, $Ar^2 = Ph$) in air gave α-cyano-*p*-nitrobenzylideneaniline instead of α-cyano-*p*-nitrobenzylaniline.[1] Hence, the reaction must involve an oxidation. α-Aryliminobenzyl cyanides (α-cyanobenzylideneanilines) (III) can generally be prepared by the reaction of benzyl cyanides with nitrosobenzenes,[2] nitrones with hydrogen cyanide,[3] or benzyl halides, α-nitrotoluene, or benzylpyridinium salts with nitrosobenzenes and cyanide ion,[4] and by permanganate oxidation of the corresponding α-cyanobenzylanilines.[5]



$$Ar^1CH{=}NAr^2 \quad (I) \qquad \underset{\displaystyle CN}{Ar^1CH}{-}NHAr^2 \quad (II) \qquad \underset{\displaystyle CN}{Ar^1C}{=}NAr^2 \quad (III)$$

The present study was undertaken to obtain information on the scope and mechanism of the formation of compounds (III) from (I) on treatment with hydrogen cyanide.

RESULTS

Products in Methanolic Solution.—Hydrogen cyanide adds readily to a series of substituted benzylideneanilines (I) in methanolic solution at room temperature except for *p*-nitrobenzilideneanilines.[1] On the other hand, the reaction of (I; $Ar^1 = p\text{-}NO_2C_6H_4$) gives α-cyano-*p*-nitrobenzylideneanilines (III) in *ca.* 50% yield with minor amount of unidentified materials[†] (*ca.* 10%) of low solubility. Thus, the reaction of *p*-nitrobenzylidene-*p*-anisidine gave (III; $Ar^1 = p\text{-}NO_2C_6H_4$, $Ar^2 = p\text{-}MeOC_6H_4$) which was identified by its m.p., elemental analysis, n.m.r., u.v., and i.r. spectra. Signals assigned to CH and NH protons are absent from the n.m.r. spectrum. The u.v. spectrum with $\lambda_{max.}$ at 405 nm resembled that of (I) rather than (II), which has no absorption maximum at longer wavelength. Further, the product from *p*-nitrobenzylideneaniline has the structure (III; $Ar^1 = p\text{-}NO_2C_6H_4$, $Ar^2 = Ph$), which was prepared by the condensation of *p*-nitrobenzyl cyanide with nitrosobenzene, from its m.p. and u.v. spectrum (Table 1). The yields approach 50%.

In the reaction of *p*-nitrobenzylidene-*p*-toluidine with hydrogen cyanide in methanol under oxygen the molar ratio of consumed oxygen to the substrate was 0·97 ± 0·10. With *p*-chloro-(*p*-nitrobenzylidene)aniline the ratio was 0·99 and hydrogen peroxide formed was estimated by iodometry to be 0·66 mol. equiv.

Table 1

Formation and physical properties of α-cyano-*p*-nitrobenzylidenearylamines (III; $Ar^1 = p\text{-}NO_2C_6H_4$)

				Electronic spectrum in $CHCl_3$			
				K band		E_2 band	
(III)	Substituent in Ar^2	M.p./°C	Yield (%)	$\lambda_{max.}$/nm	$10^{-4}\varepsilon$ / l mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$10^{-4}\varepsilon$ / l mol^{-1} cm^{-1}
a	*p*-MeO	149—151	50	416	1·44	288	1·25
						270	1·35
b	*p*-Me	120—123	63	394	1·11	288	1·80
c	H	126—127·5	64	380	0·73	287	1·81
d	*p*-Cl	135—136·5	50	387	0·89	287	1·78
e	*p*-Br	149—151	52	387	0·96	286	1·89
f	*m*-Cl	120—122	52	376	0·64	286	1·93
g	*m*-NO_2	164·5—168·5	(11) *	360	0·66	283	2·44
h	Ar^2 = β-Naphthyl	163·5—165·5		406 †	0·64	281 †	2·14

* By-product in the preparation of (IIg). † Data for methanol solution.

[†] These materials were believed to be nitrones of (III) because of the m.p. (*ca.* 250 °C), the i.r. spectra (ν_{CN} *ca.* 2200 cm^{-1}), and the strong absorptions at longer wavelength (*ca.* 400 nm) (ε *ca.* 2 × 10^4) and weak ones at *ca.* 280 nm (ε *ca.* 10^4).

[1] Y. Ogata and A. Kawasaki, *J. Chem. Soc.* (*B*), 1971, 325.

[2] F. Kroehnke, *Ber.*, 1938, **71**, 2583.

[3] F. Sachs, *Ber.*, 1901, **34**, 500; V. Bellavita, *Chem. Abs.*, 1941, **35**, 2127.

[4] J. W. Ledbetter, D. N. Kamer, and F. M. Miller, *J. Org. Chem.*, 1967, **32**, 1165; F. Kroehnke and H. H. Steuernagel, *Chem. Ber.*, 1963, **96**, 494; J. Michaelsky, *J. prakt. Chem.*, 1959, **8**, 186.

[5] F. Sachs and W. Whittacker, *Ber.*, 1902, **34**, 501.

Products in the Absence of Oxygen.—The reaction of some *p*-nitrobenzylideneanilines (I; $Ar^1 = p\text{-}NO_2C_6H_4$; $Ar^2 =$ Ph, $p\text{-}MeOC_6H_4$, or $\beta\text{-}C_{10}H_7$) with hydrogen cyanide in degassed methanol under nitrogen afforded a mixture of normal adducts (II) and their dehydrogenation products (III). Adduct (II) in solution was spontaneously oxidised on exposure to air, giving (III) (Table 2). The adducts (II) were identified by their m.p., i.r. spectra (ν_{NH} *ca.* 3350 cm^{-1}), n.m.r. spectra (τ_{OH} *ca.* 4·5; τ_{NH} *ca.* 6·0), u.v. spectra ($\lambda_{max.}$ *ca.* 240 nm), and elemental analysis. The yields are rather low (*ca.* 45%).

TABLE 2

Formation and physical properties of α-cyano-*p*-nitrobenzylanilines (II; $Ar^1 = p\text{-}NO_2C_6H_4$)

(II)	Substituent in Ar²	M.p./°C	Yield (%)	$\lambda_{max.}$/nm
a	*p*-MeO	122—123	34	241
b	*p*-Me			244 *
c	H	112—115	45	242
d	*p*-Cl	(99—120) †	(45)	250 *
e	*p*-Br	(107—150) †	(44)	253 *
f	*m*-Cl	(92—110) †	(24)	248 *
g	*m*-NO_2	132—135	17	
h	Ar² = β-Naphthyl	143—146	45	230
i	*p*-MeO ‡	74—76	39	241

* The value is based on the kinetic runs. † Contaminated with the oxidation product (III) which could not be separated. ‡ Ar¹ = *m*-Nitrophenyl.

Change in the U.v. Spectra; Kinetics.—In the reaction of *p*-nitrobenzylideneaniline (10^{-4}M) with hydrogen cyanide (0·16M) in methanol at 20 °C the maximum extinction at 340 nm decreases at first and the extinction at maximum of 370 nm increases gradually. The primary stage has an isosbestic point at 265 nm and the secondary stage at 271 nm. Hence the reaction is consecutive; the primary change corresponds to the formation of (II) ($\lambda_{max.}$ 242 nm) and the secondary one to the formation of (III) ($\lambda_{max.}$ 283 and 375 nm). Analogous changes in the u.v. spectra during the reaction with other substrates were observed in harmony with the intermediary formation of (II). Since only the addition depends on the concentration of hydrogen cyanide,[1] the rate constants for addition (k_1) and oxidation (k_2) can be evaluated separately in the presence of excess of hydrogen cyanide, *i.e.*, k_1 can be determined by initial decrease in *p*-nitrobenzylideneaniline at 340 nm and k_2 by final increase in α-cyano-*p*-nitrobenzylideneaniline at 380 nm. The rate data are in Table 3. The pseudo-first-order rate constant for addition, k_1, showed first-order dependence on the concentration of hydrogen cyanide, hence the rate of addition can be expressed as (1), as with other benzylideneanilines.[1] The rate of oxidation followed a pseudo-first-order equation (2). The concentration of oxygen dissolved

$$-d[(I)]/dt = k_1[(I)] = k[(I)][HCN] \quad (1)$$

$$d[(III)]/dt = k_2[(II)] \quad (2)$$

in methanol at 20 °C, calculated to be *ca.* 2×10^{-3}M from its solubility data is in large excess over that of the substrate (*ca.* 10^{-4}M). Therefore, the pseudo-first-order rate equation for the oxidation is reasonable.

Hammett ρ values for *p*-nitrobenzylidenearylamines were obtained to be −1·60 (σ) (correlation coefficient $r = 0·993$) for k_1/[HCN] and −0·36 (σ^+)[6] ($r = 0·979$) for k_2. In the latter case the correlation with σ is much less satisfactory. The k_2 values for the *p*-chloro-substituent show a positive deviation from the Hammett plot. If this is excluded, the correlation with σ^+ gives a ρ value of −0·38 with $r = 0·999$.

TABLE 3

Rate constants for the addition (k_1) and the oxidation (k_2) in methanol at 20 °C

Substituent in		k_1/[HCN]	
Ar¹	Ar²	l mol^{-1} min^{-1}	10^2k_2/min^{-1}
p-NO_2	*p*-OMe	0·51 ± 0·06	2·1
p-NO_2	*p*-Me	0·42 ± 0·01	1·44
p-NO_2	H	0·185 ± 0·002	1·06
p-NO_2	*p*-Cl	0·093 ± 0·002	1·16
p-NO_2	*p*-Br	0·071 ± 0·004	
p-NO_2	*m*-Cl	0·054 ± 0·001	0·75
m-NO_2	*p*-OMe	0·53 —	
ρ		−1·60 (σ)	−0·36 (σ^+)
r		0·993	0·979 *

* Except for *p*-chloro-substituent, ρ = −0·38 (σ^+) with $r = 0·999$.

Oxidation of α-Cyanobenzylanilines.—While isolated α-cyano-*p*-nitrobenzylanilines (II; $Ar^1 = p\text{-}NO_2{\cdot}C_6H_4$) is easily oxidised on dissolution in methanol, α-cyanobenzylanilines (II; $Ar^2 \neq p\text{-}NO_2{\cdot}C_6H_4$) could not be oxidised under similar conditions. Thus, α-cyano-*p*-chlorobenzyl-*p*-toluidine, α-cyano-*p*-methylbenzylaniline, and α-cyanobenzyl-*p*-anisidine were not oxidised in methanolic solution even in the presence of a small amount of potassium hydroxide, *p*-nitrotoluene, or *m*-dinitrobenzene which might act as an electron acceptor. In the case of α-cyanobenzyl-*p*-anisidine benzylidene-*p*-anisidine was isolated [reaction (3)].

α-Cyano-*m*-nitrobenzyl-*p*-anisidine was little oxidised in an equimolar mixture with α-cyano-*p*-nitrobenzyl-*p*-anisidine (IIa). However, α-cyano-*m*-nitrobenzyl-*p*-anisidine was oxidised in the presence of potassium hydroxide to give *N*-(*p*-methoxyphenyl)-*m*-nitrobenzamide but not α-cyano-*m*-nitrobenzylidene-*p*-anisidine [equation (4)].

$$PhCH(CN){\cdot}NHC_6H_4OMe\text{-}p \xrightarrow{KOH} PhCH{=}N{\cdot}C_6H_4OMe\text{-}p \quad (3)$$

$$m\text{-}NO_2C_6H_4CH(CN){\cdot}NH{\cdot}C_6H_4OMe\text{-}p \xrightarrow{KOH} m\text{-}NO_2C_6H_4{\cdot}CONH{\cdot}C_6H_4OMe\text{-}p \quad (4)$$

A methanolic solution of α-hydroxy-*p*-nitrobenzyl cyanide $p\text{-}NO_2{\cdot}C_6H_4{\cdot}CH(CN)OH$, was prepared from the reaction of the aldehyde and hydrogen cyanide, resulted in the isolation of *p*-nitrobenzaldehyde dimethyl acetal alone. *p*-Nitrobenzyl cyanide also was not oxidised, as observed by Russell and his collaborators.[7]

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[6] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, 1958, **80**, 4979.

[7] G. A. Russell, A. J. Moye, and K. Nagpal, *J. Amer. Chem. Soc.*, 1962, **84**, 4154; G. A. Russell and E. G. Janzen, *ibid.*, p. 4153; G. A. Russell and R. C. Williamson, jun., *ibid.*, 1964, **86**, 2357.

Base Catalysis.—Oxidation of α-cyano-*p*-nitrobenzylaniline is subject to base catalysis by potassium hydroxide or triethylamine. The rate of reaction increased with an increase of base concentration, but the catalysis is more remarkable than expected from the first-order dependence on the base concentration. This complexity is probably due to carbon dioxide dissolved in methanol (*ca.* 10^{-4}M). This assumption is consistent with the fact that the rate of oxidation is much more rapid in absolute methanol dried (over Mg) and distilled. Hydrochloric acid retarded the oxidation.

Ionisation of (II) was detected. On addition of potassium hydroxide the methanolic solution of *p*-nitrobenzyl cyanide became red. The colour is stable in air, indicating the ion

$p\text{-}NO_2\cdot C_6H_4\cdot \bar{C}HCN$ (IV)

$p\text{-}NO_2\cdot C_6H_4\cdot \bar{C}(CN)\cdot NHAr^2$ (V)

(IV). Addition of potassium hydroxide changed the colour of a methanolic solution of α-cyano-*p*-nitrobenzylaniline to yellow, *i.e.*, the colour of α-cyano-*p*-nitrobenzylideneaniline, through a transient red colour, suggesting rapid oxidation. On the other hand, the solution in degassed methanolic solution under nitrogen had the persistent red colour of (V) on addition of potassium hydroxide. This colour changed rapidly to yellow on exposure to air.

Table 4

Effect of potassium hydroxide on the rate of oxidation of α-cyano-*N*-(*p*-nitrobenzyl)-*p*-anisidine at 20 °C in undistilled methanol

10^4[KOH]/M	0·41	0·80	0·82	1·0	1·2
10^2k_2/min^{-1}	1·9	2·9	3·3	3·3	3·9
10^4[KOH]/M	1·6	2·4	3·3		
10^2k_2/min^{-1}	8·7	61	(170) *		

* Very rapid.

Reaction of α-Cyanobenzylideneanilines (III) *with Bases.*—The reaction of (III) with methanolic potassium hydroxide was carried out at room temperature. The reaction of α-cyano-*p*-nitrobenzylideneaniline with methanolic potassium hydroxide was found to afford methyl *N*-phenyl-*p*-nitrobenzimidate (VI) and the reaction with aqueous methanolic (1 : 4) potassium hydroxide to give *p*-nitrobenzanilide (VII). Neither hydrogen peroxide nor hydrogen cyanide reacted with α-cyano-*p*-nitrobenzylideneaniline even under basic conditions, where *p*-nitrobenzanilide was isolated in aqueous methanol.

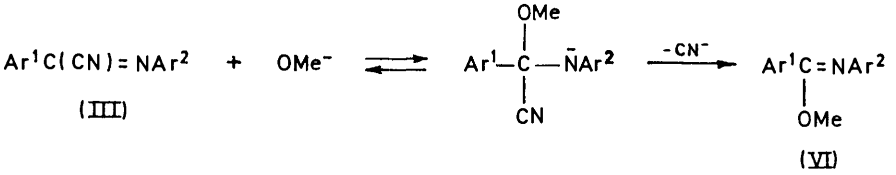
Effect of Additives on Oxidation.—Hydrogen peroxide and formaldehyde did not affect the oxidation of (II). *p*-Nitrotoluene and *m*-dinitrobenzene had virtually no effect on the rate of oxidation, nor did cupric chloride or sulphate if less than five mol. equiv. were added to the substrate.

DISCUSSION

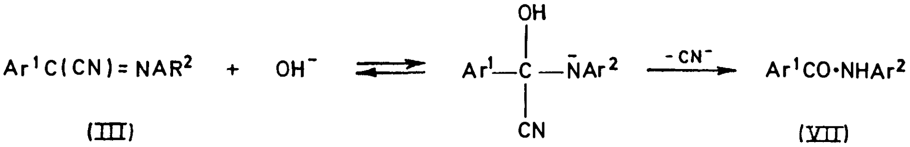
The results indicate a new simple route to α-cyanobenzylideneanilines (III). The reaction may proceed *via* consecutive steps, *i.e.*, addition of hydrogen cyanide to (I) giving α-cyanobenzylanilines (II), followed by spontaneous oxidation. This procedure at present is applicable only to *p*-nitrobenzylidene derivatives probably because the oxidation should require the deprotonation of intermediate (II) under neutral or weakly basic conditions, while the strongly basic conditions introduce subsequent reactions with bases resulting in amide or imidate formation. α-Cyano-*m*-nitrobenzylaniline and the other derivatives without a *p*-nitro-substituent are not oxidised under weakly basic conditions. Oxygen up to the amount equivalent to (I) is consumed during the reaction; at the same time, (II) and hydrogen peroxide are formed [reaction (7)].

$$(I) + HCN \xrightarrow{k_1} (II) \xrightarrow{O_2,\,k_2} (III) + H_2O_2 \qquad (7)$$

The reaction at high concentration of hydrogen cyanide proceeds by consecutive first-order steps.

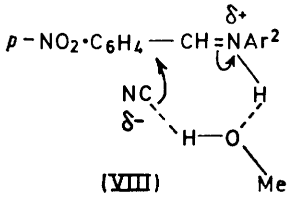


$$\underset{(III)}{Ar^1C(CN){=}NAr^2} + OMe^- \rightleftharpoons Ar^1\text{—}\overset{OMe}{\underset{CN}{C}}\text{—}\bar{N}Ar^2 \xrightarrow{-CN^-} \underset{(VI)}{Ar^1\underset{OMe}{C}{=}NAr^2} \qquad (5)$$



$$\underset{(III)}{Ar^1C(CN){=}NAR^2} + OH^- \rightleftharpoons Ar^1\text{—}\overset{OH}{\underset{CN}{C}}\text{—}\bar{N}Ar^2 \xrightarrow{-CN^-} \underset{(VII)}{Ar^1CO\cdot NHAr^2} \qquad (6)$$

Additions.—It is likely that the addition of hydrogen cyanide to (I) (first step) is acid-catalysed, since an electron-releasing group in the anilino-group increases the rate ($\rho = -1·60$) as in the case of other benzylideneanilines ($\rho = -1·39$) [1] and protic solvents increase the rate.[1] The data agree with the formation of the transition state (VIII), involving an attack of solvated cyanide ion on the conjugate acid of the Schiff bases.[1] A moderate negative ρ value may be due to the opposing effects of a large ρ value for the protonation equilibrium and a smaller positive ρ value for the rate of cyanide attack. An attack of cyanide ion on the more electrophilic *p*-nitrobenzylidene derivatives would be less sensitive to the polar effect, resulting in a little larger

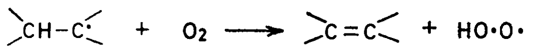


(VIII)

negative ρ value of −1·60 for the overall rate, compared with that of −1·39 for the other benzylidene derivatives.

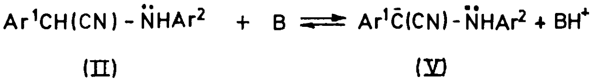
Oxidations.—A molecule of α-cyano-*p*-nitrobenzylanilines (II) reacts with a molecule of oxygen to give α-cyano-*p*-nitrobenzylideneanilines (III) and hydrogen peroxide, that is, dehydrogenation of (II) by molecular oxygen. Russell and his co-workers have studied the autoxidations of hydrocarbons [7] and their carbanions.[8,9] They suggested radical-chain mechanisms whose main steps are (8) and (9). Selection between reactions (8)

$$R\cdot + O_2 \longrightarrow RO\cdot O\cdot \qquad (8)$$

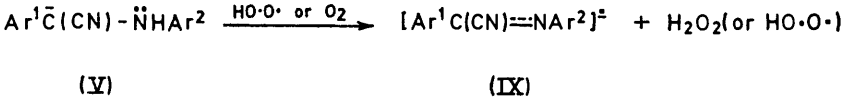


$$>CH-C< + O_2 \longrightarrow >C=C< + HO\cdot O\cdot \qquad (9)$$

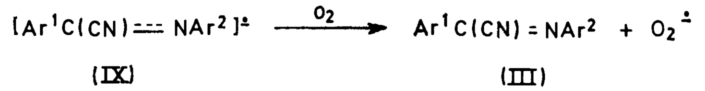
and (9) depends on the temperature, product stability, and oxygen pressure.[10] Reaction (9) is involved in oxidations such as those of cyclohexa-1,4-diene, dinitrobibenzyl, secondary alcohols, and tetraphenylethane.[10,11]



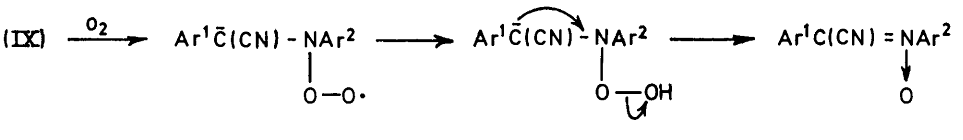
$$\underset{(\mathrm{II})}{Ar^1CH(CN)\text{-}\ddot{N}HAr^2} + B \rightleftharpoons \underset{(\mathrm{V})}{Ar^1\bar{C}(CN)\text{-}\ddot{N}HAr^2} + BH^+ \qquad (10)$$



$$\underset{(\mathrm{V})}{Ar^1\bar{C}(CN)\text{-}\ddot{N}HAr^2} \xrightarrow{HO\cdot O\cdot \text{ or } O_2} \underset{(\mathrm{IX})}{[Ar^1C(CN)\overset{\cdots}{=}NAr^2]^{\dot{-}}} + H_2O_2(\text{or } HO\cdot O\cdot) \qquad (11)$$



$$\underset{(\mathrm{IX})}{[Ar^1C(CN)\overset{\cdots}{=}NAr^2]^{\dot{-}}} \xrightarrow{O_2} \underset{(\mathrm{III})}{Ar^1C(CN)=NAr^2} + O_2^{\dot{-}} \qquad (12)$$



$$(\mathrm{IX}) \xrightarrow{O_2} \underset{\overset{|}{O-O\cdot}}{Ar^1\bar{C}(CN)\text{-}NAr^2} \longrightarrow \underset{\overset{|}{O-OH}}{Ar^1\bar{C}(CN)\text{-}NAr^2} \longrightarrow \underset{\overset{\downarrow}{O}}{Ar^1C(CN)=NAr^2} \qquad (13)$$

The present reaction belongs formally to type (9) because of the stability of (III). The observed base catalysis and a very rapid autoxidation of the conjugate base of (II) suggest that the anion is preferentially oxidised. The acidity of (II) may be similar to that of *p*-nitrobenzyl cyanide, which has pK_a *ca.* 11·5. The inertness for oxidation of *p*-nitrobenzyl cyanide or α-hydroxy-*p*-nitrobenzyl cyanide which have similar acidity suggests that the presence of the α-anilino-group in (II) is important for this oxidation. A probable scheme is as in reactions (10)—(12). The initiation is a hydrogen-atom abstraction or a one-electron transfer followed by deprotonation (11) from the nitrogen atom assisted by the α-carbanion and it should obey the ρσ$^+$ correlation, for it gives a species such as Ar$^1\bar{C}$(CN)–$\dot{N}$Ar^2 (IX) or Ar$^1\bar{C}$(CN)–$\overset{\cdot+}{N}$Ar^{2}H (IX + H$^+$). The hydrogen-atom abstraction seems more likely as in sequence (11) in view of small effect of the addition of *p*-nitroaromatic compounds [12] or cupric ions on the rate.

If an anion radical (IX) could couple with molecular oxygen, a cyano-nitrone would be formed as a minor product. Hence, the scheme (10)—(13) is compatible with the results.

The radical Ar$^1\dot{C}$(CN)–NHAr^2 might couple with molecular oxygen at the carbon atom to give a peroxy-radical or a hydroperoxide, followed by alcohol formation and subsequent dehydration to give (III). This is less plausible, since α-cyano-α-anilinobenzyl alcohol (X), once formed, would give the corresponding anilide under the present weakly basic conditions as observed [reaction (6)].

The overall rate of oxidation depends on the equilibrium concentration of (V) in reaction (10) as well as the rate of formation of (IX) in reaction (11). Substituents in the benzylidene ring chiefly affect the ionisation (10), while those in the anilino-ring principally step (11). Hydrogen abstractions by electrophilic radicals like

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[8] G. A. Russell and A. G. Bemis, *J. Amer. Chem. Soc.*, 1966, **88**, 5491.

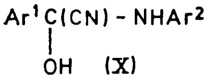
[9] G. A. Russell, A. J. Moye, E. G. Janzen, S. Mak, and E. R. Talaty, *J. Org. Chem.*, 1967, **32**, 137.

[10] G. A. Russell, 'Peroxide Reaction Mechanisms, ed. J. O. Edwards, Interscience, New York, 1962, p. 107.

[11] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 457.

[12] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Amer. Chem. Soc.*, 1965, **87**, 4520; G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, 1964, **86**, 1807.

Bu^{t}O· in the α-position to the phenyl group have been shown to have correlations with Brown's σ^+ parameter and rather small negative ρ values,[13,14] suggesting the contribution (XI) in the transition state. For example, $\rho = -0{\cdot}35$ (σ^+) for substituted toluenes,[14] $\rho = -0{\cdot}53$ (σ^+) for substituted ethylbenzenes,[15] and $\rho = -0{\cdot}74$, $-1{\cdot}49$ (σ^+) for substituted phenols,[16] while $\rho = -0{\cdot}41$ (σ) for the β-hydrogen abstraction of substituted anisoles.[17]



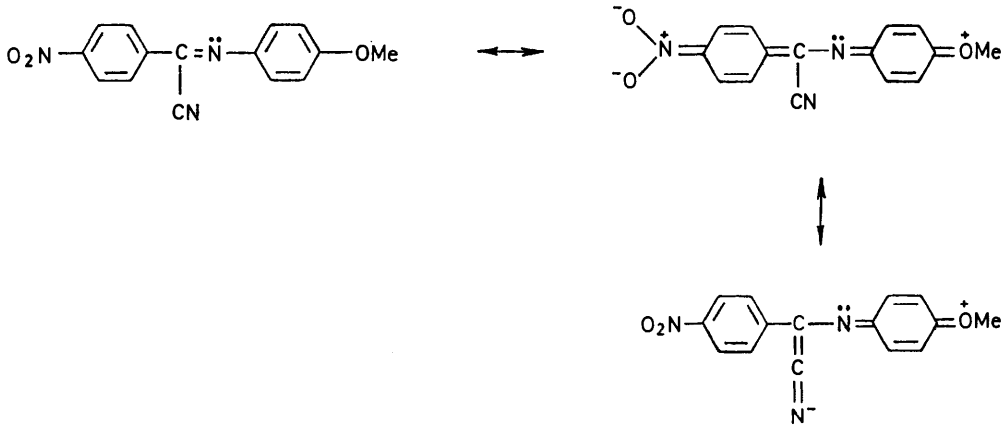
$$\mathrm{Ar^1C(CN)(OH){-}NHAr^2}\quad\text{(X)}$$

$$[\,\mathrm{R{:}H{\cdot}X} \longleftrightarrow \overset{+}{\mathrm{R}}{\cdot}\mathrm{H}{:}\overset{-}{\mathrm{X}} \longleftrightarrow \mathrm{R}{\cdot}\overset{\bullet}{\mathrm{H}}{\cdot}\mathrm{X}\,]$$

(XI)

The observed positive deviation for *p*-Cl from the Hammett plot has been reported for the hydrogen abstraction of phenols,[16] dibenzyl ethers,[18] and toluenes[19] and is ascribed to its radical-stabilising ability.

Electronic Spectra of (III).—The electronic spectra of (III) above 250 nm are composed of two bands corresponding to those of (I),[20] that is, the *K* band at *ca.* 400 nm and E_2 band at *ca.* 280 nm. The bathochromic shift in the *K* band of (III) compared with that of (I) may be due to the effect of the cyano-group[4] and a reduced intensity in the *K* band to non-planarity of (III) compared with (I).[20] It has been reported that the dihedral angle in (I) is *ca.* 60°, and is not affected by the substituents in benzylideneaniline.[20] However, conjugation between the benzylidene and the anilino-groups is important. As shown in Table 1, an electron-releasing group causes a bathochromic shift with an increase in intensity, which can be explained by increased conjugation between the benzylidene and the anilino-groups (XII). Thus, the ratio of the intensity of the E_2 band to that of the *K* band changed from 0·9 for *p*-MeO to 3·7 for *m*-NO_2 in the aniline ring. This might affect the dihedral angle.



(XII)

EXPERIMENTAL

The electronic spectra were recorded on a Hitachi spectrophotometer, model 124, the i.r. spectra on a Perkin-Elmer spectrophotometer, model 337, and n.m.r. spectra on a JEOL C-60HL spectrometer, with tetramethylsilane as an internal standard. A Hitachi photoelectric spectrophotometer, model EPU-2A, equipped with a cell compartment with circulating thermostatted water, was employed for the kinetic measurements.

Materials.—Substituted benzylideneanilines and a hydrogen cyanide solution were prepared as reported previously.[1] M.p.s are as follows: *p*-nitrobenzylidene-*p*-anisidine (Ia), 136—139 °C; *p*-nitrobenzylidene-*p*-toluidine (Ib), 125—127 °C; *p*-nitrobenzylideneaniline (Ic), 90—91 °C; *p*-chloro-(*p*-nitrobenzylidene)aniline (Id), 134—136 °C; *p*-bromo-(*p*-nitrobenzylidene)aniline (Ie), 164—166·5 °C; *m*-chloro-(*p*-nitrobenzylidene)aniline (If), 107—109 °C; *m*-nitro-(*p*-nitrobenzylidene)aniline (Ig), 154—156 °C; *p*-nitrobenzylidene-2-naphthylamine (Ih), 122—123 °C; *m*-nitrobenzylidene-*p*-anisidine (Ii), 82·5—83·5 °C.

p-*Nitro*-α-p-*tolyliminobenzyl Cyanide* (IIIb).—*Procedure A*. To a solution of (Ib) (1·0 g, 4·2 mmol) in methanol–chloroform (100 ml–30 ml) in a 500 ml flask equipped with a gas burette was added a 4·5M-hydrogen cyanide solution (4·0 ml, 18 mmol). The apparatus was filled with oxygen and the solution was stirred magnetically at 20 °C. After 24 h the absorption of oxygen (90 ml, 4·1 mmol) had stopped. A small amount of precipitate was filtered off and a part of the filtrate (20 ml) was poured into water (20 ml). After extraction with chloroform (20 ml) the aqueous layer was used to detect hydrogen peroxide by iodometry. The crude product (0·45 g, 53%) obtained

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[13] H. Sakurai and K. Tokumaru, 'Chemistry of Free Radicals,' Nankodo, Tokyo, 1967, p. 359.

[14] H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, 1967, **89**, 458.

[15] E. P. Chang, R. L. Huang, and K. H. Lee, *J. Chem. Soc.* (*B*), 1969, 878.

[16] K. U. Ingold, *Canad. J. Chem.*, 1963, **41**, 2816; J. A. Howard and K. U. Ingold, *ibid.*, p. 1744.

[17] H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, 1970, **35**, 993.

[18] R. L. Huang and O. K. Yeo, *J. Chem. Soc.*, 1959, 3190.

[19] K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1960, 1446.

[20] V. I. Minkin, Y. A. Zhdanov, E. A. Medyantseva, and Yu. A. Astroumov, *Tetrahedron*, 1967, **23**, 3651.

from another part of the filtrate and recrystallisation from methanol, gave pure *compound* (IIIb) (0·34 g, 42%), m.p. 120—123 °C (Found: N, 15·6. $C_{15}H_{11}N_3O_2$ requires N, 15·8%). Compounds (IIId—f) were obtained similarly.

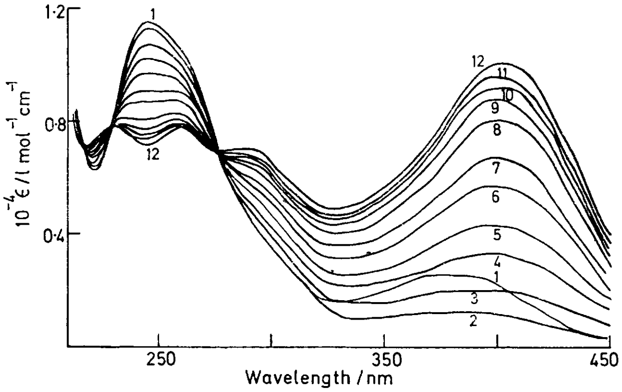
α-p-*Chlorophenylimino*-p-*nitrobenzyl Cyanide* (IIId).—According to procedure A (Id) (0·97 g, 3·8 mmol) was made to react with hydrogen cyanide with absorption of oxygen (84 ml, 3·75 mmol) at 20 °C for 44 h. The solution was filtered and poured into water (100 ml). After extraction with chloroform (80 ml and 3 × 20 ml), hydrogen peroxide in the aqueous layer was estimated by iodometry to be 2·5 ± 0·1 mmol [66% based on (I)]. The chloroform solution gave 0·67 g of crude *product* (69%). On recrystallisation from ethanol it had m.p. 135—136·5 °C (Found: N, 14·6. $C_{14}H_8ClN_3O_2$ requires N, 14·7%).

α-p-*Methoxyphenylimino*-p-*nitrobenzyl Cyanide* (IIIa).—*Procedure B. p*-Nitrobenzylidene-*p*-anisidine (Ia) (1·0 g, 3·9 mmol) was made to react with stirring with excess of hydrogen cyanide in methanol under air. After 24 h the solution was evaporated to give the *product*. Recrystallisation from ethanol gave pure (IIId) (0·57 g, 50%), m.p. 149—151 °C (Found: N, 15·1. $C_{15}H_{11}N_3O_3$ requires N, 14·9%), τ ($CDCl_3$) 1·74 (4H, $NO_2C_6H_4$), 2·70 (2H, *meta* to OMe), 3·20 (2H, *ortho* to OMe), and 6·17 (3H, OMe).

α-p-*Methoxyanilino*-p-*nitrobenzyl Cyanide* (IIa).—A chloroform solution (7 ml) of *p*-nitrobenzylidene-*p*-anisidine (Ia) (0·512 g, 2 mmol) and a methanolic solution of hydrogen cyanide (15 mmol, 3 ml) were placed in a flask with separate compartments, degassed, and mixed under nitrogen. The mixture after 3 h at 20 °C gave 0·19 g (34%) of (IIa), m.p. 122—123 °C, $\nu_{max.}$ (KBr) 3360 (NH), 1510 (NO_2), 1340 (NO_2), 1240 (C–O–C), and 825 (1,4-disubstituted benzene) cm^{-1}, τ ($CDCl_3$) 1·82 (2H, *ortho* to NO_2), 2·30 (2H, *meta* to NO_2), 3·31 (4H, $MeOC_6H_4$), 4·60 (1H, =CH), and 6·33 (4H, NH and OMe). From the filtrate 0·11 g (24%) of (IIIa) was obtained, m.p. 149—153 °C. Other adducts were prepared similarly as described: α-anilino-*p*-nitrobenzyl cyanide (IIc), (45%), $\nu_{max.}$ (KBr) 3335 (NH), 1510 (NO_2), 1340 (NO_2), 840 (1,4-disubstituted benzene), and 785 and 696 (phenyl) cm^{-1}, τ ($CDCl_3$) 1·80 (2H, *ortho* to NO_2), 2·25 (2H, *meta* to NO_2), and 2·6—3·5 (5H, Ph) [compound (IIIc) was obtained as a by-product, m.p. 127·5—132 °C]; α-2-Naphthylamino-*p*-nitrobenzyl cyanide (IIh), (45%), $\nu_{max.}$ (KBr) 3380 (NH), 1520 (NO_2), 1340 (NO_2), and 830 (1,4-disubstituted benzene) cm^{-1}, τ ($CDCl_3$) 1·75 (2H, *ortho* to NO_2), 2·22 (2H, *meta* to NO_2), 1·8—3·2 (7H, $C_{10}H_7$), 4·4 (1H, =CH), and 5·8 (1H, NH). In addition (IIIh) (20%) was obtained from the filtrate and had m.p. 163·5—165·5 °C, τ ($CDCl_3$) 1·70 (4H, $NO_2C_6H_4$) and 2·0—2·7 (7H, $C_{10}H_7$).

Attempted Oxidation of α-p-*Methoxyanilino*-m-*nitrobenzyl Cyanide* (IIg).—A methanolic solution (100 ml) of (IIg) (0·15 g) was stirred for 24 h in the presence of potassium hydroxide (0·15M). The solution was poured into water. Extraction with ether and evaporation gave yellow needles of *N*-(*p*-methoxyphenyl)-*p*-nitrobenzamide, m.p. 179—181 °C. In the absence of potassium hydroxide (IIi) was recovered. α-Cyano-*p*-chlorobenzylaniline was unchanged under the same conditions. No α-cyanobenzylidene-*p*-anisidine was obtained from the methanolic solution of α-cyanobenzyl-*p*-anisidine (0·2 g) containing *p*-nitrotoluene (0·02 g) in ten days. Instead, benzylidene-*p*-anisidine was obtained, m.p. 66—70 °C.

Reaction of Compound (IIIc) *with Potassium Hydroxide*.—A methanolic solution (100 ml) of (IIIc) (0·5 g) was made to react with potassium hydroxide (0·8 g) at 30—40 °C for 1·5 h. Addition of water and extraction with chloroform gave 0·3 g (60%) of yellow liquid methyl *N*-phenylbenzimidate, $\nu_{max.}$ (film) 1660 (C=N), 1520 and 1350 (NO_2), 2825 (OCH_3), 850 (1,4-disubstituted benzene), and 695 and 735 (phenyl) cm^{-1}. A similar reaction in aqueous methanol (1 : 4 v/v) gave 0·11 g (23%) of *p*-nitrobenzanilide, m.p. 214—216·5 °C.



U.v. spectral study of the reaction of (Ia) with hydrogen cyanide in undistilled methanol. $[(Ia)]_0 = 0·67 \times 10^{-4}$M. $[HCN]_0 =$ 1·5M. Curve 2 corresponds to (IIa) and curve 12 to (IIIa); curve 1, 1 min; curve 2, 5 min; curve 5, 25 min; curve 10, 90 min; curve 12, 1200 min

Reaction of Compound (IIIc) *with Hydrogen Peroxide*.—Hydrogen peroxide (60%, 0·5 ml) was added to the solution of (IIIc) (0·36 g) in methanolic potassium hydroxide (0·01 g). During 6 h the u.v. spectrum did not change. Further addition of methanolic potassium hydroxide (0·01 g) gave 0·05 g (15%) of *p*-nitrobenzanilide, m.p. 214—216 °C. In the absence of base the substrate was unchanged.

Kinetic Measurements.—The reaction was followed by the procedure described previously.[1] The rate of addition of hydrogen cyanide was followed spectrophotometrically by a decrease in [(I)] (at *ca*. 340 nm) and the rate of oxidation by an increase in [(III)] (at *ca*. 380 nm). Pseudo-first-order rate constants (k_1 and k_2) were calculated.

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