Comparative Reactivity of Substituted 4-Nitrobenzylidene Dichlorides with Alkali

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A comparative study of the reactions of substituted 4-nitrobenzylidene dichlorides $ArCHCl_2$ ($Ar = 3-Cl-4-NO_2C_6H_3$, $2-Cl-4-NO_2C_6H_3$, $4-NO_2C_6H_4$, $3,5-Me_2-4-NO_2C_6H_2$, and $2-Me-4-NO_2C_6H_3$) with aqueous alcoholic alkali shows that chlorine substitution enhances the electron-transfer-radical mechanism, whereas methyl substitution favours the solvolysis pathway. Changes in reactivity and mechanism are discussed.

THE reactions of 4-nitrobenzyl chloride and other structural analogues with base have been the subject of several studies.¹⁻¹⁰ Compelling evidence ^{1,9,11} has been accumulated to show that the reactions of many 4nitrobenzyl derivatives with base are radical in nature. In the simple reaction of 4-nitrobenzyl chloride with sodium hydroxide it was demonstrated 1,2 that $\alpha \text{-}$ elimination did not occur but rather nitrobenzylic radicals were involved in the formation of dimeric products. A similar mechanism has been shown ¹¹ to operate for the reaction of 4-nitrobenzylidene dichloride with sodium hydroxide. Interest in these and related systems has continued unabated.¹¹⁻¹⁵ Recently kinetic studies 16,17 of the reaction of 4-nitro- and 4,4'-dinitrobenzhydryl chlorides have appeared. Our earlier studies ^{10,11} on 4-nitrobenzylidene dichloride have prompted us to examine further the scope of this reaction involving simple nuclear substituted derivatives, the results of which are now reported.

RESULTS AND DISCUSSION

A number of substituted 4-nitrobenzylidene dichlorides (1a---d) were prepared for this study from the corresponding aldehydes. With the exception of 2-methyl-4-nitrobenzaldehyde, these aldehydes could readily be obtained by the chromium trioxide oxidation of the appropriately substituted nitrotoluenes. Oxidation of 2-methyl-4-nitrotoluene gave a mixture of two methylnitrobenzaldehydes, the major one being 2methyl-5-nitrobenzaldehyde. The desired 2-methyl-4nitrobenzaldehyde could be synthesized from 2-methyl-4nitrobenzyl bromide in reasonably good yields by the Sommelet reaction ¹⁸ or by reaction with p-nitrosodimethylaniline hydrochloride.¹⁹

 $\begin{array}{c} {\rm ArCHCl}_2 \\ (1) \\ {\rm a}; \ {\rm Ar} = {\bf 3}, {\rm 5-Me}_2 {\rm -4-NO}_2 {\rm C}_6 {\rm H}_2 \\ {\rm b}; \ {\rm Ar} = {\rm 2-Me} {\rm -4-NO}_2 {\rm C}_6 {\rm H}_3 \\ {\rm c}; \ {\rm Ar} = {\rm 3-Cl} {\rm -4-NO}_2 {\rm C}_6 {\rm H}_3 \\ {\rm d}; \ {\rm Ar} = {\rm 2-Cl} {\rm -4-NO}_2 {\rm C}_6 {\rm H}_3 \end{array}$

The reactions of the nitrobenzylidene dichlorides (la—d) with sodium or potassium hydroxide were carried out under an atmosphere of nitrogen, since traces of oxygen are known to adversely affect the reactions of

these and other closely related compounds.^{2,11} Among the compounds (1a—d) studied it was found that the methyl-substituted derivatives (1a and b) were fairly unreactive; reactions with 2.4M potassium hydroxide in 95% methanol took *ca*. 5 days at 50 °C to complete. On the other hand the chloro-substituted derivatives (1c and d) were relatively more reactive, being of comparable reactivity to the parent 4-nitrobenzylidene dichloride. Differences in reactivity were also reflected in the reaction products, these being either dimers or simply aldehydes and acetals arising from solvolysis. The two reaction pathways are depicted below.

$$ArCHCl_{2} + OH^{-}-MeOH -$$

$$(1a-d)$$

$$ArCCl_{2} + OH^{-}-MeOH -$$

$$ArCCl_{2} + OH^{-}-MeOH -$$

$$ArCCl_{3} + ArC = CAr$$

$$[from (1c and d)]$$

The reaction products from chloronitrobenzylidene dichlorides (1c and d) were a mixture of dimers and had to be separated by column chromatography before identification by ¹H n.m.r. and mass spectroscopy. Table 1 shows the dimeric products (2) - (5) which were

TABLE 1
¹ H N.m.r. spectra ^a of dimeric products

		-		-				
		δ						
Com-								
pound	m.p. (°C)	2-H	6-H	3-H	5-H			
(<i>E</i>)-(4b)	185 - 186		7.64 (d)	8.40 (d)	8.25 (dd)			
(Z) - (3b)	182 - 183		7.44 (d)	8.19 (d)	7.98 (dd)			
(5b)	202 - 203		7.77 (d)	8.37 (d)	8.16 (dd)			
(E)-(4a)	196 - 198	7.78 (d)	7.60 (dd)		7.96 (d)			
(Z)-(3a)	1 7818 0	7.50 (d)	7.16 (dd)		7.74 (d)			
(5a)	198	7.69 (d)	7.50 (dd)		7.89 (d)			
(2)	187	7.81 (br s ^b)	7.81 (br s ^b)		7.91 (br s ^b)			

^a 60-MHz N.m.r. spectra in CDCl₃ solutions, δ downfield from internal SiMe₄. ^b The AA'B system appears as two broad singlets in the 60-MHz spectrum.

isolated and characterised. The geometric isomers (3) and (4) were distinguished by differences in their ¹H n.m.r. spectra; the protons of the Z-isomers (3) absorb at higher field than those of the E-isomers (4). This is characteristic of stilbene derivatives, where there is considerable anisotropic effect of the aromatic rings on each other in the *cis* configuration.^{1,20} Empirically the assignments are also verified by the melting-point data,

where *trans*-isomers generally are found to melt at higher temperatures than the *cis*-compounds.

The distribution of reaction products is summarised in Table 2 where it may be seen that, except for the methylsubstituted derivatives (la and b), which gave mainly solvolysis products, the others furnished essentially dimeric-type products. Although the reaction conditions may not be exactly the same in view of slight differences in reactivity among 4-nitrobenzylidene dichloride and the chloro-substituted derivatives (lc and d), the close similarity of the products is indicative that a similar mechanistic pathway must be responsible for their formation. It may be pointed out that minor differences in the products do occur; the most conspicuous result comes from the reaction of 2-chloro-4-nitroless reactive than (1c) and a prolonged reaction time was required. Thus, even if a dimeric product of type (2) was formed it could be consumed in further reactions, especially if it happens to be soluble in the solvent. The distribution of products from the reaction of 3-chloro-4nitrobenzylidene dichloride (1c) parallels closely that of the parent 4-nitrobenzylidene dichloride. In the series of compounds studied, (1c) was the most reactive being about ten times more reactive than 4-nitrobenzylidene dichloride.

The reactions of (1c) and (1d) fit well into the mechanistic scheme involving carbanion formation, electron transfer, and radical coupling, as shown below. Dimeric products can be expected to predominate once radicals ArCHCl and ArCCl₂ are generated. The formation of

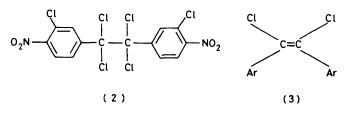
TABLE 2

Percentage product ^a distribution in the reactions of substituted 4-nitrobenzylidene dichloride ArCHCl₂

	(E)-ArCCl=	(Z)-ArCCl=	1.0701	ArCCl ₂ -		
Ar	CClAr	CClAr	ArC≡CAr	CCl ₂ Ar	ArCH ₂ Cl ^b	∘ ArCHO
$3-Cl-4-O_2NC_6H_3$	26	16	6	31	14	
$4-O_{2}NC_{6}H_{4}$	22	16	12	34	12	
$2-Cl-4-O_2NC_6H_3$	28	26	20	d		2
$3,5-Me_2-4-O_2NC_8H_2$						>95%
$2-Me-4-O_2NC_6H_3$						> 95%
		0.0/ 1./*		1 1 07101	(TD)	

^{*a*} All reactions were carried out to 95–99% completion and yields are based on ArCHCl₂. The reactions of the chloronitrobenzylidene dihalides were conducted in aqueous ethanol and the rest in aqueous methanol. ^{*b*} Yield given includes $ArCH_2OEt$ or $ArCH_2OMe$ derived by reaction with solvent. ^{*c*} Yield given includes $ArCH(OMe)_2$ or $ArCH(OEt)_2$. ^{*d*} 3% $ArCO_2Et$.

benzylidene dichloride (1d). Firstly, a tetrachloroethane dimer similar to (2) was not found. Secondly, 2-chloro-4-nitrobenzyl chloride was not detected, whereas the corresponding derivatives were readily detectable in



a; Ar = $3 - Cl - 4 - O_2NC_6H_3$ b; Ar = $2 - Cl - 4 - O_2NC_6H_3$



a;
$$Ar = 3 - Cl - 4 - O_2 NC_6 H_3$$

b; $Ar = 2 - Cl - 4 - O_2 NC_6 H_3$
b; $Ar = 2 - Cl - 4 - O_2 NC_6 H_3$
b; $Ar = 2 - Cl - 4 - O_2 NC_6 H_3$

the other two reactions. Instead, it was observed that noticeable quantities of S_N reaction products, *i.e.* aldehyde and acetal, were obtained. Part of the reason must be due to the fact that compound (1d) is relatively

ArCH₂Cl or its solvolysis derivative ArCH₂OMe, however, is not so obvious. This is explained in the scheme as arising from hydrogen donation of ArCHCl₂ to ArCHCl. An alternative pathway could be by a carbanion interchange of ArCCl₂ with ArCHCl₂ to ArCCl₃ and ArCHCl, a process which may not be likely from thermodynamic considerations. The former pathway is more attractive since it shows that there is an excess of ArCCl₂ over ArCHCl radicals and this would account for the significant amounts of the dimer (2). This dimer, however, was absent in the reaction of 2-chloro-4-nitrobenzylidene dichloride (1d). Although no detailed experimental studies were made, it may be surmised that this dimeric product could have been further solvolysed by the solvent, since in comparison to the other 3-chlorosubstituted derivative (1c), (1d) was much more unreactive requiring prolonged reaction times. Further-

$$\begin{array}{c} \operatorname{ArCHCl}_{2} + \operatorname{OH}^{-} \rightleftharpoons \operatorname{ArCCl}_{2} + \operatorname{H}_{2}\operatorname{O} \\ \operatorname{ArCCl}_{2} + \operatorname{ArCHCl}_{2} \twoheadrightarrow \operatorname{ArCCl}_{2} + \operatorname{ArCHCl}_{2}^{-} \\ \operatorname{ArCHCl}_{2}^{-} \dashrightarrow \operatorname{ArCHCl} + \operatorname{Cl}^{-} \\ \operatorname{ArCCl}_{2} + \operatorname{ArCHCl} \longrightarrow \xrightarrow{\operatorname{OH}^{-}} \operatorname{ArCCl}_{2} \\ \operatorname{CCl}_{2} \longrightarrow \operatorname{ArCCl}_{2} \\ \operatorname{CCl}_{2} \longrightarrow \operatorname{ArCCl}_{2} \\ \operatorname{CCl}_{2} \operatorname{ArC} \\ \operatorname{ArCHCl} \longrightarrow \xrightarrow{\operatorname{OH}^{-}} \operatorname{ArC}_{2} \\ \operatorname{ArCHCl} + \operatorname{ArCHCl}_{2} \longrightarrow \operatorname{ArCH}_{2} \\ \operatorname{CL}_{2} \operatorname{ArCHCl}_{2} \\ \operatorname{ArCHCl}_{2} \xrightarrow{} \operatorname{ArCHCl}_{2} \\ \operatorname{ArCHCl}_{2} \\ \operatorname{ArCHCl}_{2} \\ \operatorname{ArCHCl}_{2} \xrightarrow{} \operatorname{ArCHCl}_{2} \\ \operatorname{ArCHCl}_{2$$

more 3% ethyl 2-chloro-4-nitrobenzoate, which can arise by base-initiated solvolytic cleavage of the dimer (2), was isolated.

The present results demonstrate that slight changes in steric and electronic factors can alter the course of the base-induced reactions of substituted 4-nitrobenzylidene dichlorides. Although the 4-nitro-substituent is an important requisite for the radical pathway, further methyl substitution can suppress this reaction in favour of the $S_N 2$ reaction. An important step in the radical reaction is the electron-transfer step from carbanion ArCCl₂ to the acceptor molecule ArCHCl₂. Methyl substitution appears, by a combination of steric and electronic effects, to depress carbanion formation and decrease the electron-acceptor property of ArCHCl₂; the reaction therefore becomes dominated by S_N solvolysis. Similar observations have also been reported ²¹ in the effect of methyl substitution on the reactivity of 4nitrobenzyl chloride. Chlorine substitution, however, is very favourable, particularly in the 3-position. An electron-withdrawing group at this position enhances the electron-acceptor property of the molecule, which is conducive to both carbanion formation as well as electron transfer. Chlorine substitution at the 2-position appears to exert a slightly unfavourable steric effect on the carbanion and radical centre, resulting in the observed lower reactivity.

The present results confirm the view ^{1,2,5-11} that the radical mechanism is important in the reactions of 4nitrobenzylic derivatives in the presence of base. Electron-withdrawing and radical-stabilizing groups will favour this mechanistic pathway, although the competing substitution pathway can still remain significant, especially in the presence of nucleophilic solvents.

EXPERIMENTAL

¹H N.m.r. spectra were obtained with a Perkin-Elmer Hitachi R20 60-MHz spectrometer. Electron-impact mass spectra and gas chromatography-mass spectrometry (g.c.m.s.) were recorded on an AEI MS3074 mass spectrometer.

Preparation of Substituted Nitrobenzaldehydes.—The synthesis of 3,5-dimethyl-4-nitrobenzaldehyde by the chromium with p-nitrosodimethylaniline hydrochloride,¹⁹ in 34 and 35% yield, respectively.

Preparation of Substituted 4-Nitrobenzylidene Dichlorides.—The reaction of the aldehydes prepared above with a 20% molar excess of phosphorus pentachloride at 90—100 °C for 6 h, followed by quenching in ice, provided the crude nitrobenzylidene dichlorides. Recrystallization from ethanol usually gave the pure products (see Table 3). The more reactive 3-chloro-4-nitrobenzylidene dichloride also solvolyses to some extent in ethanol; to avoid this the product was purified by distillation under reduced pressure to yield a light yellow liquid; m/e 239 $(M^+, 19\%)$, 204 (100), 174 (15), 146 (13), and 123 (35) (Found: M^+ , 238.928, C₇H₄Cl₃-NO₂ requires M, 238.931).

Reactions of 3,5-Dimethyl-4-nitrobenzylidene and 2-Methyl-Dichlorides .--- 3.5-Dimethyl-4-nitro-4-nitrobenzylidene benzylidene dichloride (1.4 g, 6 mmol) was dissolved in deoxygenated 95% aqueous methanol (25.6 ml) under nitrogen and potassium hydroxide in 95% methanol (34.4 ml, 4.2M) was then added. The reaction mixture was kept under nitrogen at 50 °C for 5 days, after which the reaction mixture was quenched by acidification with concentrated hydrochloric acid, and the mixture extracted with chloroform (5 imes 20 ml). After drying over sodium sulphate, the solvent was removed by rotary evaporation to give a yellow oil, the n.m.r. spectrum of which indicated a mixture of 3,5-dimethyl-4-nitrobenzaldehyde and 3,5dimethyl-4-nitrobenzaldehyde dimethyl acetal (ratio 7:3). Both these compounds could be isolated by thick-layer chromatography on silica gel. The acetal had $\delta(CCl_4)$ 2.30 (s, 6 H, 2 \times Me), 3.21 (s, 6 H, 2 \times OMe), 5.25 (s, 1 H, ArCH), and 7.11 (s, 2 H, Ar). Small amounts (<5%) of presumably dimeric products were not examined further.

2-Methyl-4-nitrobenzylidene dichloride was similarly treated to give the corresponding aldehyde and acetal (ratio 7:3). The acetal had δ (CDCl₃) 2.47 (s, 3 H, Me), 3.35 (s, 6 H, 2 × OMe), 5.49 (s, 1 H, ArCH), and 7.8-8.3 (m, 3 H, Ar).

Reaction of 3-Chloro-4-nitrobenzylidene Dichloride.—3-Chloro-4-nitrobenzylidene dichloride (0.962 g, 4 mmol) was dissolved in deoxygenated ethanol (36.6 ml) under nitrogen. Potassium hydroxide (3.4 ml, 2.5M) in ethanol was added and the reaction mixture was kept at *ca.* 28 °C for

TABLE 3

Syntheses of substituted 4-nitrobenzylidene dichlorides and precursors

ArCH(OAc) ₂			ArCHO			ArCHCl ₂		
Yield (%)	m.p. (°C)	$\delta[CH(OAc)_2]^{a}$	Yield (%)	m.p. (°C)	δ(CHO) ·	Yield (%)	m.p. (°C)	δ(CHCl ₂) α
43	7778	7.51	78	5859	10.0	66	b	6.69
36	105 - 107	7.77	66	6870	10.51	54	35 - 36	7.12
34	128 - 129	7.41	30	51 - 53	9.92	70	8384	6.53
60	123 - 125	7.72	65	49 - 51	10.23			
с			35	6970	10.39	55	70-71	6.90
	43 36 34	Yield (%) m.p. (°C) 43 77—78 36 105—107 34 128—129	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Yield (%)m.p. (°C) δ [CH(OAc)2]Yield (%)m.p. (°C) δ (CHO)4377-787.517858-5910.036105-1077.776668-7010.5134128-1297.413051-539.9260123-1257.726549-5110.23	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

" Chemical shifts in carbon tetrachloride from internal SiMe₄. B.p. 118-122/0.27 mmHg. Not isolated.

trioxide oxidation of nitromesitylene has been described previously.²¹ Application of this method was also successful for the preparation of 2- and 3-chloro-4-nitrobenzaldehydes, and the results are summarised in Table 3. Oxidation of 3,4-dimethylnitrobenzene, followed by hydrolysis, gave 2-methyl-5-nitrobenzaldehyde admixed with a smaller amount (15%) of 2-methyl-4-nitrobenzaldehyde. The latter compound was prepared from 2-methyl-4-nitrobenzyl bromide ²² by the Sommelet reaction ¹⁸ or by the reaction of 2-methyl-4-nitrobenzylpyridinium bromide

24 min. The reaction mixture was acidified by concentrated hydrochloric acid and cooled in ice. The precipitated products were filtered off on a sintered funnel and washed with cold water. Extraction of the filtrate with chloroform afforded a further crop of products. A portion of the products was chromatographed on a 65×3 -cm column of silica gel and eluted with light petroleum (b.p. 60-80 °C), benzene, chloroform, and finally methanol. The eluted fractions were rotary-evaporated, pumped to constant weight, and analysed by t.l.c. and n.m.r. spectroscopy. The order of elution was 3-chloro-4-nitrobenzyl chloride, (2), (4a), (5a), and ethyl 3-chloro-4-nitrobenzyl ether. Most of the dimers were only partially separated but could be isolated in crystalline form by repeated fractional recrystallization, and the final results are given in Table 2.

3-Chloro-4-nitrobenzyl chloride was a yellow liquid, δ(CCl₄) 4.52 (s, 2 H, ArCH₂) and 7.27-7.95 (m, 3 H, Ar), (Found: M⁺, 204.973. C₇H₅Cl₂NO₂ requires M, 204.970).

1,2-Bis-(3-chloro-4-nitrophenyl)tetrachloroethane (2)crystallized readily from benzene as almost colourless prisms; $\lambda_{max.}$ (95% EtOH) 253 (e 1.1×10^4) and 208 nm (3.5 \times 10⁴). The electron-impact mass spectrum did not show a molecular ion, the highest fragment being m/e 406

(M - 2Cl, 35%) with a base peak at 238 (NO₂C₆H₃ClCCl₂), [Found: $M^+ = 2$ Cl, 405.908. $C_{14}H_6Cl_4N_2O_4$ requires (M = 12Cl), 405.908].

(E)- $\alpha, \alpha', 3, 3'$ -Tetrachloro-4,4'-dinitrostilbene (4a) was crystallized from benzene as almost colourless rods; λ_{max} . (95% EtOH) 294 (ε 1.1 × 10⁴) and 211 nm (3.3 × 10⁴). The mass spectrum gave molecular-ion peaks characteristic of a tetrachloro-compound at m/e 410 (M^+ + 4, 50%), 408 $(M^+ + 2, 100)$, and 406 $(M^+, 77)$ (Found: $M^+, 405.908$, $C_{14}H_6Cl_4N_2O_4$ requires M, 405.908).

(Z)- $\alpha, \alpha', 3, 3'$ -Tetrachloro-4,4'-dinitrostilbene (3a) crystallized from benzene as almost colourless needles. In solution it slowly isomerized to the E-isomer. The mass spectrum showed molecular-ion peaks expected for a tetrachlorocompound at m/e 412 $(M^+ + 6, 10\%)$, 410 $(M^+ + 4, 49)$, 408 $(M^+ + 2, 100)$, and 406 $(M^+, 78)$ (Found: $M^+, 405.908$. $C_{14}H_6Cl_4N_2O_4$ requires M, 405.908).

was 3,3'-Dichloro-4,4'-dinitrodiphenylacetylene (5a) obtained as yellow needles from benzene; $\lambda_{max.}$ (EtOH) 306 (z 2.4 × 10⁴) and 211 nm (3.1 × 10⁴). The mass 306 ($\epsilon 2.4 \times 10^4$) and 211 nm (3.1×10^4). spectrum showed molecular-ion peaks for a dichlorocompound at m/e 340 $(M^+ + 4, 11\%)$, 338 $(M^+ + 2, 66)$, and 336 (M⁺, 100) (Found: M⁺, 335.970. C₁₄H₆N₂O₄Cl₂ requires M, 335.970).

3-Chloro-4-nitrobenzyl ethyl ether was isolated as a yellow liquid; $\delta(\text{CDCl}_3)$ 128 (t, J 6 Hz, 3 H), 3.58 (q, J 6 Hz, 2 H), and 7.35-7.95 (m, 3 H).

Reaction of 2-Chloro-4-nitrobenzylidene Dichloride.-2-Chloro-4-nitrobenzylidene dichloride (0.962 g, 4 mmol) was dissolved in deoxygenated ethanol (24 ml). Potassium hydroxide (15.6 ml, 3.08M) in ethanol was added and the reaction mixture was kept at ca. 28 °C for 100 min under nitrogen. After acidification with concentrated hydrochloric acid and cooling, the solid products were filtered off through sintered glass, washed with cold water, and vacuum-dried to give 0.67 g of solids. Extraction of the filtrate with chloroform yielded a further crop of products (0.13 g). Chromatography through Florisil as described above gave (3b), (4b), (5b), 2-chloro-4-nitrobenzaldehyde, ethyl 3chloro-4-nitrobenzoate, and 2-chloro-4-nitrobenzaldehyde diethyl acetal; yields are in Table 2.

The dimeric products (3b), (4b), and (5b) were readily isolated crystalline and their spectra are in Table 1. (Z)- $\alpha, \alpha', 2, 2'$ -Tetrachloro-4,4'-dinitrostilbene (3b) had a mass spectrum showing molecular ions characteristic of a tetrachloro-compound at m/e 412 $(M^+ + 6, 8\%)$, 410 $(M^+ + 4, 4)$ 46), 408 $(M^+ + 2, 100)$, and 406 $(M^+, 76)$ (Found: M^+ , 405.908. $C_{14}H_6Cl_4N_2O_4$ requires M, 405.908).

(E)- $\alpha, \alpha', 2, 2'$ -Tetrachloro-4,4'-dinitrostilbene (3b) crystallized from benzene as almost colourless rods and showed molecular-ion peaks expected of a tetrachlorocompound at m/e 412 $(M^+ + 6, 9\%)$, 410 $(M^+ + 4, 46\%)$, 408 $(M^+ + 2, 100)$, and 406 $(M^+, 73)$ (Found: $M^+, 405.907$. $C_{14}H_6Cl_4N_2O_4$ requires M, 405.908).

2,2'-Dichloro-4,4'-dinitrodiphenylacetylene (5b) crystallized from chloroform as straw-coloured rods; $\lambda_{max.}$ (95% EtOH) 339 ($\epsilon 2.7 \times 10^4$), 224sh (2×10^4), and 210 nm $(2.19 imes10^4)$. The mass spectrum gave molecular ions of a dichloro-compound at m/e 340 $(M^+ + 4, 10\%)$, 338 $(M^+ + 2, 65)$, and 336 $(M^+, 100)$ (Found: $M^+, 335.967$. $C_{14}H_6Cl_2N_2O_4$ requires M, 335.970).

2-Chloro-4-nitrobenzaldehyde was identified by g.c.m.s., on a 4-ft \times 1/8-in 3% OV-17 column, 100--240 °C at 6 °C min⁻¹; m/e 185 $(M^+, 32\%)$, 184 (36), 111 (17), and 75 (100) (Found: M⁺, 184.992. Calc. for C₇H₄ClNO₃: M, 184.988). The diethyl acetal was obtained as a vellow liquid: $\delta(CCl_4)$ 1.22 (t, $\int 7 Hz$, 6 H), 3.56 (q, $\int 7 Hz$, 4 H), 5.65 (s, 1 H), and 7.65–8.28 (m, 3 H); m/e 214 (M^+ – OEt, 100%), 186 (91), and 140 (19) (Found: $M^+ - OEt$, 214.024. C₉H₉ClNO₃ requires 214.027).

Ethyl 2-chloro-4-nitrobenzoate was obtained as a yellow liquid; δ(CCl₄) 1.42 (t, J 7 Hz, 3 H), 4.39 (q, J 7 Hz, 2 H), and 7.75--8.37 (m, 3 H). G.c.-m.s. using the same conditions as above gave a mass spectrum with $m/e 229 (M^+, 1\%)$, 201 (79), 184 (100), 154 (14), 138 (45), 126 (23), 110 (31), and 75 (68) (Found: M⁺, 229.027. C₉H₈ClNO₄ requires M, 229.014).

The reaction of 4-nitrobenzylidene dichloride was also carried out in aqueous methanol, and the results obtained are comparable to those reported previously.^{10,11}

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