

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 methyl-substituted derivatives (1a 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 (1c 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-nitro-

less 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-4-nitrobenzylidene 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.

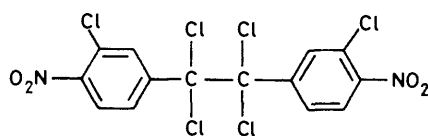
The reactions of (1c) and (1d) fit well into the mechanistic scheme involving carbanion formation, electron transfer, and radical coupling, as shown below. Dimeric products can be expected to predominate once radicals $\text{Ar}\dot{\text{C}}\text{HCl}$ and $\text{Ar}\dot{\text{C}}\text{Cl}_2$ are generated. The formation of

TABLE 2
Percentage product ^a distribution in the reactions of substituted 4-nitrobenzylidene dichloride ArCHCl_2

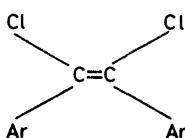
Ar	(E)-ArCCl=CClAr	(Z)-ArCCl=CClAr	$\text{ArC}\equiv\text{CAr}$	$\text{ArCCl}_2\text{-CCl}_2\text{Ar}$	ArCH_2Cl^b	ArCHO ^c
3-Cl-4-O ₂ NC ₆ H ₃	26	16	6	31	14	
4-O ₂ NC ₆ H ₄	22	16	12	34	12	
2-Cl-4-O ₂ NC ₆ H ₃	28	26	20	d		2
3,5-Me ₂ -4-O ₂ NC ₆ H ₃						> 95%
2-Me-4-O ₂ NC ₆ H ₃						> 95%

^a All reactions were carried out to 95–99% completion and yields are based on ArCHCl_2 . 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 $\text{ArCH}(\text{OMe})_2$ or $\text{ArCH}(\text{OEt})_2$. ^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

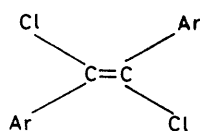


(2)



(3)

a; Ar = 3-Cl-4-O₂NC₆H₃
b; Ar = 2-Cl-4-O₂NC₆H₃



(4)

a; Ar = 3-Cl-4-O₂NC₆H₃
b; Ar = 2-Cl-4-O₂NC₆H₃

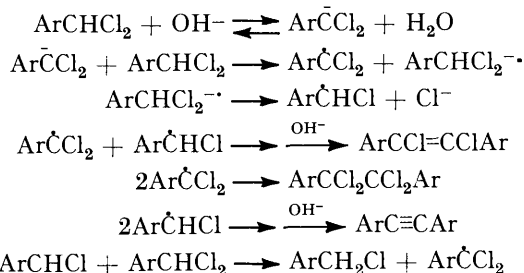


(5)

a; Ar = 3-Cl-4-O₂NC₆H₃
b; Ar = 2-Cl-4-O₂NC₆H₃

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

ArCH_2Cl or its solvolysis derivative ArCH_2OMe , however, is not so obvious. This is explained in the scheme as arising from hydrogen donation of ArCHCl_2 to ArCHCl . An alternative pathway could be by a carbanion interchange of $\text{Ar}\bar{\text{C}}\text{Cl}_2$ with ArCHCl_2 to ArCCl_3 and $\text{Ar}\bar{\text{C}}\text{HCl}$, 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 $\text{Ar}\bar{\text{C}}\text{Cl}_2$ over $\text{Ar}\dot{\text{C}}\text{HCl}$ 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-chloro-substituted derivative (1c), (1d) was much more unreactive requiring prolonged reaction times. Further-



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_N2 reaction. An important step in the radical reaction is the electron-transfer step from carbanion $\text{Ar}\bar{\text{C}}\text{Cl}_2$ to the acceptor molecule ArCHCl_2 . Methyl substitution appears, by a combination of steric and electronic effects, to depress carbanion formation and decrease the electron-acceptor property of ArCHCl_2 ; the reaction therefore becomes dominated by S_N solvolysis. Similar observations have also been reported²¹ in the effect of methyl substitution on the reactivity of 4-nitrobenzyl 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 4-nitrobenzyl 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, $\text{C}_7\text{H}_4\text{Cl}_3\text{NO}_2$ requires M , 238.931).

Reactions of 3,5-Dimethyl-4-nitrobenzylidene and 2-Methyl-4-nitrobenzylidene Dichlorides.—3,5-Dimethyl-4-nitrobenzylidene 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 × 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 3,5-dimethyl-4-nitrobenzaldehyde dimethyl acetal (ratio 7 : 3). Both these compounds could be isolated by thick-layer chromatography on silica gel. The acetal had $\delta(\text{CCl}_4)$ 2.30 (s, 6 H, 2 × Me), 3.21 (s, 6 H, 2 × 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 $\delta(\text{CDCl}_3)$ 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

Ar	ArCH(OAc) ₂			ArCHO			ArCHCl ₂		
	Yield (%)	m.p. (°C)	$\delta[\text{CH}(\text{OAc})_2]^a$	Yield (%)	m.p. (°C)	$\delta(\text{CHO})^a$	Yield (%)	m.p. (°C)	$\delta(\text{CHCl}_2)^a$
3-Cl-4-O ₂ NC ₆ H ₃	43	77–78	7.51	78	58–59	10.0	66	<i>b</i>	6.69
2-Cl-4-O ₂ NC ₆ H ₃	36	105–107	7.77	66	68–70	10.51	54	35–36	7.12
3,5-(CH ₃) ₂ -4-O ₂ NC ₆ H ₂	34	128–129	7.41	30	51–53	9.92	70	83–84	6.53
2-CH ₃ -5-O ₂ NC ₆ H ₃	60	123–125	7.72	65	49–51	10.23			
2-CH ₃ -4-O ₂ NC ₆ H ₃	<i>c</i>			35	69–70	10.39	55	70–71	6.90

^a Chemical shifts in carbon tetrachloride from internal SiMe₄. ^b B.p. 118–122/0.27 mmHg. ^c 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 bromide²² by the Sommelet reaction¹⁸ 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, $\delta(\text{CCl}_4)$ 4.52 (s, 2 H, ArCH_2) and 7.27–7.95 (m, 3 H, Ar), (Found: M^+ , 204.973. $\text{C}_7\text{H}_5\text{Cl}_2\text{NO}_2$ requires M , 204.970).

1,2-Bis-(3-chloro-4-nitrophenyl)tetrachloroethane (2) crystallized readily from benzene as almost colourless prisms; λ_{max} (95% EtOH) 253 (ϵ 1.1×10^4) and 208 nm (3.5×10^4). The electron-impact mass spectrum did not show a molecular ion, the highest fragment being m/e 406 ($M - 2\text{Cl}$, 35%) with a base peak at 238 ($\text{NO}_2\text{C}_6\text{H}_3\text{Cl}_2\text{Cl}_2^+$), [Found: $M^+ - 2\text{Cl}$, 405.908. $\text{C}_{14}\text{H}_6\text{Cl}_4\text{N}_2\text{O}_4$ requires ($M - 2\text{Cl}$), 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 1.1×10^4) and 211 nm (3.3×10^4). 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. $\text{C}_{14}\text{H}_6\text{Cl}_4\text{N}_2\text{O}_4$ 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 tetrachloro-compound at m/e 412 ($M^+ + 6$, 10%), 410 ($M^+ + 4$, 49), 408 ($M^+ + 2$, 100), and 406 (M^+ , 78) (Found: M^+ , 405.908. $\text{C}_{14}\text{H}_6\text{Cl}_4\text{N}_2\text{O}_4$ requires M , 405.908).

3,3'-Dichloro-4,4'-dinitrodiphenylacetylene (5a) was obtained as yellow needles from benzene; λ_{max} (EtOH) 306 (ϵ 2.4×10^4) and 211 nm (3.1×10^4). The mass spectrum showed molecular-ion peaks for a dichloro-compound at m/e 340 ($M^+ + 4$, 11%), 338 ($M^+ + 2$, 66), and 336 (M^+ , 100) (Found: M^+ , 335.970. $\text{C}_{14}\text{H}_6\text{N}_2\text{O}_4\text{Cl}_2$ requires M , 335.970).

3-Chloro-4-nitrobenzyl ethyl ether was isolated as a yellow liquid; $\delta(\text{CDCl}_3)$ 1.28 (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 3-chloro-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 ($M^+ + 4$, 46), 408 ($M^+ + 2$, 100), and 406 (M^+ , 76) (Found: M^+ , 405.908. $\text{C}_{14}\text{H}_6\text{Cl}_4\text{N}_2\text{O}_4$ 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 tetrachloro-compound at m/e 412 ($M^+ + 6$, 9%), 410 ($M^+ + 4$, 46%), 408 ($M^+ + 2$, 100), and 406 (M^+ , 73) (Found: M^+ , 405.907. $\text{C}_{14}\text{H}_6\text{Cl}_4\text{N}_2\text{O}_4$ requires M , 405.908).

2,2'-Dichloro-4,4'-dinitrodiphenylacetylene (5b) crystallized from chloroform as straw-coloured rods; λ_{max} (95% EtOH) 339 (ϵ 2.7×10^4), 224sh (2×10^4), and 210 nm (2.19×10^4). 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. $\text{C}_{14}\text{H}_6\text{Cl}_2\text{N}_2\text{O}_4$ 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 $\text{C}_7\text{H}_5\text{ClNO}_2$: M , 184.988). The diethyl acetal was obtained as a yellow liquid: $\delta(\text{CCl}_4)$ 1.22 (t, J 7 Hz, 6 H), 3.56 (q, J 7 Hz, 4 H), 5.65 (s, 1 H), and 7.65–8.28 (m, 3 H); m/e 214 ($M^+ - \text{OEt}$, 100%), 186 (91), and 140 (19) (Found: $M^+ - \text{OEt}$, 214.024. $\text{C}_9\text{H}_9\text{ClNO}_3$ requires 214.027).

Ethyl 2-chloro-4-nitrobenzoate was obtained as a yellow liquid; $\delta(\text{CCl}_4)$ 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. $\text{C}_9\text{H}_8\text{ClNO}_4$ 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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