Elimination Reactions. Part I. Reaction of Bis-(4-nitrophenyl)methyl Chloride with Sodium Hydroxide in Aqueous Dioxan

By **Rasmy Tewfik,** Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
Fouad M. Fouad and **Patrick G. Farrell,*** Department of Chemistry, McGill University, P.O. Box 6070, Montreal 101, Canada

The reaction between bis-(4-nitrophenyl)methyl chloride and sodium hydroxide in aqueous dioxan under air gives tetrakis-4-nitrophenylethylene and 4,4'-dinitrobenzophenone, whereas the reaction under nitrogen yields the ethylene as the sole product. The carbanion formed in the fast and reversible base-catalysed α-proton extraction from bis-(4-nitrophenyl)methyl chloride attacks aldehydes of different reactivities, under nitrogen, to yield the corresponding epoxides, the order of reactivity of the benzaldehydes used being 4-NO_2 > 3-NO_2 > 2-NO_2 > H > 4-OMe. The kinetics show first-order dependence upon the chloride and possible reaction mechanisms are discussed.

THE action of alkali upon 4-nitrobenzyl chloride (II) yields predominantly 4,4'-dinitrostilbene. Because of the difference in behaviour between this halide and other similar halides, which in general react to yield the corresponding alcohols, a number of studies of this reaction have been carried out. Earlier kinetic studies showed the reaction to be first order in the organic chloride and a mechanism involving the intermediate carbene was proposed.[1] The alternative radical-anion mechanism was excluded as the reaction proceeded without photochemical excitation and the rate for the dark reaction was the same as that for the illuminated one.[2,3] A more recent study, however, reports that the kinetics are second order in organic chloride and that the radical mechanism, together with a major competing S_N2 contribution, is the more probable.[4]

In view of the strong electronic or steric influence of substituents upon this reaction,[5,6] the effect of an extra 4-nitrophenyl group in (II) has been studied. The action of alkali upon bis-(4-nitrophenyl)methyl chloride (I) in 60 and 70% aqueous dioxan at various temperatures and reactant conditions has been examined. The extra 4-nitrophenyl group is expected to increase the acidity of

---

[1] S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 1961, 217.

[2] G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, 1968, **90**, 341; R. C. Kerber, G. Wurry, and N. Kornblum, *ibid.*, 1964, **86**, 3904.

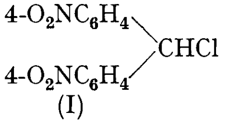
[3] A. A. Abdallah, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 1969, 1178.

[4] G. L. Closs and S. H. Goh, *J.C.S. Perkin II*, 1972, 1473.

[5] S. B. Hanna, Y. Iskander, and A. Salama, *J. Chem. Soc.*, 1961, 221.

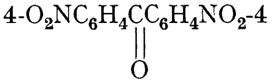
[6] D. M. Doleib and Y. Iskander, *J. Chem. Soc. (B)*, 1967, 1154.

the benzylic proton, thus increasing the rate of α-proton extraction and decreasing the probability of either an S_N2 or a radical mechanism. It should also stabilise the resulting conjugate base, retard any *E*1cB ejection of chloride ion leading to carbene formation, and thus reduce the total rate of chloride ion elimination.


(I)

$4\text{-}O_2NC_6H_4CH_2Cl$
(II)

$(4\text{-}O_2NC_6H_4)_2C{=}C(C_6H_4NO_2\text{-}4)_2$
(III)


$4\text{-}O_2NC_6H_4\underset{\underset{\displaystyle O}{\|}}{C}C_6H_4NO_2\text{-}4$
(IV)

EXPERIMENTAL

Solvents.—Commercial dioxan was purified according to the standard methods.[7] Doubly distilled water was boiled to expel dissolved air, cooled, and used immediately.

Materials.—Bis-(4-nitrophenyl)methyl chloride was prepared by nitrating diphenylmethane, oxidizing the bis-(4-nitrophenyl)methane to 4,4′-dinitrobenzophenone, and reducing the latter with aluminium isoproproxide to the alcohol. This was chlorinated with phosphorus pentachloride and bis-(4-nitrophenyl)methyl chloride was recrystallised several times from carbon tetrachloride, m.p. 111—112° (lit.,[8] 111—112°).

4-, 3-, and 2-nitrobenzaldehyde were commercial products repeatedly crystallized to sharp m.p. Commercial benzaldehyde and 4-methoxybenzaldehyde were distilled under reduced pressure immediately before use.

Qualitative Experiments under Kinetic Conditions.—The chloride (I) (0·1463 g), was dissolved in peroxide-free dioxan (30 ml) and distilled water (10 ml) added, followed by sodium hydroxide solution (10 ml; 0·05M). The mixture (dark violet) was kept for 10 days. Two compounds were isolated by dilution, tetrakis-4-nitrophenylethylene[9] (III) (32%) and 4,4′-dinitrobenzophenone (IV) (68%).

When the concentrations of reactants were 0·01M in (I) and 0·1M in sodium hydroxide, in 60% dioxan the amounts of (III) and (IV) isolated by dilution, were: (III) 60%; (IV) 40%. When these two experiments were repeated in the absence of air (N_2), tetrakis-4-nitrophenylethylene (III) was the sole product.

Epoxidations.—The chloride (I) (0·1463 g) and 4-nitrobenzaldehyde (0·0756 g) in dioxan (30 ml), were treated with sodium hydroxide (20 ml; 0·02M) under nitrogen and kept for three hours. After work-up *tris-4-nitrophenylethylene oxide* was obtained as a light yellow solid which, after recrystallisation from 1 : 1 dioxan–water had m.p. 178° (Found: C, 58·95; H, 3·05; N, 10·5. $C_{20}H_{13}N_3O_7$ requires C, 58·95; H, 3·1; N, 10·3%). The epoxide structure was confirmed by spectroscopy and by treatment with PCl_5 which affords the chloro-olefin.[10] Experiments carried out using 2-nitro-, 3-nitro-, 4-methoxy-benzaldehyde, and benzaldehyde all gave the corresponding epoxides.[11]

4-Nitrobenzyl chloride (0·0858 g) and 4,4′-dinitrobenzophenone (0·1360 g) were dissolved in dioxan (37·5 ml). Distilled water (2·5 ml) was added, followed by sodium hydroxide (10 ml; 0·5M). The same epoxide as obtained above was formed immediately.

N.m.r. Spectra.—Measurements were taken for $[^2H_6]$-acetone solutions (silanor-A) using a Varian T-60 spectrometer.

Dipole Moments.—The measurements were carried out at 25° using spectrophotometric grade carbon tetrachloride (Baker analysed), with a dipolemeter type DMo1 (Wissenschaftlich–Technische Werkstätten) and cell type MFL1.

Kinetic Measurements.—All reactions were carried out in aqueous dioxan. The rates of reaction were determined by following the rates of liberation of chloride ion by an electrometric method.[1] Typical experimental data are given in Table 1 and the linearity of the third-order plots for the epoxidation reactions is illustrated in Figure 1. The rate coefficients quoted in Tables 1 and 2 are the averaged values of several runs.

DISCUSSION

As can be seen from the results presented above, the reaction is first order in (I), rather than second order, and the S_N2 mechanism for stilbene formation is therefore inapplicable. Under the conditions of the kinetics experiments, quantitative conversion into tetrakis-4-nitrophenylethylene (III) was obtained and the normal analytical techniques revealed no traces of any minor products. Under nitrogen, the carbanion decomposed slowly to yield the observed product. These observations are in accord with the earlier work of Iskander and his co-workers[1] on (II), but are in marked contrast to the recently reported study by Closs and Goh of the reaction of (II) with bases.[4] These latter authors found

TABLE 1

(*a*) First-order rate constants for the reaction of (I) (0·01M) with sodium hydroxide (0·1M) in aqueous dioxan under nitrogen, at various temperatures, together with the derived thermodynamic parameters

	$10^4k/\text{min}^{-1}$			$E_a/$	$-\Delta S^\ddagger_{298}/$
Temperature (°C)	20°	25°	30°	kJ mol^{-1}	J K^{-1} mol^{-1}
60% aq. dioxan	48·9	71·8	89·8	44·7	102
70% aq. dioxan	51·2	88·4	108·7	55·5	64

(*b*) Typical data for the reaction between (I) (0·01M) and sodium hydroxide (0·1M) in 60% dioxan at 30° under nitrogen

t/min	10	20	30	40	50	60	70
Reaction (%)	11·6	16·7	22·4	29·3	36·5	45·0	53·4
$10^4k_1/\text{min}^{-1}$ (graphically)	89·8						

After 45% reaction, k_1 increases as the reaction proceeds.

TABLE 2

Third-order rate coefficients, k_3, for the reactions of (I) with alkali, in aqueous dioxan, in the presence of substituted benzaldehydes. All reactants were 0·1M. Estimated maximum error ±5%

	$10^{-2}k_3/\text{l}^2\ \text{mol}^{-2}\ \text{min}^{-1}$					
	60% aq. dioxan			70% aq. dioxan		
XC_6H_4CHO	20°	25°	30°	20°	25°	30°
X = H	0·55		0·80	0·70		1·27
X = 2-NO_2	5·1	7·1	8·8	4·7	8·5	9·7
X = 3-NO_2	25·0	36·7	41·5	26·0	42·6	53·5
X = 4-NO_2	41·2	71·7	74·5	50·0	88·2	92·0
X = 4-OMe		0·43	0·45	0·46		0·73

---

[7] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1966, p. 117.

[8] Y. Iskander and Y. Riad, *J. Chem. Soc.*, 1961, 2397.

[9] Y. Iskander, R. Tewfik, and Y. Riad, *J. Chem. Soc.*, 1962, 3232.

[10] Y. Iskander, E. M. E. Mansour, A. G. Rehiem, Y. Riad, and A. A. Youssef, *Chem. Comm.*, 1968, 976.

[11] R. Tewfik, unpublished work.

overall third-order kinetics for the reaction of (II) with sodium hydroxide in aqueous dioxan under nitrogen [second order in (II)], and suggested that an electron-transfer mechanism accompanied by S_N2 substitution accounted for stilbene formation. Furthermore, some 10% bis-(4-nitrophenyl)acetylene was isolated from the reaction of (II) with base by Closs and Goh, whereas no side-products had been previously reported. Because of these discrepancies we have attempted to confirm some of the recently reported work.

Upon mixing (I) with sodium hydroxide in aqueous dioxan, under nitrogen, an immediate violet colour developed, whose intensity decreased with time as the product was formed. Similar behaviour was observed on mixing 4-nitrophenyl(phenyl)methyl chloride with alkali-metal t-butoxides in t-butyl alcohol under nitrogen[12] and we also observed the immediate formation of a violet colour on mixing (I) with a solution of potassium t-butoxide in t-butyl alcohol. Mixing (II) with potassium t-butoxide in t-butyl alcohol under the conditions reported by Closs and Goh led to the immediate formation of a yellow solution, the colour of which changed to violet over 10—30 min. The violet solution decayed slowly as the product was formed and these solutions were stable in air. The colours in dioxan were attributed to the carbanions and in no case were products other than the stilbene obtained (*cf.* uninvestigated black material[4]). Dilute solutions of all the carbanions were stable for several days but we were unable to obtain e.s.r. signals from any of the compounds studied, at any concentration ratio (substrate : base). However, neither the observation of unidentified e.s.r. signals from solutions of (II) in an excess of potassium t-butoxide–t-butyl alcohol, nor their absence, provides any evidence concerning the electron-transfer mechanism under the conditions of the kinetic studies. Similar attempts to obtain e.s.r. signals from solutions of (I) in various basic media failed. We are therefore unable to confirm the recently reported results for (II) and also unable to obtain any evidence of radical intermediates in the reaction of (I) with bases. Both S_N2 and electron-transfer mechanisms thus appear unlikely for the reaction of (I) with alkali in dioxan.

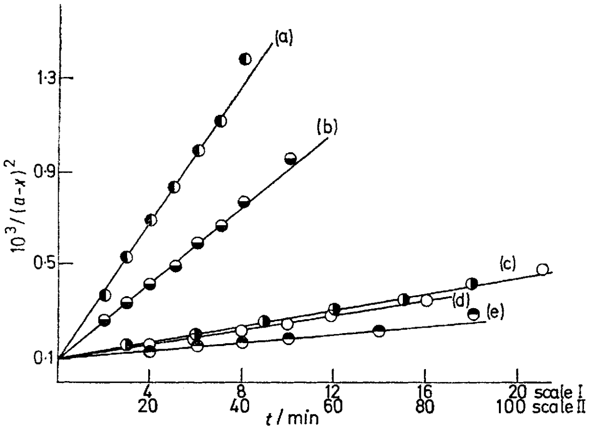


FIGURE 1 The variation with time of the chloride ion concentration in the presence of added aldehydes in 60% dioxan at 30°, plotted as a third-order reaction. The plots represent the addition of (a) 4-nitrobenzaldehyde; (b) 3-nitrobenzaldehyde; (c) 2-nitrobenzaldehyde; (d) benzaldehyde; (e) 4-methoxybenzaldehyde. Plots (a)—(c) are represented by scale I; plots (d) and (e) by scale II

From the results it can be seen that the reaction of (I) with alkali under nitrogen occurs at a slower rate than that of (II), k_1^{I} in 60% dioxan at $30° = 89·8 \times 10^{-4}$ min^{-1}, k_1^{II} in 50% dioxan at $30° = 96·8 \times 10^{-4}$ min^{-1}. The specific rate constants for both the reaction of (I) with alkali and its epoxidation decrease as the water : dioxan ratio increases. It therefore appears that the extra 4-nitrophenyl group, which increases the possibility of α-proton extraction, does indeed stabilise the resulting chloro-carbanion. The n.m.r. spectra imply that the benzylic proton of (I) is more acidic than those of (II) or benzyl chloride, the relevant chemical shifts δ being 6·74, 4·82, and 4·68 respectively.[13]

The ease of carbanion formation may be due in part to the fact that the bis-(4-nitrophenyl)methyl chloride molecule may not exist as a regular tetrahedral structure, but is somewhat deformed due to the steric interaction of the two neighbouring 4-nitrophenyl groups. The dipole moments for (I) and (II), in carbon tetrachloride as solvent, are 3·21 and 3·55 D respectively. These data may be interpreted to suggest that the $O_2NC_6H_4$–C–$C_6H_4NO_2$ bond angle in (I) is greater than tetrahedral, whereas the $O_2NC_6H_4$–C–H bond angle in (II) is smaller than tetrahedral. Thus (I) may prefer a rapid α-proton extraction to give the relaxed, planar carbanion in which the two 4-nitrophenyl groups are at 120° to each other; k_1 will then be fast in (I) as compared with (II) under the conditions employed.

The epoxidation occurs through the attack of the formed carbanion on the aldehyde present in the medium, rather than through insertion of the carbene into the carbonyl group of the aldehyde, as the reaction exhibits third-order kinetics, *i.e.* first order in organic chloride, in alkali, and in aldehyde. The rate of epoxidation varies with changes in the species and concentration of the intercepting aldehyde, and change in the alkali concentration. The slower rate of epoxidation, k_2', than of conjugate base protonation, k_{-1}, as shown by both the kinetic form and deuterium incorporation from D_2O, plus the fact that the rate of epoxidation of (I) with 4-nitrobenzaldehyde is faster than that with (II), further confirms that the rate of α-proton extraction, k_1, is faster in (I) than (II) [equations (1)—(3)]. This may be contrasted with the reaction of 4-nitro-3-methylbenzyl chloride in the presence of 4-nitrobenzaldehyde, where $k_2' > k_{-1}$[14] and with the conjugate base resulting from the chloride (II) which only intercepts the more

---

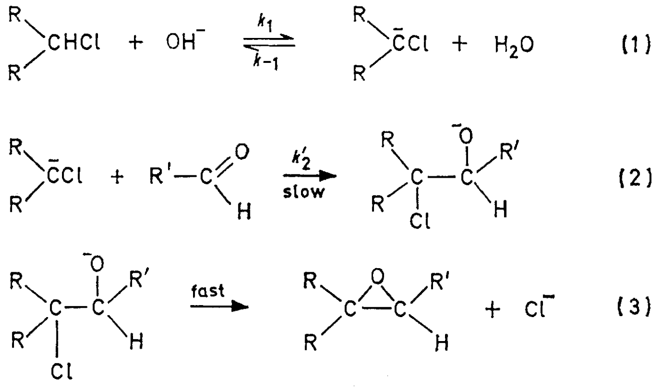
[12] D. Bethell and A. F. Cockerill, *J. Chem. Soc.* (*B*), 1966, 920.

[13] *Cf.* δ 4·63 and 4·50 for (II) and benzyl chloride respectively, measured as 5% solutions in carbon tetrachloride; J. B. Hyne and R. Willis, *J. Amer. Chem. Soc.*, 1963, **85**, 3650.

[14] D. M. Doleib and Y. Iskander, *J. Chem. Soc.* (*B*), 1967, 1159.

reactive 4-nitrobenzaldehyde and 4,4′-dinitrobenzophenone.

The rate of interception by benzaldehydes lies in the order, 4-NO_2 > 3-NO_2 > 2-NO_2 > H > 4-OMe. The faster interception of 3- than 2-nitrobenzaldehyde may be due to (*a*) the difficult attack of the bulky carbanion on the carbonyl carbon *ortho* to the nitro group, and (*b*) decreased partial positive charge on the carbon atom of the carbonyl group, this being partially satisfied by an oxygen atom of the nitro-group.[15]



R = 4−$O_2NC_6H_4$

The plots of log k_3 against σ values [16] give straight lines of slopes (ρ) 3·0 and 2·8 in 60 and 70% aqueous dioxan respectively, from which σ(2-NO_2) is found to be $+0·4 \pm 0·02$. (Figure 2). A wide range of σ values has been observed for the 2-NO_2 substituent [17] and it is difficult to ' interpret ' these values. The values obtained here are close to those found for the ionisation or esterification with diphenyldiazomethane, of 2-nitrophenylpropiolic acid in aqueous ethanol and aqueous dioxan respectively.[18]

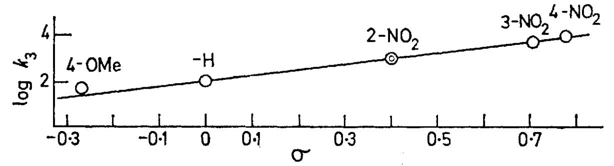


FIGURE 2 The variation of the logarithms of the third-order rate constants, k_3, measured in 60% dioxan at 30°, with the Hammett substituent constants σ. The value of σ(2-NO_2) has been interpolated using the experimental rate constant

The rate-determining step of the reaction thus involves loss of the chloride ion and two mechanisms have been considered for similar reactions in basic media. Loss of chloride ion to yield the carbene, which may attack the anion or dimerise (less probable) to give the ethylene, was the preferred mechanism of Iskander and his co-workers for the reaction of (II) with bases,[1] and of Rothberg and Thornton for the reaction of *p*-nitrobenzylsulphonium ions with aqueous sodium hydroxide.[19] The slow dissociation of the rapidly formed ion pair, followed by fast reaction of the anion with a neutral molecule and fast hydrogen halide elimination was preferred by Bethell and his co-workers in their study of the formation of bifluorenylidene from some 2-substituted 9-halogenofluorenes in t-butyl alcohol.[20]

The major objection to the carbene mechanism has been the extreme selectivity which must be invoked for the proposed intermediate and the failure to trap this carbene by the usual methods. Generation of the carbene derived from (II) in ethyl acetate or carbon tetrachloride in the presence of *cis*- or *trans*-but-2-ene does lead to the expected cyclopropanes *etc.*,[21] but we are unable to find any reports of the reactions of this species under the kinetic conditions employed.

The isolation of 4,4′-dinitrobenzophenone from experiments carried out under air would support either a carbene or a free radical mechanism, and the reaction proceeds at a rate faster than that found under nitrogen, $k_1{}^{\mathrm{I}}$ in 60% aqueous dioxan at 30° under air = $352·0 \times 10^{-4}$ min^{-1}. The addition of sodium peroxide to the reaction, or the use of unpurified dioxan, increased both the reaction rate and the amount of benzophenone formed. In the presence of a 10-fold excess of added peroxide, *only* benzophenone was formed. It is possible that this product arises *via* a free radical mechanism although this was rejected by Shipp and Kaplan in their study of stilbene formation from 2,4,6-trinitrobenzyl chloride under the influence of alkali.[22] The 2,4,6-trinitrobenzyl anion does not react with oxygen to give the 2,4,6-trinitrobenzyl radical under conditions where the *p*-nitrobenzyl anion does transfer an electron, leading to bibenzyl derivatives.[22] No evidence of any tetra-arylethane was found in the present study, but the carbene mechanism, although unlikely,[20] is not *necessarily* eliminated.

The formation of 4,4′-dinitrobenzophenone in experiments carried out under air, rather than tetrakis-4-nitrophenylethylene epoxide, implies that the anion from (I) is not trapped by this ketone. This is in contrast to the reaction of 4-nitrobenzyl chloride with base in the presence of 4,4′-dinitrobenzophenone, which leads to tris-4-nitrophenylethylene epoxide. However, Bethell and Cockerill reported [12] only 4-nitrobenzophenone (81%) and the tetra-arylethylene (18%) from the reaction of 4-nitrophenyl(phenyl)methyl chloride with potassium t-butoxide in air and these results may imply that steric interactions hinder attack by the carbanion upon the substituted benzophenones (*cf.* 2-nitrobenzaldehyde discussed above). Attempts to trap the anion from (I) with 4,4′-dinitrobenzophenone were unsuccessful.

---

[15] Y. Iskander, R. Tewfik, and S. Wassif, *J. Chem. Soc.* (*B*), 1966, 424.

[16] M. S. Newman, ' Sterics Effects in Organic Chemistry,' Wiley, London, 1955, p. 571.

[17] M. Charton, *Progr. Phys. Org. Chem.*, 1971, **8**, 235.

[18] I. J. Solomon and R. Filler, *J. Amer. Chem. Soc.*, 1963, **85**, 3492.

[19] I. Rothberg and G. R. Thornton, *J. Amer. Chem. Soc.*, 1964, **86**, 3302.

[20] D. Bethell, A. F. Cockerill, and D. B. Frankham, *J. Chem. Soc.* (*B*), 1967, 1287.

[21] G. L. Closs and S. H. Goh, *J.C.S. Perkin I*, 1972, 2103.

[22] K. G. Shipp and L. A. Kaplan, *J. Org. Chem.*, 1966, **31**, 857.

Reaction *via* the ion pair would seem unlikely in the highly aqueous media employed here, although there is some evidence for ion pairing in dioxan–water mixtures.[23] Ion pairs undergoing rapid internal return within a solvent cage might dissociate more slowly than the subsequent reaction of the anion with another molecule of (I), thus leading to first-order kinetics as is observed, but this seems improbable. Although we do not have direct evidence of the chloride loss step, our results do not support the radical or S_N2 mechanisms, except *via* an ion pair, and the latter does not provide an obvious pathway for ketone formation. Work is continuing on other systems to identify the mechanisms of halide ion loss.

We are grateful to a referee for valuable comments.

[3/184 *Received, 25th January,* 1973]

---

[23] *E.g.* G. Atkinson and S. K. Kor, *J. Phys. Chem.*, 1965, **69**, 128; J. C. D. Brand, D. D. MacNicol, and D. G. Williamson, *Chem. Comm.*, 1965, 123; F. Butera, M. Goffredi, and R. Triolo, *Atti Accad. sci. Lett. Arti Palermo Parte I*, 1966–1967, **27**, 191.