# Elimination Reactions. Part II.[1] Base-catalysed Formation of Stilbene Derivatives from α-Phenyl- and α-(4-Nitrobenzyl)-substituted 4-Nitrobenzyl Chloride

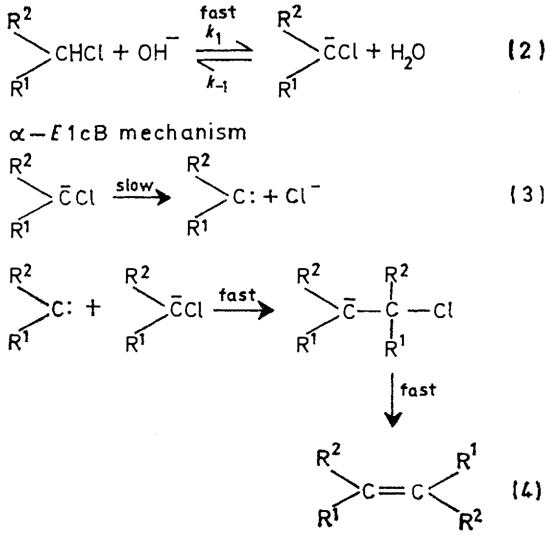
By **Rasmy Tewfik,** Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
**Fouad M. Fouad** and **Patrick G. Farrell,*** Department of Chemistry, McGill University, P.O. Box 6070, Station A, Montreal, Canada H3C 3G1

The reactions of 4-nitrophenyl(phenyl)methyl chloride and 1,2-bis-(4-nitrophenyl)ethyl chloride with sodium hydroxide in aqueous dioxan have been studied, and shown to yield stilbene derivatives. The overall rate of reaction of the former is slower than that of 4-nitrobenzyl chloride under the same conditions, presumably because of the stabilization of the carbanion by the extra phenyl group, whereas the latter compound reacts *ca.* 5 times faster than 4-nitrobenzyl chloride. The results imply that, in the absence of oxygen, the reactions do not occur *via* radical pathways.

In spite of a considerable number of kinetic *etc.* studies of the reactions of aqueous alkali upon 4-nitrobenzyl halides and their derivatives (both ring- and methylene-substituted), some controversy still exists over the mechanism of olefin formation from the chlorides in mixed solvents. Whereas the hydrolysis of 4-nitrobenzyl chloride (I) by aqueous alkali yields 4-nitrobenzyl alcohol as expected,[2] the addition of ethanol, acetone, or dioxan to the mixture results, under nitrogen, in almost quantitative formation of 4,4′-dinitrostilbene [3] [equation (1)]. The product is almost exclusively the *trans*-isomer.

$$\underset{\text{(I)}}{4\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}} + {}^-\text{OH} \longrightarrow 4\text{-NO}_2\text{C}_6\text{H}_4\text{CH=CHC}_6\text{H}_4\text{NO}_2\text{-4} \quad (1)$$

The reaction in aqueous acetone or aqueous dioxan was reported to obey first-order kinetics and α-*E*1cB ejection of chloride ion from the initially formed carbanion, leading to the carbene, was proposed to account for this [3] [equations (2)—(4)].



Although the lack of any products arising from the reaction of the intermediate carbene with the solvent necessitated the attribution of ' high selectivity ' to the species, some support for this mechanism was provided by studies of the reactions of 4-nitrobenzylsulphonium ions with aqueous hydroxide by Thornton and his co-workers.[4] These workers showed that rate-determining

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[1] Part I, R. Tewfik, F. M. Fouad, and P. G. Farrell, *J.C.S. Perkin II*, 1974, 31.

[2] *Cf.* *o*-nitrobenzyl chloride, H. G. Soderbaum and O. Widman, *Ber.*, 1892, **25**, 3291.

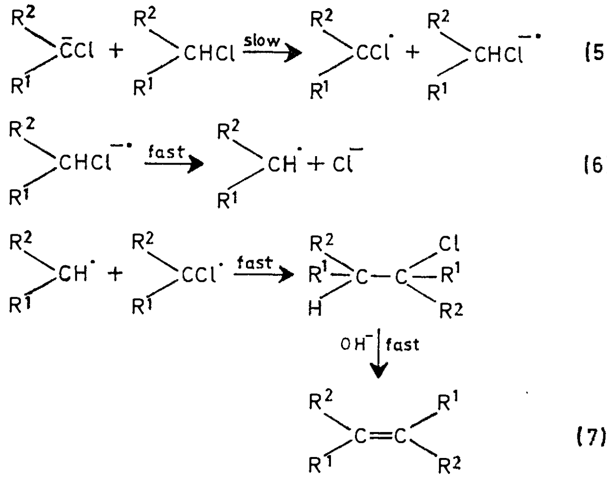
[3] S. B. Hanna, Y. Iskander, and Y. Riad, *J. Chem. Soc.*, 1961, 217.

[4] I. Rothberg and E. R. Thornton, *J. Amer. Chem. Soc.*, 1964, **86**, 3296, 3302; see also C. G. Swain and E. R. Thornton, *ibid.*, 1961, **83**, 4033.

4-nitrophenylcarbene formation was consistent with, but not essential for, the results obtained. The subsequent studies of Iskander and his co-workers upon derivatives of (I) were also interpreted in terms of the effects of substituents upon the α-elimination reaction.[5-8]

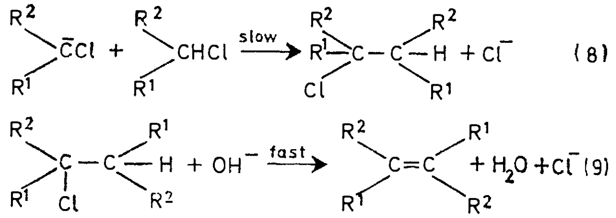
More recently, third-order kinetics have been reported for the 4-nitrobenzyl chloride reaction in aqueous dioxan and the combination of a free-radical and an $S_N2$ mechanism was proposed to account for these results, the latter followed by rapid base-catalysed elimination of HCl[9]

Radical mechanism



(5)
(6)
(7)

$S_N2$ mechanism

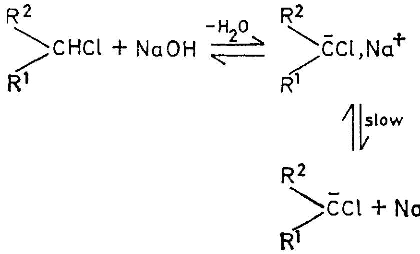


(8)
(9)

[equations (5)—(9)]. In all the proposed mechanisms, the initial proton abstraction was assumed to be the fast step [equation (2)].

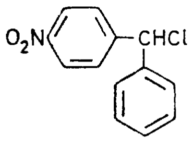
In Part I[1] we showed that the influence of an extra 4-nitrophenyl group upon this reaction [*i.e.* the reaction of bis-(4-nitrophenyl)methyl chloride] is two-fold: it increases the acidity of the benzylic proton and it stabilizes the resulting carbanion, thus decreasing the total reaction rate. We were not able to identify any free-radical component in that system and suggested that reaction *via* either the carbene or the less likely ion-pair mechanism[10] [equation (10), followed by (8) or (9), both fast steps] was consistent with the observed first-order kinetics.

In an effort to identify any free radical component of this reaction we have studied the reaction of 4-nitrophenyl(phenyl)methylchloride (II) with alkali in aqueous dioxan. [The base catalysed proton removal from (II) in t-butyl alcohol has been studied previously, but no mechanistic study of stilbene formation was reported.[11]] The free-radical mechanism requires the intermediacy of Ar•CHCl and Ar•CH$_2$ (Ar = 4-O$_2$NC$_6$H$_4$) and formation of such radicals from the corresponding methanes is disfavoured by replacement of a hydrogen atom by a phenyl group, presumably because of resonance stabilization of the carbanions.[12] Although this substitution will also stabilize the carbanion derived from the chloromethane derivative, decreased stability of a radical intermediate should be reflected in the products.



(10)

All the above mechanistic schemes for the parent 4-nitrobenzyl chloride involve the intermediacy of 1,2-bis-(4-nitrophenyl)ethyl chloride (III) or the anion (IV) derived therefrom, but only the α-*E*lcB mechanism leads directly to (IV) *via* attack of the carbene upon its precursor anion. By analogy with benzene derivatives, the proton attached to C-1 of (III) should be the more acidic and base-catalysed elimination of HCl from (III) should therefore be much slower than that from (IV). To confirm that the elimination of HCl from (III) occurs faster than the overall elimination reaction from (I), we have synthesized (III) and studied the kinetics of HCl elimination therefrom.



(II)

4-O$_2$NC$_6$H$_4$CH$_2$CHClC$_6$H$_4$NO$_2$-4

(III)

4-O$_2$NC$_6$H$_4\bar{C}$HCHClC$_6$H$_4$NO$_2$-4

(IV)

(4-O$_2$NC$_6$H$_4$)$_2$CHCl

(V)

EXPERIMENTAL

The rates of reaction in aqueous dioxan were determined by following the chloride ion elimination by an electrometric method.[3] Reaction products were identified by m.p., mixed m.p. with authentic specimens, and spectroscopy. N.m.r. spectra were measured for $[^2H_6]$acetone solutions (silanor-A) using a Varian T-60 spectrometer.

*Solvents.*—Commercial dioxan was carefully purified according to standard methods[13] to ensure the absence of

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[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.

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

[8] A. A. Abdallah, Y. Iskander, and Y. Riad, *J. Chem. Soc.* (*B*), 1969, 1178.

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

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

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

[12] G. A. Russell, A. J. Moye, and K. Nagpal, *J. Amer. Chem. Soc.*, 1962, **84**, 4154.

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

peroxides. Doubly distilled water was boiled to expel dissolved air, cooled, and used immediately.

*Materials.*—4-Nitrophenyl(phenyl)methyl chloride (II) was prepared by the reduction of 4-nitrobenzophenone to the corresponding alcohol using aluminium isopropoxide in isopropyl alcohol, followed by chlorination of this alcohol in benzene–ether solution with dry hydrogen chloride in the presence of anhydrous zinc chloride. The product was recrystallized from benzene–light petroleum, m.p. 46° (lit.,[14] 41—42°).

1,2-Bis-(4-nitrophenyl)ethyl chloride (III) was prepared in low yield by the photochemically initiated chlorination of 4,4′-dinitrobibenzyl by *N*-chlorosuccinimide in carbon tetrachloride solution. The photolysis was carried out over 24 h using 300 nm lamps in a Rayonet reactor. The filtrates from several experiments were combined and evaporated *in vacuo*, and the product was separated by preparative t.l.c. using benzene as eluant. The *product*, light yellow needles, was crystallized from benzene, then methanol, and had m.p. 149—150° (Found: $M^+$, 306·0406. $C_{14}H_{11}ClN_2O_4$ requires *M*, 306·0408). In addition to the aromatic signals, the n.m.r. spectrum showed δ 3·60 (d) and 5·60 (t).

4-Nitrobenzaldehyde was a commercial product repeatedly crystallized to sharp m.p. Commercial benzaldehyde and 4-methoxybenzaldehyde were distilled under reduced pressure immediately before use.

*Product Determination.*—The chloride (II) (0·619 g) was dissolved in peroxide-free dioxan (125 ml) and sodium hydroxide solution (125 ml; 0·2M) was added. The red mixture was kept for 10 days. Three compounds were isolated by dilution and extraction: 4-nitrobenzophenone (35%) and *cis*- (4%) and *trans*-4,4′-dinitrotetraphenylethylene (61%). The yields of the ethylene isomers were determined spectrophotometrically. When the experiment was repeated in the absence of air ($N_2$), only the ethylenes were obtained: 94% *trans*, m.p. 227—229° (lit.,[15] 228—229°); 6% *cis*, m.p. 214—215° (lit.,[15] 215—216°). The corresponding alcohol, 4-nitrophenyl(phenyl)methanol, was also treated as described above. After 10 days, the carbinol was recovered almost quantitatively (>95%) and no traces of 4-nitrobenzophenone were detected.

The chloride (II) (0·619 g) and 4-nitrobenzaldehyde (0·750 g) in dioxan (125 ml) were treated with sodium hydroxide (125 ml; 0·2M) under nitrogen and kept for 2 days. Quantitative formation of a 1 : 1 mixture of *cis*- and *trans*-4,4′-dinitrotriphenylethylene oxides was obtained, the isomers being separated by fractional crystallization from chloroform. After recrystallization from benzene, the trans-*isomer* had m.p. 194—195° (Found: C, 66·25; H, 3·9; N, 7·7. $C_{20}H_{14}N_2O_5$ requires C, 66·3; H, 3·9; N, 7·75%). The cis-*isomer* was recrystallized from chloroform and had m.p. 164—165° (Found: C, 66·25; H, 3·9; N, 7·7%). The epoxide structures were confirmed both by spectroscopy and by treatment with $PCl_5$ followed by base-catalysed elimination from the vicinal dichloride,* which yields the chloro-olefin.[16] Attempts to form the corresponding epoxides from 4-nitrobenzophenone, benzaldehyde, or 4-methoxybenzaldehyde were unsuccessful.

Treatment of (III) 0·092 g) in dioxan (25 ml) with sodium hydroxide solution (25 ml; 0·2M) resulted in the immediate formation of a deep violet colour, followed by precipitation of 4,4′-dinitrostilbene with concomitant fading of the violet colour.

## RESULTS AND DISCUSSION

*Reaction of Compound* (II).—Under the conditions of a ten-fold excess of base, in aqueous dioxan, elimination occurs from (II) to give, under nitrogen, the tetra-arylethylene, as found by other workers for the reaction of (II) with potassium t-butoxide in t-butyl alcohol.[11] The kinetics are first order in (II) and the rate data obtained are shown in Table 1, together with corresponding data for (I) [3] and bis-(4-nitrophenyl)methyl chloride (V).[1]

TABLE 1

(*a*) Typical rate data for the reaction of (II) with NaOH in aqueous 70% dioxan (v/v) at 30°, obtained by analysis of liberated $Cl^-$

Initial concentrations: [(II)] $10^{-2}$M; [NaOH] $10^{-1}$M

| *t*/h | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|
| Reaction (%) | 10·9 | 14·2 | 17·7 | 21·2 | 26·1 | 32·8 | 41·5 |

$10^4k_1$ 8·5 min$^{-1}$

(*b*) Derived first-order rate coefficients and thermodynamic parameters for the reaction of (II) with NaOH

| Dioxan (v/v %) | | 50 | 60 | 70 |
|---|---|---|---|---|
| $10^4k_1$/min$^{-1}$ (±5%) | 30° | 15·2 | 9·4 | 8·5 |
| | 25° | 9·4 | 5·9 | |
| | 20° | 7·6 | 4·8 | |
| $E_a$/kJ mol$^{-1}$ (±4 kJ mol$^{-1}$) | | 50·2 | 50·2 | |
| $\Delta S^‡$/J K$^{-1}$ mol$^{-1}$ | | −114·1 | −117·9 | |

(*c*) Comparable data for (I) and (V)

Corresponding rate data for (I) in 50% dioxan [3]

$10^4k_1$/min$^{-1}$ (30°) = 96; $E_a$/kJ mol$^{-1}$ = 68·1; $\Delta S^‡$/J K$^{-1}$ mol$^{-1}$ = −100

Corresponding rate data for (V) in 60% dioxan [1]

$10^4k_1$/min$^{-1}$ (30°) = 89·8; $E_a$/kJ mol$^{-1}$ = 44·7; $\Delta S^‡$/J K$^{-1}$ mol$^{-1}$ = −135·8

For these latter compounds, increasing the percentage (v/v) of dioxan increases the reaction rate and *vice versa* but allows a greater range of reactant concentrations to be studied. Thus the first-order rate coefficient for bis-(4-nitrophenyl)methyl chloride (V) in 50% dioxan (v/v) is considerably less than the value shown in Table 1 for 60% dioxan (v/v) solution. The first-order kinetic plots show some curvature towards zero order after 25—45%

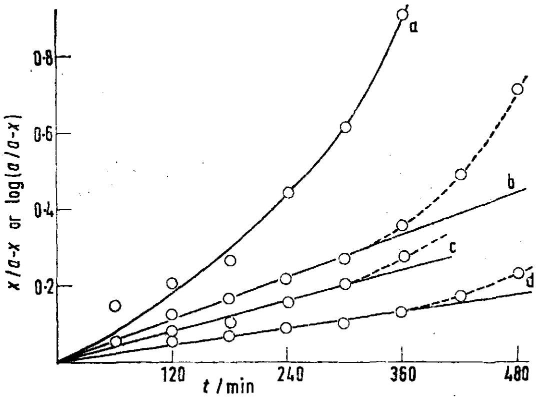

FIGURE 1 First- and second-order kinetic plots for the reactions of (II) with base in 50 and 70% aqueous dioxan: a, b, second-order plots in 50 and 70% dioxan respectively; c, d, corresponding first-order plots

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* In Part I, we omitted to point out that this step is necessary to obtain the olefin.

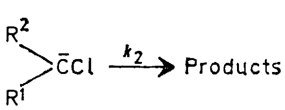
[14] S. Altscher, R. Baltzly, and S. W. Blackman, *J. Amer. Chem. Soc.*, 1952, **74**, 3649.

[15] R. Kuhn and D. Blum, *Chem. Ber.*, 1959, **92**, 1483 (*Chem. Abs.*, 1959, **53**, 21,805i).

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

reaction, depending upon solvent composition. In all experiments the agreement with first-order was better than with second-order kinetics (Figure 1) but the second-order reaction competes more favourably in the solvents containing more dioxan. Curvature of the plots in solvents richer in dioxan sets in after smaller percentages of reaction, possibly due to the lower rate of elimination from the intermediate 1,2-diphenyl-1,2-bis-(4-nitrophenyl)ethyl chloride in these solvents [equations (8) and (9)]. This would lead to a decreasing dependence upon the concentration of (II) and we are currently investigating this possibility.

As was the case with the replacement of a benzylic hydrogen atom of 4-nitrobenzyl chloride by $4\text{-}O_2NC_6H_4$, the introduction of the phenyl group enhances α-proton extraction, stabilizes the resulting carbanion, and decreases the overall reaction rate (relative to 4-nitrobenzyl chloride), although the overall influence of the substituent is, by definition, a composite one. Assuming that a slow, first-order reaction of the carbanion formed in equation (1) is the rate-determining step, *i.e.* equation (11), then,



$$R^1R^2\bar{C}Cl \xrightarrow{k_2} \text{Products} \qquad (11)$$

from the rates of epoxidation of 4-nitrobenzyl chloride and (IV) with 4-nitrobenzaldehyde, the ratio $k_{-1}[H_2O]/k_2$ may be calculated.[7]

In the presence of a ten-fold excess of base, (II) reacts with 4-nitrobenzaldehyde to give the *cis*- and *trans*-epoxides. The reaction follows first-order kinetics and is independent of the concentration of the aldehyde, implying that the rate-determining step is the proton extraction from (II).[7] The values of $k_{-1}[H_2O]/k_2$ for 4-nitrobenzyl chloride and (II) respectively are *ca.* 2 [7] and 83 (Table 2). The rate-determining step in the epoxidation of bis-(4-nitrophenyl)methyl chloride is the attack of the carbanion on the aldehyde implying that $k_{-1}$ is extremely large and these data thus reflect the difficulty of oxidation of the carbanions.[17]

TABLE 2

(*a*) Typical rate data for epoxidation of (II) with 4-nitrobenzaldehyde in the presence of sodium hydroxide (1 : 3 : 10). Solvent 60% dioxan (v/v); temperature 20°; $[(II)]_0 = 10^{-2}$M

| $t$/min | 3 | 8 | 13 | 18 | 23 | 28 | 33 |
|---|---|---|---|---|---|---|---|
| Reaction (%) | 8·0 | 29·1 | 41·2 | 51·1 | 58·5 | 65·1 | 70·5 |

(*b*) Derived first-order rate coefficients and thermodynamic parameters for epoxidation. Errors as for Table 1.

| [(II)] : [OH⁻] : [ArCHO] | | 1 : 10 : 1 | 1 : 10 : 2 | 1 : 10 : 3 |
|---|---|---|---|---|
| $10^4k_1$/min⁻¹ | 30° | 664·8 [a] | 783·0 | 794·5 [b] |
| | 25° | | | 530·0 |
| | 20° | | | 332·1 |

$E_a$/kJ mol⁻¹ = 62·7; $\Delta S^{\ddagger}$/J mol⁻¹ K⁻¹ = −93

[a] This value is low, presumably because of competition from the Cannizarro reaction. [b] *Cf.* value of $10^4k_1$ for (I) = 280·8 min⁻¹ in 50% aqueous dioxan.[3]

A careful analysis of the reaction products of the reaction of (I) with base, under oxygen, failed to reveal any traces of 4-nitrobenzoic acid or 4,4′-dinitrobibenzyl. These are the major reaction products of the oxidation of *p*-nitrotoluene in basic solution (t-butyl alcohol–dimethyl sulphoxide; potassium t-butoxide), which has been shown to proceed *via* a radical pathway.[17,18] Other workers have similarly failed to find these reaction products, which throws some doubt upon the radical mechanism for stilbene formation in this reaction, even though carried out in a different solvent.[19] Furthermore, the major product of the photochemical decarboxylation of the 4-nitrophenylacetate ion in aqueous solution is bis-(4-nitrophenyl)ethane [20] and, by analogy the corresponding vicinal dichloride would be an expected initial product from the 4-nitrobenzyl ion [equation (2)]. This product should undergo base-catalysed elimination to the acetylene which was reported in 10% yield by Closs and Goh,[9] although we have so far been unable to detect this product. We have also been unable to find any evidence of the 4,4′-dinitrotetraphenylethylene epoxide, which might be expected from (II) *via* the vicinal dichloride and the chloro-alcohol, in the present work. It thus appears that the influence of the phenyl group in (II) is mainly confined to the first step of the reaction [equation (2)] and that the products are essentially unaffected by the replacement of a benzylic hydrogen by a phenyl group.

The free radical mechanism for the oxidation of 4-nitrotoluene in basic t-butyl alcohol–dimethyl sulphoxide solutions assumed that the proton abstraction by base was fast, relative to electron transfer.[17] Russell and his co-workers failed to observe the formation of radical anions from nitroaromatic compounds in which conversion into anions is very rapid, and the ease of oxidation of these compounds was found to be 4-nitrotoluene > 4-nitrophenyl(phenyl)methane > bis-(4-nitrophenyl)-methane in t-butyl alcohol.[17] The similarity of reactions, products, *etc.*, for the substituted 4-nitrobenzyl halides studied to date [1,3,5–9] suggests that a uniform mechanism is operative, and the results for (II) support this. Experiments in the presence of *p*-dinitrobenzene showed no evidence of rate retardation [21] or of an induction period,[22] further implying that the free radical mechanism is not operative under oxygen-free conditions, although ketone formation in the presence of oxygen or peroxides is compatible with the $S_{RN}1$ mechanism.

*Reaction of Compound* (III).—The rate of base-catalysed elimination of HCl from (III) in aqueous 62·5% dioxan (v/v) was measured at various temperatures and, in the presence of a ten-fold excess of base, is first order in both substrate and base. Typical first-order plots are shown in Figure 2. Although the majority of earlier work on the formation of 4,4′-dinitrostilbene from (I) was performed using 50% aqueous dioxan (v/v) as solvent,[3,9] the higher percentage of dioxan

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

[18] G. A. Russell and E. G. Janzen, *J. Amer. Chem. Soc.*, 1962, **84**, 4153.

[19] H. D. Burrows and E. M. Kosower, *J. Phys. Chem.*, 1974, **78**, 112; M. Mohammad, J. Hadju, and E. M. Kosower, *J. Amer. Chem. Soc.*, 1971, **93**, 1792.

[20] J. D. Margerum, *J. Amer. Chem. Soc.*, 1965, **87**, 3772.

[21] J. F. Wolfe, J. C. Green, and T. Hudlicky, *J. Org. Chem.*, 1972, **37**, 3199.

[22] G. A. Russell and W. C. Danen, *J. Amer. Chem. Soc.*, 1968, **90**, 347.

used here allows both a greater range of concentration to be studied and a higher concentration of product to remain in solution (see above). This results in deviations from linearity of the first-order plot only after *ca.* 70% reaction.

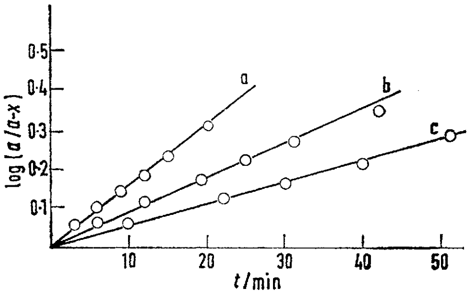

FIGURE 2 Typical first-order plots for the reaction of (III) with hydroxide ion in aqueous dioxan solution and their temperature variation: $[(\mathrm{III})]_0$ $3{\cdot}75 \times 10^{-3}$M; [base] : [(III)] 10 : 1. Values obtained at a, 20·6°; b, 15°; c, 9·4°

A comparison of the pseudo-first-order rate coefficient for chloride ion elimination from (III) in 50% aqueous dioxan at 30° ($10^4k_1$ 485 $\mathrm{min}^{-1}$) with that from (I) in the same solvent ($10^4k_1$ 96 $\mathrm{min}^{-1}$) [3] shows that the former reacts *ca.* 5 times faster. A similar rate ratio is obtained in solutions containing 62·5% dioxan and such a value supports all proposed stilbene formation mechanisms (α-*E*1cB, $S_N2$, radical), as the elimination of HCl from (III) or $Cl^-$ from (IV) is postulated as a fast step [equations (4) and (9)]. However, only the α-*E*1cB or the ion-pair mechanism is in accordance with the observed first-order kinetics.[3,10] From the pseudo-first-order rate coefficients the energy of activation is found to be 62·7 kJ $\mathrm{mol}^{-1}$ and the corresponding entropy −92·0 J $\mathrm{K}^{-1}$ $\mathrm{mol}^{-1}$. The activation energy for the elimination from (III) is slightly less than that for the overall elimination from (I) (68·1 kJ $\mathrm{mol}^{-1}$) as expected and the entropy slightly higher than that for the latter compound (−100 J $\mathrm{K}^{-1}$ $\mathrm{mol}^{-1}$).[3] The entropy seems somewhat low for an *E*2 elimination reaction, but reactions carried out in deuteriated solvent show <10% deuterium incorporation in the recovered starting material (after 50% reaction) and no deuterium in the isolated stilbene derivative. (These results were obtained by mass spectrometry.) Thus the elimination reaction is faster than exchange (of the α-proton) and only a small fraction of the overall reaction proceeds *via* an alternative mechanism (*e.g.* α-*E*1cB followed by insertion into an adjacent C–H bond [23]).

*Conclusions.*—From both the kinetic [3] and the product analysis the results suggest that the $S_{RN}1$ mechanism is not operative in the reactions studied here and, by analogy, is probably not operative in similar systems under oxygen-free conditions. The results do not allow the halide-loss mechanism to be unequivocally identified although the first-order kinetics are in accord only with the α-*E*1cB [3] or ion-pair [10] mechanisms.

We are grateful to the National Research Council of Canada for financial support.

[4/855 *Received, 29th April,* 1974]

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[23] D. G. Hill, W. A. Judge, P. S. Skell, S. W. Kantor, and C. R. Hauser, *J. Amer. Chem. Soc.*, 1952, **74**, 5599.