Dehalogenation Reactions of Vicinal Dihalides. Part V.[1] Kinetic Study of the Reactions of 1,2-Dihalogeno-1,2-diphenylethanes with Triphenylphosphine

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Triphenylphosphine-promoted dehalogenation reactions of *meso*-1,2-dibromo-1,2-diphenylethane and some *para*-substituted derivatives have been studied in dimethylformamide. Substituent effects on the reaction rate are in agreement with a concerted *anti*-elimination mechanism and do not support a stepwise mechanism involving bridged intermediates. The effect of solvent has also been investigated and the nucleophilicity of triphenylphosphine towards bromine is briefly discussed.

Two possible mechanisms have been suggested for the dehalogenation reactions of 1,2-dibromo-derivatives.[2] The first is a concerted *anti*-elimination process identical with that suggested for the base-induced *E*2 eliminations of HX. The second is a multi-step mechanism involving a bridged structure in which the bromine atom attacked by the nucleophile can interact with the α-carbon thereby aiding C_α–Br ionization.

Evidence favouring the latter mechanism has been found in reactions of (±)-1,2-dibromo-1,2-diphenylethane[3] where, however, a concerted *anti*-elimination is made energetically unfavourable by steric factors (*cis*-effect). For the reactions of *meso*- and *erythro*-forms the choice is more difficult, the indications for both the concerted and the stepwise mechanism being rather tenuous. A study of substituent effects on the rate of dehalogenation from *erythro*-1,2-dibromo-1,2-diaryl-

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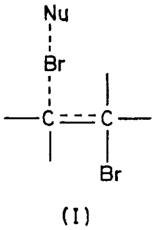
[1] Part IV, E. Baciocchi and C. Lillocci, *J.C.S. Perkin II*, 1975, 802.

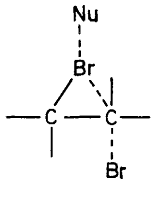
[2] W. H. Saunders, jun., and A. F. Cockerill, ' Mechanisms of Elimination Reactions,' Wiley, New York, 1973, p. 332. In some dehalogenations promoted by carbanions an electron transfer mechanism with the formation of a radical anion has been suggested: see D. C. Korzan, F. Chen, and C. Ainsworth, *Chem. Comm.*, 1971, 1953.

[3] (*a*) C. S. T. Lee, I. M. Mathai, and S. I. Miller, *J. Amer. Chem. Soc.*, 1970, **92**, 4602; (*b*) W. K. Kwok and S. I. Miller, *ibid.*, p. 4599; (*c*) I. M. Mathai, K. Schug, and S. I. Miller, *J. Org. Chem.*, 1970, **35**, 1733; (*d*) I. M. Mathai and S. I. Miller, *ibid.*, p. 3416; (*e*) W. K. Kwok, I. M. Mathai, and S. I. Miller, *ibid.*, p. 3420; (*f*) W. K. Kwok and S. I. Miller, *ibid.*, p. 1034.

ethanes promoted by halide ion gave results interpreted in terms of a concerted elimination mechanism.[4] The small size of the effects and the fact that both electron-releasing and -attracting substituents increase the dehalogenation rate are in agreement with a nearly synchronous reaction with a transition state (I) in which little charge is developed at both α- and β-carbon atoms and the formation of the C=C double bond is far advanced.



(I)



(II)

However, with these results, a stepwise mechanism cannot be excluded since small substituent effects are also expected for such a mechanism if the first step is rate determining and the transition state is (II).[3a]

Although discrimination, on the basis of substituent effects, between stepwise and concerted mechanisms has not been possible for the halide ion-promoted dehalogenations, this may be feasible when reactions with other nucleophiles are considered. The nature of the nucleophile could change the structure of the transition state in a significant way and therefore modify the sensitivity of the reaction to the electronic effects of substituents. This should be especially true when the reaction mechanism is concerted for which, if the analogy with *E*2 eliminations of HX may be stretched so far, a spectrum of transition states with varying amounts of positive charge on the α- and negative charge on the β-carbon should be possible.

On the basis of these considerations we have undertaken a quantitative study of the dehalogenation of vicinal dibromides promoted by triphenylphosphine (Ph_3P). The choice of Ph_3P from possible nucleophiles was suggested by the fact that the reactions of phosphorus derivatives with vicinal dihalides have recently received some attention of a qualitative nature.[5] Moreover, in one of these reports [5a] it was suggested that dehalogenations promoted by Ph_3P may proceed through the formation of a carbanion intermediate. At the same time it also seemed useful to acquire additional quantitative information on the nucleophilicity of trivalent phosphorus toward bromine.

In this paper we report a kinetic study of the reactions of *meso*-1,2-dibromo-1,2-diphenylethane (III) and some *para*-substituted derivatives with Ph_3P in *NN*-dimethylformamide (DMF) and of (III) with Ph_3P in ethanol. A product analysis for the reaction of (±)-1,2-dibromo-1,2-diphenylethane with Ph_3P in DMF has also been carried out.

RESULTS AND DISCUSSION

The reaction of Ph_3P and (III) proceeds according to equation (1). In preparative experiments (see Experimental section) the yields of isolated *trans*-stilbene and Ph_3PO (derived from Ph_3PBr_2 after reaction with CH_3OH) were 97.2 and 98.0%, respectively. The yields of substituted *trans*-stilbenes obtained in the reactions of the substituted-derivatives were determined spectrophotometrically and found to be quantitative in all cases. In contrast, the reaction of Ph_3P with (±)-1,2-dibromo-1,2-diphenylethane was not stereospecific, affording 55.5% *cis*- and 44.5% *trans*-stilbene under conditions where no *cis* ⇄ *trans* isomerization takes place.

$$\underset{\text{(III)}}{\mathrm{PhCHBr{-}CHBrPh}} + \mathrm{Ph_3P} \longrightarrow \underset{\textit{trans}}{\mathrm{PhCH{=}CHPh}} + \mathrm{Ph_3PBr_2} \quad (1)$$

The kinetics of the dehalogenation of (III) and its derivatives were carried out by following spectrophotometrically the appearance of *trans* stilbene or substituted *trans*-stilbene. A large excess of Ph_3P was used and good first-order plots were obtained in each experiment. The second-order rate constants (k_2) were independent of the concentration of the nucleophile. The kinetic data are collected in Table 1.

Substituent Effects.—According to the data in Table 1 the dehalogenation of (III) promoted by Ph_3P appears to be significantly influenced by the nature of the substituent present in the *para*-position of the phenyl ring. A *p*-nitro-group gives a 29-fold rate increase, 58-fold if the statistical factor is considered. The effect of a second *p*-nitro-group is much smaller, the difference in rate between the di- and mono-nitro-derivatives being only 2.6-fold after statistical correction. For the *p*-methoxy-group a 1.5-fold rate increase is observed. Because of the small effect it is reasonable to suggest that in the *p*-methoxy-derivative of (III) the two bromine atoms have nearly equal reactivity towards nucleophilic attack. Thus a statistical correction is unnecessary. A second *p*-methoxy-group produces a rate increase very similar

TABLE 1

Kinetic data for the dehalogenation of *erythro*-1,2-dibromo-1-(4-$R^1C_6H_4$)-2-(4-$R^2C_6H_4$)ethanes promoted by triphenylphosphine in DMF at 50°

R^1	R^2	k_2/l mol^{-1} s^{-1} [a]
H	H	0.010 7
H	NO_2	0.310
NO_2	NO_2	1.69
OCH_3	OCH_3	0.037 5
H	OCH_3	0.016 4
OCH_3	NO_2	0.344

[a] Average of two or three kinetic runs. Error *ca.* ±3%.

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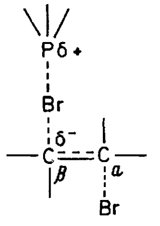
[4] E. Baciocchi and A. Schiroli, *J. Chem. Soc.* (*B*), 1969, 554.

[5] (*a*) C. J. Derlin and B. J. Walker, *J.C.S. Perkin I*, 1972, 249; (*b*) I. J. Borowitz, D. Weiss, and R. Crouch, *J. Org. Chem.*, 1971, **36**, 2377; (*c*) J. P. Schroeder, L. B. Tew, and V. M. Peters, *ibid.*, 1970, **35**, 3181.

to that of the first. However, the kinetic effect of the methoxy-group on the dehalogenation rate is decreased by the presence in the substrate of the strongly activating *p*-nitro-group. Thus the 4-methoxy-4′-nitro-derivative of (III) is only 1.07 times more reactive than the 4-nitro-compound. In conclusion, dehalogenations promoted by Ph_3P are favourably influenced by both electron-releasing and -withdrawing substituents. However, the latter exert a much larger kinetic effect than the former.

This pattern, which is quite different from that observed for halide ion-promoted dehalogenation, where the effects of both methoxy- and nitro-groups are very small, may be rationalized on the basis of a not completely synchronous $E2$ mechanism. The significant activating effect of the *p*-nitro-group is indicative of a substantial negative charge in the transition state. Moreover, the fact that, in contrast, the introduction of a second *p*-nitro-group produces only a small rate enhancement clearly suggests that the negative charge is stabilized by only one of the two nitro-groups. These observations are therefore consistent with a transition state (IV), where C_β–Br bond breaking is more advanced than C_α–Br bond breaking, thus allowing accumulation of negative charge on C_β.

The amount of this charge is however substantially less than in the transition state of eliminations involving loss of HX. Accordingly, in sodium ethoxide-induced elimination from 1-chloro-1,2-diphenylethane a *p*-nitro group in the 2-phenyl ring produces a rate increase of 770-fold.[6] As a further consequence the C=C double bond is formed to a significant extent in the transition state of the Ph_3P-promoted debromination. On the basis of this conclusion the small activating effect of the *p*-methoxy-group may be due to favourable conjugative interactions of that group with the incipient double bond in the transition state. The small effect of the second nitro-group may have the same origin.



(IV)

While in agreement with a concerted mechanism the data in Table 1 do not fit a stepwise mechanism involving a transition state such as (II). Since no rupture of C_β–Br bond occurs in (II) there is no way to rationalize the significant effect on the rate produced by the *p*-nitro-substituent. Even if formation of the Ph_3P–Br_β bond in the transition state were much more advanced than that of the bond between Br_β and C_α no direct conjugative interaction would be possible between the negative charge accumulating on the bromine atom and the remote NO_2 group.* Moreover, in this case, a negative kinetic effect of the *p*-methoxy-group would be expected. Thus, substituent effects on the reaction rate clearly indicate a concerted *anti*-elimination mechanism for Ph_3P-promoted dehalogenation from (III) and its derivatives.

The reasons, in dehalogenation promoted by Ph_3P, for the shift in transition state structure towards the carbanion side relative to the corresponding halide ion-promoted reaction are not clear. Unlike eliminations involving loss of HX,[8] the basicity of the nucleophile does not seem to affect the transition state significantly, as shown by the fact that dehalogenations in DMF promoted by I^-, Br^-, and Cl^- exhibit very similar substituent effects in spite of the different basicity of the three halides.[4] This is not surprising since a nucleophile–bromine bond is being formed in the transition state of these reactions, not a nucleophile–hydrogen bond. Probably other factors, not recognized at present, are of importance. The neutral character of the nucleophile Ph_3P could also play a role in this respect since the incipient positive charge on the phosphorus atom should help to stabilize the incipient negative charge on C_β, favouring a transition state with carbanion character.

On the basis of results obtained using 1,2-dibromo-1-nitro-2-phenylethane as the substrate the mechanism of Ph_3P-induced debromination of vicinal dibromides has been recently discussed in terms of an initial attack of Ph_3P on bromine to give a carbanion intermediate.[5a] Clearly, this conclusion cannot be applied to our system since the activating effect of a *p*-nitro-group is too small to be consistent with a carbanionic mechanism. Nevertheless, the fact that in strongly activated systems (*e.g.* with a nitro-group directly attached to the β-carbon) such a mechanism is operative gives further support to the idea that dehalogenation proceeds by the same mechanism as elimination involving loss of HX.[9]

In eliminations as in dehalogenation the nature of the substrate and of the nucleophile will determine the reaction mechanism and influence the structure of the transition state. Thus halide ion-promoted dehalogenation occurs by an $E2$ mechanism with a transition state halfway along the reaction coordinate. When the nucleophile is Ph_3P we still have $E2$ elimination, but the transition state has a certain amount of carbanionic character. Finally, when in the substrate a powerful $-I$, $-R$ substituent is bonded directly to the β-carbon, dehalogenation promoted by Ph_3P is no longer a concerted process but takes place through the formation of a carbanion, in this case a very stable species.

Clearly these conclusions specifically refer to the reac-

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* In the equilibrium $YC_6H_4CHOHCH_2X \rightleftharpoons YC_6H_4CHO-CH_2X$, K_{eq} is only *ca.* three-fold larger when Y is a *p*-nitro group than when Y is hydrogen.[7]

[6] E. Baciocchi, P. Perucci, and C. Rol, *J.C.S. Perkin II*, 1975, **329**.

[7] A. C. Knipe, *J.C.S. Perkin II*, 1973, 589.

[8] S. Alunni and E. Baciocchi, *Tetrahedron Letters*, 1973, **47**, 4665.

[9] J. F. Bunnett, *Survey Progr. Chem.*, 1969, **5**, 53.

tions of *meso*- and *erythro*-forms of vicinal dibromides. With (±)- and *threo*-diastereoisomers the mechanism of Ph_3P-promoted dehalogenation may be different, as shown by the lack of stereospecificity exhibited by the reaction of (±)-1,2-dibromo-1,2-diphenylethane. A multi-step mechanism is probable, even though, at this stage, competitive *syn*- and *anti*-debrominations can not be ruled out.

Solvent Effects.—Table 2 reports kinetic data and activation parameters for the reactions of (III) with PPh_3 in DMF and EtOH. The reactivity is practically the same in the two solvents as expected for a reaction involving two uncharged species which are not hydrogen-bond donors.[10] However, $\Delta H^‡$ and $\Delta S^‡$ exhibit important changes in going from DMF to EtOH which compensate for each other in their effect on $\Delta G^‡$. $\Delta S^‡$ is more negative in DMF than in EtOH whereas the reaction in EtOH has a larger $\Delta H^‡$ than that in DMF.

TABLE 2

Kinetic data and activation parameters for the dehalogenation of *meso*-1,2-dibromo-1,2-diphenylethane promoted by triphenylphosphine in DMF and EtOH [a]

Solvent	Temp. (°C)	10^2k_2/ l mol^{-1} s^{-1}	$\Delta H^‡$/ kcal mol^{-1}	$\Delta S^‡$/ cal mol^{-1} K^{-1}
DMF	41.1	0.559	13.2	−27.0
	50.0	1.07		
	59.8	1.94		
EtOH	41.1	0.510	17.7	−12.7
	58.6	2.86		
	68.5	6.04		

[a] The activation parameters were calculated by least-square analysis of the equation $\log k_2/T = 10.319 + \Delta S^‡/4.574 - \Delta H^‡/4.574T$. Estimated errors: $\Delta H^‡ \pm 1$ kcal mol^{-1}; $\Delta S^‡ \pm 3$ cal mol^{-1} K^{-1}.

Evidently, the transition state for Ph_3P-promoted debromination is more solvated in DMF, which is a very good solvator of dipoles, than in EtOH, leading to a more negative $\Delta S^‡$ in the former solvent. On the other hand, increased solvation of the transition state in DMF produces a smaller $\Delta H^‡$ than in EtOH, since less energy is required to reach the transition state. Clearly, DMF must surpass EtOH to a large extent in its capacity to solvate the transition state since it is expected that the reagents are more solvated in DMF than in EtOH.[11] It is also possible that the charge separation is less advanced in the transition state for the reaction in EtOH than in DMF. Interestingly a similar pattern of activation parameters is exhibited by the reaction between $(CH_3)_2S$ and CH_3Br when data in 88% methanol–water are compared with those in dimethylacetamide.[12,*]

Nucleophilic Reactivity of Triphenylphosphine.—In Table 3 the reactivity of Ph_3P towards (III) in DMF and EtOH is compared with that of some halide ions. In DMF Ph_3P is slightly less effective than I^- but much more reactive than Br^- as a debrominating agent. On the contrary, in protic solvents the reactivity towards bromine of PPh_3 is significantly larger (10-fold) than that of I^-. Probably a slightly greater difference would have been observed if the reaction with Ph_3P had been carried out in MeOH.[13] Interestingly, when the nucleophilicity of I^- and Ph_3P are compared for the reaction with CH_3I (attack to a saturated carbon) in CH_3OH the reverse situation is observed, I^- being more reactive than Ph_3P.[14] Clearly, bromine is a softer electrophile than saturated carbon and Ph_3P is a softer nucleophile than I^-: as a consequence the nucleophilicity of Ph_3P towards bromine is higher than that of I^-; the reverse situation applies for carbon nucleophilicity.

TABLE 3

Kinetic data for the dehalogenation of *meso*-1,2-dibromo-1,2-diphenylethane promoted by Ph_3P, I^-, and Br^-, in protic and aprotic solvents at 25°

Nucleophile	Solvent	k_2/l mol^{-1} s^{-1}
I^-	DMF	5.20×10^{-3} [a]
	MeOH	1.09×10^{-4} [b]
Br^-	DMF	7.35×10^{-5} [a]
	MeOH	$\leqslant 10^{-6}$ [b]
Ph_3P	DMF	1.70×10^{-3} [c]
	EtOH	1.14×10^{-3} [c]

[a] Data from ref. 4. [b] Data from E. Baciocchi and P. Bocca, *Ricerca sci.*, 1967, **37**, 1182. [c] Calculated from data at higher temperatures.

EXPERIMENTAL

Materials.—*NN*-Dimethylformamide (Erba R.P.) was dried over molecular sieves (B.D.H.; type AM; 8—12 mesh beads), then distilled under nitrogen and at reduced pressure. Absolute ethanol was refluxed with sodium and diethylphthalate and fractionally distilled. Triphenylphosphine (B.H. Schilling R.P.) was recrystallized from ethanol and had m.p. 80—81° (lit.,[15] 80—81°). (±)-1,2-Dibromo-1,2-diphenylethane was prepared by addition of bromine to *cis*-stilbene in CS_2, m.p. 113—114° (lit.,[16] 114°). 4-Methoxy-*trans*-stilbene was obtained by treating 1-chloro-2-(4-methoxyphenyl)-1-phenylethane with Bu^tOK in Bu^tOH. The olefin has m.p. 140—141° (lit.,[17] 140—141.5°),

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[*] In our case we compare data for solvents of different dielectric constant. However this should not significantly modify the conclusions since similar rates have been observed for the reaction of PPh_3 with ethyl iodide in MeOH and EtOH.[13]

[10] A. J. Parker, *Adv. Phys. Org. Chem.*, 1967, **5**, 201.

[11] A. J. Parker, *Chem. Rev.*, 1969, **69**, 1; C. F. Ko and A. J. Parker, *J. Amer. Chem. Soc.*, 1968, **90**, 6447.

[12] Y. C. Mac, W. A. Miller, A. J. Parker, and D. W. Watts, *J. Chem. Soc.* (*B*), 1967, 525.

[13] W. A. Henderson, jun., and S. A. Buckler, *J. Amer. Chem. Soc.*, 1960, **82**, 5794.

[14] R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, 1968, **90**, 319.

[15] 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 1971.

[16] R. E. Buckles, J. M. Beder, and R. J. Thurmaier, *J. Org. Chem.*, 1962, **27**, 4523.

[17] J. T. Hewitt, W. Lewcok, and F. G. Pope, *J. Chem. Soc.*, 1912, **101**, 606.

$\lambda_{max.}$ (DMF) 318 nm (ε 29 600). The remaining olefins and the substrates were prepared as described in Part II[4] and had the properties reported.

Product Analysis.—Reaction of (±)-1,2-*dibromo*-1,2-*diphenylethane with triphenylphosphine.* A solution 0.1M in dibromide and *ca.* 1M in PPh_3 was kept in a thermostatted bath at 60°. After 16 and 24 h, portions (3 ml) were withdrawn, poured into H_2O, and extracted with CCl_4. The concentrated solution was analysed at 190 °C using a Carlo Erba gas chromatograph (model G1), equipped with a flame ionization detector. A 2 m × 2 mm column of 10% SE 30 on Chromosorb was employed with nitrogen as carrier gas. Blank experiments showed no *cis* $\rightleftharpoons$ *trans* isomerization for the conditions used.

Reaction of meso-1,2-*dibromo*-1,2-*diphenylethane with triphenylphosphine.* To *meso*-1,2-dibromo-1,2-diphenylethane (3.326 g, 9.79 mmol) in DMF (100 ml), PPh_3 (2.825 g, 10.75 mmol) was added. The solution was kept at 40° for 3.6 h and then the solvent was removed under reduced pressure. MeOH (100 ml) was added to the residue and the solid formed was filtered and dried, and was found to be *trans*-stilbene (5.74 mmol), m.p. 123°. Further *trans*-stilbene (13.82 mmol) was obtained by column chromatography of the solution together with triphenylphosphine oxide (9.60 mmol), m.p. 152—153° (lit.,[15] 155°), and PPh_3 (0.94 mmol), m.p. 79—80°.

Kinetics.—The appearance of *trans*-stilbene or substituted *trans*-stilbene was followed spectrophotometrically at the wavelength corresponding to the absorption maximum, with the exception of the unsubstituted compound (λ = 324 nm) and its mono- and di-methoxy-derivatives (λ = 340 nm).

Solutions were prepared in a stoppered two limb cell and placed in the thermostatted compartment of a Beckman DB-GT spectrophotometer. After *ca.* 0.5 h the solutions were mixed thoroughly and the cell was rapidly replaced in the compartment of the spectrophotometer.

When the solvent was DMF the concentration of Ph_3P normally ranged from 2×10^{-3} to 10^{-2}M and that of the substrate was *ca.* 5×10^{-5}M. With mono- and di-methoxy derivatives higher concentrations of Ph_3P (2×10^{-2}—10^{-1}M) were necessary owing to a competitive reaction of these substrates with the solvent. In order to nullify the high absorbance of PPh_3 at these concentrations, reactions were carried out in a volumetric flask placed in a thermostatted bath, the concentration of the substrates being 5×10^{-4}M. At appropriate times, portions (1 ml) were withdrawn and diluted to 10 ml with DMF; the optical density was then measured at the appropriate wavelength. For the reaction of (III) in EtOH a saturated solution of the dibromide was used.

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