Elimination Reactions of 1,2-Diaryl-1-chloroethanes promoted by Sodium Ethoxide in Ethanol. The Kinetic Effects of α- and β-Phenyl Substituents

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The kinetics of the elimination reactions of several substituted 1,2-diaryl-1-chloroethanes promoted by sodium ethoxide in ethanol have been studied. On the basis of the kinetic effects of β-phenyl substituents a ρ value of +2·26 has been calculated. This value is slightly less positive than that (+2·50) found in the corresponding elimination from substituted phenylethyl chlorides, thus showing that the introduction of an α-phenyl group does not modify substantially the carbanionic character of the transition state in the elimination reactions of β-phenyl activated substrates. Small kinetic effects are observed for α-phenyl substituents. Electron-withdrawing α-phenyl substituents produce an increase in the reaction rate; it appears therefore that these substituents exert their influence mainly through a favourable interaction with the partial negative charge present on C_β in the transition state.

IT is accepted that the structure of the transition state of an E_2 elimination reaction may vary across the mechanistic spectrum shown in the Scheme.[1] Evidence on the position of the transition state along this spectrum has been furnished by extensive kinetic studies on the

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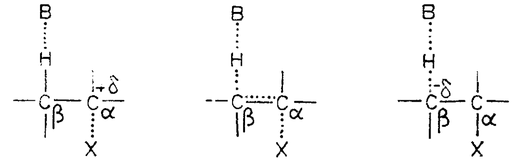
[1] J. F. Bunnett, *Progr. Chem.*, 1969, **5**, 53.

phenethyl system.[2] The determination of the effects of β-phenyl substituents upon the reaction rate has given *detailed information* on the excess of negative charge which accumulates on C_β (carbanionic character) in the



near *E*1 central near *E*1cb

SCHEME

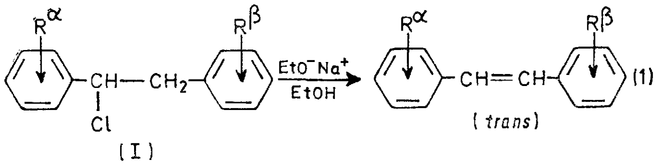
transition state as a function of the nature of nucleophile, solvent, and leaving group.

In contrast, much less information is available on the charge distribution at C_α. As far as we know, only studies of the elimination reactions of α-phenylethyl bromides[3] and α-phenylethyltrimethylammonium ions[4] have dealt with this problem.*

In this paper we present kinetic data for the elimination reactions of 1,2-diaryl-1-chloroethanes promoted by sodium ethoxide in ethanol. The aim of this work was to acquire information on the charge distribution in the transition state at both C_α and C_β.

RESULTS AND DISCUSSION

The reaction studied is shown in equation (1). The rates of reaction were determined by spectrophotometric



(1)

(I)

a; $R^\alpha = R^\beta =$ H
b; $R^\alpha =$ H, $R^\beta =$ *p*-Me
c; $R^\alpha =$ H, $R^\beta =$ *p*-Cl
d; $R^\alpha =$ H, $R^\beta =$ *p*-NO_2
e; $R^\alpha =$ *p*-Cl, $R^\beta =$ H
f; $R^\alpha =$ *m*-Cl, $R^\beta =$ H
g; $R^\alpha =$ *p*-Me, $R^\beta =$ H
h; $R^\alpha =$ *p*-NO_2, $R^\beta =$ H

analysis for *trans*-stilbene or substituted *trans*-stilbene in the case of compounds (Ia—f and h). The concentration of sodium ethoxide was in the range 0·08—0·48M, and was always in large excess over that of the substrate. Kinetics of (Ig) were followed by titrimetric analysis of Cl^-; for this substrate, elimination induced by the solvent was a concurrent reaction and it was necessary to use concentrations of sodium ethoxide between 0·7 and 1·3M, unsuitable for spectrophotometric analysis, in order to make negligible the unimolecular mechanism of elimination.

In each case, clean first-order kinetics were observed up to 70—80% of reaction and the second-order rate constants were practically independent of the concentration of sodium ethoxide. The formation of *trans*-stilbene or substituted *trans*-stilbene was nearly quantitative in each case, spectrophotometric or g.l.c. analysis indicating a yield >95%. No attempt was made to search for small amounts, if any, of *cis*-olefin or substitution product.

The kinetic results are reported in the Table. Rate data for compounds (Ia—d) allow the determination of the effect of substituents in the β-phenyl ring. A plot of log k_2 against the Hammett σ values of substituents (for the NO_2 group the σ^- value[5] was used) exhibited excellent linearity. A ρ value of +2·26 (*s* 0·07, *r* 0·999) was calculated.† This value indicates that the transition state has significant carbanionic character. A more positive value of ρ (+2·50) has been found for elimination from phenethyl chlorides promoted by EtONa–EtOH at 50°.[2f,j] Thus, as expected on the basis of variable transition state theory for *E*2 eliminations,[1] the introduction of an α-phenyl group in the phenethyl system has shifted the transition state structure somewhat towards the central region. The shift is, however, not large and moreover a very small increase (six fold when the statistical factor ‡ is allowed for) in the rate of

Kinetic data for the elimination reactions from 1-chloro-1-(R^α-phenyl)-2-(R^β-phenyl)ethanes in EtONa–EtOH at 50°

Rα	Rβ	$10^4 k_2$ [a]/l mol⁻¹ s⁻¹
H	H	1·67 ± 0·17
H	*p*-Me	0·97 ± 0·02
H	*p*-Cl	6·81 ± 0·2
H	*p*-NO_2	1290 ± 150
p-Cl	H	3·45 ± 0·08
m-Cl	H	3·27 ± 0·09
p-Me	H	2·17 ± 0·09
p-NO_2	H	~11 [b]

[a] Each k_2 value is the average of at least four determinations.
[b] Approximate value since (see Experimental section) it was not possible to obtain compound (Ih) with a purity >80%. Moreover, we experienced some difficulty in obtaining a constant value of the optical density at infinite time.

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* After this paper was submitted for publication we learnt (W. H. Saunders and A. F. Cockerill, 'Mechanisms of Elimination Reactions,' Wiley–Interscience, New York, 1973, p. 64) that the same kinetic work as ours has been carried out [J. G. Griepenburg, Ph.D. Thesis, University of Rochester, 1971; *Diss. Abs. Int. B*, 1971, **32**(**6**), 3252].

† Griepenburg obtains a ρ value of +2·0 using substituents covering a smaller reactivity range (*m*-chloro in the place of the *p*-nitro). For α-phenyl substituents the same author reports kinetic data only for the *m*- and *p*-chloro-substituted compounds from which a ρ value of +0·6 is calculated.

‡ The rate of elimination from phenethyl chloride must be divided by two to give the rate per hydrogen atom, since *trans*-olefin is practically the only product from 1-chloro-1,2-diphenylethane.

[2] (*a*) C. H. De Puy and D. H. Froemsdorf, *J. Amer. Chem. Soc.*, 1957, **79**, 3710; (*b*) W. H. Saunders, jun., and R. A. Williams, *ibid.*, p. 3712; (*c*) W. H. Saunders, jun., C. B. Gibbons, and R. A. Williams, *ibid.*, 1958, **80**, 4099; (*d*) W. H. Saunders, jun., and D. H. Edison, *ibid.*, 1960, **82**, 138; (*e*) C. H. De Puy and C. A. Bishop, *ibid.*, p. 2532; (*f*) C. H. De Puy and C. A. Bishop, *ibid.*, p. 2535; (*g*) A. F. Cockerill, S. Rottschaefer, and W. H. Saunders, jun., *ibid.*, 1967, **89**, 901; (*h*) A. F. Cockerill, *J. Chem. Soc.* (*B*), 1967, 964; (*i*) W. H. Saunders, jun., D. G. Bushman, and A. F. Cockerill, *J. Amer. Chem. Soc.*, 1968, **90**, 1775; (*j*) C. H. De Puy, D. L. Storm, J. T. Frey, and C. G. Naylor, *J. Org. Chem.*, 1970, **35**, 2746; (*k*) J. Banger, A. F. Cockerill, and G. L. O. Davies, *J. Chem. Soc.* (*B*), 1971, 498; (*l*) L. F. Blackwell, P. D. Buckley, K. W. Jolley, and A. K. H. MacGibbon, *J.C.S. Perkin II*, 1973, 169; (*m*) A. F. Cockerill and W. J. Kendall, *ibid.*, p. 1352; (*n*) S. Alunni and E. Baciocchi, *Tetrahedron Letters*, 1973, 4665.

[3] P. J. Smith and S. K. Tsui, *Tetrahedron Letters*, 1972, 917.

[4] T. Yoshida, Y. Yano, and S. Oae, *Tetrahedron*, 1971, **27**, 5343.

[5] P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1969, p. 29. For the use of σ^- value in the case of the NO_2 substituent see also refs. 2*b* and *g*.

elimination is observed. These results clearly show that in β-phenyl activated systems the breaking of the C_α–leaving group bond has a much less important effect on the reaction rate than the breaking of the C_β–hydrogen bond.

A larger activating effect by the α-phenyl group (a factor of *ca.* 30) was observed in the elimination reactions of ethyl bromide promoted by EtO^- in EtOH.[6] According to variable transition state theory elimination from this substrate should occur through a transition state which has less carbanionic character than that in the corresponding reaction of phenethyl chloride, since bromide is a better leaving group than chloride and the β-hydrogen atoms are less acidic. As a consequence the breaking of the C_α–leaving group bond is more advanced in the transition state and the factors which favour this rupture (α-phenyl group) become more important. In Bu^tOK–Bu^tOH the elimination reaction of ethyl bromide utilizes a transition state with more carbanionic character than in EtO^-–EtOH; accordingly, in this base–solvent system a smaller kinetic effect by the α-phenyl group (*ca.* 8) has been observed,[7] similar to that found in the present work.

However it should be noted that the accelerating effect of the α-phenyl group could also reside in its electron-withdrawing polar effect, the decrease in ρ being due to the fact that less delocalization by the β-aryl ring of the negative charge on C_β is now required.* In this case the kinetic effect of an α-phenyl group would become a measure of the carbanionic character of the transition state and the figures discussed above would lead to completely different conclusions about the transition state structure since they would indicate a decrease of the carbanionic character of the transition state in passing from ethyl bromide to phenethyl chloride and from EtONa–EtOH to Bu^tOK–Bu^tOH. Interestingly, these conclusions are in agreement with Thornton's predictions[8] concerning substituent and medium effects on the transition state structure of *E*2 eliminations.

As expected for a reaction with a transition state of significant carbanionic character the kinetic effects of α-phenyl substituents are rather small [see rate data of compounds (Ie—h)]. More significantly, we observe that electron-withdrawing substituents [compounds (Ie, f, h)] exert an accelerating effect on the reaction rate, despite the fact that they are expected to make more difficult the breaking of the C_α–Cl bond. The favourable effect on the partial negative charge which develops on C_β, even if depressed by the intervening methylene group, is therefore still more important than the unfavourable effect of strengthening the C_α–Cl bond. The existence of these two opposite effects is probably the cause of the lack of good correlation between the rate constants and the σ or σ^+ values of the α-phenyl substituents.

A slight increase in rate is observed for compound (Ig) which has an electron-releasing methyl substituent. Probably in this case, there is a nearly perfect balance between the effect on C_α and that on C_β, with the former slightly prevailing. In addition, conjugation between the substituent and the double bond which develops in the transition state could explain the accelerating effect of the methyl group, and, on the same basis also the fact that the *p*-chloro-substituted compound (Ie) exhibits a slightly larger rate constant than the *m*-chloro-substituted compound (If) could be rationalized. However, this proposal does not appear consistent with the small kinetic effect of the α-phenyl group discussed above. Clearly this effect indicates that in the transition state of the elimination reaction of β-phenyl activated systems there is very little development of double bond character.

A more important role, for compound (Ig), of the elimination reaction promoted by sodium ethoxide ion pairs, could be suggested, since for this compound larger base concentrations were used than for the other substrates. However, this cannot be the cause of the positive kinetic effect, since ion pairs should be less reactive than dissociated ions.

Also in the elimination reactions of α-arylethyl bromides in EtONa–EtOH[4] the trend of the effects of α-aryl substituents is qualitatively similar to that found in our systems. In spite of this trend, these reactions, on the basis of the β-hydrogen kinetic isotope effect and of the effect on the rate of a β-methyl group, were suggested to occur *via* a 'nearly *E*1' transition state. Of course, the transition state for the elimination reactions of α-arylethyl bromides is expected to have less carbanionic character than that of the reactions of 1,2-diarylethyl chlorides since the former systems lack the acidic β-phenyl group and have a better leaving group; however, in our opinion, a positive kinetic effect of electron-withdrawing α-aryl substituents is not compatible with the presence of a substantial positive charge at C_α in the transition state. A 'central' rather than a 'nearly *E*1' transition state seems therefore more plausible for the elimination reactions of α-arylethyl bromides in EtONa–EtOH. It may be mentioned, in this respect, that, for the halide ion induced eliminations in dipolar aprotic solvent a 'nearly *E*1' transition state was excluded on the basis that these reactions exhibit little sensitivity to the nature of α-aryl substituents.[9]

If the above reasoning is correct bimolecular eliminations which utilize a 'nearly *E*1' transition state are very unusual reactions; in fact, we do not know of any *E*2 elimination for which a transition state of this type has been clearly established. Probably the most common situation in bimolecular β-eliminations is that,

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* We thank a referee for this suggestion.

[6] E. D. Hughes, C. K. Ingold, and V. J. Shiner, jun., *J. Chem. Soc.*, 1953, 3827.

[7] G. Biale, D. Cook, D. J. Lloyd, A. J. Parker, I. D. R. Stevens, J. Takahashi, and S. Winstein, *J. Amer. Chem. Soc.*, 1971, **93**, 4735.

[8] E. R. Thornton, *J. Amer. Chem. Soc.*, 1967, **89**, 2915; L. J. Steffa and E. R. Thornton, *ibid.*, p. 6149.

[9] D. J. Lloyd and A. J. Parker, *Tetrahedron Letters*, 1970, 5029.

in the transition state, the degree of C_β–H bond breaking is larger than or equal to the degree of C_α–leaving group bond breaking.

Finally, it seems of interest that the general conclusion that electron-withdrawing α-phenyl substituents exert a favourable effect on the rate of elimination could be taken as evidence against the recent proposal that *E*2 elimination reactions from α-phenyl substituted systems can occur *via* ion pair intermediates.[10] Accordingly, on the basis of this proposal, the observed kinetic effects of the electron-withdrawing α-phenyl substituents would require that the effect (unfavourable) of these substituents on the formation of the ion pair, a reaction which produces a positive charge at C_α, is overcome by the effect (favourable) they exert in the subsequent reaction of the ion pair with the base.

EXPERIMENTAL

Materials.—Compounds (Ia, b, e, f, and h) were prepared by the treatment of the corresponding alcohols with $SOCl_2$. With the exception of 1-*p*-nitrophenyl-2-phenylethanol the alcohols were obtained, according to standard procedures, by the reaction between the appropriately substituted benzylmagnesium chlorides and benzaldehyde or phenylmagnesium bromide and the appropriately substituted benzaldehyde. 1-*p*-Nitrophenyl-2-phenylethanol was prepared from *p*-nitrostilbene oxide [11] according to a procedure described in the literature. Compounds (Ic and d) were prepared by the Meerwein [12] reaction between styrene and the diazonium chloride of *p*-chloro- and *p*-nitro-aniline respectively. All the chloro-derivatives were purified by column chromatography on deactivated silica gel and were obtained with a purity >95%. Compound (Ih) was an exception; in spite of several recrystallizations and much column chromatography it was not possible to obtain this compound with a purity >80%, the main impurity being 4-nitro-*trans*-stilbene.

The properties of alcohols and chlorides were as follows: 1,2-diphenylethanol, m.p. 67—68° (lit.,[13] 67°); 2-phenyl-1-*p*-tolylethanol, m.p. 67·5—68° (lit.,[14] 66·8—68·2°); 1-phenyl-2-*p*-tolylethanol, m.p. 76—78°; 1-*p*-chlorophenyl-2-phenylethanol, m.p. 53—54°; 1-*m*-chlorophenyl-2-phenylethanol, b.p. 123° at 0·01 mmHg (lit.,[15] 157° at 0·15 mmHg); 1-*p*-nitrophenyl-2-phenylethanol, m.p. 112—114° (lit.,[12] 109—110°); 1-chloro-1,2-diphenylethane, n_D^{20} 1·5818 (lit.,[16] 1·5825), τ (CCl_4) 6·79 (2H, d), 5·15 (1H, t), and 3·00 (10H, m); 1-chloro-1-*p*-tolyl-2-phenylethane, n_D^{20} 1·5796, τ ($CDCl_3$) 7·67 (3H, s), 6·65 (2H, d), 5·00 (1H, t), and 2·85 (9H, m); 1-chloro-1-phenyl-2-*p*-tolylethane, n_D^{20} 1·5770 (lit.,[16] 1·5766), τ (CCl_4) 7·79 (3H, s), 6·79 (2H, d), 5·15 (1H, t), and 3·00 (9H, m); 1-chloro-1-*p*-chlorophenyl-2-phenylethane, m.p. 35·5—37°, τ (CCl_4) 6·79 (2H, d), 5·15 (1H, t), and 2·88 (9H, m); 1-chloro-1-*m*-chlorophenyl-2-phenylethane, n_D^{20} 1·5847, τ ($CDCl_3$) 6·65 (2H, d), 5·04 (1H, t), and 2·85 (9H, m); 1-chloro-1-phenyl-2-*p*-chlorophenylethane, m.p. 75·7—77° (lit.,[16] 75°), τ (CCl_4) 6·79 (2H, d), 5·15 (1H, t), and 3·00 (9H, m); 1-chloro-1-phenyl-2-*p*-nitrophenylethane, m.p. 91—91·5° (lit.,[16] 84—85°), τ (CCl_4) 6·64 (2H, d), 5·00 (1H, t), and 2·79 (9H, m); 1-chloro-1-*p*-nitrophenyl-2-phenylethane, m.p. 62—66°, τ (CCl_4) 6·76 (2H, d), 5·03 (1H, t), and 2·91 (9H, m).

trans-Stilbene was a commercial product (Fluka purissimum) recrystallized from light petroleum. Substituted stilbenes were obtained by the reaction of the chloro-derivatives (Ia—g) with EtO^- in EtOH. Their properties were as follows: *trans*-stilbene, m.p. 122—123° (lit.,[17] 124°), $\lambda_{max.}$ (EtOH) 296 nm (ε 2·84 × 10^4) [lit.,[18] 294 nm (2·85 × 10^4)]; *p*-chloro-*trans*-stilbene, m.p. 130—131° (lit.,[19] 128°), $\lambda_{max.}$ (EtOH) 299 nm (ε 3·15 × 10^4); *p*-methyl-*trans*-stilbene, m.p. 125—126° (lit.,[20] 119°), $\lambda_{max.}$ (EtOH) 297·5 nm (ε 2·82 × 10^4); *p*-nitro-*trans*-stilbene, m.p. 154—155°, $\lambda_{max.}$ (EtOH) 348 nm (ε 2·20 × 10^4) [lit.,[21] 154—155°; 348 nm (2·20 × 10^4)]; *m*-chloro-*trans*-stilbene, m.p. 74·5—75·5° (lit.,[22] 73—74°), $\lambda_{max.}$ (EtOH) 298 nm (ε 3·22 × 10^4).

Ethanol was purified as described [23] and carefully fractionated with a Todd column.

Kinetics.—For all compounds, except (Ig), the appearance of stilbene or substituted stilbene was followed spectrophotometrically. A solution (2 ml) of known concentration of the desired compound was placed in a volumetric flask (25 ml) and a solution of sodium ethoxide of the appropriate concentration was added to the calibration mark. Both solutions were previously equilibrated thermally in a thermostatted bath. After adequate agitation, the flask was placed in a thermostatted bath and allowed to come to thermal equilibrium. Portions (1 ml) were then withdrawn periodically and poured into a dilute solution of HCl (or $HClO_4$) in absolute EtOH placed in a volumetric flask (25 ml). Ethanol was added to the calibration mark and the optical density of the solution measured at the absorption maximum of the particular stilbene formed in the reaction.

For the very reactive compound (Id) the solutions (each 1·5 ml) were prepared in a stoppered two-limb cell. The cell was 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 placed again in the compartment of the spectrophotometer.

A large excess of base (at least 500 fold) was used in each case and pseudo-first-order rate constants were determined from the slope of a plot of log $(D_\infty - D_t)$ against time. The yield of olefin was determined from the value of D_∞ (optical density at infinite time).

The spectrophotometric method was not completely satisfactory for compound (Ig), for which very large (0·7—1·3M) base concentrations had to be used. In this case

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[23] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1964, p. 168.

kinetics were followed by determining the chloride ion produced in the reaction. The concentration of substrate was *ca.* $1{\cdot}5 \times 10^{-2}$M. Portions of the kinetic solution were withdrawn periodically and poured into a separatory funnel containing pentane (40 ml), water (30 ml), and 6N-HNO_3 (2 ml). After rapid mixing the aqueous phase was separated and the organic layer further washed with water (2 × 25 ml). The combined aqueous phases were titrated potentiometrically with 0·02N-$AgNO_3$. The yield of olefin formed in the reaction was determined either spectrophotometrically (after 250 fold dilution of the mixture with absolute EtOH) or by g.l.c. analysis (2 m; 10% SE30 on 60—80 mesh Chromosorb W; 186°) with 1,2-diphenylethane as internal standard, and practically identical results were obtained. Some kinetic experiments on compound (If) were carried out also according to this procedure and the results were in good agreement with those obtained by the spectrophotometric method.

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