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Reactions of diaryl-halogeno-ethylenes with sodium ethoxide - Part IV. Cis-and trans-1-p-anysil-1-phenyl-2-chloro-ethylenes. Kinetics and Mechanism

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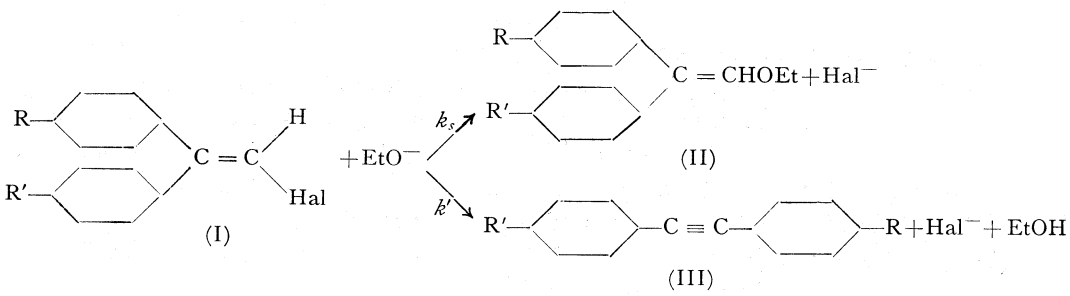
Chimica fisica. — *Reactions of diaryl–halogeno–ethylenes with sodium ethoxide* – Part IV. Cis– *and* trans–*1–p–anysil–1–phenyl–2–chloro–ethylenes. Kinetics and Mechanism* [(*)]. Nota di PAOLO BELTRAME e GABRIELE CORTILI, presentata [(**)] dal Corrisp. M. SIMONETTA.

The competitive α–elimination (F.B.W. rearrangement) [1] and nucleophilic substitution occurring in some 1,1–diaryl–2–halogeno–ethylenes (I) in the presence of ethoxide ion in ethanol



a: R = H ; R′ = OMe (*cis*)
b: R = OMe ; R′ = H (*trans*)
c: R = R′ = H
d: R = R′ = Me
e: R = R′ = OMe
(Hal = Cl or Br)

have been studied previously [2] by (i) varying R and R′ on one or both of the phenyl groups and (ii) varying the halogen.

Substituent effects were measured in particular for the *p*–methoxy group, through the study of the *cis*– and *trans*– monosubstituted bromoderivatives (I–a–Br and I–b–Br) [2 *a*] and the disubstituted derivatives I–e–Br and I–e–Cl [2 *b*]. For bromide ion as the leaving group, an increasing tendency towards α–elimination and rearrangement was found in the order (R , R′): H , H < H, *cis*–OMe < *trans*–OMe , H < OMe , OMe.

These kinetic studies have an inherent limitation, because the second order rate constant k', obtained for the α–elimination, appears to be the combination of an equilibrium and a rate constant. Indeed, the F. B. W. reaction is very probably a two-step process, a fast abstraction of the proton being followed by slow rearrangement of the vinyl anion with concerted

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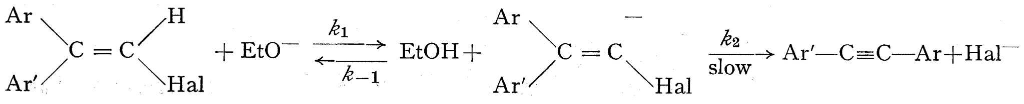
(*) Work done at the Istituto di Chimica fisica – Università di Milano.
(**) Nella seduta del 13 novembre 1965.

removal of the halide ion [3, 4, 5, 6]:



(I) (IV) (III)

Application of the steady state approximation gives $k' = k_1 k_2/(k_{-1} + k_2)$, that reduces to

$$k' = k_1 k_2/k_{-1} \tag{1}$$

if $k_2 \ll k_{-1}$. This is apparently fulfilled in the case of *t*–butoxide in *t*–butyl alcohol as a base, since the rate of deuterium exchange of 1, 1–diphenyl–bromoethylene has been found to be much higher than the rate of conversion to diphenyl–acetylene [3*b*]. Although the corresponding behaviour of substrates (I) in ethoxide/ethanol solution has not been checked directly, it seems probable that eq. (1) holds, that is (I) and (IV) can be considered in equilibrium. In any case the measured effects would be a combination of influences on the acid–base equilibrium and on the subsequent reaction.

For a better understanding of the reaction mechanism, the kinetic behaviour of the *cis* and *trans* isomers of 1–*p*–anisyl–1–phenyl–2–chloro–ethylene (I–a–Cl and I–b–Cl) has been studied, in order to compare them with the other compounds of the series.

EXPERIMENTAL.

Materials and products. — Dry ethanol for kinetics was prepared from "99.9%" commercial ethanol by treatment with magnesium and distillation. The solvent used for the U. V. measurements was methanol R. S. (C. Erba).

Preparation of *cis*– and *trans*– *1–p–Methoxyphenyl–1–phenyl–2–chloro–ethylenes* (I–a–Cl and I–b–Cl) and identification of the products of reaction with ethoxide ion have been previously described [7].

Kinetics. — A weighed amount of organic compound was dissolved in a freshly prepared solution of sodium ethoxide in ethanol using a calibrated volumetric flask. Concentrations were ca. 0.04 M in substrate and ca. 0.5 M in ethoxide ion. The concentration of ethoxide ion was determined by titration with 0.5 N hydrochloric acid.

5 ml samples were pipetted into Pyrex tubes, sealed and introduced in a thermostat kept within less than ± 0.2°. Timed samples were withdrawn, quenched by cooling and the content of the tube diluted to 50 ml with methanol in a volumetric flask, care being taken to dissolve the small sodium chloride crystals in the bottom of the tube. Samples (3 ml) were pipetted out of this flask and further diluted for the spectrophotometric analysis of *p*–anisyl–phenyl–acetylene, effected by measurements at 305 mμ. The residual solution was used for the potentiometric titration of chloride ion by means of 0.05 M silver nitrate. Reactions were followed usually to ca. 70% completion.

Second-order overall rate constants (K) were obtained graphically from linear plots of $[2.303/(b-a)] \log [(b-x)/(a-x)]$ vs. time; b = initial conc. of ethoxide ion; a = initial conc. of organic chloride; x = concentration of chloride ion at time t.

The concentration of acetylenic product (y) at time t was obtained from the equation;

$$y = \frac{\varepsilon - \varepsilon_0}{25650 - \varepsilon_0} \cdot a. \tag{2}$$

where ε_0 and ε are molar extinction coefficients of the reaction mixture at $\lambda = 305\ m\mu$, at time zero and at time t respectively, whilst 25650 represents the theoretical value for complete conversion to *p*-anisyl-phenyl-acetylene [2*a*]. At each time the ratio of the amount of acetylenic product to the total amount of organic chloride reacted (y/x) was evaluated; averaging along the course of the kinetic run a " fraction of elimination " F_y could be calculated:

$$F_y = \left(\frac{y}{x}\right)_{av} \tag{3}$$

Some (y/x) values were discarded, since their deviation from the average value was more than twice the mean deviation. The second order rate constant (k') of the elimination-rearrangement reaction was thus obtained for each run by the equation:

$$k' = K \cdot F_y . \tag{4}$$

Both overall and elimination rate constants were corrected for solvent expansion, by means of ratio (d_{20}/d_T).

Rate constants for the substitution reaction (k_s) were obtained by difference: $k_s = K - k'$. Arrhenius activation energies ΔE_A were evaluated from plots of the logarithms of the rate constants vs. $1/T$. Activation entropies at 130° were calculated from the equation: $\Delta S_A = 4.576 \log A - 61.130$ (cal/mole °K), where A is the frequency factor ($l \cdot mol^{-1} sec^{-1}$). Probable errors of rate constants and of other kinetic parameters were evaluated by standard methods. A typical run (I-a-Cl ; temp. = 139.6° ; $a = 0.0401$ M ; $b = 0.5668$ M; $\varepsilon_0 = 386$) gave the following results:

time (min)	0.0497 M $AgNO_3$ (ml)	$10^4 \cdot x$	ε	$10^4 \cdot y$	y/x
1105	0.405	42.8	1160	13.4	0.313
3860	1.12	118	3323	50.8	(0.429)
5225	1.41	149	3791	58.9	0.395
6820	1.74	184	4708	68.6	0.373
8110	1.97	208	4950	72.5	0.349
9630	2.19	231	5124	75.2	0.326
10985	2.37	251	5452	80.4	0.320
13855	2.65	280	6076	90.4	0.323

It was therefore obtained: $(y/x)_{av} = F_y = 0.343$; $K = 3.093 \cdot 10^{-6}$ $l \cdot mol^{-1}$ sec^{-1} ; $k' = 1.060 \cdot 10^{-6}$ $l \cdot mol^{-1}$ sec^{-1}.

RESULTS.

Overall rate constants (K) from titration of chloride ion and " fractions of elimination " (F_y) from spectrophotometric determination of the acetylenic product are shown in Table I; α–elimination rate constants ($k' = K \cdot F_y$) and substitution rate constants ($k_s = K - k'$) are also listed.

TABLE I.

Kinetic results for reactions of I–a–Cl *and* I–b–Cl *with sodium ethoxide.*

(K , k' and k_s in $l \cdot mol^{-1}$ sec^{-1}).

Temp. (°C)	$K \cdot 10^6$	F_y	$k' \cdot 10^6$	$k_s \cdot 10^6$
Cis–1–*p*–methoxyphenyl–1–phenyl–2–chloroethylene (I–a–Cl).				
130.0	1.299	0.238	0.31	0.99
139.6	3.093	0.343	1.06	2.03
145.0	5.140	0.389	2.00	3.14
Trans–1–*p*–methoxyphenyl–1–phenyl–2–chloroethylene (I–b–Cl).				
130.0	1.106	0.327	0.36	0.75
135.1	2.067	0.398	0.82	1.25
139.6	3.006	0.464	1.39	1.61
145.0	5.503	0.545	3.00	2.50
149.0	8.259	0.534	4.41	3.85

Probable errors are less than 1 % for K, ca. 6 % for k' and 5 % for k_s values.

The Arrhenius equation is obeyed by all three types of constants in reasonable approximation. This might at first seem surprising, as K is not the rate constant of a single reaction, but the sum of k' and k_s; moreover, k' itself is probably a combination of an equilibrium and a kinetic constant. Apparently the experimental temperature range was too restricted to discover any deviation from " Arrhenius " behaviour. Therefore one can obtain the relevant parameters, but their real significance is open to discussion. The parameters referring to K are merely empirical, useful for interpolation or limited extrapolation. If k' can be written as product of an acid–base equilibrium constant K_{eq} and a rate constant k_2 for the elimination-rearrangement of the carbanion Ar(Ar′)C=C—Cl⁻ (IV–Cl), then the ΔE_A for k' is the sum of a heat of ionization ΔE_i and a true activation energy $\Delta E^{\ddagger}$; the Arrhenius equation should hold as long as ΔE_i and $\Delta E^{\ddagger}$ are temperature independent. Similarly, each value of the apparent activation entropy ΔS_A obtained from k' should be the sum of an ionization and true activation value.

Arrhenius and thermodynamic parameters referring to k' and k_s are given in Table II. Interpolated or extrapolated rate constants were calculated from these data as required.

TABLE II.

Apparent activation energy (ΔE_A ; Kcal/mole), *frequency factor* (A ; $l \cdot mol^{-1} sec^{-1}$) *and activation entropy* (ΔS_A ; cal/(mole °K)) *for reactions of* I–a–Cl and I–b–Cl.

ISOMER	F.B.W. REACTION			SUBSTITUTION REACTION		
	ΔE_A	log A	ΔS_A (130°)	ΔE_A	log A	ΔS_A (130°)
I–a–Cl (*cis*)	41.8	16.1	+ 12.7	25.6	7.9	— 25.1
I–b–Cl (*trans*)	44.8	17.9	+ 20.7	28.2	9.2	— 19.2

Probable errors are 1–2 Kcal for ΔE_A ; 0.5–1 for log A; 2–4 e.u. for ΔS_A .

DISCUSSION.

The *cis*– and *trans*– isomers, I–a–Cl and I–b–Cl respectively, can be compared, as to their kinetic behaviour, with the corresponding I–a–Br and I–b–Br, for which kinetic data at 120° are available. The effect of the leaving group is quite large for k' and very small for the substitution rate constants:

$$\frac{k'_{RBr}}{k'_{RCl}} = 35.6\ (cis)\ ; \quad 46.7\ (trans) \text{ at } 120^0$$

$$\frac{k_{s(RBr)}}{k_{s(RCl)}} = 1.4\ (cis)\ ; \quad — \quad \text{at } 120^0.$$

The importance of *p*–substitution on the reactivity of diaryl–chloro-ethylenes results from the sequence of data in Table III.

The nature of the leaving group and of the *p*–substituents has a remarkably different influence on the rate coefficiencts k' and k_s : while the substitution reaction has some S$_N$Ar character (Cl $\sim$ Br, with electron-releasing substituents decreasing the constant), the F. B. W. reaction has a strong "element effect", in agreement with values previously found [2*b*] and is favoured by methyl and methoxy substituents.

TABLE III.

p–Substituents effect on F. B. W. and substitution reactions of some diaryl–chloro–ethylenes (I–Cl) *with ethoxide ion.*

Temp. = 130.0° k' and k_s in $l \cdot mol^{-1} sec^{-1}$

REACTANT	I–c–Cl [2 *b*]	I–d–Cl [2 *b*]	I–a–Cl	I–b–Cl	I–e–Cl [2 *b*]
R =	H	CH_3	H	OCH_3	OCH_3
R′=	H	CH_3	OCH_3	H	OCH_3
$k' \cdot 10^6$	0.20	0.25	0.31	0.36	0.52
Relative rates	1	1.25	1.55	1.8	2.6
$k_s \cdot 10^6$	2.25	0.44	0.99	0.75	0.53
Relative rates	1	0.20	0.44	0.33	0.24

The effect of the leaving group on the latter reaction corresponds to a dehydrohalogenation in which C–Hal bond breaking is advanced in the transition state of the rate limiting step. One might envisage complete α–elimination preceding the rearrangement, but such a hypothesis has been discarded because the *trans*–stereospecificity usually displayed by the F. B. W. reaction [3*a*, 4] is hardly consistent with a carbene intermediate (1).

The enhancement of k' due to methoxy groups follows a well-defined sequence (R , R′ : H , H < H , *cis*–OMe < *trans*–OMe , H < OMe , OMe) that is also found for compounds I–Br. As to the numerical significance of such an effect, it should be remembered that electron-releasing *p*–substituents cannot but depress the acid ionization of the substrate, and therefore, the

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(1) The only reported example of non-stereospecificity refers to reactions with sodium hydroxyethoxide in boiling ethylene glycol [8] but such a high temperature could have led to isomerization.

increase in k' should be the net result of a negative effect on the pre-equilibrium and a positive effect on the subsequent slow reaction, with the latter predominating.

Since the F. B. W. reaction is favoured more by a methoxy group on the *trans* (migrating) than on the *cis* (non migrating) benzene ring, an internal nucleophilic attack of the migrating aryl-group on the C–Hal bond is indicated. The presence of a carbanionic charge at the site of attack does not provide a prohibitive barrier because C–Hal bond breaking should be so much advanced with respect to the migration of the aryl-group that the charge is largely displaced from carbon to the halogen atom (Hal = Br or Cl).

Molecular orbital calculations [9] have shown that a *p*–methoxy substituent should lead to a gain in π–electron energy for the F. B. W. rearrangement, on both the fixed phenyl or the migrating phenyl, but the effect has been shown to be greater for the methoxy substituent on the migrating group, favouring the order of reactivity found experimentally.

Apparent activation energies and entropies from k_s constants are reasonable values for a vinylic non-activated substitution with a fairly rigid transition state. The values for ΔE_A and ΔS_A of the F. B. W. reaction fall in a typical range for this kind of process [2 *b*]; their high values result from a combination of ionization and true activation values, but so far they cannot be split into the respective terms.

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RIASSUNTO. — È stata studiata, nel campo di temperature da 130 a 149° C, la cinetica delle reazioni del *cis*– e del *trans*–1–fenil–1–*p*–metossifenil–2–cloroetilene con ioni etilato in etanolo; le due reazioni di α–eliminazione con trasposizione a fenil–*p*–metossifenil–acetilene e di sostituzione nucleofila sono state seguite mediante titolazione degli ioni cloro e determinazione spettrofotometrica del prodotto acetilenico.

I risultati sono confrontati con quelli ottenuti in precedenza da altri diaril–alogeno–etileni.