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Kinetic study of base-promoted elimination reactions of some 1,1,1-trihalo-2,2-bis(dimethoxyphenyl)ethanes in alcoholic solutions

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ABSTRACT: The base–promoted elimination reactions of 1,1,1-trichloro-2,2-bis(dimethoxyphenyl)ethanes were investigated. The bis(3,4-dimethoxyphenyl)ethane was found to be more reactive than the bis(2,5-dimethoxyphenyl)ethane and the latter more reactive than the bis(2,4-dimethoxyphenyl)ethane. Kinetic data relative to 1,1,1-trihalo(chloro or bromo)-2,2-bis(3,4-dimethoxyphenyl)ethanes show that the tribromo reacts faster than trichloro derivative and that the reactions are general-base promoted with Brønsted β values of about 0.6. A kinetic isotope effect, with k_H/k_D ratio ranging from 3.5 to 5.7, for the base-promoted elimination reaction of 1,1,1-trichloro-2,2-bis(3,4-dimethoxyphenyl)ethane was found. Tunneling occurs for methoxide and ethoxide ion-promoted eliminations. Activation parameters for alkoxy-promoted elimination show a similar trend for chloride and bromide derivatives. The data collected seem to confirm that there is contiguity between $E1cB_{irr}$ and $E2$ mechanisms. © 1998 John Wiley & Sons, Ltd.

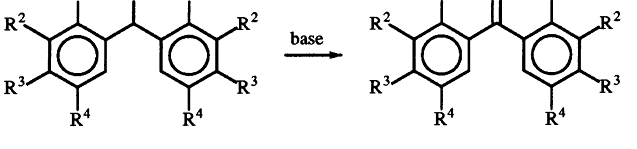
KEYWORDS: 1,1,1-trihalo-2,2-bis(dimethoxyphenyl)ethanes; base-promoted elimination; reaction mechanism

INTRODUCTION

The dehydrohalogenation reaction[1] is one among the most studied organic reactions. It is well known that both the electronic and steric properties of a β-aryl substituent affect the reactivity of base-promoted elimination of 2-arylethyl halides. For example, both the observed variation in reactivity for methoxide ion-promoted elimination of a series of 1,1,1-trichloro-2,2-bis(4-substituted phenyl)ethanes (**la**)[2] and the relative reactivities of the hydroxide ion-promoted reactions of 2-(2,4-dinitrophenyl)ethyl bromide, 2-(4-nitrophenyl)ethyl bromide and 2-phenylethyl bromide in aqueous solutions (7400:110:1) were well explained by electronic effects of the β-aryl group.[3] In contrast, the abnormally slow elimination of 2-(2,4,6-trinitrophenyl)ethyl bromide, which reacts at the same rate as the dinitro derivative, was attributed to steric effects that reduce the efficiency of the electron-withdrawing 2,4,6-trinitrophenyl group.[3]

The interest in the properties of 1,1-diarylethanes[4] induced us to investigate the base-promoted elimination reaction of the bis(3,4-dimethoxphenyl) (**lb**), bis(2,5-dimethoxyphenyl) (**1c**). and bis(2,4-dimethoxyphenyl) (**1d**) derivatives[5].

We now report a kinetic study undertaken with a view to determining the dependence of the reactivity and the mechanism for compounds **1b–d** on the electronic and proximity effects. An *E*1*cB* mechanism has been suggested[5] for the base-promoted dehydrochlorination of **la**. In order to verify whether this mechanism works also in our case and to study the effect of the chlorine atoms by more bulky bromine atoms, we collected kinetic



1 : Y = CX_3

2 : Y = CX_2

a : X = Cl;	$R^1 = R^2 = R^4 = H$	R^3 = variable substituent
b : X = Cl;	$R^1 = R^4 = H$	$R^2 = R^3 = OMe$
c : X = Cl;	$R^2 = R^3 = H$	$R^1 = R^4 = OMe$
d : X = Cl;	$R^2 = R^4 = H$	$R^1 = R^3 = OMe$
e : X = Br;	$R^1 = R^4 = H$	$R^2 = R^3 = OMe$

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data relative to base-promoted elimination reactions of **1b–d**, of the 2-^{2}H derivative (**1bD**) and of **1e** to give the corresponding 1,1-dichloro- (**2b–d**) and 1,1-dibromo- (**2e**) 2,2-bis(3,4-dimethoxyphenyl)ethenes. The kinetic studies were performed in the temperature range 20–50°C using MeO^-, EtO^-, Bu^tO^-, $C_6H_5O^-$ and p-$NO_2C_6H_4O^-$ as bases.

RESULTS AND DISCUSSION

We observed that in the base-promoted dehydrochlorination of some 1,1,1-trichloro-2,2-dimethoxyphenylethanes, changes in the aryl structure gave rise to substantial changes in reactivity. A comparison among the rate constants for base-promoted eliminations of the bis(3,4-dimethoxyphenyl) (**1b**), bis(2,5-dimethoxyphenyl) (**1c**) and bis(2,4-dimethoxyphenyl) **1d**) derivatives shows (Table 1) a decrease in reactivity in the order **1b** > **1c** > **1d**, with a rate increase from **1d** to **1b** of about four orders of magnitude.

For **1b–d**, assuming that the electronic substituent effects of methoxy groups are additive, the reactivity order **1b** ≈ **1c** > **1d** should be observed if only electronic effects operate and the order **1b** > **1c** > **1d** if both electronic and steric effects operate. However, since in **1b–d**, the aryl rings have at least one unsubstituted *ortho* position, a steric effect such as that assumed for 2-(2,4,6-trinitrophenyl)ethyl bromide should have little or no influence on reactivity. Because of the low reactivity of **1c** and **1d**, we did not carry out a complete kinetic investigation on these derivatives.

The kinetic data showed that the rate of elimination reaction of **1b, 1bD** and **1e** depends on the concentration of all basic species present in reaction mixture. The elimination reactions of **1b, 1bD** and **1e** follow the rate of equation (1) for bases such as alkoxide ions (MeO^-, EtO^- and Bu^tO^-) and equation (2) for phenoxide ions ($C_6H_5O^-$ and p-$NO_2C_6H_4O^-$):

$$k_{obsd} = k_{RO^-}[RO^-] \qquad (1)$$

where k_{obsd} is the pseudo-first-order rate constant and k_{RO^-} is the second-order rate constant for alkoxide ion-promoted reactions, and

$$k_{obsd} = k_{EtO^-} + k_{PhO^-}[PhO^-] \qquad (2)$$

where k_{EtO^-} and k_{PhO^-} are the rate constants for the ethoxide (from the solvent) and phenoxide ion-promoted reactions. Rate constants for phenoxide ion-promoted reactions were obtained from the slopes of plots of k_{obsd} against phenoxide ion concentration at a constant phenoxide to phenol concentration ratio; under this condition, the ethoxide ion concentration coming from the equilibrium $PhO^- + EtOH = PhOH + EtO^-$ is constant. For all of the bases used a good straight line was obtained by plotting k_{obs} *versus* base concentration.

In Table 1 are reported the Brønsted β values for the reactions of **1b, 1bD** and **1e**. Since the change in solvent, going from EtOH to MeOH or Bu^{t}OH, can affect the β values, because of different solvent effects, determined the β values (*ca* 0.6) by plotting log k values obtained for elimination reactions of **1b, 1bD** and **1e** promoted by ethoxide, phenoxide and p-nitrophenoxide ions as base catalysts, against the pK_a values[6] of the bases in EtOH. However, Brønsted β values of *ca* 0.5, i.e. slightly smaller than 0.6, were calculated when data relative to all five bases were used. In this case for methoxide and *tert*-butoxide ions we calculated the pK_a values in EtOH from those in water[7] since a good correlation was found between pK_a values in these two solvents.

Under the reaction conditions reported here, Scheme 1 depicts the commonly accepted mechanisms for base-promoted β-elimination reactions, either via carbanion intermediates (free or ion-paired) in a stepwise mechanism (*E*1*cB*) or via a one-step concerted mechanism (*E*2).

Table 1. Second-order rate constants (dm^3 mol^{-1} s^{-1})^a, Brønsted β values and relative halogen leaving group abilities for the base-promoted eliminations of **1b, 1bD, 1c, 1d** and **1e** at 40°C

Compound	k_{RO^-}						
	MeO^-	EtO^-	Bu^tO^-	$C_6H_5O^-$	p-$NO_2C_6H_4O^-$	β^b	β^c
1b	1.04×10^{-3}	3.46×10^{-3}	1.47×10^{-2}	5.00×10^{-6}	1.80×10^{-7}	0.61	0.54
1bD	2.12×10^{-4}	6.11×10^{-4}	4.93×10^{-3}	1.10×10^{-6}	5.15×10^{-8}	0.58	0.53
1c	1.77×10^{-6}						
1d	$< 10^{-7}$						
1e	2.71×10^{-2}	9.50×10^{-2}	3.83×10^{-1}	2.02×10^{-4}	9.40×10^{-6}	0.57	0.50
k_H/k_D	4.91	5.66	3.53	4.55	3.5		
k_{Br}/k_{Cl}	26.1	27.5	22.0	40.4	52.2		
pK_a^{d}	20.1^e	20.3	22.8^e	15.8	13.3		

[a] The rate constants are accurate to within ± 3%.

[b] β Values calculated by using the bases, EtO^-, $C_6H_5O^-$ and p-$NO_2C_6H_4O^-$.

[c] β Values calculated by using all five bases.

[d] In ethanol.

[e] Calculated from pK_a values in water reported in Ref. 7.

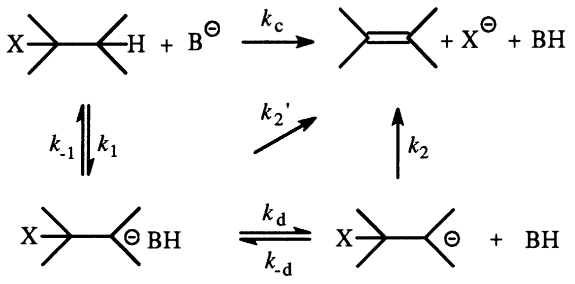
Table 2. Activation parameters[a] and Arrhenius pre-exponential factors (*A*)[a] for the base-promoted eliminations of **1b, 1bD** and **1e**.

Compound	MeO$^-$			EtO$^-$			Bu^{t}O$^-$		
	$H‡$[b] (kJ mol^{-1})	$-S‡$[c] (J K^{-1} mol^{-1})	A (dm^3 mol^{-1} s^{-1})	$H‡$[b] (kJ mol^{-1})	$-S‡$[c] (J K^{-1} mol^{-1})	A (dm^3 mol^{-1} s^{-1})	$H‡$[b] (kJ mol^{-1})	$-$**S**$‡$[c] (J K^{-1} mol^{-1})	A (dm^3 mol^{-1} s^{-1})
1b	71.9	72	2.68×10^9	67.7	75	1.75×10^9	51.8	112	2.24×10^7
1bD	86.1	41	1.30×10^{11}	82.7	42	1.04×10^{11}	55.2	113	2.10×10^7
1e	62.3	76	1.90×10^9	60.6	71	3.10×10^9	44.7	110	3.04×10^7

[a] Calculated from kinetic data collected in the temperature range 20–40°C. Because turbidity was observed in kinetics with Bu^{t}O$^-$ at 20°C, the range 30–50°C was used.
b Calculated at 40°C; experimental uncertainly *ca* 3 kJ mol^{-1}.
c Calculated at 40°C; experimental uncertainty *ca* 8 J K^{-1} mol^{-1}.

The observation of general-base catalysis with Brønsted β values of *ca* 0.6 rules out mechanisms in which breakdown of either an ion-paired or hydrogen-bonded carbanion (k_2') or free carbanion (k_2) is rate limiting because these mechanisms would either not show general-base catalysis (k_2 rate limiting) or give rise to Brønsted β values approaching unity (k_2' rate limiting). General-base catalysis with β values in the range reported here are instead consistent with either $E2$ (via k_c) or $E1cB_{irr}$ mechanisms (k_1 rate-limiting), in which the rate-limiting step involves hydrogen transfer.

The data in Table 1 show that the rate constants for base-promoted eliminations of **1b** and **1e** agree with the order of carbon–halogen bond strength, *i.e.* the tribromo derivative reacts faster than the corresponding trichloro derivative. For various bases and substituents to the leaving group, a k_{Br}/k_{Cl} ratio in the range 5–30 is considered[8] to be consistent with an $E2$ mechanism in which there is partial cleavage of the carbon–halogen bond in the transition state. However, the measured k_{Br}/k_{Cl} ratios make at difficult to rule out the possibility that **1b** and **1e** may also react via an $E1cB_{irr}$ mechanism. An element effect of the kind observed here might also be the result of anionic hyperconjugation, in which the negative charge on the β-carbon is stabilized by anionic hyperconjugation due to overlapping between the β-electron pair and the C—X orbitals. Hyperconjugation should be greatest for carbanions that are poorly delocalized[9] such as those derived from **1b** and **1e**. MNDO calculations show that the β-electron pair lies in the plane of the aryl rings. The observed k_{Br}/k_{Cl} leaving group effect arises from the fact that, as has been suggested,[10] anionic hyperconjugative stabilization energies follow the order Br > Cl and overshadow the polar effect of the halogens. This suggestion has been criticized[11] and Br and Cl have been considered to have similar hyperconjugative effects.



Scheme 1

The fact that the Brønsted β value does not change on going from the bromide to the corresponding chloride derivative is considered to be consistent with an $E1cB_{irr}$ mechanism. In contrast, an increase in β values as the leaving group is made less nucleofugic is a characteristic of $E2$ reactions (and of a variable $E2$ transition-state structure).[12] The data in Table 1 also show that the relative leaving group ability of a bromine atom increases as the catalyst is made less basic. This is the result expected for an $E1cB_{irr}$ mechanism in which the breakdown of the C—H bond in the transition state is greater with a less basic catalyst. In this case the charge density on the β-carbon is higher and consequently hyperconjugation is more effective. Since it is difficult to distinguish between the $E1cB_{irr}$ and $E2$ mechanisms because they would show essentially the same characteristics, a similar trend in reactivity should be observed for an $E2$ mechanism with a variable transition-state structure.

The data in Table 1 show a kinetic isotope effect for base-promoted eliminations of chloride compounds **1b** and **1bD**, the k_H/k_D ratio ranging from 3.5 to 5.7 and increasing as the catalyst is made more basic. For an $E1cB_{irr}$ mechanism the k_H/k_D values should show a maximum when the pK_a of the substrate reaches that of the catalyst.[13] We have not reach at this condition because a pK value (*ca* $\approx$ 30) in ethanol, *ca*. 10 units greater than that of the more basic catalyst used, can be evaluated for **1b**. The pK_a value for **1b** was calculated as suggested by McLennan and Wong.[14]

An analysis of Arrhenius pre-exponential factors indicates an effect of tunneling on methoxide-and ethoxide-promoted eliminations. In fact, for these bases small values (*ca* 0.02) of the ratio A^H/A^D can be calculated from the data in Table 2.

Although the rate constants for methoxide ion-promoted elimination of **1b** are affected by tunneling, the k_H/k_D ratio value for **1b** with the MeO$^-$ –MeOH catalyst system at 45°C was used to calculate the k_H/k_T ratio by means of the Swain–Schaad equation:[15]

$$\log k_H/k_T = 1.44 \log(k_H/k_D) \qquad (3)$$

Equation (3) can be used without corrections[16] since tunneling should not cause[17] major deviations in proton transfers via highly unsymmetrical transition states.

The k_T value (1.87×10^{-4} dm^3 mol^{-1} s^{-1}) so obtained is close to those measured by Streitwieser *et al*.[18] for $E1cB_{irr}$ detritiation reactions of fluorene and indene derivatives. Indeed a good linear correlation ($s = -0.37 \pm 0.02$; $i = 5.09 \pm 0.41$; $r = 0.986$; $n = 10$) was obtained when $\log k_T$ for **1b** and for fluorene and indene derivatives were plotted *versus* the pK_a values.

Table 2 shows a similar trend in the activation parameters for alkoxide ion-promoted eliminations of each compound. In particular, for each compound the same activation parameters for MeO$^-$–MeOH and EtO$^-$–EtOH catalyst systems are observed, whereas a smaller value of the enthalpy and a more negative value of the entropy for Bu^{t}O$^-$–Bu^{t}OH were found. Similar enthalpy values have been calculated for methoxide-promoted $E1cB_{irr}$ elimination of some 1,1,1-trichloro-2,2-diphenyl-substituted ethanes.[1] Furthermore, the trend in entropy values is also consistent with carbanion formation. For this reaction, it has been suggested[19] that the entropy of activation becomes more negative as the difference in pK_a values between the substrate and base decreases. Enthalpy and entropy values more and less negative respectively, than those reported here have been calculated for ethoxide-promoted $E2$ eliminations for 1-bromo-2-phenyl-ethane and-propane.[20]

In conclusion, as mentioned previously, it is difficult to distinguish between $E1cB_{irr}$ and $E2$ mechanism, because the $E2$ mechanism would be expected to show most of the characteristics of an $E1cB_{irr}$ mechanism. The leaving group effect seems to be explained better by an $E2$ mechanism, but the absence of changes in β and activation parameter values between the chloro (**1b**) and bromo **(1e)** derivatives seems to indicate an $E1cB_{irr}$ mechanism. The data collected in this work could provide further confirmation that the $E1cB_{irr}$ mechanism is transformed into the $E2$ mechanism with very little change in the transition-state structure.[21]

EXPERIMENTAL

The melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. IR spectra were obtained with a Perkin-Elmer model 1310 IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-E 250 MHz spectrometer in deuterochloroform solutions. Chemical shifts are reported as δ values (ppm) relative to TMS as an internal standard. Kinetic experiments were performed on a Beckman DU 650 UV–visible spectrophotometer.

Materials. The MeOH,[22] EtOH[22] and Bu^{t}OH[23] solvents and the base solutions were purified and/or prepared as reported. Compounds **1b, 1c**[24], **1d**[25] and **1e**[26] were prepared by published methods.

1,1,1-Trichloro-2-(3,4-dimethoxyphenyl)[2-^{2}H]ethanol. LiAlD$_4$ (1.2 g, 0.03 mol) was added to suspension of 2,2,2-trichloro-3′,4′-dimethoxyacetophenone[27] (8.5 g, 0.03 mol) in anhydrous diethyl ether (75 cm^3) and after normal work-up 83% of 1,1,1-trichloro-2-(3,4-dimethoxyphenyl)[2-^{2}H]ethanol was obtained. The compound was recrystallized from ethanol; m.p. 135°C (found: C, 41.84; H, 4.28; Cl, 37.18. $C_{10}H_{10}DCl_3O_3$ requires C, 41.91; H, 4.21; Cl, 37.12%); IR, ν_{max} 3420 cm^{-1} ^{1}HNMR, δ_H(250 MHz, CDCl$_3$) 3.33 (1 H, s, br exangeable with D$_2$O, OH), 3.90 (6 H, s, 2 OMe), 6.87 (1 H, d, J 8.1 Hz, 5-H), 7.15 (1 H, dd, J 2.0 and 8.1 Hz, 6-H), 7.17 (1 H, d, J 2.0 Hz, 2-H).

1,1,1-Trichloro-2,2-bis(3,4-dimethoxyphenyl)[2-^{2}H]ethane (1bD). A solution of 1,1,1-trichloro-2-(3,4-dimethoxyphenyl)[2-^{2}H]ethanol (0.21 mol) in glacial acetic acid (150 cm^3) was added dropwise to a stirred solution of 1,2-dimethoxybenzene (0.21 mol) in glacial acetic acid–98% sulphuric acid (1:1, v:v) (200 cm^3) while the temperature was maintained below 20°C. After standing at room temperature overnight, the mixture was poured on to crushed ice and the oil obtained was extracted with ethyl acetate. After neutralization, the solvent was removed under reduced pressure. The residue was steam distilled in order to remove any unreacted 1,2-dimethoxybenzene. The distillation residue was extracted with ethyl acetate, dried and evaporated. Crystallization of the crude product from ethanol afforded **1bD** as white crystals, yield 95%, m.p. 116°C (found: C, 53.20; H, 5.00; Cl, 26.20. $C_{18}H_{18}DCl_3O_4$ requires C, 53.16; H, 4.95; Cl, 26.15%); 1H NMR, δ_H (250 MHz, CDCl$_3$) 3.85 (6 H, s, 2 OMe), 3.87 (6 H, s, 2 OMe), 6.84 (2 H, d, J 8.3 Hz, 2 5-H), 7.14 (2 H, d, J 2.1 Hz, 2 2-H), 7.20 (2 H dd, J 2.0 and 8.1 Hz, 2 6-H); ^{13}C NMR δ_C (62.5 Mz, CDCl$_3$) 55.77 (2 OCH$_3$), 55.93 (2 OCH$_3$), 70.14 (t, J 24 Hz, CD), 102.38 (CCl$_3$), 110.70 (2 CH), 113.37 (2 2-C), 122.38 (2 6-C), 130.75 (2 1-C), 148.45 (2 3-C), 148.70 (2 4-C).

Kinetics. Reaction mixtures for kinetic measurements were prepared by mixing thermostated volumes of base and substrate solutions. The substrate concentrations used were 1×10^{-4}–2.5×10^{-4} M for alkoxide ion-promoted eliminations and *ca* 10^{-2} M for phenoxide ion-promoted eliminations and for **1c** and **1d**. For *p*-nitrophenoxide ion-promoted eliminations, 1×10^{-3} M of base and variable (1.2×10^{-2}–6×10^{-2} M) substrate concentrations were used. The base solutions were MeO$^-$–MeOH, EtO$^-$–EtOH, Bu^{t}O$^-$–Bu^{t}OH, C$_6$H$_5$O$^-$–EtOH and *p*-NO$_2$C$_6$H$_4$O$^-$–EtOH.

For the kinetics followed spectrophotometrically, reaction mixtures were placed in cuvettes that had been temperature equilibrated for at least 15 min. For the kinetics followed titrimetrically, the reaction mixtures were placed in a thermostat. Portions (10 cm^3) were withdrawn at appropriate times and quenched in ethanol containing an excess of dilute nitric acid before analysis.

The kinetics of the alkoxy-promoted eliminations were studied by following spectrophotometrically the appearance of 1, 1-dihalo-2,2-bis(3,4-dimethoxyphenyl)ethenes at a wavelength of 295 nm, where the largest difference between the absorbance spectra of the reagents and products was observed. The kinetics of *p*-nitrophenoxy-promoted eliminations were studied by following spectrophotometrically the disappearence of the base at a wavelength of 400 nm. The kinetics of the phenoxy-promoted eliminations were followed using a titrimetric method, *i.e*. by following the release of chloride ions according to the Volhard technique.

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