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Reactivity of some tertiary chlorides with olefinic and methoxy neighboring groups. A case of extended π, n-participation[†]

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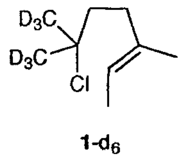
ABSTRACT: Tertiary 2-chloro-2-methyl-5-methoxypentane (**2**) solvolyzes with a significantly reduced secondary β-deuterium kinetic isotope effect (substrate with two trideuteromethyl groups), and with smaller entropy and enthalpy of activation than the reference saturated analog **4** [$k_H/k_D = 1.35 \pm 0.01$ VS $k_H/k_D = 1.79 \pm 0.01$; $\Delta\Delta H^{\neq} = -11$ kJ mol^{-1}; $\Delta\Delta S^{\neq} = -30$ J mol^{-1} K^{-1}, in 80% (v/v) aqueous ethanol], indicating participation of the methoxy group in the rate-determining step. 2-Chloro-2,5-dimethyl-8-methoxy-5(*E*)-octene (**3**) solvolyzes with a further reduction of the isotope effect, and drastically smaller activation parameters [$k_H/k_D = 1.16 \pm 0.01$; $\Delta\Delta H^{\neq} = -33$ kJ mol^{-1}; $\Delta\Delta S^{\neq} = -106$ J mol^{-1} K^{-1}, in 80% (v/v) aqueous ethanol], suggesting that the solvolysis of **3** proceeds with extended π, n-participation, i.e. the assistance of both neighboring groups occurs in the rate-determining step. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: Secondary β-deuterium isotope effects; tertiary chlorides; extended π, n-participation; solvolysis

INTRODUCTION

Substrates having a neighboring group properly located with respect to the reaction center solvolyze with neighboring group participation.[1] The abilities of the double bond and the methoxy group to participate in solvolytic reactions are comparable.[2–4] They both act as intramolecular nucleophiles and stabilize the carbocation intermediate and the transition state. The similar behavior of the double bond and the methoxy group is due to their similar nucleophilicities. Mayr *et al.* investigated the reactivity of carbocations with different nucleophiles,[5] and found that the reaction rates of 4,4-dichlorobenzhydryl cation with a trisubstituted double bond (2-methyl-2-butene) and with various ethers are of the same order of magnitude (H. Mayr, personal communication).

In a previous communication,[6] we showed that the solvolytic behaviors of tertiary chlorides **1** and **2** are very alike. The most significant result reported is the reduction of the secondary β-deuterium kinetic isotope effects (KIEs). Thus, tertiary chloride **1** has a considerably lower secondary β-deuterium KIEs in solvolysis [$k_H/k_D = 1.30 \pm 0.03$, in 80% (v/v) aqueous ethanol (80E); $k_H/k_D = 1.29 \pm 0.02$, in 97% (**w/w**) aqueous 2,2,2-trifluoroethanol (97T)] in comparison with its saturated analog ($k_H/k_D = 1.79 \pm 0.01$, in 80E; $k_H/k_D = 1.81 \pm 0.01$, in 97T), demonstrating the assistance of the double bond in the rate-determining step. Essentially the same result was obtained with tertiary chloride **2** ($k_H/k_D = 1.35 \pm 0.01$, in 80E; $k_H/k_D = 1.34 \pm 0.01$, in 97T), indicating that the 5-methoxy group takes part in the reaction. The existence of n-participation of the methoxy group and formation of a five-membered oxonium ion intermediate were stipulated earlier on the basis of product analysis[7] and the ρ^+ value of the corresponding benzyl derivatives.[4]



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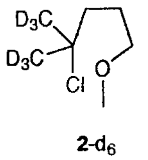

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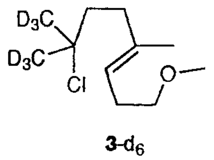

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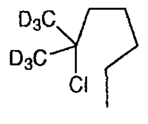

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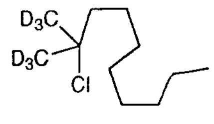

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In this work, we examined a model substrate in which simultaneous assistance of π- and n-electrons could occur, i.e. we studied whether extended π, n-participation

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Table 1. Solvolysis rate constants and activation parameters of some tertiary chlorides having the methoxy group in the side-chain

Compound	Solvent[a]	t(°C)	$k(10^{-4}\ \mathrm{s}^{-1})$[b]	$\Delta H^{\neq}(\mathrm{kJ\ mol^{-1}})$[c]	$-\Delta S^{\neq}(\mathrm{J\ K^{-1}\ mol^{-1}})$[c]
2	80E	45	1.55 (2)	77 ± 2	76 ± 7
		55	3.64 (2)		
		65	8.74 (6)		
		25	0.204		
	97T	25	2.95 (1)	71 ± 4	73 ± 13
		35	8.57 (3)		
		45	23.9 (2)		
2-d_6	80E	50	1.91 (1)	—	—
	97T	25	2.18 (1)		
3	80E	50	2.37 (5)	56 ± 6	142 ± 17
		60	4.10 (7)		
		70	8.51 (4)		
		25	0.41		
	97T	35	11.3 (1)	64 ± 8	92 ± 25
		45	30.3 (5)		
		55	55.7 (2)		
3-d_6	80E	50	2.05 (3)	—	—
	97T	35	10.10 (2)		

[a] 80E is 80% (v/v) aqueous ethanol; 97T is 97% (w/w) aqueous 2,2,2-trifluoroethanol.

[b] The uncertainties of the last reported figure (standard deviation of the mean) are shown in parentheses. The rate constants lacking standard errors are extrapolated.

[c] Uncertainties are standard deviations.

of the neighboring groups occurs. This phenomenon has not been reported earlier. Therefore, we sought more information about the model in which there is simple n-participation, as in the case of chloride **2**, and to examine the solvolytic behavior of the tertiary chloride **3**, since it combines the structural characteristics of both chlorides **1** and **2**. We decided to determine whether enhancement of the solvolytic reactivity, decrease in activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) and, most significantly, depression of the secondary β-deuterium KIEs[8] occur in solvolysis of **2** and **3**, in comparison with the same parameters of the saturated tertiary substrates. Chloride **4** is a suitable reference for chloride **2** (both side-chains consist of five carbon atoms), and chloride **5** is an appropriate reference model for chloride **3** (the side-chains consist of eight carbon atoms). Reaction rates and activation parameters obtained in the solvolysis of both reference chlorides were reported earlier.[9]

Table 2. Relative solvolysis rates and β-deuterium secondary kinetic isotope effects of some tertiary chlorides

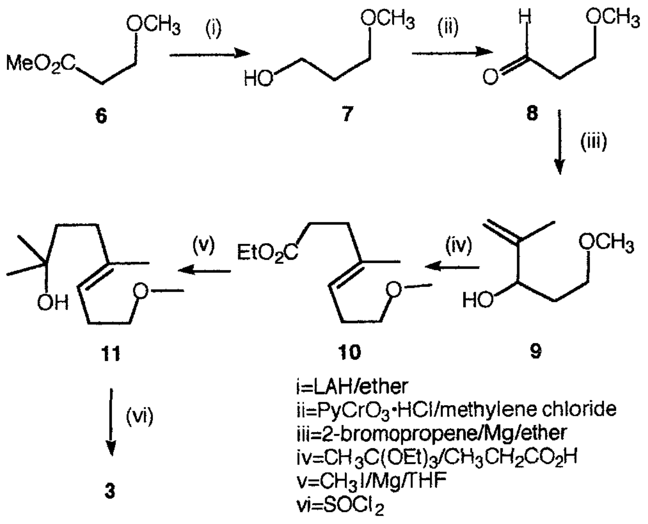
Compound	Solvent	k_u/k_s[a]	k_H/k_D[b]	Ref.
4	80E	—	1.79 (1)	9
	97T	—	1.81 (1)	
1	80E	0.6	1.30 (3)	6
	97T	—	1.29 (2)	
2	80E	0.93	1.34 (1)	6
	97T	0.52	1.35 (1)	
3	80E	2.97	1.16 (1)	—
	97T	—	1.12 (1)	

[a] k_u is the rate constant of the substrate with the neighboring group, k_s is the substrate with adequate length of the alkyl side-chain, k_u/k_s at 25 °C.

[b] The uncertainty of the last reported figures (standard deviation of the mean) is shown in parentheses.

RESULTS AND DISCUSSION

Substrates were prepared according to Scheme 1. The *trans*-trisubstituted double bond was introduced according to Johnson *et al.*'s procedure.[10] The deuterated



Scheme 1

compound **3**-d_6 was obtained according to the same procedure, but using methyl-d_3 iodide.

Chlorides **2, 3** and **3**-d_6 were solvolyzed in 80E and 97T. Solvolysis rates were followed with a pH-stat. The activation parameters were calculated from the rate constants determined at several temperatures. The rate constants and activation parameters are shown in Table 1. Secondary β-deuterium KIEs obtained with **1** and **3**, along with some reference chlorides, are given in Table 2.

It has been proved that only a large rate enhancement in the solvolysis of a compound having a neighboring group in comparison with the corresponding compound that lacks the neighboring group can be taken as valid proof of neighboring group participation.[11] A modest rate effect, as obtained with **3**, or even an inverse rate effect, as obtained with **2** (Table 2), can conceal considerable assistance. Therefore, in such a case, the participation or its lack must be proved by other methods.

We demonstrated earlier that the activation parameters in the solvolysis of saturated tertiary chlorides, which proceed through non-assisted reaction, are essentially the same, regardless of the chain length. For example, the activation parameters obtained with **4** are $\Delta H^{\neq} = 89.7 \pm 8.3$ kJ mol^{-1} and $-\Delta S^{\neq} = 36.6 \pm 2.6$ J K^{-1} mol^{-1}, and those obtained with **5** are $\Delta H^{\neq} = 88.9 \pm 1.8$ kJ mol^{-1} and $-\Delta S^{\neq} = 39.7 \pm 5.5$ J K^{-1} mol^{-1}.[9] Therefore, $\Delta H^{\neq} \approx 90$ kJ mol^{-1} and $-\Delta S^{\neq} \approx 35$ J K^{-1} mol^{-1} can be taken as standard values for the non-assisted reaction under given conditions.

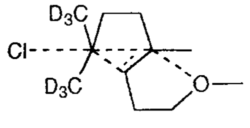
The solvolysis of the tertiary chloride **2** proceeds through a five-membered oxonium ion. Bridging in the transition state results in smaller $\Delta H^{\neq}$ and $\Delta S^{\neq}$ (Table 1) than the above set of reference values. The lower values of the activation parameters for **2** compared with **4** ($\Delta\Delta H^{\neq} = -11$ kJ mol^{-1}; $\Delta\Delta S^{\neq} = -30$ J mol^{-1}K^{-1}; 80E) are consistent with a mechanism involving two-electron assistance. The entropy changes are mainly due to the loss of some internal rotations, which is converted to stiffer vibrations. Similar activation parameters were obtained with chloride **1** having a double bond as a neighboring group ($\Delta H^{\neq} = 82 \pm 3$ kJ mol^{-1} and $-\Delta S^{\neq} = 67 \pm 10$ J K^{-1} mol^{-1}).[12]

As shown in Table 1, the activation parameters obtained for chloride **3** are dramatically different from the values for the reference compounds. This result can be rationalized only if extended participation is considered. $\Delta H^{\neq}$ values smaller than those for **1** and **2** (for ca 15 kJ mol^{-1}) arise from a further charge delocalization in the transition state. The assumed extended π-participation mechanism requires a particular conformation in the transition state which demands a considerably higher degree of order, causing a very negative $\Delta S^{\neq}$ value. A significant decrease in $\Delta S^{\neq}$ in comparison with **1** and **2** (ca 70 J K^{-1} mol^{-1}, Table 1) is due to the loss of three internal rotations around the three single C—C bonds in **3** located between the double bond and the oxygen atom in the side-chain. Extended π-participation mechanism fits excellently the values of $\Delta S^{\neq}$, since it is known that the loss of one internal rotation in the transition state decreases $\Delta S^{\neq}$ for ca 20 J mol^{-1} K^{-1}.[13]

It was pointed out earlier that the secondary β-deuterium KIEs are the most sensitive probe for proving the participation of the neighboring group.[14]

Substrates deuterated at the β-position relative to the reaction center show a rate depression relative to the protio analogs. The cause of this KIE is the hyperconjugative electron release from the neighboring C—H(D) bond to the incipient empty p-orbital in the transition state. Because of the charge delocalization, less hyperconjugative interaction between the p-orbital of the reaction center and the β-CH(D) bonds of the methyl group occurs, resulting in a lower secondary β-deuterium KIE. Recognizing that the kinetic isotope effects are cumulative, the magnitudes of β-deuterium KIEs with hexadeuterated substrates can show the extent of the participation most clearly.

Numerous dimethylalkyl chlorides with the alkyl side-chain ranging from ethyl to squalanyl,[11,15] whose reactions proceed via unassisted processes, solvolyze with the same secondary β-deuterium KIEs ($k_H/k_D = 1.8$) for two deuterated methyl groups adjacent to the reaction center. The existence of one neighboring group that participates with its electrons in the rate-determining step reduces that value by more than 50%.[9] Thus, almost the same reduction of the β-deuterium KIE for chlorides **1** and **2**, as shown in Table 2, indicates assistance of their π- and n-electrons, respectively. However, the reduction of the secondary β-deuterium KIE is considerably more pronounced in the case of **3** ($k_H/k_D = 1.17$ in 80E and 1.12 in 97T) than in the case in which simple n- or π-participation takes place. Since β-KIEs are often interpreted as a measure of the charge at the reaction center in the transition state, it is apparent that the partial charge on the reaction center in **3-TS** is substantially lower than in the substrates with one neighboring group (**1** and **2**). It is therefore, obvious that the effects of neighboring π- and n-electrons are additive, since the second neighboring group (methoxy) further delocalizes the positive charges in the transitions state. This consideration inevitably leads to the conclusion that extended π,n-participation mechanism is operative. This conclusion is strongly supported with the above-considered activation parameters, particularly $\Delta S^{\neq}$. To the best of our knowledge, this is the first case in which extended π, n-participation has been reported.



3-d₆

EXPERIMENTAL

Substrate preparation

3-Methoxypropanol (7).[16]. To a stirred solution of $LiAlH_4$ (7.6 g, 0.20 mol) in 40 ml of dry diethyl ether, a solution of methyl-3-methoxypropionate (**6**) (23.6 g, 0.20 mol) in 50 ml of diethyl ether was added dropwise at such a rate as to keep the reaction mixture refluxing. Refluxing and stirring were continued for 3 h. The reaction mixture was cooled, and the excess hydride was decomposed with gradual addition of water. The precipitate was washed with diethyl ether, and the combined organic layer was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel. Impurities were removed with methylene chloride and the pure product with diethyl ether. The yield of pure alcohol **7** was 13.5 g (75%). ^{1}H NMR ($CDCl_3$): δ 1.81–1.85 (m, 2H), 2.98 (s, 1H), 3.35 (s, 3H), 3.54–3.58 (m, 2H), 3.73–3.77 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 31.78, 58.60, 61.16, 71.33.

3-Methoxypropanal (8). Pyridinium chlorochromate (22.7 g, 0.11 mol) was suspended in methylene chloride (40 ml) and 3-methoxypropanol (**7**) (9.5 g, 0.11 mol) was rapidly added at room temperature. After 2 h, the oxidation was complete. The dark reaction mixture was diluted with 10 ml of dry diethyl ether, the solvent was decanted and the dark solid was washed twice with diethyl ether. The product was isolated by filtration of the organic extracts through Florisil and evaporation of the solvent at reduced pressure. The crude product was distilled (b.p. 108–110 °C), yielding 3.4 g (36.8%) of the pure product (**8**). ^{1}H NMR ($CDCl_3$): δ 2.68–2.70 (m, 2H), 3.39 (s, 3H), 3.71–3.75 (m, 2H), 9.80 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 43.66, 58.77, 29.45, 66.04, 201.03.

2-Methyl-5-methoxy-1(*E*)-penten-3-ol (9). 2-Bromopropene (16.5 g, 0.14 mol) was dissolved in 15 ml of THF and an aliquot of 1 ml of was added to magnesium (6.6 g, 0.27 mol) and a crystal of iodine at once. The mixture was heated until the THF started to reflux. The remainder of the 2-bromopropene solution was added dropwise at such a rate as to maintain the mixture refluxing. Refluxing and stirring of the reaction mixture were continued for 1 h, then the reaction mixture was cooled to 0 °C and 3-methoxypropanal (**8**) (3 g, 3.4 mmol) in 15 ml of THF was added slowly. Stirring was continued for 1 h at room temperature. The Grignard complex was hydrolyzed with a saturated solution of NH_4Cl, the water layer was washed three times with diethyl ether. The combined ether layers were washed with saturated aqueous solution of NaCl and dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by silica gel column chromatography, eluting with light petroleum followed by light petroleum–dichloromethane (1:1). The yield of pure alcohol **9** was 1.79 g (40.5%). ^{1}H NMR ($CDCl_3$): δ 1.74 (s, 3H), 1.81–1.83 (m, 2H), 3.36 (s, 3H), 3.54–3.57 (m, 2H), 4.21–4.25 (m, 1H), 4.85 (s, 1H), 5.01 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 18.04, 34.43, 58.73, 70.93, 74.49, 110.44, 146.89.

Ethyl 4-methyl-7-methoxy-4(*E*)-heptenoate (10). A mixture of 2-methyl-5-methoxy-1(*E*)-penten-3-ol (**9**) (1 g, 7.69 mmol), triethyl orthoacetate (6.55 g, 54 mmol) and propionic acid (0.18 g, 2.56 mol) was heated at 140 °C for 1 h under conditions for distillative removal of ethanol through a Vigreux column. The excess of orthoacetate was then removed by distillation under reduced pressure. The crude product was purified by column chromatography on silica gel, eluting first with light petroleum and then with light petroleum–dichloromethane (3:1). Ester **10** was obtained in 85% yield. ^{1}H NMR ($CDCl_3$): δ 1.11–1.13 (m, 3H), 1.77 (s, 3H), 1.94–2.01 (m, 2H), 2.08–2.19 (m, 2H), 22.34–22.39 (m, 2H), 3.35 (s, 3H), 33.38–3.43 (m, 2H), 4.13–4.19 (m, 2H), 5.31–5.35 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 13.91, 18.00, 27.65, 28.18, 32.81, 58.54, 68.78, 74.10, 125.23, 143.05, 173.47.

2,5-Dimethyl-8-methoxy-5(*E*)-octen-2-ol (11). Grignard reagent obtained from magnesium (0.97 g, 40 mmol) and iodomethane (5.7 g, 40 mmol) in 5 ml of dry THF, as described above, was cooled to 0 °C, and a solution of ester **10** (4 g, 20 mmol) in THF was added slowly to the cold mixture. The reaction mixture was heated under reflux (1–2 h). When the reaction was completed, and the Grignard complex was destroyed with saturated aqueous NH_4Cl (2 × 20 ml). The product was extracted with diethyl ether (3 × 25 ml). The combined ether layers were dried over Na_2SO_4, the solvent was evaporated and the crude product was subjected to column chromatography on silica gel, eluting first with light petroleum–dichloromethane (3:1) and then with light petroleum–dichloromethane (1:1). Evaporation of the pooled alcohol-containing fractions yielded the pure alcohol **11** as a viscous oil. ^{1}H NMR ($CDCl_3$): δ 1.25 (s, 6H), 1.38–1.42 (m, 2H), 1.73 (s, 1H), 1.83–1.88 (m, 2H), 2.26–2.33 (m, 2H), 3.31 (s, 3H), 3.34–3.36 (m, 2H), 5.28–5.32 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 17.70, 29.27, 29.90, 32.50, 40.16, 58.09, 68.45, 71.78, 121.34, 142.71.

1, 1, 1-d_3-2, 2, 2-d_3-Methyl-5-methyl-8-methoxy-5(*E*)-octen-2-ol (11-d_6). The procedure is the same as described above. From 0.17 g (7 mmol) of magnesium, 1 g (7 mmol) of iodomethane-d_3 (99% deuterium) and 0.55 g (3.5 mmol) of ester **10**, 0.24 g (46%) of pure alcohol **11**-d_6 was obtained. ^{1}H NMR ($CDCl_3$): δ 1.37–1.42 (m, 2H), 1.72 (s, 1H), 1.83–1.88 (m, 2H), 2.25–2.33 (m, 2H), 3.31 (s, 3H), 3.34–3.36 (m, 2H), 5.28–5.32 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 17.50, 28.21, 31.42, 40.11, 58.23, 69.23, 71.80, 121.11, 142.31.

Chlorides 3 and 3-d_6. 2-Chloro-2,5-dimethyl-8-methoxy-5(E)-octene (**3**) and 2-chloro-1, 1, 1-d_3-2,2,2-d_3-methyl-5-methyl-8-methoxy-5(E)-heptene (**3**-d_6), were prepared from alcohols **11** and **11**-d_6, respectively. Alcohol (1 equiv.) was dissolved in light petroleum (b.p. 40–60 °C), the solution was cooled to -15 °C, and $SOCl_2$ (1 equiv.) was added dropwise. The reaction mixture was stirred for 2 h under reduced pressure (about 520–560 mmHg), to remove the liberated HCl and SO_2 continuously. Then the light petroleum was evaporated and the crude chloride was used for kinetic measurements. Further purification proved to be unnecessary since the solvolysis rates were found to be independent of contamination.

Kinetic measurements

Solvolysis rates were followed in 80% (v/v) and 95% (v/v) aqueous ethanol (80E and 95E, respectively) and 97% (w/w) aqueous 2,2,2-trifluoroethanol (97T) titrimetrically with a pH-stat. Typically, 0.01 mmol of the substrate was dissolved in 20 ml of the solvent at the required temperature (±0.05 °C), and the liberated hydrochloric acid was continuously titrated with a 0.004 M solution of sodium hydroxide in the same solvent mixture. Individual measurements could be described by a first-order law from 15% up to at least 80% completion. First-order rate constants were calculated from about 100 determinations by using a non-linear least-squares program. Measurements were usually repeated 3–7 times. Activation parameters were calculated from rate constants at three different temperatures.

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