JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 10, 879–884 (1997)

SOLVOLYSIS OF 1-ALKYL-1-CHLORO-1-(4-METHYL)PHENYLMETHANES. NUCLEOPHILIC SOLVENT INTERVENTION AND EXTENDED Y_{BnCl} SCALE

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The solvolysis of 1-alkyl-1-chloro-1-(4-methyl)phenylmethanes (4a–d) in aqueous acetone, aqueous ethanol, aqueous methanol and ethanol–trifluoroethanol was studied. Grunwald–Winstein-type correlation analysis using the Y_{BnCl} scale suggests significant nucleophilic solvent intervention in the case of 1-chloro-1-(4-methyl)phenylethane (4a). Increasing bulkiness of the 1-alkyl substituent from methyl (4a) to ethyl (4b), to isopropyl (4c) and to *tert*-butyl (4d) resulted in a gradual change to limiting S_N1 mechanisms. The observed excellent linear correlations with Y_{BnCl} and the good solubility in high-water-containing binary solvents made 4d a suitable reference standard for deriving more Y_{BnCl} values. A positive azide salt effect was realized in the solvolysis of 4a but not 4d. A small decrease in the β-deuterium kinetic isotope effect from 4a to 1-chloro-1-(4-methoxyphenyl)propane (5) suggested the presence of additional stabilization of the benzylic cationic transition state. Howver, no relationship between $k(CH_3)/k(CD_3)$ and the solvent effect was found. The superiority of employing the Y_{BnCl} scale over the combination of Y_{Cl} and I scales in the mehanistic study was observed. © 1997 John Wiley & Sons, Ltd.

J. Phys. Org. Chem. **10**, 879–884 (1997)   No. of Figures: 3   No. of Tables: 6   No. of References: 27

Keywords: solvolysis; correlation analysis; azide salt effect; *β*-deuterium kinetic isotope effect; Y_{BnCl}; 1-alkyl-1-chloro-1-(4-methyl)phenylmethanes

Received 31 March 1997; revised 9 May 1997; accepted 19 May 1997

INTRODUCTION

Correlation analysis with the Grunwald–Winstein equation (1)[1] or (2)[2] has long been employed as a diagnostic tool for the study of solvent effects on solvolytic mechanisms:

$$\log(k/k_0)=mY \qquad (1)$$

$$\log(k/k_0)=mY+lN \qquad (2)$$

A variety of scales of solvent ionizing power Y, a kind of empirical solvent polarity scale,[3] have been developed.[4] Recently, new Y_{BnX} scales were suggested to be superior to Y_X scales in the study of several secondary and tertiary benzylic bromides,[5] chlorides,[6] *p*-nitrobenzoates[7] and tosylates.[8]

Depression of the data point corresponding to log k values measured in an isodielectric ethanol–trifluoroethanol mixture[9] from the linear plots was observed for the solvolysis of several 2-aryl-2-propyl derivatives (**1**), and nucleophilic solvent intervention was then deduced from the variation in the electronic and steric factors of substituents.[10, 11] Kevill and co-workers,[12] on the other hand, suggested a general preference for Y_X scales. In addition, they proposed the use of new multiparameter equations (3 and 4) containing the aromatic ring parameter I[13] to interpret the solvolytic behavior of benzylic substrates:

$$\log(k/k_0)=mY+hI \qquad (3)$$

$$\log(k/k_0)=mY+lN+hI \qquad (4)$$

However, several drawbacks and disadvantages of such approaches have been pointed out recently.[14] More work seems to be needed to ascertain which one is more suitable for interpreting solvolytic mechanisms.

We have also extended our studies on benzylic solvolyses to several other systems. One of them was 1-alkyl-1-aryl-1-halomethanes. Previous work on both 1-aryl-1-chloroethanes (**2**)[15] and 1-aryl-1-*tert*-butyl-1-chloromethane (**3**)[16] under different reaction conditions led to the conclusion that an S_N1 mechanism occurred in most cases. The kinetic solvent isotope effect on the methanolysis of **2** suggested ion-pair formation with the attack of the solvent molecule at the carbocation in the pre-equilibrium.[15e] On the other hand, an S_N2+ mechanism was found in the acetolysis of 1-*tert*-butyl-1-chloro-1-(4-methoxy)phenylmethane.[16b] Addition of thiourea in the solvolysis of 1-chloro-1-phenylethane and 1-*tert*-butyl-

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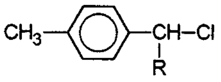
1-chloro-1-phenylmethane resulted in a change in mechanism.[17]

In this paper, we provide kinetic evidence to demonstrate the presence of nucleophilic solvent intervention in the solvolysis of 1-alkyl-1-chloro-1-(4-methylphenyl)methane (**4**) and the importance of steric hindrance to this effect. Moreover, an extended Y_{BnCl} scale to include the values for high-water-containing solvents based on the solvolytic reactivity of 1-*tert*-butyl-1-chloro-1-(4-methylphenyl)methane (**4d**) is provided to circumvent the limitation of the use of 2-aryl-2-chloroadamantane[6] as a reference standard.

RESULTS

The desired substrates were prepared by conventional methods. 1-Alkyl-1-aryl-1-chloromethanes (**4a**–**d**) and 1-chloro-1-(4-methoxyphenyl)propane (**5**) were synthesized by Grignard addition of arylmagnesium bromide to appropriate acyl chlorides, followed by reduction with sodium borohydride and then chlorination with thionyl chloride. Grignard reaction of methyl-d_3-magnesium iodide with the corresponding benzaldehyde, followed by the treatment



4a R = CH_3
4b R = C_2H_5
4c R = $CH(CH_3)_2$
4d R = $C(CH_3)_3$

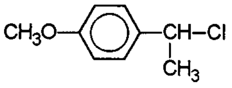


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Table 1. Solvolytic rate constants for chlorides **4a**–**d**

Solvent[a]	k(25 °C) (s^{-1})[b] 4a	4b	4c	4d
100E	$1{\cdot}04\times10^{-5}$			
90E	$1{\cdot}22\times10^{-4}$			
80E	$5{\cdot}55\times10^{-4}$			$9{\cdot}78\times10^{-7}$[c]
70E	$1{\cdot}61\times10^{-3}$	$3{\cdot}80\times10^{-4}$	$9{\cdot}86\times10^{-5}$	$3{\cdot}86\times10^{-6}$[d]
60E	$5{\cdot}10\times10^{-3}$	$1{\cdot}27\times10^{-3}$	$3{\cdot}46\times10^{-4}$	$1{\cdot}18\times10^{-5}$
50E		$4{\cdot}57\times10^{-3}$	$1{\cdot}37\times10^{-3}$	$4{\cdot}96\times10^{-5}$
40E				$2{\cdot}56\times10^{-4}$
80A	$3{\cdot}25\times10^{-5}$			
70A	$2{\cdot}42\times10^{-4}$	$4{\cdot}97\times10^{-5}$		$4{\cdot}59\times10^{-7}$[e]
60A	$1{\cdot}10\times10^{-3}$	$3{\cdot}02\times10^{-4}$	$8{\cdot}26\times10^{-5}$	$2{\cdot}73\times10^{-6}$[f]
50A		$1{\cdot}58\times10^{-3}$	$4{\cdot}98\times10^{-4}$	$1{\cdot}60\times10^{-5}$
40A				$1{\cdot}15\times10^{-4}$
100M	$1{\cdot}24\times10^{-4}$			
90M	$6{\cdot}48\times10^{-4}$	$1{\cdot}74\times10^{-4}$	$5{\cdot}13\times10^{-5}$	$2{\cdot}57\times10^{-6}$[g]
80M	$2{\cdot}21\times10^{-3}$	$7{\cdot}29\times10^{-4}$	$2{\cdot}36\times10^{-4}$	$1{\cdot}01\times10^{-5}$[h]
70M				$3{\cdot}68\times10^{-5}$
60M		$8{\cdot}22\times10^{-3}$	$2{\cdot}89\times10^{-3}$	$1{\cdot}26\times10^{-4}$
50M				$4{\cdot}25\times10^{-4}$
100T	$1{\cdot}00\times10^{-1}$	$3{\cdot}88\times10^{-2}$	$2{\cdot}83\times10^{-2}$	$1{\cdot}27\times10^{-3}$
80T–20E	$9{\cdot}43\times10^{-3}$	$4{\cdot}21\times10^{-3}$	$2{\cdot}33\times10^{-3}$	$9{\cdot}79\times10^{-5}$
60T–40E	$1{\cdot}12\times10^{-3}$	$5{\cdot}34\times10^{-4}$	$2{\cdot}49\times10^{-4}$	$1{\cdot}04\times10^{-5}$[i]
70Tw				$1{\cdot}36\times10^{-3}$
50Tv				$1{\cdot}59\times10^{-3}$

[a] Abbreviations: A, acetone; E, ethanol; M, methanol; T, 2,2,2-trifluoroethanol. The numbers denote the volume percentage of the specific solvent in the solvent mixture.
[b] Maximum error ±3%.
[c] Calculated from $k=5.03\times10^{-4}\ s^{-1}$ (75 °C), $k=1{\cdot}70\times10^{-4}\ s^{-1}$ (65 °C) and $k=5{\cdot}19\times10^{-5}\ s^{-1}$ (55 °C).
[d] Calculated from $k=7{\cdot}86\times10^{-4}\ s^{-1}$ (70 °C), $k=1{\cdot}64\times10^{-4}\ s^{-1}$ (55 °C) and $k=4{\cdot}88\times10^{-5}\ s^{-1}$ (45 °C).
[e] Calculated from $k=2{\cdot}15\times10^{-4}\ s^{-1}$ (75 °C), $k=7{\cdot}25\times10^{-5}\ s^{-1}$ (65 °C) and $k=2{\cdot}30\times10^{-5}\ s^{-1}$ (55 °C).
[f] Calculated from $k=3{\cdot}23\times10^{-4}\ s^{-1}$ (65 °C) and $k=3{\cdot}45\times10^{-5}\ s^{-1}$ (45 °C).
[g] Calculated from $k=8{\cdot}36\times10^{-4}\ s^{-1}$ (75 °C), $k=2{\cdot}93\times10^{-4}\ s^{-1}$ (65 °C), $k=1{\cdot}09\times10^{-4}\ s^{-1}$ (55 °C) and $k=3{\cdot}13\times10^{-5}\ s^{-1}$ (45 °C).
[h] Calculated from $k=3{\cdot}65\times10^{-4}\ s^{-1}$ (55 °C), $k=1{\cdot}24\times10^{-4}\ s^{-1}$ (45 °C) and $k=3{\cdot}59\times10^{-5}\ s^{-1}$ (35 °C).
[i] Calculated from $k=3{\cdot}25\times10^{-4}\ s^{-1}$ (55 °C) and $k=1{\cdot}11\times10^{-4}\ s^{-1}$ (45 °C).

Table 2. Correlation analyses against Y_{BnCl} and N_T[a]

	Y_{BnCl}	Y_{BnCl} and N_{T}	
Substrate	*m*	*m*	*l*
4a	0·734 (*R*=0·972, *n*=14)	0·834	0·146 (*R*=0·976, *n*=14)
4b	0·735 (*R*=0·975, *n*=11) 0·756 (*R*=0.965, *n*=12)	0·817	0·098 (*R*=0·978, *n*=11)
4c	0·835 (*R*=0·988, *n*=10) 0·856 (*R*=0·983, *n*=11)	0·830	− 0·005 (*R*=0·988, *n*=10)
4d	0·886 (*R*=0·996, *n*=12) 0·884 (*R*=0·997, *n*=15)[b]		

[a] Standard deviation is between 0·02 and 0·08.

[b] Using the data in Table 6.

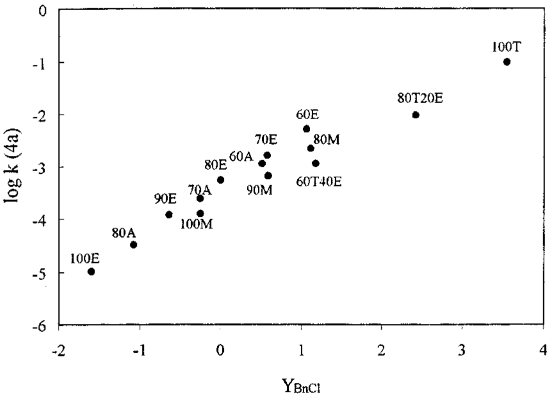

Figure 1. Correlations of log *k* for **4a** against Y_{BnCl}. Abbreviations for solvents as in Table 1.

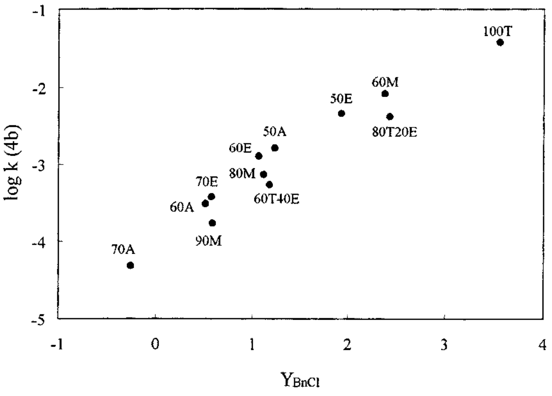

Figure 2. Correlations of log *k* for **4b** against Y_{BnCl}. Abbreviations for solvents as in Table 1.

with thionyl chloride, yielded the α-trideuteriomethyl compounds **4a**-d_3 and **5**-d_3. Solvolytic rate constants within ±2% error were obtained by the conductimetric method unless mentioned otherwise. Pertinent data are reported in Table 1.

Good agreement of the rate constants with literature data[15a] for **4a** and **5** was found. Correlation analyses of log *k* against Y_{BnCl} [equation (1)][6b] and against Y_{BnCl} and N_{T}[18] [equation (2)] were carried out and the results are given in Table 2. Plots of log *ks* vs Y_{BnCl} for **4a** and **b** are given in Figures 1 and 2, respectively. Comparison of the correlation analysis using equation (1) with Y_{Cl},[4] equation (2) with Y_{Cl} and N_{T},[18] equation (3) with Y_{Cl} and *I*[13b] and equation (4) with Y_{Cl}, N_{T} and *I* is shown in Table 3, although only a limited number of data are available for the multiparameter correlation equation (4).

Kinetic salt effects induced by adding sodium azide and sodium perchlorate, respectively, were monitored titrametrically for **4a** and **d**. The data are presented in Table 4.

For the study of the β-deuterium kinetic isotope effect, the substrate pairs **4a** and **4a**-d_3 and **5** and **5**-d_3 were solvolyzed under identical experimental conditions and were measured conductimetrically. The reproducibility of the measured individual rate constant was found within ±1% error in triplicate experiments. The results are given in Table 5.

DISCUSSION

The comparison of Tables 2 and 3 clearly indicates that the correlation of log*k* with Y_{Cl} is not good (*R*=0·92–0·96) and shows a random change for substrates **4a**–**4d**, while the variations of both *m* and *R* show a reasonably increasing trend from the correlation with Y_{BnCl}. The excellent linear correlation[19] (*R*=0·996–0·997) with $m(Y_{\mathrm{BnCl}})$ of about 0·9 observed in the case of **4d** suggests that a limiting $S_{\mathrm{N}}1$ process is involved in the solvolysis. The *m* value decreases and the correlation changes from excellent (*R*>0·99) to less satisfactory (*R*=0·96–0·97) as the bulkiness of the α-alkyl substituent decreases from *tert*-butyl to ethyl and methyl groups. The solvolysis mechanisms are likely to be non-limiting for **4a** and **4b** and to be a borderline case for **4c**. Steric hindrance is therefore probably an important factor governing the solvolytic mechanism. The coalescence of lines in the log k–Y_{BnCl} plots as the α-alkyl substituent becomes bulkier, e.g. *tert*-butyl (Figure 3), could be interpreted by the diminishing intervention of the nucleophilic solvent due to steric hindrance, in harmony with what has been observed in the solvolysis of 1-alkyl-1-chloro-1-phenylethanes.[11b]

Splitting of lines made from data points measured in different solvent systems was found in the log k–Y_{BnCl} plots for **4a** (Figure 1) and **4b** (Figure 2), in which the line defined by those measured in isodielectric and low nucleophilic ethanol–trifluoroethanol solvent systems was with the smallest *m* value (0·822 for **4a** and 0·784 for **4b**). Obviously, nucleophilic solvent intervention is present in those cases as

Table 3. Correlation analyses against Y_{Cl}, N_T and I[a]

	Y_{Cl}	Y_{Cl}	N_T	I		
Substrate	m	m	l	h		h/m
4a	0·732 (R=0·964, n=14)	0·690	− 0·053		(R=0·965, n=14)	
		0·715		0·580	(R=0·976, n=13)	0·811
		0·751	0·059	0·640	(R=0·978, n=13)	0·852
4b	0·849 (R=0·943, n=12)	0·788	− 0·070		(R=0·942, n=11)	
		0·827		0·628	(R=0·973, n=11)	0·759
		0·932	0·119	0·780	(R = 0·980, n = 11)	0·837
4c	0·869 (R=0·919, n=11)	0·618	− 0·263		(R=0·950, n=10)	
		0·895		0·871	(R=0·980, n=10)	0·973
		0·892	− 0·003	0·877	(R=0·980, n=10)	0·983
4d	0·944 (R=0·943, n=18)	0·806	− 0·217		(R=0·952, n=15)	
		0·945		1·003	(R=0·983, n=14)	1·06
		0·999	0·077	1·12	(R=0·984, n=14)	1·12

[a] Standard deviations are 0·05–0·17 for m, 0·09–0·13 for l and 0·24–0·30 for h.

in the solvolysis of tertiary benzylic substrates.[10, 11] Application of the dual-parameter equation (2) with Y_{BnCl} and N_T (Table 2) indicated little improvement, although a decrease in l could be found from **4a** to **b**. With Y_{Cl} and N_T (Table 3), even worse results including negative l values were obtained. Therefore, factors other than the solvent nucleophilicity would be also influential. The outcome of the use of equations (3) and (4) (Table 3) was not any better. Irregular variation of l values and h/m ratios for **4a**–**d** suggested that those types of correlation including the aromatic ring character I were insensitive to structural change, and hence less useful in mechanistic studies than the correlation with Y_{BnCl}.

Table 4. Salt effects in solvolyses of **4a** and **d**

Substrate	[Salt] (M)	$k(NaN_3)$ (s^{-1})	$k(NaClO_4)$ (s^{-1})	$k(NaN_3)/k(NaClO_4)$	RN_3 (%)
4a[b]	0	$3{\cdot}25\times10^{-5}$	$3{\cdot}25\times10^{-5}$		
	0·04	$5{\cdot}78\times10^{-5}$	$4{\cdot}10\times10^{-5}$	1·41	20·8
	0·08	$7{\cdot}21\times10^{-5}$	$4{\cdot}42\times10^{-5}$	1·63	31·4
4d[c]	0	$3{\cdot}45\times10^{-5}$	$3{\cdot}45\times10^{-5}$		
	0·02	$4{\cdot}09\times10^{-5}$	$3{\cdot}95\times10^{-5}$	1·03	

[a] By titrametric method, maximum error is ±3%.

[b] 0·005 M in 80% acetone at 25 °C.

[c] 0·003 M in 60% acetone at 45 °C

The study of salt effects[20] with sodium azide and sodium perchlorate indicated a significant rate enhancement for **4a** but not for **4d** in aqueous acetone (Table 4). The observed azide salt effects, $k(NaN_3)/k(NaClO_4)$ at equal salt-to-substrate ratios, were 1·41 (0·04 M [salt]/0·005 M [RCl]) and 1·63 (0·08 M [salt]/0·005 M [RCl]) in the case of **4a**. Solvolysis of **4d**, however, showed only a negligible effect of 1·03 at similar salt-to-substrate ratio (0·02 M [salt]/0·003 M [RCl]). In agreement with the result of correlation analysis with equation (2) (see above), the significant azide salt effect suggests the involvement of nucleophilically assisted process in solvolysis of **4a**.

The β-deuterium kinetic isotope effect has been considered a useful tool for elucidating solvolytic mechanisms.[21, 22] In a study of the solvolysis of **2**, Shiner *et al.*[15a] observed a small decrease in $k(CH_3)/k(CD_3)$ with increasing electron-donating character of substituents from hydrogen to *p*-methoxy and also with increasing electron-withdrawing character of substituents from hydrogen to *p*-nitro in the aromatic moiety. A change in the demand of hyperconjugative stabilization from the β-methyl group to

Table 5. β-Deuterium kinetic isotope effects in solvolysis of **4a** and **5** at 25 °C

Substrate	Solvent[a]	$k(CH_3)$ (s^{-1})	$k(CD_3)$ (s^{-1})	$k(CH_3)/k(CD_3)$
4a	100E	$(1{\cdot}044\pm0{\cdot}012)\times10^{-5}$	$(8{\cdot}218\pm0{\cdot}008)\times10^{-5}$	1·270 ± 0·015
4a	90E	$(1{\cdot}223\pm0{\cdot}017)\times10^{-4}$	$(1{\cdot}022\pm0{\cdot}014)\times10^{-4}$	1·197 ± 0·023
4a	80E	$(5{\cdot}551\pm0{\cdot}028)\times10^{-4}$	$(4{\cdot}809\pm0{\cdot}053)\times10^{-4}$	1·155 ± 0·014
4a	80A	$(3{\cdot}252\pm0{\cdot}016)\times10^{-5}$	$(2{\cdot}736\pm0{\cdot}013)\times10^{-5}$	1·189 ± 0·008
4a	70A	$(2{\cdot}421\pm0{\cdot}024)\times10^{-4}$	$(2{\cdot}065\pm0{\cdot}036)\times10^{-4}$	1·141 ± 0·022
5	100E	$(2{\cdot}168\pm0{\cdot}008)\times10^{-2}$	$(1{\cdot}958\pm0{\cdot}014)\times10^{-2}$	1·107 ± 0·009
5	90E	$(2{\cdot}453\pm0{\cdot}004)\times10^{-1}$	$(2{\cdot}295\pm0{\cdot}016)\times10^{-1}$	1·068 ± 0·008
5	80A	$(7{\cdot}213\pm0{\cdot}023)\times10^{-2}$	$(6{\cdot}412\pm0{\cdot}037)\times10^{-2}$	1·125 ± 0·007

[a] See Table 1 for abbreviations.

Table 6. Compilation of extended Y_{BnCl} values

Solvent[a]	Y_{BnCl}[b]	Solvent[a]	Y_{BnCl}[b]
100E	−1·61	80M	1·12
90E	−0·645	70M	1·72[c]
80E	0·00	60M	2·37[c]
70E	0·571	50M	2·97[c]
60E	1·07	100T	3·55
50E	1·92[c]	85T	3·57
40E	2·72[c]	70T	3·60
90A	−2·28	50T	3·62[c]
80A	−1·09	70Tw	3·54
70A	−0·259	80T–20E	2·42
60A	0·518	60T–40E	1·18
50A	1·23	40T–60E	0·18
40A	2·33[c]	*i*-PrOH	−2·71
100M	−0·253	HOAc	−1·97
90M	0·585	Formamide	1·38

[a] Abbreviations: A, acetone; E, ethanol; M, methanol; T, 2,2,2-trifluoroethanol; HOAc, acetic acid; *i*-PrOH, propan-2-ol. The numbers denote the volume percentage of the specific solvent in the solvent mixture with the exception of 70Tw, which denotes weight percentage.

[b] From Ref. 6b unless mentioned otherwise.

[c] This work.

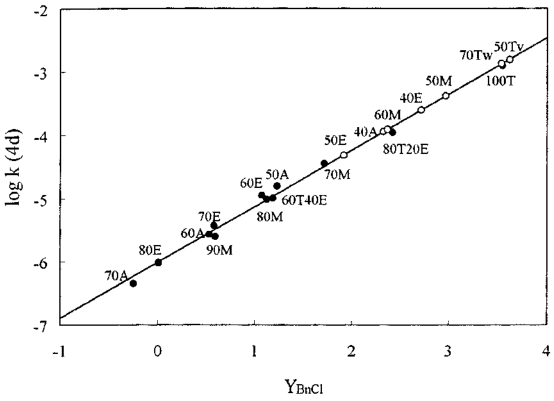

Figure 3. Correlations of log *k* for **4d** against Y_{BnCl}. The open circles denote the points of interpolation. Abbreviations for solvents as in Table 1.

the benzylic reaction in solvolysis and a partly nucleophilic mechanism for substrates containing *m*-Br and *p*-NO_2 substituents were concluded to be involved.[15a] The proposal of a decreasing hyperconjugative effect with electron-donating substituents was confirmed in the present study (Table 5), and had also been found with certain tertiary benzylic systems.[23] However, the proposed relationship between the decrease in $k(CH_3)/k(CD_3)$ and the presence of nucleophilic solvent intervention[15a] is questionable. The extrapolation of rate data from solvents of different ionizing power and nucleophilicity to give 'isotope effects corrected to the value expected in 50% ethanol'[15a] seems to be unreliable. In the present study, the data in Table 5 reveal that the magnitude of β-deuterium kinetic isotope effects varies significantly with solvent composition. Moreover, the trends of the variation are not the same for different substrates. For instance, the ratio $k(CH_3)/k(CD_3)$ in 90% ethanol is greater than that in 80% acetone for **4a**, but a reversed order is found for **5**. Therefore, a decrease in the ratio $k(CH_3(/k(CD_3)$ cannot be considered a necessary condition for nucleophilic attack of solvents. In other words, a decrease in the β-deuterium kinetic isotope effect could indicate a larger electronic stabilization due to electron-donating substituents, but could not be considered diagnostic for determining nucleophilic mechanisms. Variation of hyperconjugative stabilization with the solvent might account for the observed correlation coefficient R of 0·976–0·978 in the regression with dual-parameter equation (2) (Table 2) for the solvolysis of **4a** and **4b**.

The importance of nucleophilic solvent intervention in the solvolysis of 1-alkyl-1-chloro-1-(4-methyl)phenylmethanes diminishes with increasing bulkiness of the 1-alkyl group. The present study confirms the limiting S_N1 character for the solvolysis of 1-*tert*-butyl-1-chloro-1-(4-methyl)phenyl-methane (**4d**) in acetone–water, ethanol–water, methanol–water and ethanol–trifluoroethanol solvent systems. Excellent linear *mY* correlations with the Y_{BnCl} scale, R=0·996, are realized from Table 2. Since the Y_{BnCl} scale was developed with the use of 2-chloro-2-(3-chloro)phenyladamantane and other 2-aryl-2-chloroadamantanes, the value for high-water-containing solvents is not available owing to their high reactivities and low solubilities. Consequently, more values of the Y_{BnCl} scale can be obtained from interpolation of the log *k* (**4d**)–Y_{BnCl} plots (Figure 3). The data in 30% acetone, 30% ethanol, 40% methanol or solvents containing more water were not reliable, and were therefore discarded, because of the low solubility of **4d** in these solvents at 25 °C. A compilation of available Y_{BnCl} values is given in Table 6.

EXPERIMENTAL

Capillary melting points were uncorrected. NMR spectra were determined on a Bruker Model AM-300 or AC-200 instrument using tetramethylsilane as an internal standard. IR spectra were measured on a Perkin-Elmer Model 983G spectrometer.

Materials. Spectral-grade or reagent-grade solvents were purified according to standard methods[24] for kinetic studies. Dry solvents for preparative purposes were freshly distilled before use if necessary. Doubly deionized water was used to prepare aqueous solvent mixtures for solvolysis. Starting materials for the preparation of substrates were reagent-grade chemicals available commercially.

The chlorides **4a**–**d** and **5** were synthesized according to the following conventional procedures: Grignard addition of the corresponding arylmagnesium bromide to the appropriate acyl chlorides in tetrahydrofuran to give the ketones, which were purified by column chromatography on silica gel. The ketone was then reduced with sodium borohydride in methanol to form the desired alcohol, followed by chlorination with thionyl chloride in carbon tetrachloride. The resultant chloride was purified by recrystallization or by column chromatography on triethylamine-washed silica gel with hexane–ethyl acetate as eluent. 1-Chloro-1-(4-methylphenyl)ethane (**4a**),[15a] 1-chloro-1-(4-methylphenyl)propane (**4b**),[25] 1-chloro-2-methyl-1-(4-methylphenyl)propane (**4c**)[26] and 1-chloro-1-(4-methoxyphenyl)ethane (**5**)[15a] were obtained in the pure liquid state and 1-chloro-2,2-dimethyl-1-(4-methylphenyl)propane (**4d**)[27] was isolated as a solid, m.p. 28–29 °C. Their IR and proton and carbon NMR data were found to be in line with the assigned structures.

The α-trideuteriomethyl compounds **4a**-d_3 and **5**-d_3 were prepared by Grignard reaction of methyl-d_3-magnesium iodide (99% isotopically pure) with the corresponding benzaldehyde, followed by the treatment of the resultant alcohol with thionyl chloride.

Kinetic measurements. Conductimetric rate constants were measured for general solvolytic studies. The conductivity cells were placed in a thermostat with a temperature variation of ±0·02 °C. A solution of 1×10^{-4}–2×10^{-5} M was used. In some cases, a small amount (0·1%) of 2,6-lutidine was added to the solution to prevent curvature of the rate constant plot. For studying the kinetic isotope effect, the solvolyses of the isotopic pairs were run side-by-side in the same thermostat. The potentiometric titration method was employed in the study of salt effects. The concentration of substrate was 0·003–0·005 M.

ACKNOWLEDGEMENTS

We are grateful to the National Science Council, Republic of China, for financial support of this research, and to Mr Hung-I Chen for checking some rate data.

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