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STRUCTURAL EFFECTS ON THE GRUNWALD–WINSTEIN CORRELATIONS IN THE SOLVOLYSIS OF SOME SIMPLE TERTIARY ALKYL CHLORIDES

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The rates of solvolysis in various solvents at 25 °C were determined for five tertiary alkyl chlorides: 2-chloro-2,4,4-trimethylpentane (4), 2-chloro-2,4-dimethylpentane, 2-chloro-2-methylpentane, 1-chloro-1,3,3-trimethylcyclopentane (7) and 1-chloro-1-methylcyclopentane. The rate data were analysed on the basis of the original and extended Grunwald–Winstein-type equation [$\log(k/k_0)=mY_{Cl}+c$ and $\log(k/k_0)=lN_T+mY_{Cl}+c$] and the results were compared with those reported for 2-chloro-2-methylpropane (1) and 2-chloro-2,3,3-trimethylbutane (3). The rate data for 4 in 18 solvents give an excellent correlation with $l=0{\cdot}00\pm0{\cdot}02$ and $m=0{\cdot}74\pm0{\cdot}01$. The neopentyl group in 4 more effectively shields the rear-side of the reaction center than the *tert*-butyl group in 3 that is correlated by $l=0{\cdot}10\pm0{\cdot}04$ and $m=0{\cdot}81\pm0{\cdot}04$. The rate ratio between 4 and 1 at 25 °C is 275 in TFE and predicted to increase to 950 in TFA. The previous 4/1 rate ratio of 21 in 80% ethanol evidently underestimates the B-strain effect on the solvolysis rate of 4 by a factor of at least 40. The remote methyl groups in 7 works to increase rear-side shielding without increasing B-strain. The marked difference in the effect of the remote methyl groups between 4 and 7 suggests that the leaving chloride ion in 4 takes a locus that is nearly antiperiplanar to the *tert*-butyl group. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

The extended Grunwald–Winstein correlation [equation (1)] is one of the most useful linear free energy relationships in the study of solvolysis reactions.[1] The equation includes the nucleophilic (N) and electrophilic (Y) parameters of solvents, where k_0 and k refer to the specific rates of solvolysis in 80% aqueous ethanol and a given solvent, respectively, and c is the intercept.[1]

$$\log(k/k_0)=lN+mY+c \quad (1)$$

As the N parameters, the N_{OTs} scale based on methyl tosylate,[1b] N_T and N_{KL} scales based on *S*-methyldibenzothiophenium ion[2a,b] and triethyloxonium ion,[2c] respectively, and N'_{OTs} scale[2a] (improved N_{OTs}) are generally used. On the other hand, it has been found that the electrophilic parameters (Ys) are dependent on nucleofuges, and more than a dozen Y scales have been developed.[1d,1f,3] In this paper, we specifically deal with the solvolyses of tertiary alkyl chlorides.

In 1948, Grunwald and Winstein[4] defined an ionizing power scale Y by using 2-chloro-2-methylpropane (**1**) as a typical S_N1 substrate. In 1982, Bentley and Carter reported that **1** is susceptible to nucleophilic solvent intervention, and redefined the Y_{Cl} scale depending upon 1-chloroadamantane (**2**) as a standard substrate ($l=0{\cdot}000$, $m=1{\cdot}000$).[5] At present, a recommended equation for solvolyses of alkyl chlorides is a function of N_T and Y_{Cl}:[1e]

$$\log(k/k_0)=lN_T+mY_{Cl}+c \quad (2)$$

In 1990, Liu *et al.*[6] suggested that by using the Y_{Cl} scale even 2-chloro-2,3,3-trimethylbutane (**3**), which has a bulky *tert*-butyl group directly attached to the reaction center, might be subject to nucleophilic solvent intervention in aqueous ethanol solvents. Since then, there have been no efforts to seek open-chain chloroalkanes that solvolyze without nucleophilic solvent intervention.

Recently, we reported that 2-chloro-2,4,4-trimethylpentane (**4**) is an open-chain tertiary alkyl substrate that undergoes essentially limiting S_N1 solvolysis.[7] In this paper, we compare the behavior of **4** with that of 2-chloro-2,4-dimethylpentane (**5**) and 2-chloro-2-methylpentane (**6**) in the Grunwald–Winstein-type correlations, and show the effectiveness of the neopentyl group in rear-side shielding in solvolysis. Comparisons of the rates of solvolysis of **4** and **6** with those of the structurally similar cyclopentyl derivatives **7** and **8** support the previous conclusion[7] on the

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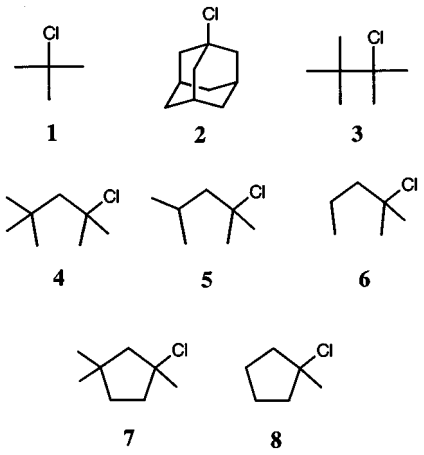


direction of departure of the leaving chloride ion in the solvolysis of **4**.

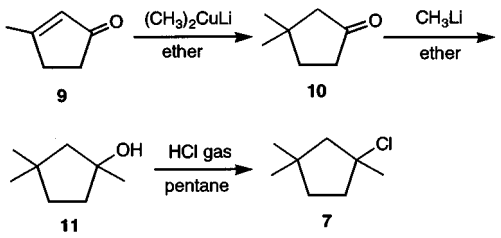
RESULTS AND DISCUSSION

Synthesis

The known chlorides **4**, **5**, **6** and **8** were prepared following literature procedures. 1-Chloro-1,3,3-trimethylcyclopentane (**7**) was prepared by hydrochlorination of the corresponding alcohol **11** that was derived from commercially available 3-methylcyclopent-2-enone (**9**) (Scheme 1).

Solvolysis rates of chlorides 4–8

The rates of solvolysis of **4**–**8** were determined in various solvents by a titrimetric or a conductimetric method mostly in the presence of 2,6-lutidine. Acetolysis was conducted in the presence of sodium acetate. The low solubilities of **4** and solvolysis products in aqueous solvents hampered the rate studies in 40% acetone, 50% methanol and 50% ethanol and their more aqueous mixtures. The rates of **4** in low-nucleophilicity solvents such as trifluoroacetic acid (TFA), formic acid, and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP) were expected to be too fast to be measured; therefore, these solvents were not included, and only 70% HFIP was subjected to a rate study. Since the cyclopentyl system was studied only for comparative purposes, the rate study of **7** and **8** was limited to several selected solvents. The specific rates are summarized in Table 1. The specific rates of **6** in 80% ethanol[8a] and 80% acetone[8b] are literature values. The rate of **8** in ethanol has also been reported.[8c]



Scheme 1

Correlations of log *k* values with Y_{Cl}

Correlations of log *k* values for **4**–**6** with Y_{Cl} are shown in Figure 1. For comparison, similar plots are also shown for **1**[4,9] and **3**[6] by using selected reported data.

It has been well recognized that downward deviations of the points for fluorinated alcohols (TFE and HFIP) and carboxylic acids (TFA, HCO_2H and AcOH) in the correlation with Y_{Cl} indicate the involvement of nucleophilic solvent intervention in non-fluorinated alcohols and aqueous organic solvents, such as aqueous ethanol, aqueous acetone and aqueous dioxane.[1c,d] As Figure 1 shows the perfect fit of the points of AcOH, TFE, 70% TFE, 50% TFE and 70% HFIP for **4** to a single straight line ($m = 0.74 \pm 0.01$, $r = 0.999$) is in accord with essential absence of nucleophilic solvent intervention in the transition state of ionization.

As is obvious from the plots in Figure 1, the downward deviation of the TFE and aqueous TFE points from the line defined by EtOH, MeOH, their aqueous mixtures and aqueous acetone points increases in the order **4** (no deviation) < **5** ≈ **3** < **6** < **1**. This suggests that the nucleophilic

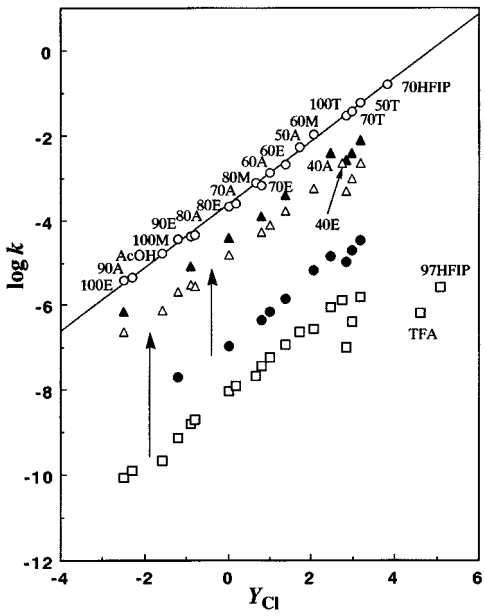


Figure 1. Plots of log *k* against Y_{Cl} for the solvolyses of **1** (□), **3** (●), **4** (○), **5** (▲) and **6** (△) at 25 °C. The points for **1** and **3** are shifted downwards by 3 and 2 units, respectively, for clarity. For references to Y_{Cl} and rate data for **1** and **3**, see text

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Table 1. Rate constants of solvolysis of **4**–**8** at 25·0 °C

	10^5k (s^{-1})[b]				
Solvent[a]	**4**	**5**	**6**	**7**	**8**
100E	0·373[c]	0·0679[d]	0·0241[e,f]	0·799[g]	0·568[h]
90E	4·19	0·801	0·297		
80E	20·3[i]	3·82	1·533[j]	35·8	36·4
70E	65·9	12·5	5·28		
60E	205[k]	39·5	16·2	350[k]	410[k]
40E			224[l]		
100M	3·54[m]		0·202[n]	6·43[o]	4·65[p]
80M	79·4				
60M	1040[k]		55·6		
90A	0·454				
80A	4·61		0·29[j]		
70A	24·5				
60A	129[k]		7·79		
50A	521[k]				
40A		398[k]			
AcOH	1·61[q,r]		0·0777[q,s]	2·25[q,t]	1·29[q,u]
100T	2860[v]	273[v]	50·7	2550[v]	1350[v]
70T	3590[v]	400[v]	96·7[v]		
50T	5790[v]	777[v]	227[v]		
70HFIP	15700[e,w]				

[a] E, M, A, T and HFIP denote ethanol, methanol, acetone, 2,2,2-trifluoroethanol and 1,1,1,3,3,3-hexafluoropropan-2-ol, respectively. The numbers before E, M and A indicate the volume % of the organic components in aqueous mixtures at 25 °C and those before T and HFIP indicate the weight % of T and HFIP.

[b] Determined titrimetrically within an experimental error of ±2% in the presence of 0·025 mol l^{-1} 2,6-lutidine unless noted otherwise.

[c] $k = 9{\cdot}70 \times 10^{-5}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 24.4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -1{\cdot}7$ cal K^{-1} mol^{-1} (1 cal = 4·184 J).

[d] $k = 1{\cdot}80 \times 10^{-5}$ (50·0 °C), $2{\cdot}91 \times 10^{-4}$ s^{-1} (75·0 °C); $\Delta H^{\ddagger} = 24{\cdot}4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -4{\cdot}9$ cal K^{-1} mol^{-1}.

[e] Extrapolated from data at other temperatures.

[f] $k = 6{\cdot}40 \times 10^{-6}$ (50·0 °C), $1{\cdot}06 \times 10^{-4}$ s^{-1} (75·0 °C); $\Delta H^{\ddagger} = 24{\cdot}5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -6{\cdot}6$ cal K^{-1} mol^{-1}.

[g] $k = 1{\cdot}79 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 23{\cdot}2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -4{\cdot}0$ cal K^{-1} mol^{-1}.

[h] $k = 1{\cdot}31 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 23{\cdot}4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -3{\cdot}9$ cal K^{-1} mol^{-1}. A reported value[8c] at 25 °C is $5{\cdot}62 \times 10^{-6}$ s^{-1}.

[i] A reported value[10a] is $2{\cdot}06 \times 10^{-4}$ s^{-1}.

[j] Ref. 8a.

[k] Determined conductimetrically within an experimental error of ±0·5% in the presence of 0·025 mol l^{-1} 2,6-lutidine.

[l] Ref. 8b.

[m] $k = 7{\cdot}30 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 22{\cdot}6$ kcal mol^{-1}; $\Delta S^{\ddagger} = -3{\cdot}2$ cal K^{-1} mol^{-1}.

[n] $k = 5{\cdot}15 \times 10^{-5}$ s^{-1} (50·0 °C), $6{\cdot}37 \times 10^{-4}$ s^{-1} (75·0 °C); $\Delta H^{\ddagger} = 23{\cdot}2$ kcal mol^{-1}; $\Delta S^{\ddagger} = -6{\cdot}8$ cal K^{-1} mol^{-1}.

[o] $k = 1{\cdot}19 \times 10^{-3}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 21{\cdot}8$ kcal mol^{-1}; $\Delta S^{\ddagger} = -4{\cdot}7$ cal K^{-1} mol^{-1}.

[p] $k = 8{\cdot}61 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 21{\cdot}8$ kcal mol^{-1}; $\Delta S^{\ddagger} = -5{\cdot}4$ cal K^{-1} mol^{-1}.

[q] Determined titrimetrically within an experimental error of ±2% in the presence of 0·025 mol l^{-1} NaOAc.

[r] $k = 2{\cdot}89 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 21{\cdot}5$ kcal mol^{-1}; $\Delta S^{\ddagger} = -8{\cdot}3$ cal K^{-1} mol^{-1}.

[s] $k = 2{\cdot}46 \times 10^{-5}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 25{\cdot}9$ kcal mol^{-1}; $\Delta S^{\ddagger} = 0{\cdot}3$ cal K^{-1} mol^{-1}.

[t] $k = 5{\cdot}17 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 23{\cdot}4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -1{\cdot}3$ cal K^{-1} mol^{-1}.

[u] $k = 3{\cdot}07 \times 10^{-4}$ s^{-1} (50·0 °C); $\Delta H^{\ddagger} = 23{\cdot}7$ kcal mol^{-1}; $\Delta S^{\ddagger} = -1{\cdot}5$ cal K^{-1} mol^{-1}.

[v] Determined conductimetrically within an experimental error of ±0·5% in the presence of 2×10^{-4} mol l^{-1} 2,6-lutidine.

[w] The rates at lower temperatures were determined conductimetrically within an experimental error of ±1% in the absence of a buffer. $k = 0{\cdot}0178$ (2·8 °C), 0·0406 (10·5 °C), 0·0812 s^{-1} (18·0 °C); $\Delta H^{\ddagger} = 15{\cdot}4$ kcal mol^{-1}; $\Delta S^{\ddagger} = -10{\cdot}7$ cal K^{-1} mol^{-1}.

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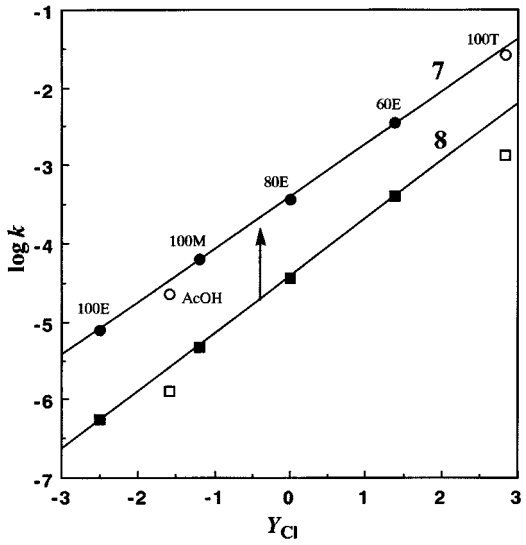


Figure 2. Plots of log *k* against Y_{Cl} for the solvolyses of **7** (●, ○) and **8** (■, □) at 25 °C. The points for **8** are shifted downwards by 1 unit for clarity. The data for AcOH and 100T are not included in the regression analyses

solvent assistance to ionization increases in this order. The results will be more quantitatively treated in the following section by the evaluation of *l* values.

A similar tendency is found in the correlations of log *k* values for **7** and **8** with Y_{Cl} (Figure 2). Although the points of AcOH and TFE for **7** deviate only slightly downwards from the regression line passing through EtOH, 80E, 60E, and MeOH points, the deviations of the AcOH and TFE points for **8** are considerably larger.

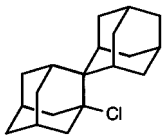
Despite the marked similarity in the effect on the mY_{Cl} correlations of introducing two methyl groups into the γ position of **8** and **6** to form **7** and **4**, respectively, the effects on solvolysis rates are very different. The rate ratio in TFE, the least nucleophilic solvent examined, is 1.9 for **7**/**8** compared with 56 for **4**/**6**. This shows that one of the two remote methyl substituents in **7** works to shield the rear-side of the cationic carbon without increasing the back strain (B-strain) in the ground state. On the other hand, the remote methyl groups in **4** work to increase both of the rear-side shielding and the B-strain. As will be discussed later, the remote methyl groups in **4** appear to have a marked effect in controlling the conformation of the transition state of ionization.

The rate data in this study also give an important insight into the magnitude of the relief of B-strain involved in the solvolysis of **4**. Brown and co-workers[10] compared the rate of **4** with that of 2-chloro-2-methylpropane (**1**) in 80% ethanol at 25 °C and obtained the **4**/**1** rate ratio of 21. The enhanced rate of **4** was attributed to the acceleration of solvolysis of **4** by B-strain in the ground state.[10,11] As discussed above, the nucleophilic solvent assistance is large in **1** and is essentially absent in **4**. Therefore, if the B-strain effect is to be evaluated, the rates should be compared in a solvent of as low nucleophilicity as possible. The **4**/**1** rate ratio obtained in this work in TFE is 275 by using the specific rate $1{\cdot}04\times10^{-4}\,s^{-1}$ for **1**.[9b] Extrapolation of the plot for **1** in Figure 1 predicts the specific rates in TFA ($Y_{Cl}=4{\cdot}6$)[1d] and 97% HFIP ($Y_{Cl}=5{\cdot}08$)[1d] to be 0·61 and $1{\cdot}4\,s^{-1}$, respectively. By using these predicted specific rates and reported values for **1** in TFA[9c] and 97% HFIP[9d,e] at 25 °C ($6{\cdot}4\times10^{-4}$ and $2{\cdot}69\times10^{-3}\,s^{-1}$, respectively), we obtain the respective **4**/**1** rate ratios of 950 and 520. Evidently, the previously assigned B-strain effect for **4** as measured by the solvolysis rate ratio has been underestimated by a factor of at least 40.

Correlations of log(k/k_0) values with lN_T+mY_{Cl}

The rate data in Table 1 were analysed by using equation (2): the *l*, *m* and *c* values are summarized in Table 2 with associated standard errors. The correlation analysis for **1** was performed on 20 data by excluding TFA, for which the N_T value is unavailable. Extensive correlation analysis for **1** by using 46 data and equation (2) has been reported by Kevill and D'Souza[2b] to give l=0·38±0·03, m=0·86±0·02 and c=0·00±0·19 with r=0·993. The *l* value increases in the order **4** (l=0·00±0·02)<**7** (0·05±0·02)<**5** (0·09±0·04)≈**3** (0·10±0·04)<**6** (0·15±0·03)≈**8** (0·16±0·02)<**1** (0·38±0·03), showing that the nucleophilic solvent intervention increases in this order. As expected from the good straight line for **4** in Figure 1, its *l* value is essentially zero (0·00±0·02). Notably, the isobutyl group in **5** is as effective as the *tert*-butyl group in **3** in rear-side shielding.

Previously, we pointed out that the less reactive the chloride is in TFE, the greater the *m* value becomes.[7] By comparing the rates and *m* values for **1**, **3** and **4**, we suggested that 'a lower *m* value of a more activated chloride due to greater B-strain is in accord with an earlier transition state and, therefore, a reduced sensitivity to changes in solvent ionizing power'.[7] It appears that a correlation holds, but more data would be required before we can conclude whether our postulate is appropriate or not. The relatively small *m* value (0·89±0·06) for very reactive 1-chloro-[1]diadamantane (**12**) has been attributed to an earlier transition state.[12]



12

Solvent effect and structure of the transition state

The solvolysis of **4** is characterized by two findings. One is the very small *l* value of nearly zero, which suggests the essential absence of nucleophilic solvent intervention. The

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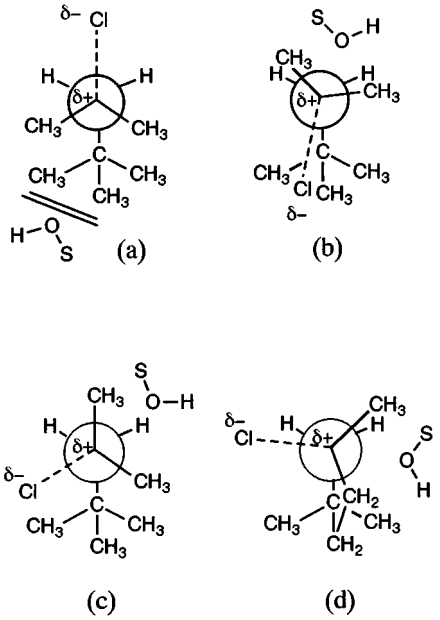
Table 2. Correlation of specific rates of solvolysis of **1** and **3**–**8** against N_T[a] amd Y_{Cl}[b] by using the extended Grunwald–Winstein equation (2)

Substrate	n[c]	l[d]	m[d]	c[d]	r[e]
1	20	0·32±0·03	0·83±0·02	0·05±0·04	0·996
3	10	0·10±0·04	0·81±0·04	0·09±0·05	0·996
4	18	0·00±0·02	0·74±0·01	0·05±0·02	0·999
5	9	0·09±0·04	0·76±0·03	0·03±0·04	0·998
6	14	0·15±0·03	0·75±0·02	0·02±0·03	0·998
7	6	0·05±0·02	0·70±0·01	0·05±0·03	0·999
8	6	0·16±0·02	0·76±0·02	0·06±0·03	0·999

[a] Refs 2a and 2b.
[b] Ref, 5.
[c] Number of solvents.
[d] Using equation (2); with associated standard errors.
[e] Correlation coefficient.

other is the very fast rate of solvolysis that is attributed to a marked B-strain effect in the ground state. The two characteristics may be reasonably accounted for assuming a transition state where the leaving chloride ion takes a locus that is nearly antiperiplanar to the *tert*-butyl group [Scheme 2(a)]. In this conformation the nucleophilic solvent intervention would be hampered by the bulky *tert*-butyl group. The reason for favouring this conformation would be that the transition state (b) is energetically unfavorable because of the steric hindrance to departure of the leaving group.



Scheme 2

Steric hindrance to ionization has been demonstrated in the solvolyses of various U-shaped molecules.[11]

Conformation (c) is similar to the transition state of 1-chloro-1,3,3-trimethylcyclopentane (d), where the leaving chloride ion takes a locus that is nearly perpendicular to the cyclopentane ring. We first postulated that a relief of possible 1,3-dimethyl interaction (B-strain) might increase the rate of **7** compared with **8**; in actuality, however, the **7**/**8** ratio was only 1·9 in TFE (see above). Therefore, the transition state (c) or the like where the B-strain is not relieved would not account for the **4**/**1** rate ratio as large as 275 in TFE. In addition, the possible occurrence of nucleophilic solvent intervention in the transition state (c) is not in harmony with the good mY_{Cl} correlation with $l = 0{\cdot}00 \pm 0{\cdot}02$.

It would be appropriate here to consider briefly the meaning of 'nucleophilic solvent intervention' in the solvolysis of *simple tertiary* compounds that may not undergo classical S_N2 reactions. In the analysis by using equation (1), all possible factors to stabilize the carbocation part are included in the lN term, despite the fact that the N scales have been determined on the basis of S_N2 reactivity of a given standard substrate with solvents. Bentley and Carter[5] interpreted the appreciable l value of 0·3 for **1** by the S_N2 (intermediate) mechanism that involves the formation of loosely bonded intermediate by nucleophilic solvation of a developing carbocation. On the other hand, this appreciable l value could also be interpreted to mean that nucleophilic solvation of the incipient *tert*-butyl cation might be much better than the solvation of the incipient 1-adamantyl cation in the solvolysis of 1-chloroadamantane (**2**).[1g,13]

Richard *et al.*[14] suggested the greater importance of the solvation by Brønsted base-type interaction (solvation by hydrogen bonding) with an α-methyl group (or more generally, β-hydrogens) than the Lewis base-type interaction (nucleophilic solvation) toward the cumyl cation. In the less hindered *tert*-butyl cation, the importance of the latter effect would increase. In contrast, in heavily con-

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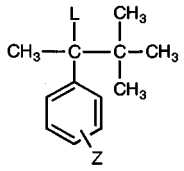
gested compounds both types of interaction would decrease, and finally become less solvated than the 1-adamantyl system. Recent results in this laboratory support the importance of Brønsted base-type interactions in stabilizing incipient carbocations, which will be reported elsewhere.



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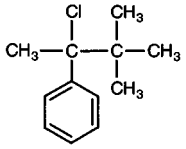

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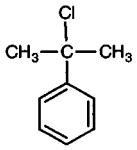

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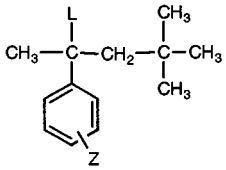

16

Solvolysis products

The products of solvolysis of **4** were examined in methanolysis and acetolysis at 50 °C under buffered conditions. GLC and ^{1}H NMR analyses for the product mixtures after 10 or 15 half-lives showed that the products were the expected two olefins, 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene, and the expected substitution product; no other components were observed. The ratio between these products was 63:11:26 in methanolysis and 86:12:2 in acetolysis.

Significance of the solvolysis of neopentylcarbinyl systems

At present, the most reliable systems that undergo limiting S_N1 solvolysis are cage-shaped bridgehead compounds.[1c,1d,15,16] A typical example is the 1-adamantyl system.[5] However, the bridgehead compounds are tertiary as they are; therefore, it is impossible to examine the effect of a substituent on the reaction center. The 2-adamantyl system is another candidate that exhibits k_c solvolyses.[1b] Liu[1f] used 2-aryl-2-adamantyl compounds as standard substrates for the evaluation of the ionizing power of solvents specifically for benzylic compounds, and developed Y_{BnCl}, Y_{BnBr} and Y_{BnOPNB}. One drawback of the 2-adamantyl system is the difficulty in examining the steric course of reactions. The neopentylcarbinyl systems are expected to find a solution to this point, provided that some convenient methods to prepare optically active tertiary neopentylcarbinols are developed.

In open-chain systems, a *tert*-butyl group is often used as a substituent on the α-carbon to inhibit nucleophilic solvent intervention,[1f] although 2-chloro-2,3,3-trimethylbutane (**3**) has been suspected to be subject to nucleophilic solvent intervention.[6] In the solvolysis of 1-aryl-1,2,2-trimethylpropyl systems (**13**), steric hindrance to resonance[17] is evident. For example, 2-chloro-3,3-dimethyl-2-phenylbutane (**14**) solvolyzes 10^3 time more slowly than cumyl chloride (**15**).[18] Therefore, **14** would not be an ideal system for use as a surrogate of **15** to preclude nucleophilic solvent intervention. Perhaps the neopentylcarbinyl system (**16**) will satisfy the requirement. Investigation of molecular models indicates that the resonance stabilization would not be hindered by the neopentyl substituent. Application to secondary solvolyses will also shed light on the solvolysis mechanisms of borderline cases[19] and retentive solvolyses of 1-arylethyl systems.[20]

EXPERIMENTAL

IR spectra were recorded as solutions. ^{1}H NMR spectra were recorded at 90 or 270 MHz in $CDCl_3$. ^{13}C NMR spectra were recorded at 22·5 or 68 MHz in the same solvent. Gas chromatographic analyses were conducted on a PEG-20M column (2 m × 3 mm i.d.). The known chlorides **4**, **5**, **6** and **8** were prepared by hydrochlorination[21] of the corresponding olefin (for **4**) or alcohols. Solvolysis solvents were purified by previously described methods.[22] Anhydrous solvents used for synthesis were purified by standard procedures. 2,6-Lutidine was distilled over CaH_2. Other commercially available reagents were of a reagent-grade quality and used as received.

1-Chloro-1,3,3-trimethylcyclopentane (7)

3,3-Dimethylcyclopentanone (10). Following a literature procedure,[23] freshly distilled 3-methylcyclopent-2-enone (**9**) (7·12 g, 0·074 mol) was treated with lithium dimethylcuprate to give 5·3 g (63%) of **10**; b.p. 83–84 °C/80 Torr (1 Torr = 133·3 Pa) (lit.[23] 75 °C/84 Torr).

1,3,3-Trimethyl-1-cyclopentanol (11). Treatment of **10** (5·04 g, 0·045 mol) with excess methyllithium in diethyl ether gave **11** (4·8 g, 83%); b.p. 83–84 °C/50 Torr; IR (CCl_4), 3612, 3200–3500 br, 2954, 1374, 1364 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ 0·99 (s, 3H), 1·12 (s, 3H), 1·33 (s, 3H), 1·4–1·9 (m, 6H), 1·94 ppm (s, 1H); ^{13}C NMR ($CDCl_3$), δ 80·6 (C), 56·2 (CH_2), 41·3 (CH_2), 40·1 (CH_2), 38·6 (C), 30·8

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(CH_3), 30·5 (CH_3), 29·8 ppm (CH_3); HRMS (EI), calculated for $C_8H_{16}O$, 128·1202; found, 128·1177.

1-Chloro-1,3,3-trimethylcyclopentane (7). A solution of **11** (1·00 g, 7·8 mmol) in pentane (10 ml) was treated with dry HCl gas at 0 °C for 40 min. The reaction mixture was dried with $CaCl_2$ and excess HCl was swept off with N_2. Filtration followed by evaporation of solvent afforded **7** as a colorless liquid (1·06 g, 94%); ^{1}H NMR ($CDCl_3$), δ 1·01 (s, 3H), 1·19 (s, 3H), 1·5–2·3 (m, 6H), 1·68 ppm (s, 3H);^{13}C NMR ($CDCl_3$), δ 78·2 (C), 58·5 (CH_2), 44·3 (CH_2), 40·4 (CH_2), 38·8 (C), 32·3 (CH_3), 31·3 (CH_3), 30·9 ppm (CH_3). The crude chloride was essentially pure by ^{13}C NMR spectroscopy and used for rate studies without further purification.

Product of solvolysis of 4

Methanolysis. A solution of **4** (0·297 g, 2·00 mmol) in 0·050 M 2,6-lutidine in methanol (50 ml) was kept at 50·0 °C for 160 min (10 half-lives). The reaction mixture was mixed with pentane, washed with 10% NaCl and dried. GLC analysis showed the formation of a mixture of the two expected olefins (74%) and the expected methyl ether (26%). Most of the pentane was slowly distilled off through a 20 cm Vigreux column, and the residue was examined by ^{1}H NMR spectroscopy. The formation of 2-methoxy-2,4,4-trimethylpentane was confirmed by the methoxy signal at δ 3·17. The ratio between the two olefins, 2,4,4-trimethylpent-1-ene and 2,4,4-trimethylpent-2-ene, was determined by the integration of the olefinic protons.

Acetolysis. A solution of **4** (0·297 g, 2·00 mmol) in 0·050 M NaOAc in acetic acid (50 ml) was heated for 10 h (15 half-lives). The reaction mixture was mixed with pentane, washed with water and saturated $NaHCO_3$ solution and dried. Product analysis was conduced in the manner described under *Methanolysis*. The formation of the expected acetate was confirmed by the agreement of the GLC retention time with that of an authentic sample.

Authentic 1,1,3,3-tetramethylbutyl acetate. This was prepared by treating 2,4,4-trimethylpentan-2-ol (0·400 g. 3·07 mmol) with acetic anhydride (0·47 g, 4·6 mmol) in triethylamine (0·64 ml) in the presence of 4-(*N*,*N*-dimethylamino)-pyridine (0·038 g, 0·31 mmol) at room temperature overnight. The reaction mixture was diluted with pentane, washed with 10% HCl and saturated NaCl solution and dried. Evaporation of the solvent afforded essentially pure 1,1,3,3-tetramethylbutyl acetate; ^{13}C NMR ($CDCl_3$), δ 170·4 (CO), 83·6 (C), 52·3 (CH_2), 31·4 (C), 31·3 (CH_3), 28·3 (CH_3), 22·7 ppm (CH_3).

Kinetic studies

The preparation of solvents and kinetic procedures followed the methods described previously.[22]

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