Solvent Effects and Steric Course in the Solvolysis of 1,3,3-Trimethyl-2-oxocyclopentyl Mesylate in Comparison with 1,1,3,3-Tetramethyl-2-oxobutyl System

Ken'ichi Takeuchi,* Takuhiro Ushino, Takao Okazaki, Toshikazu Kitagawa, Tomomi Kinoshita, Yasushi Ohga,[#] Koichi Tanaka,[†] and Fumio Toda*,[†,##]

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501

† Department of Applied Chemistry, Faculty of Engineering, Ehime University, Matsuyama, Ehime 790-8577

(Received September 18, 2000)

The rates of solvolysis in various solvents were determined for 1,1,3,3-tetramethyl-2-oxobutyl tosylate (**1**OTs) and 1,3,3-trimethyl-2-oxocyclopentyl mesylate (**4**OMs). The rate data for **1**OTs reinforced that the linear Grunwald–Winstein (GW) relationship of **1**OMs previously reported by Creary for non-aqueous solvents must also hold for aqueous organic solvents. **4**OMs showed a markedly dispersed GW relationship that is, on the other hand, well correlated with an extended GW equation involving a nucleophilicity parameter. Such solvent dependence, such marked effects of added sodium azide on rates, and the 100% inversion of configuration of the solvolysis product showed that the solvolysis of **4**OMs would be categorized to S_N2(intermediate), whereas **1**OMs and **1**OTs solvolyze via limiting S_N1. The negligible susceptibility of **1**OTs toward nucleophilicity of solvent and azide probe indicates that the nucleofuge leaves along the C=O axis in such a manner that the back-strain (B-strain) in the ground state is efficiently relieved in the transition state. Comparison of solvolysis rates of **1**OMs and **4**OMs with those of the corresponding parent substrates suggests that the transition states of these substrates would not be stabilized by carbonyl π conjugation. The origin of the unexpectedly fast rates of solvolysis of **1**OMs has been discussed.

The chemistry of carbocations that are destabilized by a strongly electron-withdrawing substituent has been a subject of considerable interest for the past two decades in the field of physical organic chemistry.[1] Some carbocations having a carbonyl or a cyano substituent on the α carbon have been spectroscopically observed under stable ion conditions.[1e] The α-carbonyl cation stabilized by *p*-methoxyphenyl substituents has even been isolated.[2] These works appear to have brought about an impression that the α-carbonyl cations were much more stable than had been thought before.[3]

The solvolyses of various α-carbonyl substrates have been extensively carried out by Creary and co-workers.[1c–e] They demonstrated that many α-carbonyl cations can be relatively easily formed as solvolysis intermediates: for example, 1,1,3,3-tetramethyl-2-oxobutyl methanesulfonate (mesylate) (**1**OMs) solvolyzes 55 times faster than isopropyl mesylate (**2**OMs) in 97% 1,1,1,3,3,3-hexafluoro-2-propanol containing 3% water (97HFIP).[4] Since **1**OMs had been postulated to solvolyze 10^4–10^5 times as slow as **2**OMs, the enormous amount of acceleration was ascribed to possible contribution of the carbonyl substituent to stabilize the incipient cation by the mesomeric (+M) effect[5] **3a** ↔ **3b** (Chart 1).[1,4]

Previously, we have suggested that the mesomeric stabilization as described by **3a** ↔ **3b** would be improbable by comparing the solvolysis rates of various 2-oxo bridgehead compounds.[6] We herein report the full account of a previous communication[7] on the solvolysis of 1,3,3-trimethyl-2-oxocy-

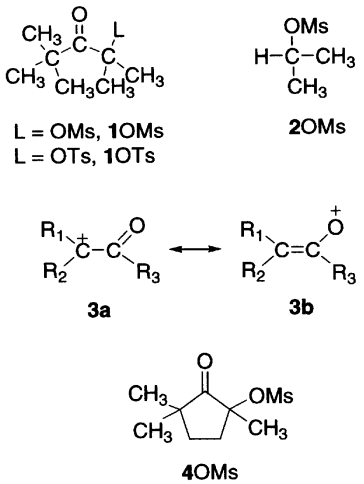


Chart 1.

Department of Chemistry, Faculty of Engineering, Oita University, Oita 870-11

Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridai-cho, Okayama 700-0005

clopentyl mesylate (**4**OMs), a cyclopentyl version of **1**OMs. By comparing markedly different behavior between **4**OMs and **1**OMs in the solvent effects on solvolysis rates and azide probe experiments, and by examining the stereochemistry of substitution, we obtained further evidence suggesting that **1**OMs may not be an appropriate model to test the mesomeric contribution **3a** ↔ **3b**.

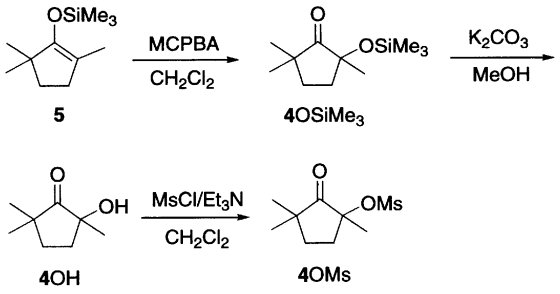
Results and Discussion

Synthesis of Substrates. In order to obtain more solvolysis data, we wished to prepare **1**OMs in a reasonable amount, but the synthesis required methanesulfinyl chloride and oxidation of the resulting methanesulfinate.[4b] These synthetic processes were not necessarily straightforward in this laboratory: consequently, we chose a *p*-toluenesulfonate (tosylate) in place of a mesylate and were able to obtain **1**OTs in a good yield.

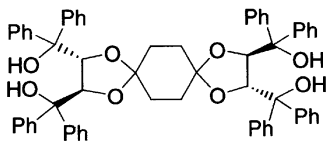
The preparation of 2-hydroxy-2,5,5-trimethylcyclopentanone (**4**OH) is summarized in Scheme 1. Oxidative rearrangement of silyl enol ether **5**[8] by *m*-chloroperbenzoic acid[9] afforded **4**OSiMe$_3$, which was converted to **4**OH and then to **4**OMs in usual manners.

Optical Resolution of 2-Hydroxy-2,5,5-trimethylcyclopentanone (4OH). 2-Hydroxy-2,5,5-trimethylcyclopentanone (**4**OH) was resolved by inclusion complexation with optically active host compound **6**[10] (Chart 2) derived from tartaric acid. For example, when a mixture of **6a** and (±)-**4**OH in hexane was kept at room temperature for a week, a 1:1 inclusion complex of **6a** and (–)-**4**OH was obtained as colorless prisms. Heating the inclusion complex in vacuo gave (–)-**4**OH of 49% ee in 70% yield as a distillate, and (+)-**4**OH of 30% ee was obtained from the filtrate. When the complexation of (–)-**4**OH of 49% ee with **6a** was repeated again, (–)-**4**OH of 73% ee was obtained in 36% yield. The same treatment of the (+)-**4**OH of 30% ee with **6b** followed by distillation as above gave (+)-**4**OH of 80% ee in 28% yield.

Rate Studies and Grunwald–Winstein Relationship. The first-order rate constants of solvolysis of **1**OTs and **4**OMs in various solvents have been titrimetrically determined and results are summarized in Table 1. In the previous study by the Creary group the rates of **1**OMs were determined only in nonaqueous alcohols and carboxylic acids.[4b] Therefore, we carried out the rate measurements for **1**OTs in TFE, AcOH, HCO_2H,



Scheme 1.



6

a: (*R,R,R,R*)-(–)-form
b: (*S,S,S,S*)-(+)-form

Chart 2.

Table 1. Rate Constants and Activation Parameters for the Solvolysis of **1**OTs and **4**OMs at 25.0 °C

Solvent[a)]	Compound and $10^6 \times k/s^{-1}$ [b)]	
	1OTs	**4**OMs
EtOH	0.0701[c,d)]	0.447[c,e)]
80% EtOH–20% H_2O	0.610[c,f)]	4.00[g)]
60% EtOH–40% H_2O	1.87[h)]	10.1
50% EtOH–50% H_2O	3.72	17.4
40% EtOH–60% H_2O		32.5
MeOH		1.35[i)]
80% acetone–20% H_2O		0.513[c,j)]
TFE	8.19[k)]	0.384[c,l)]
97% HFIP–3% H_2O		1.03[m)]
AcOH	0.206[c,n,o)]	0.0818[c,n,p)]
HCO_2H	85.7[q)]	19.8[q,r)]
TFA		14.2[s)]

a) TFE, HFIP, and TFA denote 2,2,2-trifluoroethanol, 1,1,1,3,3,3-hexafluoro-2-propanol, and trifluoroacetic acid, respectively. The percentages mean volume% for aqueous ethanol and aqueous acetone and weight% for HFIP.
b) Determined titrimetrically within an experimental error ± 2% in the presence of 0.025 mol dm^{-3} 2,6-lutidine unless otherwise noted.
c) Extrapolated from data at higher temperatures.
d) $k = 2.30 \times 10^{-6}$ s^{-1} (50.0 °C), 4.57×10^{-5} s^{-1} (75.0 °C); $\Delta H^{\ddagger} = 109$ kJ mol^{-1}; $\Delta S^{\ddagger} = -15.1$ J mol^{-1} K^{-1}.
e) $k = 8.83 \times 10^{-6}$ s^{-1} (50.0 °C), 1.05×10^{-4} s^{-1} (75.0 °C); $\Delta H^{\ddagger} = 91.7$ kJ mol^{-1}; $\Delta S^{\ddagger} = -51.6$ J mol^{-1} K^{-1}.
f) $k = 1.65 \times 10^{-5}$ s^{-1} (50.0 °C), 2.78×10^{-4} s^{-1} (75.0 °C); $\Delta H^{\ddagger} = 103$ kJ mol^{-1}; $\Delta S^{\ddagger} = -18.0$ J mol^{-1} K^{-1}.
g) $k = 6.34 \times 10^{-5}$ s^{-1} (50.0 °C); $\Delta H^{\ddagger} = 86.2$ kJ mol^{-1}; $\Delta S^{\ddagger} = -59.4$ J mol^{-1} K^{-1}.
h) $k = 5.52 \times 10^{-5}$ s^{-1} (50.0 °C); $\Delta H^{\ddagger} = 106$ kJ mol^{-1}; $\Delta S^{\ddagger} = 0.8$ J mol^{-1} K^{-1}.
i) $k = 2.58 \times 10^{-5}$ s^{-1} (50.0 °C), 2.94×10^{-4} s^{-1} (75.0 °C); $\Delta H^{\ddagger} = 90.4$ kJ mol^{-1}; $\Delta S^{\ddagger} = -53.6$ J mol^{-1} K^{-1}.
j) $k = 9.18 \times 10^{-6}$ s^{-1} (50.0 °C), 1.08×10^{-4} s^{-1} (75.0 °C); $\Delta H^{\ddagger} = 89.9$ kJ mol^{-1}; $\Delta S^{\ddagger} = -63.8$ J mol^{-1} K^{-1}.
k) $k = 1.95 \times 10^{-4}$ s^{-1} (50.0 °C); $\Delta H^{\ddagger} = 99.2$ kJ mol^{-1}; $\Delta S^{\ddagger} = -10.0$ J mol^{-1} K^{-1}.
l) $k = 7.52 \times 10^{-6}$ s^{-1} (50.0 °C), 9.25×10^{-5} s^{-1} (75.0 °C), 8.61×10^{-4} s^{-1} (100.0 °C); $\Delta H^{\ddagger} = 92.5$ kJ mol^{-1}; $\Delta S^{\ddagger} = -57.3$ J mol^{-1} K^{-1}.
m) Determined by ^{1}H NMR within an experimental error ± 2% by using 0.16 mol dm^{-3} **4**OMs in the presence of 0.20 mol dm^{-3} 2,6-lutidine.
n) Determined titrimetrically within an experimental error ± 2% in the presence of 0.025 mol dm^{-3} NaOAc.
o) $k = 7.18 \times 10^{-6}$ s^{-1} (50.0 °C), 1.50×10^{-4} s^{-1} (75.0 °C); $\Delta H^{\ddagger} = 111$ kJ mol^{-1}; $\Delta S^{\ddagger} = 0.0$ J mol^{-1} K^{-1}.
p) $k = 2.37 \times 10^{-6}$ s^{-1} (50.0 °C), 4.25×10^{-5} s^{-1} (75.0 °C), 5.15×10^{-4} s^{-1} (100.0 °C), $\Delta H^{\ddagger} = 95.4$ kJ mol^{-1}; $\Delta S^{\ddagger} = -27.2$ J mol^{-1} K^{-1}.
q) Determined titrimetrically within an experimental error ± 2% in the presence of 0.025 mol dm^{-3} NaOCHO.
r) $k = 3.25 \times 10^{-4}$ s^{-1} (50.0 °C); $\Delta H^{\ddagger} = 87.0$ kJ mol^{-1}; $\Delta S^{\ddagger} = -53.6$ J mol^{-1} K^{-1}.
s) Determined by ^{1}H NMR within an experimental error ± 2% by using 0.16 mol dm^{-3} **4**OMs in the presence of 0.20 mol dm^{-3} $NaOCOCF_3$.

EtOH, and aqueous ethanol solvents, and paid attention to whether the rate data in aqueous ethanol could be accommodated to those in non-aqueous solvents. With respect to **4**OMs, we have added four rate data (50% EtOH, 80% acetone, 97% HFIP, and TFA) to the previous short communication.[7]

The limiting S_N1 nature of the solvolysis of alkyl tosylates and mesylates is usually diagnosed by using a modified Grunwald–Winstein (GW) equation (Eq. 1),[11] where k_0 and k are solvolysis rate constants in 80% ethanol–20% water (v/v) and in a given solvent, respectively, at 25.0 °C. The ionizing power of solvent, Y_{OTs}, is defined by using 2-adamantyl tosylate as a limiting S_N1 substrate and putting m = 1 by definition in Eq. 1.[11c,12] In this work, we employed Y_{OTs} values revised by Fujio, Tsuno, and their co-workers[13] (hereafter abbreviated as $Y_{OTs(FT)}$).

$$\log (k/k_0) = mY_{OTs} \quad (1)$$

The GW plot for **1**OTs against $Y_{OTs(FT)}$ is shown in Fig. 1. The good linear correlation (m = 0.64, r = 0.9921) suggests that **1**OMs would also show a nice linear GW plot including both non-aqueous and aqueous ethanol solvents.

In contrast to the case of **1**OTs, the rate data for **4**OMs showed marked dispersions. Figure 2 shows the GW plot (Eq. 1) for **4**OMs in comparison with **1**OMs, the rate data for the latter having been quoted from Ref. 4b. The GW plot for **1**OMs against $Y_{OTs(FT)}$ gives a good linear relation (m = 0.66 and r = 0.9937), as has previously been reported by using original[12] Y_{OTs} values.

In the solvolysis of **4**OMs, the solvents having similar nucleophilicities[12] (EtOH, MeOH, EtOH–H_2O) were accommodated to a single line (m = 0.49, r = 0.9989), but the solvents, AcOH, TFE, HCO_2H, 97% HFIP, and TFA, which have relatively low nucleophilicities,[12] showed considerable downward scattering. A very subtle structural modification from **1**OMs (or **1**OTs) to **4**OMs results in a remarkable change in solvolytic behavior as far as the solvent effect is concerned.

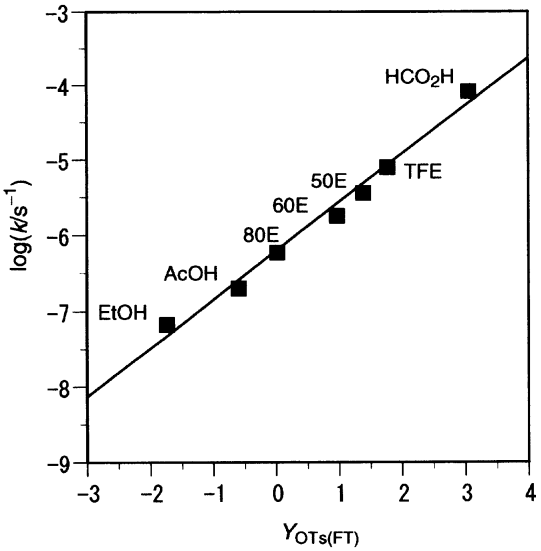


Fig. 1. A plot of log k against $Y_{OTs(FT)}$ for the solvolysis of **1**OTs at 25.0 °C; m = 0.64 (r = 0.9921). For $Y_{OTs(FT)}$ see Ref. 13.

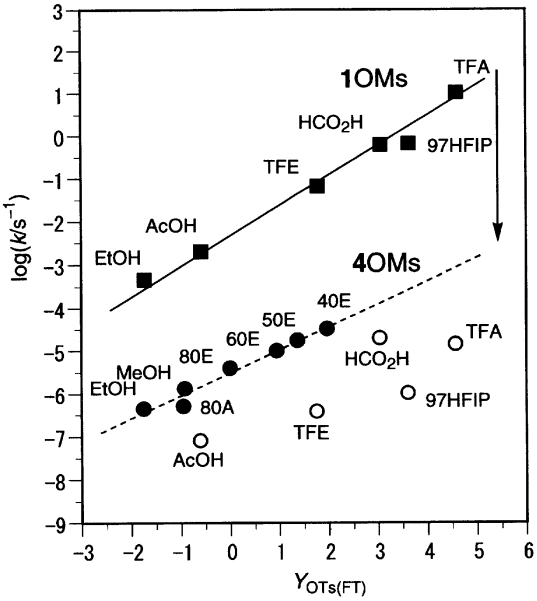


Fig. 2. Plots of log k against $Y_{OTs(FT)}$ for the solvolyses of **1**OMs and **4**OMs at 25.0 °C; for **1**OMs m = 0.66 (r = 0.9937); for EtOH, MeOH, and aqueous EtOH data points of **4**OMs, m = 0.49 (r = 0.9989). The data points for **1**OMs are shifted upward by 4 units for clarity. For the rate data of **1**OMs and $Y_{OTs(FT)}$ values, see Refs. 4b and 13, respectively.

Extended Grunwald–Winstein Relationship. The behavior of **4**OMs, i.e., the upward dispersions of the alcohols and aqueous ethanol data points relative to low-nucleophilicity solvents, is characteristic of the nucleophilic solvent participation (NSP) in ionization.[11c,12] In the previous short communication, we reported that the rate data for **4**OMs are well correlated by the extended GW equation (Eq. 2) involving original Y_{OTs}[11c,12] and nucleophilicity parameter[12] N_{OTs}, the latter being based on the solvolysis rates of methyl tosylate. We further commented that the use of Kevill's nucleophilicity parameter N_T[14] in place of N_{OTs} in Eq. 2 afforded a better fit.[7] Therefore, we employed in this work Eq. 3 consisting of N_T and $Y_{OTs(FT)}$ in place of Eq. 2. Unfortunately, the datum for TFA could not be incorporated owing to the unavailability of the N_T value.

$$\log (k/k_0) = lN_{OTs} + mY_{OTs} \quad (2)$$

$$\log (k/k_0) = lN_T + mY_{OTs(FT)} \quad (3)$$

As shown in Fig. 3, the correlation for **4**OMs with respect to Eq. 3 is very good, with l = 0.60 ± 0.02, m = 0.71 ± 0.02, and r = 0.9957. The amount of the contribution of solvent nucleophilicity is more marked than the case of cyclohexyl tosylate (l = 0.35 ± 0.03, m = 0.85 ± 0.03, and r = 0.992),[14,15] even though **4**OMs is a tertiary substrate. Evidently, the presence of the electronegative carbonyl group enhances the NSP.

The essential absence of NSP for **1**OTs (and most probably for **1**OMs) and its obvious presence for **4**OMs indicate an intrinsic difference in the solvolysis mechanism between the two compounds. In order to obtain further information on the nu-

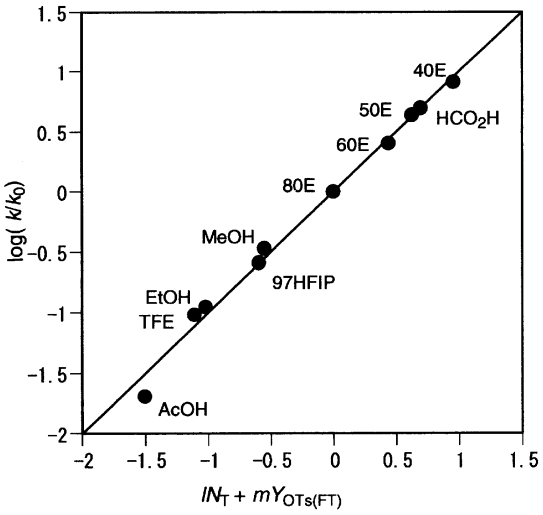


Fig. 3. A plot of $\log(k/k_o)$ against $lN_T + mY_{OTs(FT)}$ for the solvolysis of **4**OMs at 25.0 °C; slope = 1.000 (r = 0.9957). For N_T and $Y_{OTs(FT)}$, see Refs. 14 and 13, respectively.

cleophilic character in the solvolysis of **4**OMs, we examined the azide probe and the steric course of substitution

Azide Probe. A powerful tool to examine the susceptibility to NSP and S_N2 reaction is the use of an azide probe.[16] The rates of solvolysis of **1**OTs and **4**OMs in 50% ethanol in the presence of 0.02 or 0.04 mol dm^{-3} NaN_3 were determined at 25.0 °C: the results are shown in Table 2.

The solvolysis rates of both of **1**OTs and **4**OMs are accelerated by the addition of NaN_3, but the effect is much more marked in **4**OMs than in **1**OTs. The effect evaluated by the b-value of Eq. 4 is 205 ± 26 for **4**OMs, whereas it is 35 ± 6 for **1**OTs. In other words, **1**OTs is about six times *less* susceptible to azide attack than **4**OMs.

$$k = k_0(1 + b[N_3^-]) \quad (4)$$

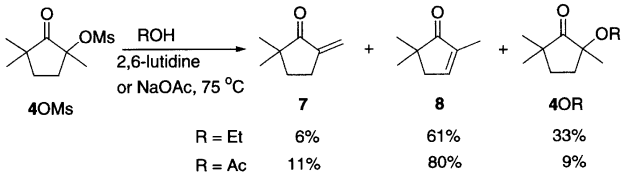
The azide probe results strongly support the conclusion that the rear-side attack is relatively easy in **4**OMs, whereas it is quite difficult in **1**OTs (and **1**OMs). The results are consistent with the marked NSP in **4**OMs and its absence in **1**OTs in the GW relationship.

Products and Steric Course of Reaction. The products of solvolysis from **1**OMs were reported by Creary in 1984.[4b] In ethanolysis, **1**OMs gave an olefin and an ethyl ether in 95% and 5% yields, respectively, and in acetolysis the substitution product was less than 1%. On the other hand, the present study showed that **4**OMs affords larger amounts of a substitution product than **1**OMs: as shown in Scheme 2, ethanolysis and acetolysis gave ethyl ether **4**OEt and acetate **4**OAc in 33% and 9% yields, respectively. No olefinic products other than **7** and **8** were found. The formation of larger amounts of the substitution product from **4**OMs than from **1**OMs is consistent with marked NSP in the former and its absence in the latter.

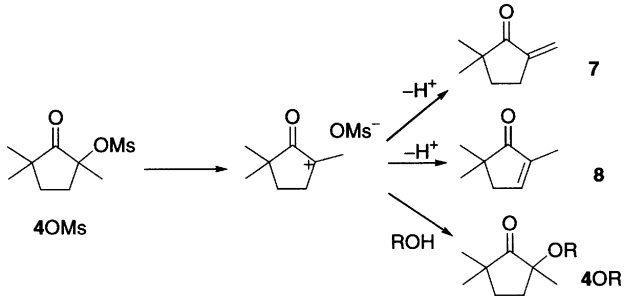
The reaction conditions employed in the present study are typical of S_N1 solvolysis. No strong bases were used. Therefore, the olefins were most probably formed by E1 process, but not by E2 pathway. We assume that the three products are formed from a common ion pair intermediate (Scheme 3).

In this context, it is intriguing to speculate what the stereochemical outcome of substitution would be. In general, solvolysis reactions of *tertiary* halides[17] and esters[18] in relatively nucleophilic solvents such as methanol, ethanol, and aqueous acetone occur with racemization, mostly accompanied by net inversion of configuration. On the other hand, the solvolyses of simple *secondary* arenesulfonates and mesylates generally occur with complete inversion of configuration.[19] Thus, we were interested in examining the stereochemical outcome of the solvolysis of tertiary **4**OMs in a solvent with relatively high nucleophilicity. Because of difficulties in relating the direction of optical rotation and the absolute configuration of an ether as a product, we chose hydrolysis in 80% aqueous acetone.

(–)-**4**OMs (ee 76.6 ± 0.4%), which was prepared from (+)-**4**OH (ee 76.6 ± 0.4%) and methanesulfonyl chloride in Et_3N/CH_2Cl_2[20] with complete retention of configuration, was solvolyzed in 80% acetone buffered with 2,6-lutidine for 10 half-lives at 75 °C ($k = 1.08 \times 10^{-4}$ s^{-1}). The product was composed of 18% **4**OH, 6% **7**, and 76% **8**. Direct analyses of the mixture on a Daicel Chiralpak AS column showed that the formed **4**OH



Scheme 2.



Scheme 3.

Table 2. Effects of Added Sodium Azide on the Rates of Solvolysis of **1**OTs and **4**OMs in 50% Ethanol at 25.0 °C[a)]

Compound	NaN_3/mol dm^{-3}	$10^5 \times k$/s^{-1} [b)]
1OTs[c)]	0.00	37.2
	0.02	56.0
	0.04	89.3
4OMs[d)]	0.00	1.74
	0.02	7.3
	0.04	16

a) The reaction was conducted in the presence of 0.025 mol dm^{-3} 2,6-lutidine. b) Titrimetrically determined. c) $[\mathbf{1}OTs]_0$ = 0.005 mol dm^{-3}. d) $[\mathbf{4}OMs]_0$ = 0.01 mol dm^{-3}.

contained (–)-**4**OH with ee of 76.6 ± 0.4%. Consequently, the complete inversion of configuration was demonstrated.

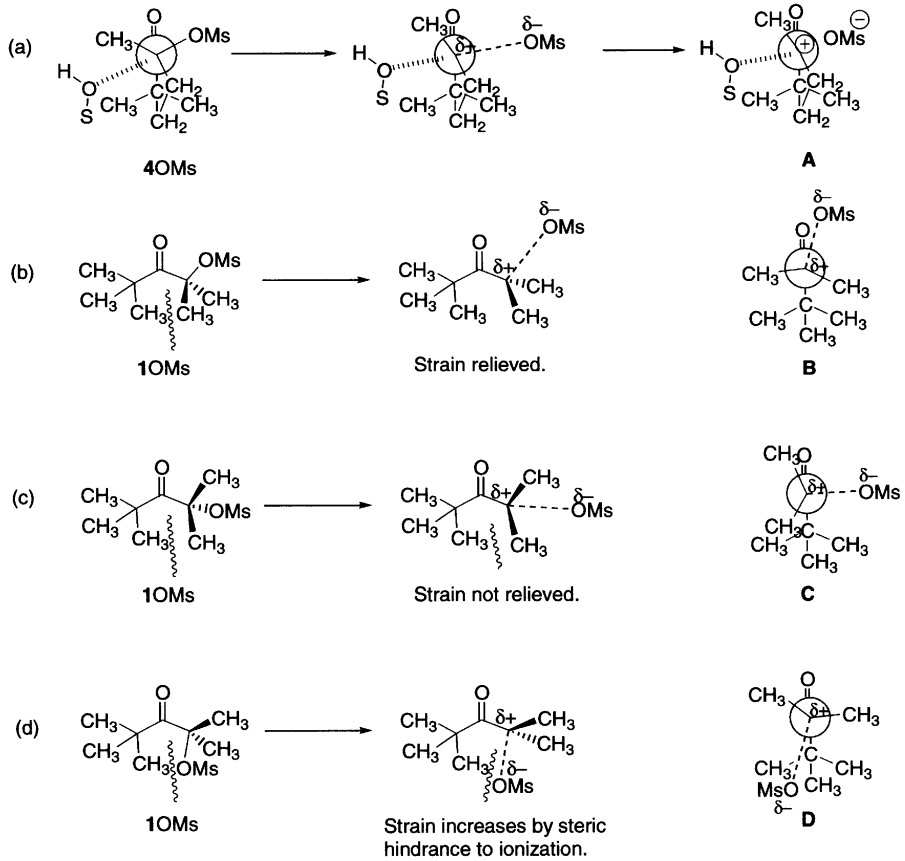
Mechanistic Considerations. The rate of ethanolysis of **1**OMs is 4.4 times slower than acetolysis, in accord with the order of Y_{OTs} values[13] (EtOH –1.75; AcOH –0.61).[4b] On the other hand, the rate of ethanolysis of **4**OMs is 5 times faster than that of acetolysis. Therefore, the ethanolysis of **4**OMs is accelerated about 20 times as much as the rate expected from acetolysis. If the substitution product were formed via a competing S_N2 pathway from **4**OMs, it would be difficult to rationalize the much faster rate in ethanol than in acetic acid, since the substitution process is too minor to control the rate. The percentages of substitution in ethanolysis and acetolysis are not much different from each other at 33% and 9%, respectively. Clearly, the marked acceleration of ethanolysis of **4**OMs does not stem from possible involvement of a competing S_N2 process. It would be reasonable to postulate that **4**OMs ionizes with appreciable NSP to give a tight ion pair **A** in Scheme 4 (a), which then gives olefins and a substitution product with complete inversion of configuration. Such a process may be categorized as the "S_N2(intermediate)" mechanism[21] that was proposed by Bentley, Schleyer et al.

The results of solvent effects, azide probe, and stereochemical outcome (for **4**OMs) give an important insight into the difference in the characteristics of the solvolytic behavior between **1**OMs and **4**OMs. The GW relationship for **4**OMs indicates that 2-oxo substrates are intrinsically susceptible to NSP. However, **1**OMs and **1**OTs are very insensitive to NSP. A plausible explanation involves the postulation of the transition state **B** in Scheme 4 (b) in which the mesylate nucleofuge leaves along the C=O axis in such a manner that the back-strain (B-strain)[22,23] between the *t*-butyl and the two methyl groups on C(1) is efficiently relieved. Investigation of molecular models indicates that the rear side of the C(1) position of the transition state of **1**OMs is effectively blocked from NSP, whereas **4**OMs is susceptible to coordination by solvent from the rear side.

The transition states having conformations **C** or **D** appear to be difficult to attain, since B-strain cannot be removed. In particular, the process (d) is energetically unfavorable because of steric hindrance to ionization.[23] The practical absence of NSP in **1**OMs suggests that the processes (c) and (d) would not be the case, since **C** and **D** may well be subject to NSP from the rear side.

These considerations lead to an important suggestion that *the developing cationic p orbital in the transition state **B** from **1**OMs cannot overlap well with the carbonyl π cloud, whereas it is possible in the transition state **A** from **4**OMs*. In other words, **1**OMs may not be a good model to examine the carbonyl π conjugation in α-carbonyl carbenium ions and that **4**OMs would be a more suitable system.

Origin of the Fast Solvolysis Rate of 1OMs. Previously, we showed that the solvolysis rate ratio between a 2-oxo bridgehead compound and the corresponding parent one [k(X = O)/k(X = H_2)] is essentially constant, being $10^{-8.2}$–$10^{-8.7}$ irre-



Scheme 4.

spective of the ring flexibility of the system (Scheme 5).[6] This was taken to indicate that the π conjugative stabilization of an incipient carbocation is unimportant at least in tertiary systems. In the case of 2-methylidene systems where allylic conjugation is available, the rate ratio [k(X = CH_2)/k(X = H_2)] increases from $10^{-3.9}$ in the rigid system to $10^{0.9}$ in the flexible bicyclo[3.3.1]nonyl system (Scheme 5).[24]

Then, why does **1**OMs solvolyze 10^4–10^5 times faster in 97% HFIP than expected from the rate of **2**OMs on the inductive basis? Previously, we concluded that a partial factor of 10^2–10^3 could be ascribed to the relief of B-strain involved in **1**OMs and the rest to geminal group interaction[25] between the leaving group and the acyl substituent.[6c] We also estimated that **1**OMs/**9**OMs rate ratio is $10^{-7.9}$ in ethanol and $10^{-8.4}$ in acetic acid (Chart 3). These values are comparable to the rate ratios for the bridgehead systems, where the carbonyl π conjugative effect could not be detected (Scheme 5).

Since **4**OMs is geometrically favorable to attain carbonyl π conjugation in the transition state of ionization (Scheme 4, **A**), the rate ratio **4**OMs/**10**OMs is expected to be greater than 10^{-8} –10^{-9} if the rate acceleration is fast enough to be detected experimentally. Unfortunately, **10**OMs is too unstable to prepare: therefore, its rate has to be estimated from that of the chloride, as in the case of **9**OMs. From the rate constant of **10**Cl in TFE at 25 °C (0.0255 s^{-1})[26] and the mesylate/chloride rate ratio in TFE for 1-adamantyl system[27,28] [0.328/(5.41 × 10^{-6}) = 6.1 × 10^4], the **4**OMs/**10**OMs rate ratio is calculated to be $10^{-9.6}$. Similarly, the **4**OMs/**10**OMs acetolysis rate ratio is evaluated to be $10^{-8.9}$.[29] Again, we are unable to obtain any supporting evidence for rate acceleration of **4**OMs in relatively low nucleophilicity solvents. Although the above estimations involve long extrapolations and assumptions, the solvolysis rate ratios between α-carbonyl and parent substrates, such as **1**OMs/**9**OMs, **4**OMs/**10**OMs, and rate ratios in Scheme 5, appear to lie at around 10^{-8}–10^{-9} irrespective of the molecular geometries permitting or restricting the carbonyl π conjugation.

Conclusions

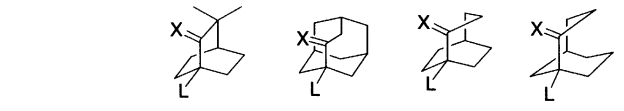
(1) The previous conclusion by Creary of the limiting S_N1 behavior of 1,1,3,3-tetramethyl-2-oxobutyl mesylate (**1**OMs) in the Grunwald- Winstein (GW) relationship has been confirmed by using the corresponding tosylate **1**OTs. In contrast, 1,3,3-trimethyl-2-oxocyclopentyl mesylate (**4**OMs) shows a markedly dispersed GW relationship against Y_{OTs}: however, a very good correlation holds with a extended GW equation ($lN_T + mY_{OTs}$). Therefore, **1**OMs and **1**OTs solvolyze without significant nucleophilic solvent participation (NSP), whereas **4**OMs is subject to marked NSP.

(2) The solvolysis of **4**OMs is markedly accelerated by added sodium azide, whereas that of **1**OTs is much less insensitive to azide. The results are in accord with the conclusion obtained from the GW relationship.

(3) Solvolysis of **4**OMs in 80% acetone affords a large amount of unrearranged olefins and a small amount of the corresponding alcohol **4**OH whose configuration is completely inverted. Consequently, the solvolysis of **4**OMs would be categorized to S_N2(intermediate), whereas that of **1**OMs is limiting S_N1.

(4) The above results suggest that the nucleofuge of **1**OMs or **1**OTs leaves along the C=O axis in such a manner that the back-strain (B-strain) in the ground state is efficiently relieved in the transition state and that the overlap between the developing cationic p orbital and the carbonyl π cloud is very unfavorable.

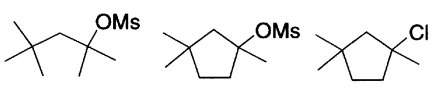
(5) The rate ratios between **4**OMs and the corresponding parent mesylate **10**OMs in TFE and AcOH are estimated to be $10^{-9.6}$ and $10^{-8.9}$, respectively, which are comparable to the corresponding rate ratios for **1**OMs/**9**OMs that are estimated to be $10^{-7.9}$ in ethanol and $10^{-8.4}$ in acetic acid. These results again support our previous conclusion that the carbonyl π conjugation is unimportant at least in tertiary carbocations.



k(X=O)/k(X=H_2)[a]	$10^{-8.4}$	$10^{-8.7}$	$10^{-8.3}$	$10^{-8.2}$
k(X=CH_2)/k(X=H_2)[a]	$10^{-3.9}$ [b]	$10^{-1.1}$	$10^{-0.8}$	$10^{0.9}$

[a] In ethanol or 80% ethanol at 25 °C. [b] For the system without methyls.

Scheme 5.



9OMs **10**OMs **10**Cl

Chart 3.

Experimental

Melting points and boiling points are uncorrected. ^{1}H NMR spectra were recorded at 90, 270, or 400 MHz. ^{13}C NMR spectra were recorded at 22.5, 67.5, 75.5, or 100 MHz. GLC analyses were conducted on a PEG 20M column (3 mm × 2 m) or a PEG 20M capillary column (0.22 mm × 25 m). Solvolysis solvents were purified by previously described methods.[27] Anhydrous solvents used for synthesis were purified by the standard procedures. 2,6-Lutidine was distilled over CaH_2. Other commercially available reagents were of a reagent-grade quality and were used as received. Medium pressure liquid chromatography (MPLC) was conducted on Merck silica gel 60 (230–400 mesh).

1,1,3,3-Tetramethyl-2-oxobutyl Tosylate (1OTs). 2-Hydroxy-2,4,4-trimethyl-3-pentanone[4b] (144 mg, 0.998 mmol) in THF (2.3 ml) was treated with 1.6 mol dm^{-3} n-BuLi in hexane (0.63 ml, 1.0 mmol) at –30 °C. To this was added a solution of p-toluenesulfonyl chloride (200 mg, 1.05 mmol) in THF (3.7 ml). The mixture was allowed to warm to room temperature. After 1 h the solvent was evaporated and the residual white oil was extracted with ether and treated with MPLC (SiO_2, hexane–ether) to afford **1**OTs as white crystals (165 mg) in 55% yield: Mp 56.0–57.0 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.20 (9H, s), 1.77 (6H, s), 2.45 (3H, s), 7.35 (2H, d, J = 8.4 Hz), and 7.83 (2H, d, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 21.5 (CH_3), 26.4 (CH_3), 26.8 (CH_3), 44.9 (C), 95.4 (C), 127.2 (CH), 129.7 (CH), 136.0 (C), 144.5 (C), and 212.7 (C). Found: C, 60.18; H. 7.27%. Calcd for $C_{15}H_{22}O_4S$: C, 60.38; H, 7.43%.

2-Hydroxy-2,5,5-trimethylcyclopentanone (4OH). To a solution of 2,5,5-trimethyl-1-(trimethylsiloxy)cyclopentene (**5**) (592 mg, 2.98 mmol) in CH_2Cl_2 (3 ml) was added *m*-chloroperbenzoic acid (MCPBA) (718 mg, 80% pure, 3.33 mmol) in CH_2Cl_2 (3 ml) over 15 min at –19––13 °C. After 4 h stirring, the reaction mixture was diluted with ethyl ether and washed with 10% NaOH and 10% NaCl, and then dried ($MgSO_4$). Evaporation of solvent afforded a liquid (713 mg), which was treated with K_2CO_3 (837 mg, 6.06 mmol) in methanol (6 ml) for 1 h in an ice bath. Most of the methanol was evaporated, the residue was dissolved in diethyl ether, and the solution was washed with 10% NaCl and dried ($MgSO_4$). Evaporation of solvent and purification with a SiO_2 open column (hexane–ether) afforded **4**OH (180 mg) in 45% yield: Bp 84 °C/13 mmHg (1 mmHg = 133.322 Pa); ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.09 (3H, s), 1.11 (3H, s), 1.27 (3H, s), 1.6–2.2 (4H, m), and 3.4 (1H, s); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 23.5 (CH_3), 24.9 ($2CH_3$), 33.5 (CH_2) , 33.9 (CH_2), 43.1 (C), 76.9 (C), and 223.9 (C). Found: C, 67.18; H. 9.99%. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92%.

1,3,3-Trimethyl-2-oxocyclopentyl Mesylate (4OMs). To a solution of **4**OH (496 mg, 3.49 mmol) and triethylamine (0.73 ml, 5.2 mmol) in CH_2Cl_2 (17 ml) was added MsCl (0.30 ml, 3.8 mmol) over 6 min at –19––9 °C. After 1 h stirring in an ice-salt bath, the reaction mixture was diluted with CH_2Cl_2, washed with cold $NaHCO_3$ and 10% NaCl, and dried ($MgSO_4$). Evaporation of solvent afforded a yellow liquid (739 mg), which was purified by MPLC (SiO_2, hexane–ether) to give **4**OMs: Mp 28.1–29.1 °C; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.13 (3H, s), 1.20 (3H, s), 1.50 (3H, s), 1.6–2.9 (4H, m), 3.14 (3H, s); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 22.7 (CH_3), 25.6 (CH_3), 26.0 (CH_3), 33.2 (CH_2), 33.6 (CH_2), 41.0 (CH_3), 43.1 (C), 90.6 (C), and 217.0 (C). Found: C, 48.94; H. 7.58%. Calcd for $C_9H_{16}O_4S$: C, 49.07; H, 7.32%.

Product Studies. (1) Ethanolysis. A solution of 0.040 mol dm^{-3} **4**OMs (147 mg, 0.665 mmol) in 0.050 mol dm^{-3} 2,6-lutidine in absolute ethanol (16.6 ml) was heated in a stoppered flask at 75 °C for 1105 min (10 half-lives). The reaction mixture was directly subjected to GLC analysis to give the product distribution shown in Scheme 2. No appreciable change in product distribution was observed at 20 half-lives. Most of the ethanol was evaporated, the residue was dissolved in diethyl ether, and the ether solution washed with water, 5% HCl, and saturated Na_2CO_3, and dried ($MgSO_4$). The solvent was evaporated, and the residue was subjected to MPLC (SiO_2, hexane–ether) to give 2-ethoxy-2,5,5-trimethylcyclopentanone (**4**OEt) (9.9 mg) and 2,2-dimethyl-5-methylenecyclopentanone (**7**) (1.3 mg). **4**OEt: liq; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.05 (3H, s), 1.10 (3H, s), 1.14 (3H, t, J = 6.8 Hz), 1.25 (3H, s), 1.6–2.1 (4H, m), and 3.39 (2H, q, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8 (CH_3), 19.4 (CH_3), 25.2 (CH_3), 25.4 (CH_3), 32.9 (CH_2), 33.8 (CH_2), 43.6 (C), 58.9 (CH_2), 81.1 (C), and 220.4 (C). **7** was obtained as a mixture with **8** and **4**OEt and the assignment of ^{1}H NMR signals was successful only for the methylidene signals at δ 5.36 and 6.02 both as a broad triplet. The ^{13}C NMR ($CDCl_3$, 67.5 MHz) signals for **7** were assigned by comparing the chart for a product mixture with authentic charts: δ 23.5 (CH_3), 25.5 (CH_2), 35.0 (CH_2), 45.0 (C), 117.9 (CH_2), 143.9 (C), and 210.3 (C). **8** was identified by NMR and GLC from comparison of the data with those of authentic samples below.

(2) Acetolysis. A solution of 0.040 mol dm^{-3} **4**OMs (400 mg, 1.82 mmol) in 0.050 mol dm^{-3} NaOAc in AcOH [containing 1% (by wt.) Ac_2O] (45.4 ml) was heated in a stoppered flask at 75 °C for 2720 min (10 half-lives). The reaction mixture was cooled and poured into ice-water (100 g) and extracted with ether. The organic layer was washed with cold saturated $NaHCO_3$ (50 ml × 7) and dried ($MgSO_4$). GLC analysis of the ether extract showed the product distribution shown in Scheme 2. The ether was evaporated and the residue was subjected to ^{1}H and ^{13}C NMR measurements. Comparisons of the spectra with those of authentic **4**OAc and **8** and with those of **7** obtained in ethanolysis permitted identification of these products. The washings were combined and acidified with 10% HCl and extracted with ether. This ether layer was washed with water, dried, and analyzed by GLC, but no appreciable peaks were detected. Also, no appreciable change in product distribution was observed at 20 half-lives.

Authentic 1,3,3-Trimethyl-2-oxocyclopentyl Acetate (4OAc). A solution of **4**OH (228 mg, 1.60 mmol) in THF (8.0 ml) was treated with 1.6 mol dm^{-3} *n*-BuLi in hexane (1.00 ml, 1.60 mmol) at –30 °C. To this was added acetyl chloride (0.114 ml, 1.60 mmol) and the mixture was allowed to warm to room temperature. After 40 min the solvent was mixed with ether, white precipitates were filtered, and the ether was evaporated. The residual white oil was treated with MPLC (hexane–ether) to afford **4**OAc as white crystals (64 mg) in 22% yield: Mp 29.0–29.5 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.11 (3H, s), 1.25 (3H, s), 1.36 (3H, s), 1.6–2.5 (4H, m), and 2.04 (3H, s); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 20.9 (CH_3), 22.6 (CH_3), 26.3 (CH_3), 26.4 (CH_3), 31.1 (CH_2), 34.0 (CH_2), 43.5 (C), 82.7 (C), 169.3 (C), 218.8 (C).

Authentic 2,5,5-Trimethyl-2-cyclopentenone (8). A mixture of **4**OMs (221 mg, 1.00 mmol) and DBU (1.50 mg, 10.0 mmol) was heated at 150 °C under N_2 for 2 h. The reaction mixture was diluted with ether and washed with cold 10% HCl and saturated NaCl, and dried ($MgSO_4$). Evaporation of the solvent gave a pale yellow oil (71 mg) in 57% yield: ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.10 (6H, s), 1.78 (3H, m), 2.42 (2H, m), and 7.22 (1H, m); ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ 10.3 (CH_3), 25.0 (CH_3), 42.7 (C), 43.4 (CH_2), 139.0 (C), 155.0 (CH), 214.3 (C).

Determination of Optical Rotation and Enantiomeric Excess. Optical rotations were determined at 589 nm by using a 1 dm cell on a JASCO DIP-1000 digital polarimeter. Enantiomeric excess percentage for optically active **4**OH used as the precursor of optically active **4**OMs and that for the solvolysis product **4**OH were determined at Kyoto University by HPLC equipped with a Daicel Chiralpak AS column (0.46 cmϕ × 25 cm). The signal intensities were recorded at 290 nm. Blank measurements on racemic **4**OH showed that the experimental error for ee was smaller than 0.02%.

Optical Resolution of 2-Hydroxy-2,5,5-trimethylcyclopentanone (4OH). A mixture of **6a**[10] (3.0 g, 3.2 mmol) and (±)-**4**OH (1.0 g, 7.0 mmol) in hexane (3 ml) was kept at room temperature for a week. A 1:1 inclusion complex of **6a** and (–)-**4**OH was formed as colorless prisms (3.4 g, no sharp m.p.), which upon heating in vacuo gave (–)-**4**OH (0.35 g, 70% yield, $[\alpha]_D$ –5.1°(*c* 0.51, MeOH)) of 49% ee as a distillate. Upon distillation of the filtrate left after separation of the inclusion complex, (+)-**4**OH (0.50 g, 100% yield, $[\alpha]_D$ +3.1°(*c* 0.52, MeOH)) of 30% ee was obtained. When the complexation of (–)-**4**OH (0.35 g) of 49% ee with **6a** (2.0 g, 2.2 mmol) was repeated again, (–)-**4**OH (0.18 g, 36% yield, $[\alpha]_D$ –7.6°(*c* 0.27, MeOH)) of 73% ee was obtained. The same treatment of the (+)-**4**OH (0.50 g) of 30% ee with **6b**[10] (3.0 g, 3.2 mmol) followed by distillation as above gave (+)-**4**OH (0.14 g, 28% yield, $[\alpha]_D$ +8.3°(*c* 0.24, MeOH)) of 80% ee. The optical purity was determined at Ehime University by ^{1}H NMR analyses of (–)- and (+)-**4**OH in $CDCl_3$ by using the chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-*d*-camphorato]europium(III), Eu(hfc)$_3$ (Aldrich).

Optically Active 1,3,3-Trimethyl-2-oxocyclopentyl Mesylate [(–)-4OMs]. (+)-**4**OH with $[\alpha]_D^{25}$ +9.0 ± 0.2°(*c* 0.0090, MeOH) or +40.6 ± 0.1°(*c* 0.0044, Et_2O) , whose ee was determined as 76.6 ± 0.4% with a Daicel Chiralpak AS column, was converted to the mesylate in the manner described for racemic **4**OMs, which showed $[\alpha]_D^{28}$ –16.4 ± 0.3°(*c* 0.0073, Et_2O).

Solvolysis of Optically Active 1,3,3-Trimethyl-2-oxocyclopentyl Mesylate (4OMs). A solution of (+)-**4**OMs (ee 76.6 ± 0.4%) (29.1 mg, 0.132 mmol) in 80% acetone (3.30 ml) containing 0.050 mol dm^{-3} 2,6-lutidine was heated in a sealed tube at 75.0 °C for 1070 min (10 half-lives). Most of the acetone was distilled off at atmospheric pressure, and the residue was diluted with diethyl ether, washed with 10% NaCl solution, and dried ($MgSO_4$). GLC analyses showed the distribution of **4**OH, **7**, and **8** as 18%, 76%, and 6%, respectively. Analyses on a Daicel Chiralpak AS column showed the formation of (–)-**4**OH with ee 76.6 ± 0.4%.

Kinetic Studies. The preparation of solvents and titrimetric kinetic studies followed the procedures described previously.[27] The reactions in 97% HFIP and TFA were conducted in a sealed NMR tube. A solution (ca. 0.4 ml) containing 0.16 mol dm^{-3} of **4**OMs and 0.20 mol dm^{-3} of a buffer (2,6-lutidine for 97% HFIP and $NaOCOCF_3$ for TFA) and a capillary containing acetone-d_6 were placed in a 5 mmϕ NMR tube. The tube was sealed and immersed in a 25.0 °C bath. At intervals, the ^{1}H NMR spectra were measured and the conversion was determined by comparing the methyl signal of the methanesulfonyl group and that of the liberated methanesulfonate ion. The former signal appeared at δ 3.1 in both solvents, but the latter one was observed at δ 2.85 in 97% HFIP containing 2,6-lutidine and at δ 2.96 in TFA buffered with $NaOCOCF_3$. The observed data followed a good first-order kinetics within an experimental error ± 2%.

This work was supported in part by the Ministry of Education, Science, Sports and Culture through a Grant-in-Aid for Scientific Research (10440188).

References

1 P. G. Gassman and T. T. Tidwell, *Acc. Chem. Res.*, **16**, 279 (1983). b) T. T. Tidwell, *Angew. Chem., Int. Ed. Engl.*, **23**, 20 (1984). c) X. Creary, *Acc. Chem. Res.*, **18**, 3 (1985). d) X. Creary, A. C. Hopkinson, and E. Lee-Ruff, "Advances in Carbocation Chemistry," ed by X. Creary, JAI Press, (1989), Vol. 1, pp. 45–92. e) X. Creary, *Chem. Rev.*, **91**, 1625 (1991).

2 K. Takeuchi, T. Kitagawa, and K. Okamoto, *J. Chem. Soc., Chem. Commun.*, **1983**, 7.

3 J. March, "Advanced Organic Chemistry," 4th ed, John Wiley & Sons, New York (1992), p. 343.

4 a) X. Creary and C. C. Geiger, *J. Am. Chem. Soc.*, **104**, 4151 (1982). b) X. Creary, *J. Am. Chem. Soc.*, **106**, 5568 (1984).

5 a) R. N. McDonald and T. E. Tabor, *J. Am. Chem. Soc.*, **89**, 6573 (1967). b) R. N. Mcdonald and R. N. Steppel, *J. Am. Chem. Soc.*, **92**, 5664 (1970).

6 a) K. Takeuchi and Y. Ohga, *Bull. Chem. Soc. Jpn.*, **69**, 833 (1996). b) K. Takeuchi, "Advances in Strained and Interesting Organic Molecules, Supplement 1," ed by K. K. Laali, JAI Press, (1999), Vol. 1, pp. 123–145. c) K. Takeuchi, Y. Ohga, M. Yoshida, K. Ikai, T. Shibata, M. Kato, and A. Tsugeno, *J. Org. Chem.*, **62**, 5696 (1997).

7 K. Takeuchi, Y. Ohga, and T. Ushino, *Chem. Lett.*, **1996**, 763.

8 C. Lion and J.-E. Dubois, *Bull. Soc. Chim. II*, **1982**, 375.

9 A. Hassner, R. H. Reuss, and H. W. Pinnick, *J. Org. Chem.*, **40**, 3427 (1975).

10 K. Tanaka, S. Honke, Z. Lipkowska, and F. Toda, *Eur. J. Org. Chem.*, in press.

11 a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948). b) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, **14**, 1 (1977). c) T. W. Bentley and G. Llewellyn, *Prog. Phys. Org. Chem.*, **17**, 121 (1990).

12 F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).

13 a) M. Fujio, T. Suzuki, M. Goto, Y. Tsuji, K. Yatsugi, Y. Saeki, S.-H. Kim, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **67**, 2233 (1994). b) M. Fujio, Y. Saeki, K. Nakamoto, K. Yatsugi, N. Goto, S.-H. Kim, Y. Tsuji, Z. Rappoport, and Y. Tsuno, *Bull Chem. Soc. Jpn.*, **68**, 2603 (1995).

14 D. N. Kevill, "Advances in Quantitative Structure-Property Relationships," ed by M. Charton, JAI Press, (1996), Vol. 1, pp. 81–115.

15 D. N. Kevill and M. H. Abduljaber, *Croatica Chemica Acta*, **65**, 539 (1992).

16 D. J. Raber, J. M. Harris, and P. v. R. Schleyer, "Ions and Ion Pairs in Organic Reactions," ed by M. Szwarc, John Wiley & Sons, New York (1974), Vol. 2, pp. 247–374.

17 E. D. Hughes, C. K. Ingold, R. J. L. Martin, and D. F. Meigh, *Nature*, **166**, 679 (1950).

18 W. v. E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 4733 (1953).

19 P. E. Dietze, "Advances in Carbocation Chemistry," ed by J. M. Coxon, JAI Press, (1995), Vol. 2, pp. 179–205.

20 R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).

21 T. W. Bentley, C. T. Bowen, D. H. Morten, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 5466 (1981).

22 H. C. Brown and R. S. Fletcher, *J. Am. Chem. Soc.*, **71**, 1845 (1949).

23 H. C. Brown, "The Nonclassical Ion Problem," with comments by P. v. R. Schleyer, Plenum Press, New York (1977).

24 K. Takeuchi, T. Kitagawa, Y. Ohga, M. Yoshida, F. Akiyama, and A. Tsugeno, *J. Org. Chem.*, **57**, 280 (1992).

25 a) W. Kirmse and B. Goer, *J. Am. Chem. Soc.*, **112**, 4556 (1990). b) Y.-D. Wu, W. Kirmse, and K. N. Houk, *J. Am. Chem. Soc.*, **112**, 4557 (1990). c) Y. Apeloig, R. Biton, and A. Abu-Freih, *J. Am. Chem. Soc.*, **115**, 2522 (1993). d) J. P. Richard, T. L. Amyes, and D. J. Rice, *J. Am. Chem. Soc.*, **115**, 2523 (1993).

26 K. Takeuchi, Y. Ohga, T. Ushino, and M. Takasuka, *J. Phys. Org. Chem.*, **10**, 717 (1997).

27 K. Takeuchi, K. Ikai, T. Shibata, and A. Tsugeno, *J. Org. Chem.*, **53**, 2852 (1988).

28 T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, **104**, 5741 (1982).

29 The rate constant for **10**OMs in acetic acid at 25 °C was estimated to be 70 s^{-1} by multiplying the rate constant of **10**Cl (2.25×10^{-5} s^{-1})[26] by 1-AdOMs/1-AdCl rate ratio (3.1×10^6) obtained from rate data in Refs. 11c and 28.