the relations utilized for the determination of the rate constants (eq 16 in cases where $[PhSH]_0 = [CA]_0$ and eq 17 when $[PhSH]_0 > [CA]_0$; $[B]_0$, $[CA]_0$, and $[PhSH]_0$ are the initial base, cycloalkenone and thiol concentrations). About 10 data points were used for each run, lying between about 10% and 80% completion of the reaction. Correlation coefficients of the lines (least squares) were generally >0.98. Estimated errors in the thermodynamic parameters are given in the tables.

Acknowledgment. The authors are indebted to Mr. Drê Oudman for synthetic assistance.

Kinetic Isotope Effect Study on Methyl Participation in Solvolysis of Neopentyl-Type Arenesulfonates[1,2]

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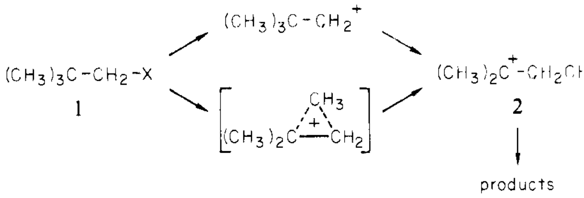
Abstract: Carbon-14 and deuterium kinetic isotope effects at various positions have been measured in the solvolysis of neopentyl arenesulfonates. In the acetolysis of neopentyl nosylate (**6**) at 100 °C, carbon isotope effects (k^{12}/k^{14}) are 1.073 at α, 1.019 at β, and 1.046 at γ. Deuterium effects (k_H/k_D) are 1.187 at α (D_2) and 1.016 at γ (D_9). In the trifluoroacetolysis of neopentyl brosylate (**7**) at 65 °C, k^{12}/k^{14} are 1.073 at α, 1.023 at β, and 1.026 at γ and k_H/k_D are 1.190 at α (D_2) and 1.012 at γ (D_9). These positive isotope effects at all the positions are compatible with the concerted nature of the solvolytic rearrangement. Kinetic isotope effects of only a migrating methyl group have been measured in the solvolysis of 2-methyl-2-adamantanemethyl brosylate (**9**), a model system of neopentyl solvolysis; k^{12}/k^{14} and k_H/k_D (D_3) are 1.037 and 1.123 in the acetolysis at 100 °C, 1.037 and 1.135 in the trifluoroacetolysis at 25 °C, and 1.035 and 1.12 in the trifluoroacetolysis at 45 °C, respectively. Combination of the results for **6** and **7** with those for **9** revealed that the carbon-14 isotope effects at γ primarily arise from the migrating methyl group and that the negligibly small D_9 effect at γ is brought about by cancellation of a normal effect of the migrating methyl group and inverse effects of the two nonmigrating methyl groups. The nature of σ participation as a composite of two formally conflicting modes, namely, hyperconjugation and bridging, is discussed on the basis of these results.

Neighboring group participation is usually classified into n-, π-, and σ-types depending on the nature of electrons used to interact with the reaction center in the same molecule.[3] A nonbonding pair of electrons is most effective in stabilizing a developing charge in nucleophilic substitution. Most of the phenomena called intramolecular catalysis belong to this category. π-Electrons of an aromatic ring or a double bond are moderately nucleophilic; their participation to an electron-deficient center has been well established.[4] σ-Electrons of a carbon–carbon or a carbon–hydrogen single bond are the least nucleophilic; participation by them is the most subtle phenomenon. The subtleness of the phenomenon is easily understandable when one regards that σ participation in the transition state corresponds to the so-called "nonclassical ion" in the intermediate. As the nonclassical ion problem has been the matter of long debate, so has the σ participation been.

Neopentyl solvolysis is the simplest among the problem systems. Neopentyl derivatives **1**, having a fully substituted carbon atom next to the reaction center, usually give rise to substitution and elimination products derived from the rearranged *tert*-amyl cation **2** under solvolytic conditions (eq 1). The timing of this rearrangement, concerted or stepwise, has been the subject of controversy.



(1)

Rate enhancement associated with the rearrangement is, if anything, too small in the usual solvents to establish methyl participation in the rate-determining transition state. Kinetic evidence for and against methyl participation has been accumulated.[5-11] Stereochemical studies favor participation,[12] and even a bridged intermediate has been claimed.[13] However, an alternative explanation by means of a tight ion pair may not be ruled out at least in solvolysis.

Kinetic isotope effects are known to be the most effective tool in studying such a subtle phenomenon. However, even this tool has so far been ineffective. Negligible intermolecular isotope effects in the hydrolysis[14] and the trifluoroacetolysis[15] of neopentyl-γ-d_9 derivatives and large intramolecular migrating ratios in the trifluoroacetolysis ($k_{CH_3}{}^{CD_3}/k_{CD_3}{}^{CH_3}$ = 1.22–1.31) led Schubert and Henson to conclude that the rearrangement occurs

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(1) Neighboring group participation in solvolysis. 12. For Part 11, see: Yukawa, Y.; Kim, S.-G.; Yamataka, H.; Matsuda, K.; Ando, T. *J. Am. Chem. Soc.*, submitted for publication.

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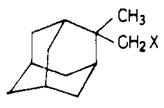
after the ionization step.[15] However, it was pointed out by Raber, Harris, and Schleyer that the negligible intermolecular isotope effects could not become unambiguous evidence in support of the stepwise mechanism because they could be brought about by cancellation of normal effects of a migrating methyl group and inverse effects of nonmigrating methyl groups.[16] Actually, inverse kinetic isotope effects by nonmigrating methyl groups were observed in the hydrolysis of isobutyl-γ-d_6 derivatives (k_H/k_D = 0.96–0.97 per D_2).[14] In the present investigation, effects of nonmigrating methyl groups have also been measured in the solvolysis of neophyl-γ-d_6 brosylate (**3**-γ-d_6) (**3** = Ph–C-$(CH_3)_2CH_2OSO_2C_6H_4Br$-*p*).

A more direct approach to elucidate the possibility of incidental cancellation must be to measure the isotope effect of only a migrating methyl group by employing an appropriate neopentyl derivative in which one particular methyl group is allowed to migrate and the other two are inhibited from migration. The 2-methyl-2-adamantanemethyl system (**4**) looks like a good candidate for this purpose.



4

Because of the uniquely strain-free structure of the adamantane skeleton in contrast to the strained one of the homoadamantane moiety,[17] the rearrangement of the ring carbon is much less favorable and only the methyl group is expected to migrate. Kinetic isotope effect study of **4** must clarify the ambiguity of the cancellation of the kinetic isotope effects.

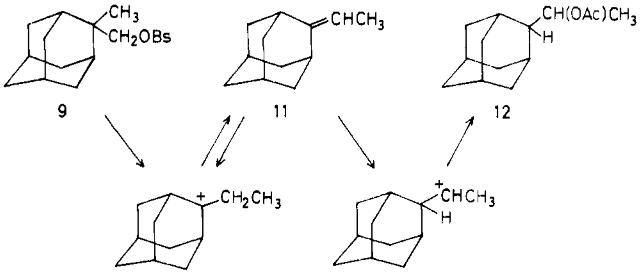
In earlier papers from our laboratory dealing with the solvolytic mechanisms of 2-phenylethyl and related derivatives, we demonstrated the usefulness of carbon-14 kinetic isotope effects for detection of phenyl participation.[1,18] In the present paper we report the results of our study on the solvolytic mechanism of neopentyl derivatives by utilizing the kinetic isotope effects, especially of carbon-14. Combining the observed isotope effects for **1** and **4** and taking advantage of the unique structure of **4**, kinetic isotope effects of γ-methyl groups can be allotted separately to migrating and nonmigrationg ones.[19] By use of these results along with the isotope effects at the α- and β-positions, a possible transition-state structure of the neopentyl solvolysis will be presented. The characteristic nature of σ participation by a methyl group in comparison with that of π participation by a phenyl group will be discussed in detail.[1]

Results

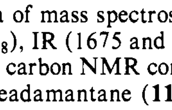
Synthesis of Labeled Compounds. Labeling of neophyl alcohol with two CD_3 groups was carried out by deuteriomethylation of benzyl cyanide with methyl-d_3 iodide in dimethyl sulfoxide.[20] Hydrolysis of the cyanide and reduction of the acid gave neophyl-γ-d_6 alcohol. The *p*-bromobenzenesulfonate (**3**-γ-d_6) was prepared by the standard procedure.[21]

Neopentyl alcohol labeled with carbon-14 at the α-position (**5**-α-^{14}C) was obtained by reduction of pivalic-*1*-^{14}C acid, which was prepared by carbonation of *tert*-butylmagnesium chloride with $^{14}CO_2$ gas.[22] The same series of reactions starting with *tert*-butyl-d_9 chloride gave **5**-γ-d_9. Labeling of the β-position of **5** ($(CH_3)_3C-CH_2OR$: **5**, R = H; **6**, R = $SO_2C_6H_4NO_2$-*p*; **7**, R = $SO_2C_6H_4Br$-*p*) with carbon-14 was carried out by use of sodium acetate-*2*-^{14}C as a starting material. Exhaustive methylation of butyl acetate-*2*-^{14}C by a combination of lithium diisopropylamide–methyl iodide gave butyl pivalate-*2*-^{14}C,[23,24] which was then reduced to neopentyl-*2*-^{14}C alcohol (**5**-β-^{14}C). Methylation of isobutyric acid with lithium diisopropylamide and methyl-^{14}C iodide[24] followed by reduction gave **5**-γ-^{14}C. **5**-α-d_2 was obtained by reduction of pivalic acid with lithium aluminum deuteride. The *p*-nitrobenzenesulfonates (nosylates, **6**) and the *p*-bromobenzenesulfonates (brosylates, **7**) of these neopentyl alcohols were prepared by the standard procedure.[21]

Scheme I



Introduction of a methyl-^{14}C group on an adamantane moiety was carried out by use of methylmagnesium-^{14}C iodide and adamantanone.[25] The Koch–Haaf reaction of thus obtained 2-methyl-2-adamantanol-*methyl*-^{14}C gave 2-methyl-2-adamantanecarboxylic-*methyl*-^{14}C acid, which was then reduced to 2-methyl-2-adamantanemethanol-*methyl*-^{14}C (**8**-γ-^{14}C).[26,27] Methylation of methyl 2-adamantanecarboxylate by use of lithium diisopropylamide and methyl-d_3 iodide[23,24] followed by reduction gave 2-methyl-2-adamantanemethanol-*methyl*-d_3 (**8**-γ-d_3). Reduction of 2-methyl-2-adamantanecarboxylic acid with lithium aluminum deuteride gave **8**-α-d_2. The brosylates (**9**) and the nosylates (**10**) of these alcohols were prepared by the standard method.[21] Deuterium contents of all the deuterated compounds used for isotope effect determination were more than 99% by NMR analysis. Molar radioactivities of carbon-14-labeled arenesulfonates were in the range of 2.7–6.2 mCi mol^{-1}.



8, R = H
9, R = $SO_2C_6H_4Br$-*p*
10, R = $SO_2C_6H_4NO_2$-*p*

Solvolysis of 2-Methyl-2-adamantanemethyl Brosylate (9). Unbuffered acetolysis of **9** at 100 °C for 9 h (8 half-lives, vide infra) gave almost exclusively an olefin (92 ± 2% yield) contaminated with a small amount of an acetate (ca. 2%) according to VPC analysis. Data of mass spectroscopy (M^+ = 162), elemental analysis ($C_{12}H_{18}$), IR (1675 and 820 cm^{-1}, trisubstituted C=C), and proton and carbon NMR confirmed the structure of the olefin as ethylideneadamantane (**11**).[25] After isolation by column chromatography, the structure of the acetate was determined as 1-(2-adamantane)ethyl acetate (**12**) by IR (1735 and

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1240 cm^{-1}) and proton and carbon NMR. The yield of **12** increased to 5% after 21 h at 100 °C, and a control experiment showed that **11** afforded **12** gradually under the reaction conditions. Monitoring of the reaction solution of the nosylate **10** in acetic acid-d_4 at 80 °C by proton NMR showed that **11** monodeuterated at the vinylic position was the sole product; no other product with the original 2-methyl-2-adamantanemethyl moiety nor with the rearranged homoadamantane structure was detected at all. Addition of sodium acetate to the acetolysis solution did not alter the mode of the reaction. These results indicate that the acetolysis of **9** (and **10**) is always accompanied by the rearrangement of the methyl group and becomes a good model of the neopentyl solvolysis as expected. The acetate **12** must be formed from protonation of **11** as a secondary reaction (Scheme I).

VPC analysis of the trifluoroacetolysis solution of **9** showed that a complex mixture was formed and that the pattern of products changed as the reaction proceeded. Detailed analysis of the products was not performed.

Kinetics. Acetolyses of **3**, **6**, and **9** were studied by the titrimetric method. Linearity of the first-order rate plots and reproducibility of the rate constants were excellent for all these compounds.

Trifluoroacetolyses of **3**, **7**, and **9** were followed by the spectrophotometric method, but the accuracy was not excellent. The inaccuracy must arise from the following disadvantages inherent to the kinetic procedures employed: (i) the troublesome nature of trifluoroacetic acid which is difficult to purify in a constant state,[28] (ii) errors during dilution of 1 mL of the reaction solution with ethanol for spectrophotometric analysis, and (iii) the lack of an adequate maximum in the absorption spectra of brosylates for following the reaction. First-order rate plots showed some scatter and correlation coefficients were between 0.9985 and 0.9997. The rate constants determined months apart by different persons using different batches of substrates and trifluoroacetic acid were accompanied by standard deviations of about 3% usually and 7% in the worst case (Table II).

Kinetic Isotope Effects. Deuterium isotope effects were determined from two or three sets of rate constants for deuterated and undeuterated compounds. It was possible to obtain the isotope effect values with considerably lower standard deviations than those expected from the errors inherent to their rate constants even for trifluoroacetolysis by carrying out reactions pairwise and simultaneously; isotope effects were calculated from pairs of runs and then averaged.

Carbon-14 isotope effects were determined according to the procedures described before.[1,29] Measurements of the radioactivities of the recovered esters were carried out two or three times per sample with the accuracy within ±0.3% usually and within ±0.5% in the case of the trifluoroacetolysis of **7**.

Calculation of carbon-14 isotope effects for all cases other than **6**- and **7**-γ-^{14}C was carried out by the linear regression method by means of eq 2, where x is the fraction of reaction calculated

$$\log A_x = \log A_0 - [1 - (k^{14}/k^{12})][\log (1 - x)] \qquad (2)$$

from the rate constant, and A_0 and A_x are the molar radioactivities of the recovered esters at $x = 0$ and $x = x$, respectively.[1] **6**- and **7**-γ-^{14}C have three methyl groups with equal possibility of rearrangement, and only one of them is labeled with carbon-14 at the tracer level of concentrations. If only one of the three methyl groups can have a chance to exhibit an isotope effect and the other two have no effect on the reaction, the isotope effect should be calculated by means of eq 3. The assumption used here means

$$\log A_x = \log A_0 - \tfrac{1}{3}[1 - (k^{14}/k^{12})][\log (1 - x)] \qquad (3)$$

that only the migrating methyl group has a primary carbon-14 isotope effect and that secondary isotope effects by the two nonmigrating methyls are negligible. The validity of the assumption will be discussed (vide infra). The results of kinetic isotope effects are summarized together with rate data in Tables I and II.

Table I. Rate Constants and Kinetic Isotope Effects in Acetolysis

	substrate (temp, °C)^a		
	6 (100.0)	**9** (100.0)	**3** (75.0)^b
$10^5 k_H$, s^{-1}	2.82 ± 0.01^c	17.3 ± 0.1^c	6.99
k_H/k_D at α	1.187 ± 0.001 (D$_2$)^{c,d}	1.190 ± 0.001 (D$_2$)^{c,d}	1.214 (D$_2$)
k^{12}/k^{14} at α	1.073 ± 0.002^e		1.093
k^{12}/k^{14} at β	1.019 ± 0.002^e		1.014
k^{12}/k^{14} at γ	1.046 ± 0.005 (Me)^f	1.037 ± 0.003 (Me)^e	1.023 (Ph-1)
k_H/k_D at γ	1.016 ± 0.006 (D$_9$)^{c,d}	1.123 ± 0.002 (D$_3$)^{c,d}	0.959 ± 0.005 (D$_6$)^{d,g}

^{a} ±0.02 °C. 0.05 M in substrate. ^{b} References 1 and 18c,d. ^{c} Average of two runs. ^{d} Deuterium isotope effects were calculated from pairs of runs and then averaged. Deuterium contents were more than 99%. ^{e} Value from single run. Error was calculated from standard deviation in the slope of eq 2. ^{f} Average of two runs, 1.050 ± 0.003 and 1.041 ± 0.006. Errors of individual runs were calculated from standard deviations in the slopes of eq 3. ^{g} Average of three runs.

Discussion

Solvolysis Rates of 2-Methyl-2-adamantanemethyl Brosylate (9). The rate ratio of **9** to **7** in acetic acid and trifluoroacetic acid can be estimated at about 25 and 40, respectively. Here, a correction factor for the ratio of a nosylate to a brosylate in acetic acid was postulated as 4, and an extrapolated rate constant for **9** in trifluoroacetic acid was compared with the observed value for **7** at 65 °C. On the other hand, McElrath and his co-workers reported that substitution of one of the three methyl groups of **7** to an isopropyl group caused a rate enhancement of 7.1 in acetic acid.[5] If the 2-adamantyl moiety is regarded as two isopropyl groups, the rate enhancement expected for the acetolysis of **9** is $(7.1)^2 = 50$. The slightly lower rate enhancement (ca. 25) actually observed in the acetolysis of **9** is not unreasonable when steric acceleration present in $R(CH_3)_2CCH_2OBs$ and absent in the adamantane derivative is taken into consideration. In trifluoroacetic acid, amplification of the polar effect must compensate for the absence of the steric acceleration. Thus, the acetolysis and trifluoroacetolysis rates of **9** suggest that neither special rate enhancement nor retardation exists in this solvolysis and that this system can become a good model of the neopentyl solvolysis.

Kinetic Isotope Effects. All the kinetic isotope effects measured in both the acetolysis and the trifluoroacetolysis of the neopentyl esters, **6** and **7**, are not unity well beyond the limit of experimental errors. The results clearly indicate that all the atoms examined are changing their bondings (force constants) in the transition state of the reaction. The fact implies that the reaction takes place in a concerted fashion. Then, how are all these atoms changing their bondings? The results of the kinetic isotope effects at the α-, β-, and γ-positions in the neopentyl (**1**) and 2-methyl-2-adamantanemethyl (**4**) systems will hereinafter be discussed separately.

α-Deuterium and Carbon-14 Effects. Secondary deuterium isotope effects at the reaction center have quite often been utilized as an effective tool to determine the mechanism of solvolysis reactions.[1,30,31] Intermediate values about halfway in between the large ones for S$_N$1 and the small ones for S$_N$2 have been reported and discussed thoroughly in the cases of the 2-phenylethyl and related solvolyses with π participation.[1,18d,30b,32,33] The results

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Table II. Rate Constants and Kinetic Isotope Effects in Trifluoroacetolysis

	substrate (temp, °C)[a]			
	7 (65.0)[b]	9 (25.0)[c]	9 (45.0)[c]	3 (0.0)[d]
$10^5 k_H$, s^{-1}	7.74 ± 0.21[e]	3.30 ± 0.09[f]	36.3 ± 2.5[g]	7.62
k_H/k_D at α	1.190 ± 0.010 (D_2)[h,i]	1.228 ± 0.001 (D_2)[h,i]	1.20 ± 0.02 (D_2)[h,i]	1.247 (D_2)
k^{12}/k^{14} at α	1.073 ± 0.002[j]			1.141
k^{12}/k^{14} at β	1.023 ± 0.001[j]			1.014
k^{12}/k^{14} at γ	1.026 ± 0.004 (Me)[k]	1.037 ± 0.002 (Me)[j]	1.035 ± 0.003 (Me)[j]	1.035 (Ph-1)
k_H/k_D at γ	1.012 ± 0.007 (D_9)[i,l]	1.135 ± 0.002 (D_3)[h,i]	1.12 ± 0.02 (D_3)[h,i]	0.916 ± 0.005 (D_6)[i,m]

[a] ±0.02 °C. [b] 0.04 M in substrate and followed at 243 nm. [c] 0.03 M in substrate and followed at 247 nm. [d] References 1 and 18c,d. [e] Average of nine runs years apart. [f] Average of four runs. [g] Average of six runs. [h] Average of two runs. [i] Deuterium isotope effects were calculated from pairs of runs and then averaged. Deuterium contents were more than 99%. [j] Value from single run. Error was calculated from standard deviation in the slope of eq 2. [k] Average of two runs, 1.022 ± 0.013 and 1.030 ± 0.010. Errors of individual runs were calculated from standard deviations in the slopes of eq 3. [l] Average of three runs. 0.03 M in substrate and followed at 247 nm. [m] Average of three runs. 0.02 M in substrate and followed at 249 nm.

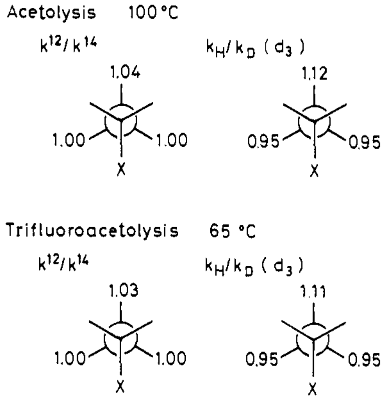
obtained in the solvolysis of **6** and **7**, i.e., k_H/k_D per deuterium are 1.089 in acetic acid at 100 °C and 1.091 in trifluoroacetic acid at 65 °C, are quite close to the typical value in the solvolysis with neighboring phenyl participation (k_Δ process), i.e., k_H/k_D of about 1.10–1.11 at 25 °C.[30b,32,33,34] Furthermore, the results of the 2-methyl-2-adamantanemethyl solvolysis are also virtually identical with those of the neopentyl solvolysis, when the difference in the reaction temperature is taken into consideration. Thus, the validity of the 2-methyl-2-adamantanemethyl solvolysis as a model system of the neopentyl solvolysis has further been confirmed.

Although the number of reports is limited, the entirely opposite tendency to that in the deuterium effects has been observed in the carbon isotope effects at the reaction center: larger values in S_N2 and smaller ones in S_N1.[35,36] Large effects in the former are attributed to a more or less symmetric, linear three-centered transition-state structure composed of a nucleophile, a reacting carbon, and a leaving group.[1,35] Considerably large carbon-14 isotope effects (k^{12}/k^{14} = 1.09–1.14) detected in the k_Δ process of the neophyl (**3**, Tables I and II) and related solvolyses are also attributable to the presence of some sort of a nucleophile forming a pseudolinear three-centered transition state together with a reacting carbon and a leaving group.[1,18d,e,37] In the solvolysis of neopentyl derivatives, direct substitution by an external nucleophile is known to hardly occur.[6,10,12] Thus, the observed data of the kinetic isotope effects at the α-carbon and deuterium are consistent with the assisted mechanism (k_Δ) by a neighboring methyl group.

β-Carbon-14 Effects. Although examples of secondary isotope effects of heavy atoms are very scarce,[38] it is sure that the magnitude of the effects must be small. Carbon-14 effects of about 2% observed in the solvolysis of **6** and **7** are significant in this sense. Similar results were already observed in the acetolysis and the trifluoroacetolysis of neophyl brosylate **3** and were attributed mainly to the weakening of the β-phenyl-1 carbon–carbon bond.[1] It is noticeable here that the β-carbon effects are larger in the neopentyl solvolysis than in the neophyl one. More weakening of the β–γ bond in the former can be intuitively concluded. Validity of the conclusion will be discussed later in detail from the viewpoint of the nature of σ participation.

γ-Deuterium and Carbon-14 Effects. Similarly to the data reported in the literature,[14,15] γ-d_9 effects of **6** in the acetolysis and **7** in the trifluoroacetolysis are negligibly small. On the contrary, γ-carbon effects of **6** and **7** are both fairly large.

Chart I



Considerable change in the bonding of the γ-methyl carbon can naturally be concluded. As described already, calculation of the γ-carbon-14 effects of **6** and **7** was carried out by use of eq 3 on the assumption that nonmigrating methyl groups have no isotope effect on the reaction. Although the assumption does not seem unreasonable,[38] it is difficult to deny without any experimental evidence the possibility of the overlap of the secondary effects by three methyl groups causing the observed isotope effects. Mathematically, a 1% effect each by three methyl groups or a 1.5% effect each by two nonmigrating methyls could make a 3% kinetic isotope effect as well. Furthermore, it is apparent that errors inherent in the isotope effects calculated by use of eq 3 are 3 times as large as those in the usual cases when one particular carbon is labeled with carbon-14 and therefore when eq 2 can be applied. Expectedly, these uncertainties have been solved unambiguously by use of the model adamantane system **4**. The carbon-14 isotope effects at γ in both the acetolysis and the trifluoroacetolysis of **9** were quite similar to those of **6** and **7** with smaller intrinsic errors. Thus, the validity of the assumption for applying eq 3 to the neopentyl solvolysis has been secured. The observed carbon-14 isotope effects at γ in **6** and **7** must result mainly from the migrating methyl group.

The observation of the distinctly positive isotope effects of the migrating CD_3 group is also important. The postulate proposed by Raber, Harris, and Schleyer,[16] who pointed out the possibility of cancellation of positive effects by a migrating CD_3 and negative effects by nonmigrating two CD_3's, has been confirmed experimentally for the first time.[19] Negative effects of nonmigrating CD_3 detected in the neighboring phenyl-assisted solvolysis of **3**-γ-d_6 reinforce the above conclusion. Thus, negligible intermolecular isotope effects concurrent with large intramolecular effects have been proved not to become evidence for the stepwise mechanism, in contradiction to the claim by Schubert and Henson.[15]

From the combination of the results for **6** and **9** cited in Table I, the observed isotope effects of carbon-14 and deuterium in the acetolysis can be allotted to the individual methyl groups by assuming that the transition states for **6** and **9** are the same. A similar calculation for the trifluoroacetolysis was undertaken by using the data for **7** observed at 65 °C and those for **9** extrapolated

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(33) Lee, C. C.; Noszko, L. *Can. J. Chem.* **1966**, *44*, 2491–2495.

(34) Although the accuracy is not clear, k_H/k_D = 1.13 (per D_2?) was reported by Winstein and his co-workers for the trifluoroacetolysis of neopentyl tosylate at 100 °C (ref 6).

(35) Fry, A. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970; Chapter 6.

(36) Burton, G. W.; Sims, L. B.; Wilson, J. C.; Fry, A. *J. Am. Chem. Soc.* **1977**, *99*, 3371–3379.

(37) Not so large effect (k^{12}/k^{14} = 1.048) was reported in the solvolysis with triple-bond participation: Collins, C. J.; Benjamin, B. M.; Hanack, M.; Stutz, H. *J. Am. Chem. Soc.* **1977**, *99*, 1669–1670.

(38) (a) Raaen, V. F.; Tsiomis, A. K.; Collins, C. J. *J. Am. Chem. Soc.* **1960**, *82*, 5502–5503. (b) Saunders, M.; Telkowski, L.; Kates, M. R. *Ibid.* **1977**, *99*, 8070–8071.

from the results at lower temperatures cited in Table II. In these calculations, the isotope effects of nonmigrating methyl groups were determined by extracting the square roots of the quotients obtained by dividing the effects of **6** or **7** by those of **9**. The results are summarized in Chart I, in which X represents a leaving group.

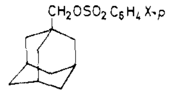
The prerequisites of this allotment, i.e., the similarity of the transition-state structures for **1** and **4**, little influence of the difference in the leaving group,[39] and the propriety of extrapolation of the kinetic isotope effects from those determined at other temperatures, must cause uncertainties in the values cited in Chart I. As mentioned above, however, errors derived from these assumptions must not be so large that discussions based on the values in Chart I must be sound as far as qualitative ones are concerned.[40]

The Transition-State Structure of Neopentyl Solvolysis and the Nature of σ Participation. The allotment of the kinetic isotope effects at the γ-position shown in Chart I gives valuable information on the transition-state structure of the neopentyl solvolysis and also on the nature of σ participation. Substitution of hydrogens at the β-position of an ethyl derivative by three methyl groups is known to influence the rate and the fate of the solvolytic reactions in various solvent systems.[6,8,9,10,12,41] The inequality of the allotted isotope effects at γ disclosed in the present investigation (Chart I) confirms that the three methyl groups are not equivalent in this influence. In other words, changes in the bondings of three methyl groups in the transition state are not the same and that of the migrating methyl group is quite different from those of the other two methyl groups.

A neighboring methyl group is considered to stabilize an incipient cation in the following three manners: inductive effect, hyperconjugation, and direct participation (bridging). Operation of the inductive effect, which is always concomitant with alkyl solvolysis, is reflected in the negative (inverse) deuterium effects of the nonmigrating methyls. Deuterium is considered as more electron releasing than hydrogen.[39b] Undetectable carbon-14 effects of these methyls suggest the insensitivity of carbon isotope effects to the inductive effect, although definite conclusion must await the direct measurement of this type of an isotope effect in a system such as **3**.

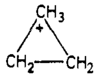
The distinct inequality of the allotted isotope effects at γ, both carbon and deuterium, can not be interpreted by the inductive effect alone but suggests the operation of the other modes of methyl group effects. Medium-sized γ-carbon effects at a particular methyl group as well as distinct β-carbon effects clearly indicate weakening of the single β-γ bond, which looks consistent with C–C hyperconjugation. However, as this bond can not be regarded as "reacting" and "moving" in C–C hyperconjugation, the kinetic isotope effect brought about at this carbon should not be a primary but a secondary one.[42a] Bigeleisen and Wolfsberg roughly estimated the "maximum" secondary isotope effects by assuming that only stretching force constants decrease by a factor of 2 on going from reactants to transition states.[42b] For the carbon-14 secondary isotope effect, the maximum is estimated at 1.023. Although the assumption is rough, it is usually considered that an effect larger than the maximum secondary effect must almost certainly be primary; the isotopic atom is actually reacting and moving in the reaction coordinate motion,[42a] which is in conflict with the definition of hyperconjugation. Thus, the observed carbon-14 isotope effects larger than 1.023 cannot be interpreted only by the operation of C–C hyperconjugation. As a conclusion, direct participation (bridging) by a methyl group must operate in the transition state of the neopentyl solvolysis, although the relative importance of the bridging is not clear at this stage. The conclusion is in accord with the large carbon-14 and the medium deuterium effects at α as mentioned above.

How much is the neopentyl solvolysis accelerated by methyl participation? It is very difficult to evaluate this acceleration by means of a linear free-energy relationship in the case of the primary alkyl solvolysis, because the contribution of the direct solvent attack and the ion pair return in each case is almost impossible to estimate.[6] A large rate ratio of neopentyl to ethyl in the trifluoroacetolysis (ca. 480)[6] might be regarded as a simple measure of the acceleration. However, the acetolysis and the formolysis of 1-adamantanemethyl arenesulfonates (**13**) revealed that the steric restriction of the alkyl migration due to the stable adamantane skeleton does not cause rate retardation at all in comparison with those of neopentyl derivatives, but actually the former solvolyzes faster than the latter.[10] This fact, together with the absence of solvent participiation in **13**,[10] implies that the reduction in the activation energy by means of bridging is not large. Other analyses by use of the substituent effect and the solvent effect on the solvolysis rates also indicate that methyl participation is not important in energetics.[5,6,9,41] Then, how can this appearent discrepancy, i.e., importance of methyl participation in kinetic isotope effects and its less importance in energetics, be solved?



13, X = CH_3, NO_2

Molecular orbial calculations showed that the relative energies of $C_3H_7^+$ isomers vary to a great extent according to the methods of calculation.[43–45] Thus, it may be concluded that the potential energy surface of the species is fairly flat and that the energies of the isomers of corner-protonated cyclopropane (**14**) and *n*-propyl cation (**15**) are similar. Although the effect of substitution of the hydrogens by two methyl groups is not clear, there is a good possibility that the transition states of the neopentyl solvolysis with and without methyl bridging, which may lead to intermediate cations correspondiong to **14** and **15**, respectively, are not so different in energy. Thus, considerable changes in force constants at γ can be consistent with the absence of strong acceleration in rate.



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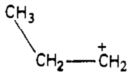

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16

Common features are apparent in the calculated structures of $C_3H_7^+$ isomers throughout cyclic and acyclic ones: shortening of the α–β bond and lengthening of the β–γ bond.[43a] It is more remarkable when one compares **14** with phenonium (ethylenebenzenium) cation **16**;[46] **14** makes a more acute triangle than **16**. These features suggest that in the transition state of the neopentyl solvolysis the α–β bond is strengthened and the β–γ bond is weakened. The conclusion is rather natural because a methyl group does not have extra electrons such as *n* or π does, and therefore, it has to use its bonding electrons of C–C or C–H σ bonds in order to interact with an electron-deficient center, no matter what the mode of interaction may be.

Quite recently, Sunko, Hehre, et al. reported that the γ-deuterium isotope effects of 1.03–1.04 (per D) were observed in the

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[39] (a) Shiner, V. J., Jr.; Seib, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 862–864. (b) Reference 30a, p 151.

[40] When our intermolecular migrating CD_3 effect (k_{CH_3}/k_{CD_3} = 1.12 ± 0.02 in trifluoroacetic acid at 45 °C) is divided by the intramolecular migrating ratios observed by Schubert and Henson (${k_{CH_3}}^{CD_3}/{k_{CD_3}}^{CH_3}$ = 1.22 ± 0.02 or 1.31 ± 0.20 in aqueous, buffered trifluoroacetic acid at 40 °C),[15] the effect of nonmigrating CD_3 (k^{CH_3}/k^{CD_3}) can be calculated as 0.92 ± 0.03 or 0.85 ± 0.13, which barely coincides with our calculated value, 0.95. Similar calculations by Shiner and Tai gave similar coincidence.[19]

[41] Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89–173.

[42] (a) Thornton, E. K.; Thornton, E. R. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970; Chapter 4. (b) Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 15–76.

[43] (a) Radom, L.; Pople, J. A.; Buss, V.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 311–321. (b) Hariharan, P. C.; Radom, L.; Pople, J. A.; Schleyer, P. v. R. *Ibid.* **1974**, *96*, 599–601.

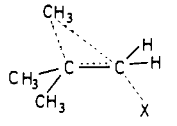
[44] (a) Bishof, P. K.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1975**, *97*, 2278–2280. (b) Dewar, M. J. S.; Ford, G. P. *Ibid.* **1979**, *101*, 783–791.

[45] Lischka, H.; Kohler, H.-J. *J. Am. Chem. Soc.* **1978**, *100*, 5297–5305.

[46] Hehre, W. J. *J. Am. Chem. Soc.* **1972**, *94*, 5919–5920.

solvolysis of 1-adamantyl-*3-d* derivatives.[47] They regard these positive effects in this nonrearranging system as a probe for C–C hyperconjugation and homohyperconjugation (1,3 interaction), the former of which was considered as a major mode of stabilization in their system. It is important that their interpretation is also in accord with our conclusion obtained in the rearranging system.

Although the importance of methyl participation in kinetic isotope effects has been verified in the present investigation, it is difficult to estimate the strength of the bridging in the above qualitative discussion.[48] At present, we are undertaking a model calculation of the transition-state structure of the neopentyl solvolysis by means of the simulation of the observed isotope effects. As a preliminary result, we can say that the structure **17** is able to reproduce the observed isotope effects by use of a model with very small α–γ interaction.[49] It is important that a large γ-carbon isotope effect does not necessarily mean strong bridging.



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Characteristic features of the transition-state structure of the neopentyl solvolysis, i.e., very weak bridging accompanied by substantial weakening of the β–γ and strengthening of the α–β bonds, show that σ participation in general is a composite phenomenon in which the two formally conflicting modes, namely, hyperconjugation and bridging, are operating at the same time.[47,51-53] In other words, hyperconjugation and bridging are not necessarily alternative but may cooperate together as the driving force of the reaction.[54] This composite nature of σ participation with less importance in enhancing the reaction must be one of the main causes of long debate concerning the nonclassical carbonium ion problem.[56] The possibility of methyl participation in the mechanism of the pinacolyl solvolysis must also be discussed considering this complexity.[57]

Experimental Section

General Data. Melting points were determined on a Yamato MP-21 capillary melting point apparatus in sealed capillaries for adamantane derivatives and a Yanagimoto MP-S2 hot stage melting point apparatus for other compounds and are all uncorrected. NMR spectra were obtained on either a JEOL JNM-FX 100 (^{1}H and ^{13}C) or a Hitachi R-24 (^{1}H) instrument in deuteriochloroform by using tetramethylsilane as an internal standard unless otherwise noted. IR spectra were recorded with a JASCO IR-G spectrophotometer. Mass spectra were taken on a Hitachi RMU-7 instrument. Analytical vapor-phase chromatography was performed on a Varian Aerograph Model 2850-30 instrument with a flame ionization detector and a Hewlett-Packard 3370B digital integrator. Elemental analyses were performed at the Material Analysis Center of the Institute of Scientific and Industrial Research, Osaka University.

Preparation of Labeled Compounds. Neophyl brosylate (**3**), neopentyl nosylate (**6**) and brosylate (**7**), and 2-methyl-2-adamantanemethyl brosylate (**9**) and nosylate (**10**) labeled with carbon-14 and deuterium at various positions were prepared by the usual series of reactions described in the text. As the sources of isotopes, methyl-d_3 iodide (Merck Sharp & Dohme, 99.5%), *tert*-butyl-d_9 chloride (Stohler Isotope Chemicals, 99%), lithium aluminum deuteride (Merck, >99%), barium carbonate-^{14}C (Radiochemical Center), sodium acetate-*2*-^{14}C (New England Nuclear), and methyl-^{14}C iodide (Radiochemical Center and New England Nuclear) were used. The physical properties were as follows: **3**, mp 81.0–81.5 °C (lit.[58] mp 80.8–81.5 °C); **3**-γ-d_6, mp 82.5–83.0 °C; **6**, mp 113.6–113.9 °C (lit.[10] mp 111.8–112.0 °C); **6**-α-^{14}C, mp 113.0–114.0 °C; **6**-β-^{14}C, mp 114.1–114.5 °C; **6**-γ-^{14}C, mp 113.3–113.8 °C; **6**-α-d_2, mp 113.5–114.2 °C; **6**-γ-d_9, mp 114.0–114.7 °C; **7**, mp 69.3–70.0 °C (lit.[5] mp 69–70 °C); **7**-α-^{14}C, mp 69.0–69.5 °C; **7**-β-^{14}C, mp 70.1–70.5 °C; **7**-γ-^{14}C, mp 69.9–70.4 °C; **7**-α-d_2, mp 69.5–70.0 °C; **7**-γ-d_9, mp 70.2–71.0 °C; **9**, mp 85.5–86.0 °C; **9**-γ-^{14}C, mp 85.0–85.5 °C; **9**-α-d_2, mp 83.0-83.7 °C; **9**-γ-d_3, mp 85.0–85.5 °C; **10**, mp 133 °C dec.

The elemental analyses of all the protio and deuterio compounds cited above and of their precursors gave satisfactory results for C, H (D), Br, N, and S.

Solvolysis Media. Acetic acid was purified as described before.[1] Trifluoroacetic acid containing 1 wt % of trifluoroacetic anhydride was prepared according to the procedure described before.[59]

Acetolysis of 9 and 10. A solution of **9** (0.05 M) in acetic acid was heated at 100 °C for 9 h in a sealed ampule. After concentration of the solution, the products were extracted with ether and then separated by column chromatography by using silica gel. After molecular distillation at 50–80 °C (bath temperature) under 15 torr, the main fraction was identified as **11**:[25] IR (neat) 1675 and 820 cm^{-1} (trisubstituted olefin); mass spectrum, *m/e* 162 (M^{+}); ^{1}H NMR ($CDCl_3$) δ 1.52 (3 H, d, *J* = 6.7 Hz, CH_3), 1.78–1.90 (12 H, m), 2.28 (1 H, br s), 2.79 (1 H, br s), 5.02 (1 H, q, *J* = 6.7 Hz, vinyl H); ^{13}C NMR ($CDCl_3$) δ 12.0, 28.8 (2 C), 31.6, 37.4, 38.7 (2 C), 39.9 (2 C), 40.6, 109.8, 147.9.

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.68; H, 11.32.

The minor product obtained from column chromatography was identified as **12**: IR (neat) 1735, 1240 cm^{-1} (acetate); mass spectrum, *m/e* 163 (M^{+} – CH_3CO_2), 43 (CH_3CO); ^{1}H NMR ($CDCl_3$) δ 1.22 (3 H, d, *J* = 6.4 Hz, CH_3), 1.83 (15 H, m), 2.03 (3 H, s, CH_3CO_2), 5.28 (1 H, dq, *J* = 9.5, 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 18.3, 21.3, 27.5, 27.9, 28.2, 29.1, 31.8, 31.9, 38.1, 38.5, 39.1, 49.3, 71.0, 170.8.

NMR monitoring of the reaction of **10** (ca. 0.03 M) in acetic acid-d_4 at 80 °C showed that as the reaction proceeded the peaks of the starting ester **10** at δ (chemical shifts from tetramethylsilane as an external standard) 1.08 (CH_3) and 4.22 (CH_2) disappeared and that of the product **11** at δ 1.51 appeared. The prominent peak of adamantane moiety at δ 1.69 gradually moved to δ 1.82. ^{1}H and ^{13}C NMR spectra of the reaction solution after 27 h showed the presence of only **11** monodeuterated at the vinylic position besides *p*-nitrobenzenesulfonic acid.

Product analysis was performed by vapor-phase chromatography using a column packed with Silicone OV1 on Chromosorb W AW at 130 and 160 °C. The reaction solution of **9** (0.05 M) after 9 h at 100 °C was directly injected on the column. The relative sensitivity of **11** to the internal standards, tetradecane and pentadecane, was calibrated by using

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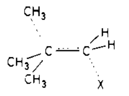
(47) Sunko, D. E.; Hirsl-Starcevic, S.; Pollack, S. K.; Hehre, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6163–6170.

(48) If we extend the definition of hyperconjugation to include considerable lenghthening of the bond β–γ to the cationic center, it is not easy to eliminate completely the possibility of the transition-state structure without bridging (**18** in place of **17**). Although we prefer the operation of direct participation (bridging) because of the close similarity between kinetic isotope effects in the neighboring phenyl assisted solvolysis and those in neopentyl solvolysis (Tables I and II), the above possibility will be reconsidered in our forthcoming paper on a model calculation of the observed isotope effects[49] in connection with Grob's "frangomeric effects".[50]



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(49) Yamataka, H.; Ando, T., to be submitted for publication.

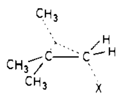
(50) (a) Grob, C. A. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 535–546. (b) *Ibid.* **1976**, *15*, 569–575. (c) Fischer, W.; Grob, C. A. *Helv. Chim. Acta* **1978**, *61*, 1588–1608. (d) Grob, C. A.; Waldner, A. *Ibid.* **1979**, *62*, 1736–1744.

(51) The idea that hyperconjugation and participation may merge has appeared repeatedly in the literature. For a recent review, see ref 3, pp 31–43.

(52) Among others, see: (a) Trayler, T. G.; Hanstein, W.; Berwin, H. J.; Clinton, N. A.; Brown, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5715–5725; (b) Reference 17b, pp 78–79; (c) Reference 45b.

(53) The composite nature of participation may be involved even in π participation, which is apparent in the acute triangle of **16**. Thus, *n*, π, and σ participation make a sort of spectrum of the composite nature.

(54) Adoptation of Olah's presentation[55] for describing the transition-state structure (**19** instead of **17** or **18**) may help us to understand the cooperative nature of hyperconjugation and bridging.



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(55) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808–820.

(56) For a recent review on the topic see: Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.

(57) Ando, T.; Morisaki, H. *Tetrahedron Lett.* **1979**, 121–122.

(58) Fainberg, A. H.; Winstein, S. *J. Am. Chem. Soc.* **1956**, *78*, 2763–2767.

(59) Ando, T.; Saito, Y.; Yamawaki, J.; Morisaki, H.; Sawada, M.; Yukawa, Y. *J. Org. Chem.* **1974**, *39*, 2465–2466.

an authentic sample. The sensitivity of **12** was calculated by the method described by Sternberg et al.[60] The absolute yield of **11** thus determined was 92 ± 2%. The yield of **12** was about 2% for the above sample, but it increased to 5% after the solution was kept at 100 °C for 21 h. A control experiment in acetic acid at 100 °C for 24 h showed that **11** afforded **12** slowly even in the absence of *p*-bromobenzenesulfonic acid.

Kinetic Procedures. Acetolysis was performed by the usual sealed-ampule method with α-naphtholbenzein as an indicator.[1,61] Trifluoroacetolysis was carried out in a similar manner as reported earlier.[59] Dilution procedures and wavelengths used were different in each case: **3**, 1 mL of 0.02 M solution was diluted to 50 mL with 95% ethanol, measured at 249 nm; **7** (except **7**-γ-d_9), 1 mL of 0.04 M solution was diluted to 50 mL and then 10 mL of this solution was again diluted to 50 mL, measured at 243 nm; **7**-γ-d_9; **9**, 1 mL of 0.03 M solution was diluted to 25 mL and then 10 mL of this solution was again diluted to 50 mL, measured at 247 nm. In the case of **3** at 0 °C and **9** at 25 °C, 1-mL aliquots were pipetted out from a reaction flask placed in a thermostatic bath. In all other cases sealed ampules were used.

Measurement of Carbon-14 Kinetic Isotope Effects. Accurate radioactivity measurement of the purified samples of unreacted esters recovered at various stages of reaction was carried out according to the procedure described earlier.[1] Concentrations of the reaction solutions were the same as those of the respective kinetic runs. The pipetting-out method was employed in the case of trifluoroacetolysis of **9** at 25 °C, and the sealed ampule method was used in all other cases. Radioactivity data for each case appear in supplementary material.

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Supplementary Material Available: Tables S1–S11 containing radioactivity data of solvolysis of **6**, **7**, and **9** used for calculating carbon-14 kinetic isotope effects (11 pages). Ordering information is given on any current masthead page.

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Deuterium Isotope Effects for Migrating and Nonmigrating Groups in the Solvolysis of Neopentyl-Type Esters[1]

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Abstract: α- and γ-deuterium rate effects on the solvolysis of (1-methylcyclohexyl)methyl, (1-methylcyclopentyl)methyl, and (1-methylcyclobutyl)methyl sulfonate esters have been measured and the solvolysis products examined by ^{2}H NMR spectroscopy. The results indicate that the products of the solvolysis of all these sulfonate esters are predominantly ($\geq$98%) rearranged. In the solvolysis of (1-methylcyclohexyl)methyl triflate, rearranged products with methyl migration slightly dominate over those with ring expansion. Normal isotope effects, 1.057 in 80E and 1.073 in 97T, are observed for the methyl-d_3 compound and an inverse effect, 0.963, is observed in 80E for the methylene-d_4 compound. However, in the solvolysis of both (1-methylcyclopentyl)methyl and (1-methylcyclobutyl)methyl sulfonates, the major products are those of ring expansion. In these examples, inverse effects are observed for the methyl-d_3-labeled species. The observed isotope effects can be separated into respective values of 0.927, 0.913 for the nonmigrating methyl-d_3 group and 1.177, 1.224 for the migrating methyl-d_3 group in the solvolysis of (1-methylcyclohexyl)methyl triflate and (1-methylcyclopentyl)methyl brosylate. This explains the relative intramolecular migratory aptitudes of CH_3/CD_3 of 1.20–1.30 and the low γ-d_9 isotope effect in the solvolysis of neopentyl sulfonates previously reported and makes them consistent with a mechanism which involves neighboring carbon participation during ionization.

Introduction

The solvolysis of neopentyl sulfonate esters yields, nearly completely,[2] products of rearranged carbon skeletal structure. Some controversy still centers around the timing of the rearrangement. Does methyl group migration occur during or after the rate-determining ionization step?[2-4]

Evidence favoring participation in neopentyl derivatives comes from (1) the dominance of rearranged products,[2,3] (2) the failure to trap the neopentyl cation,[5] (3) the observed moderate-sized γ-^{14}C effect (1.05) in the acetolysis of neopentyl *p*-nitrobenzenesulfonate,[6] (4) accelerated rates relative to some model compounds,[2a,7,8] (5) stereochemical results,[9,10] and (6) the lack of ^{18}O scrambling in the solvolytic rearrangement of bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoate.[11] However, most of these results provide permissive and suggestive, rather than compelling, evidence for participation.

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[1] (a) Taken from the thesis of J. J. Tai, submitted in partial fulfillment of the requirements for the Ph.D. degree at Indiana University, 1979. (b) A preliminary report on part of this work has appeared: Shiner, V. J., Jr.; Tai, J. J. *Tetrahedron Lett.* **1979**, 127.

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