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Solvolysis in Carboxamides. V.[1] Solvolytic Elimination of *threo*-1-Methyl-2-phenylpropyl Brosylate in *N*,*N*-Dimethylacetamide. Kinetic, Product, and Deuterium Tracer Studies

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Solvolysis of a series of ring substituted *threo*-1-methyl-2-phenylpropyl brosylates has been carried out in *N*,*N*-dimethylacetamide (DMA) as solvent. Hammett treatment of the rate data indicated that the DMA solvolysis of the unsubstituted brosylate (**1c**) falls into the category of k_s pathway (100%). In order to gain further information of the nature of the k_s pathway, the DMA solvolysis of **1c** or **1c**-2-*d* (labeled at C(2)) has been conducted. The product distribution, effect of water content on it, the composition and deuterium distribution of recovered brosylate, kinetic isotope effect, and the deuterium distribution of product have been investigated. The products consisted of the olefins ((*E*)- and (*Z*)-2-phenyl-2-butenes, and 2- and 3-phenyl-1-butenes), and, in the presence of water in DMA, the carboxylates (*erythro*- and *threo*-1-methyl-2-phenylpropyl acetates) and the small amount of diastereomeric alcohols. The major product was (*Z*)-2-phenyl-2-butene, indicating the occurrence of *anti*-*E*1 process. The deuterium was substantially scrambled in each product. These findings suggest that the reaction proceeds through tight ion-pair and subsequent processes such as *anti*-*E*1, 2,1-phenyl and -hydride shifts, solvent capture, and *threo*-*erythro* interconversion take place competitively. In view of a substantial extent of intervention of such rearrangement, the involvement of nucleophilic solvent assistance is thought to be less probable in this k_s process.

The *β*-phenyl participation in solvolytic reactions has been one of interesting subjects in organic reaction mechanism for more than twenty years.[2)] Cram has first proposed the phenonium ion as intermediate in the acetolysis of optically active *threo*- and *erythro*-1-methyl-2-phenylpropyl tosylates to account for the remarkable stereospecificity of the reaction.[3)] For example, the acetolysis of the *threo*-substrate gave acetate (53% yield) with 94% retention of configuration, accompanied with the olefin formation (35%).[3)]

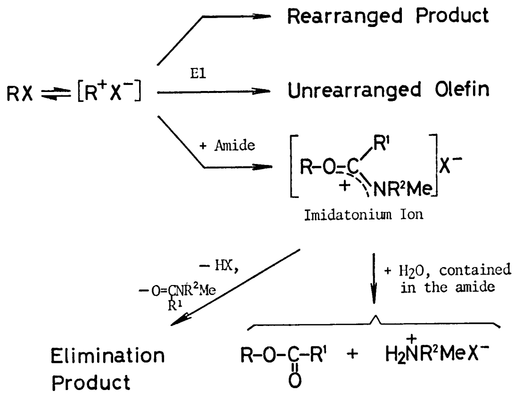
Winstein *et al.*[4)] have shown, however, that the rate enhancement expected for the *β*-phenyl participation is generally quite small. In fact, when titrimetric rate is compared, the rate of the acetolysis of *threo*-1-methyl-2-phenylpropyl tosylate was 0.6 times the rate of *s*-butyl tosylate under the same conditions.[4)]

Such an apparent discrepancy between rate data and stereospecificity of product has made it difficult to clarify the role of *β*-phenyl group in solvolytic reactions and, therefore, was the starting point of the current controversy.[2,5—13)]

Schleyer and his collaborators[6)] have recently suggested that the solvolysis of *β*-arylalkyl systems proceeds through discrete aryl-assisted (k_Δ) and/or aryl-unassisted (k_s) pathways. They have developed the method for the dissection of the observed rate constant (k_t) into its Fk_Δ and k_s components by the use of Hammett correlation.[6a)]

The application of this approach[6a)] to 2-aryl-1-methylpropyl system has been performed by Brown and Kim.[5e)] They conducted the acetolysis of a series of ring substituted *threo*-1-methyl-2-phenylpropyl brosylates and found the existence of an excellent rate-product correlation, when $100\,Fk_\Delta/k_t$ value was compared with the yield of retained acetate. However, since the rate ratio (k_Δ/k_s) of 12 for the unsubstituted derivative (**1c**) was too small to be ascribed to the mechanism involving the simultaneous formation of open and bridged ions,[6)] they have proposed a mechanism involving an open tight ion-pair as a common intermediate to which both the aryl-assisted and the aryl-unassisted pathways compete,[5e,f)] employing the original formulation of Shiner[14)] and Sneen.[15)]

In a series of our investigations with respect to the nature of carboxamide solvolysis for typical secondary cycloalkyl systems, 4-*t*-butylcyclohexyl,[16)] 7*β*-methylbicyclo[3.3.1]non-3*β*-yl,[17)] and *exo*-2-norbornyl[1)] systems, it has been revealed that the reactions proceed through an initially formed tight ion-pair intermediate $[R^+X^-]$ (classical) which undergoes various subsequent processes such as *E*1 reaction, solvent capture (formation of imidatonium ion), or rearrangements, as is outlined in Scheme 1.

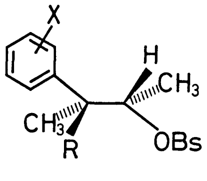


R^1, R^2=H or Me

Scheme 1.

As a principal characteristic of the carboxamide solvolysis, it has been demonstrated that the carboxamides suppress the formation of rearranged products even when the substrate has a structure prone to rearrangement and, in addition, they accelerate *syn*-*E*1 process in the cyclic substrates[1,16,17)] to result in an increase in the yield of unrearranged olefin. Based on such trends observed in the previous studies,[1,16,17)] it was anticipated that a fraction of the k_Δ pathway for **1c** might be suppressed in the carboxamide solvolysis as compared with that in the acetolysis.[5e] It appeared also of interest to examine whether the rate-product correlation, observed in the acetolysis,[5e] is observed or not in carboxamide solvolysis of such system.

In this paper, we report on a) the Hammett treatment of rate data for the DMA solvolysis of a series of ring substituted *threo*-1-methyl-2-phenylpropyl brosylates (**1a**—**g**), b) the products of the DMA solvolysis of the unsubstituted derivative **1c** in the presence of various amounts of water, c) the composition and deuterium distribution of the unchanged brosylate recovered from half-life reaction of C(2)-deuterated substrate **1c**-2-*d* in DMA solvent, d) deuterium distribution of the products produced from the DMA solvolysis of **1c**-2-*d*, and e) kinetic isotope effect for **1c**-2-*d* solvolysis in four carboxamide solvents, *i.e.*, *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA). We also discuss the generality of the mechanism (Scheme 1) and the mechanistic problem[2,5–13] of 2-aryl-1-methylpropyl solvolysis, especially on the nature of the k_s process.



1a R=H, X=*p*-MeO
1b R=H, X=*p*-Me
1c R=H, X=H
1c-2-*d* R=D, X=H
1d R=H, X=*p*-Cl
1e R=H, X=*m*-Cl
1f R=H, X=*m*-CF_3
1g R=H, X=*p*-NO_2

Results

*Rate Study and Hammett Correlation for the DMA Solvolysis of **1a**—**g**.* The rates of solvolysis of **1a**—**g** in DMA solvent were determined titrimetrically in the same manner as reported.[1] All the kinetic runs exhibited first-order behavior over two to three half lives. Pyridine, added to neutralize liberated *p*-bromobenzenesulfonic acid, did not alter the rate, presumably indicating that the reaction proceeds through typical *E*1 or S_N1 mechanism. The rate constants and activation parameters are tabulated in Table 1. The Hammett plot for the rates of **1a**—**g** at 75 °C is shown in Fig. 1, together with that for the acetolysis[5e] for the purpose of comparison.

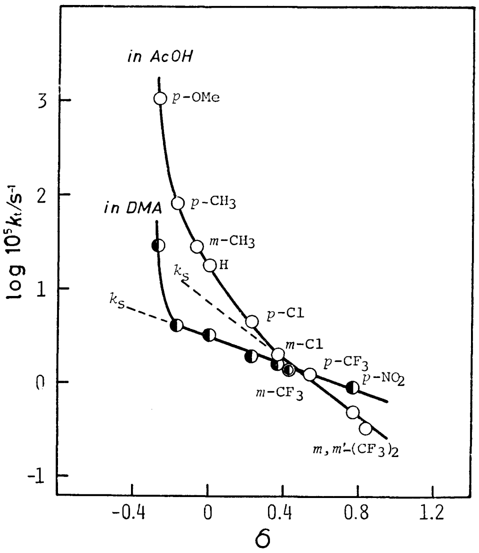


Fig. 1. Plot of $\log k_t$ (*thero*-2-aryl-1-methylpropyl brosylate) for the DMA solvolysis and acetolysis (Ref. 5e) *vs.* σ at 75 °C; ρ-value and correlation coefficient for the DMA line are −0.72 and 0.991, respectively.

A satisfactory linear relation was observed for all the substrates except for *p*-methoxyphenyl derivative **1a**. The k_s line was determined by a least-squares treatment to obtain the ρ-value of −0.72.[18] Unlike the acetolysis,[5e] the k_Δ pathway was suppressed in DMA solvent for *p*-tolyl derivative **1b** as well as the parent phenyl derivative **1c**. Thus the DMA solvolysis of **1c** turned out to be the case of 100% k_s solvolysis. This result is quite notable as compared with previously known solvolyses of unsubstituted phenyl derivatives in the system such as 2-aryl-1-methylpropyl,[5e] 2-aryl-1-methylethyl,[6a–c,19] or *trans*-2-arylcyclopentyl[5f] because these reactions are known to proceed more or less through the k_Δ pathway.

Table 1. Kinetic data for the solvolysis of *threo*-2-aryl-1-methylpropyl brosylates **1a**—**g** in *N,N*-dimethylacetamide (DMA)[a]

Substituent	$10^5/s^{-1}$ [b]				$\left(\frac{\Delta H^*}{A}\right)$ [c]	$\left(\frac{\Delta S^*}{B}\right)$ [d]
	25.0 °C[e]	50.0 °C	75.0 °C	100.0 °C		
p-OCH_3	0.124	0.299[f] 3.21	28.8		22.9	−9.1
p-CH_3	0.00952		4.15	47.1	24.5	−8.5
H	0.00844		3.34	35.9	24.4	−10.8
p-Cl	0.00443		1.90	21.4	24.4	−10.3
m-Cl	0.00341		1.59	18.5	24.7	−9.7
m-CF_3	0.00331		1.44	16.3	24.4	−10.7
p-NO_2	0.00152		0.916[e] 4.41[h]	29.7[g]	25.1	−9.5

a) [ROBs]=0.075 mol/dm³; [C_5H_5N]=0.077 mol/dm³; [H_2O]=0.003 mol/dm³. b) Mean deviation for k_t's is ±2%. c) At 25.0 °C; *A*=4.184 kJ/mol. d) At 25.0 °C; *B*=4.184 J/(K mol). e) Extrapolated from data at other temparatures. f) At 33.0 °C. g) At 110.0 °C. h) At 90.0 °C.

*Product Distribution and Effect of Water Content for the DMA Solvolysis of **1c**.* In the light of the results mentioned above, it is pertinent to investigate the nature of k_s pathway by the use of the DMA solvolysis of **1c**. The product distribution for such reaction was determined by the combined use of gas chromatography and ^{1}H NMR spectroscopy. As illustrated in Scheme 1, the carboxylates can be formed by rapid hydrolysis of the imidatonium ion. The stereochemistry of solvent capture on initial carbonium ion intermediate could be disclosed by efficient trapping of the imidatonium ion with water. This method has been successfully utilized in the previous works.[1,17] Thus the effect of water content in DMA solvent on the product distribution was examined and the results are summarized in Table 2 and illustrated in Fig. 2.

Similarly to the trends observed for cycloalkyl systems,[1,17] the olefins, (Z)-2-phenyl-2-butene (**7**), its (E)-isomer (**8**), 2-phenyl-1-butene (**9**), and 3-phenyl-1-butene (**10**), were produced in completley dried DMA. Among them, the (Z)-butene **7** was a major product (≈66%). The carboxylates, *erythro*-1-methyl-2-phenylpropyl acetate (**11**) and its *threo*-isomer (**12**), were obtained only in the presence of water and they should stem from the reaction of water and the imidatonium ions, [*erythro*-R-DMA]$^+$OBs$^-$ (**4**) or [*threo*-R-DMA]$^+$OBs$^-$ (**5**), respectively (*vide infra*). These imidatonium ions can be derived from the tight ion-pair intermediate (**2**) by solvent capture (Scheme 3, *vide infra*).

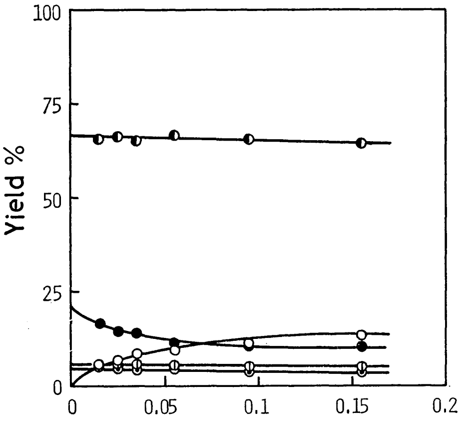
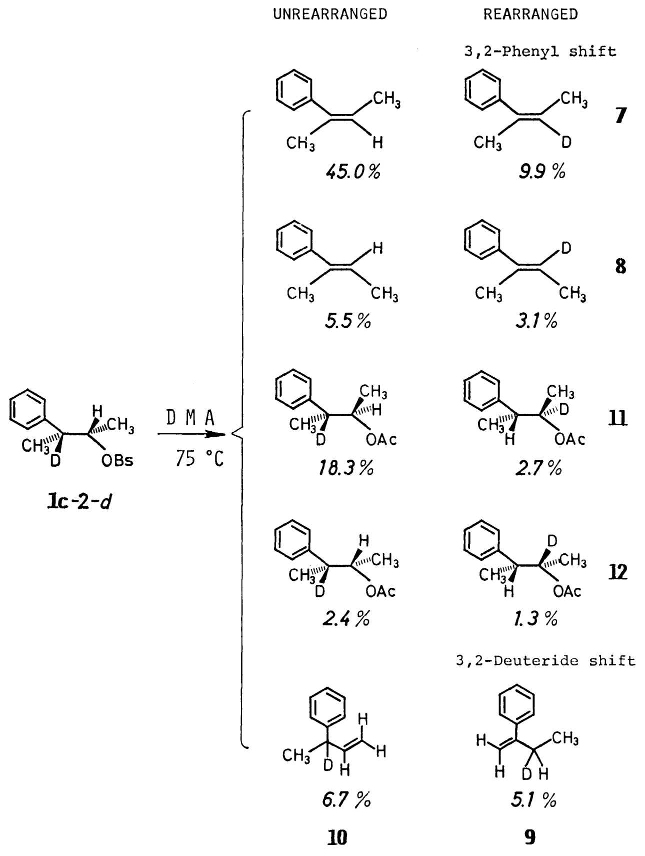


Fig. 2. Effect of water content of DMA on the formation of (Z)-olefin **7** (◐), (E)-olefin **8** (●), 2-phenyl-1-butene **9** (⊙), 3-phenyl-1-butene **10** (◐), and *erythro*-acetate **11** (○) at 75.0 °C.



Scheme 2.

*Deuterium Distribution in the Products for DMA Solvolysis and for Acetolysis of **1c**-2-d.* In the investigation of the product composition, the occurrence of 2,1-hydride shift in the tight ion-pair **2** is disclosed in view of the formation of 2-phenyl-1-butene **9**. However, 2,1-phenyl shift, if any, is impossible to be proved, unless the substrate labeled at C(2). Thus, by the use of **1c**-2-*d*, the extent of phenyl migration can be estimated from the deuterium distributions in the phenylbutenes, **7**, **8**, and **10**, and also in *erythro*- and *threo*-1-methyl-2-phenylpropyl acetates, **11** and **12**.

Table 2. Effects of added H_2O on product distribution for the DMA solvolysis of *threo*-1-methyl-2-phenylpropyl brosylate at 75.0 °C[a)]

$\left(\frac{[H_2O]}{mol/dm^3}\right)$	Product yield%						
	Olefin				Acetate		ROH[b)]
	7	**8**	**9**	**10**	**11**	**12**	
0.015	65.9	16.5	4.9	5.3	5.8	1.1	0.5
0.025	66.4	14.4	4.5	5.9	6.9	1.3	0.6
0.035	65.1	14.0	4.2	5.8	8.5	1.7	0.7
0.055	66.8	11.5	4.2	5.5	9.3	1.8	0.9
0.095	65.8	10.8	3.8	5.1	11.4	2.2	0.9
0.155	64.5	10.1	3.6	4.9	13.4	2.4	1.1

a) [ROBs]=0.075 mol/dm^3; [C_5H_5N]=0.077 mol/dm^3. b) Diastereomeric 3-phenyl-2-butanols: isomer compositions were comprable with those of the acetates.

TABLE 3. ISOTOPIC SCRAMBLING IN THE PRODUCTS FOR DMA SOLVOLYSIS AND ACETOLYSIS OF *threo*-1-METHYL-2-PHENYLPROPYL-2-*d* BROSYLATE **1c**-2-*d* AT 75 °C[a]

Product		Yield % (Composition %)[b]		
	Solvent:	wet DMA[c]	dry DMA[d]	AcOH
Butene:				
(*Z*)-2-Phenyl-2-	(**7**)	54.9	57.5	5.8
(3-H : 3-D)		(82 : 18)	(73 : 27)	(55 : 45)
(*E*)-2-Phenyl-2-	(**8**)	8.6	26.7	19.2
(3-H : 3-D)		(64 : 36)	(62 : 38)	(39 : 61)
3-Phenyl-1-	(**10**)	6.7	7.4	3.3
(3-D : 2-D)		(100 : 0)	(100 : 0)	(81 : 19)
2-Phenyl-1-	(**9**)	5.1	8.4	2.1
(3-D,H : 3-H_2)		(100 : 0)	(100 : 0)	(90 : 10[e])
Acetate:				
erythro-1-Me-2-phenylpropyl		21.0	trace[f]	2.7
(2-D : 1-D)	(**11**)	(87 : 13)		(60 : 40)
threo-1-Me-2-phenylpropyl		3.7	0.0	67.0
(2-D : 1-D)	(**12**)	(65 : 35)		(51 : 49)

a) [**1c**-2-*d*] = 0.075 mol/dm^3; $[C_5H_5N]=0.077$ mol/dm^3. b) The accuracy for NMR measurement of deuterium content was $\leq 1\%$; reproducibility$=\pm 3\%$. c) $[H_2O]=0.17$ mol/dm^3. d) $[H_2O]<0.003$ mol/dm^3. e) See text. f) Deuterium distribution was not determined.

TABLE 4. SUMMARY OF CLEAVAGE REACTION OF RECOVERED BROSYLATE FROM HALF-LIFE SOLVOLYSES OF *threo*-1-METHYL-2-PHENYLPROPYL BROSYLATE **1c** AND ITS C(2)-DEUTERATED BROSYLATE **1c**-2-*d* IN DMA AT 75 °C[a]

ROBs	% Recov.[c]	$[C_5H_5N^+HOBs^-]$ (mol/dm^3)	3-Phenyl-2-butanol, compn. %[b]			
			threo		*erythro*	
			2-D	3-D	2-D	3-D
1c-2-*d*[d]	—	—	0	100	0	0
1c	98	—	94.1		5.9	
1c	95	0.15	94.9		5.1	
1c-2-*d*	99	—	13.9	80.1	1.3	4.6

a) [ROBs]=0.075 mol/dm^3; $[C_5H_5N]=0.077$ mol/dm^3; $[H_2O]=0.17$ mol/dm^3. b) For deuterium distribution analysis: the accuracy$\leq 1\%$; reproducibility$=\pm 3\%$. c) Based on the theoretical amount. d) Control experiment.

The DMA solvolysis of **1c**-2-*d* has been carried out at 75.0 °C, and for the purpose of comparison the acetolysis of **1c**-2-*d* was also conducted at the same temperature. The isotopic distribution was measured by means of ^{1}H NMR spectroscopy in the Fourier transform mode for all the products, which were separated by the use of column chromatography, preparative gas chromatography, and/or an appropriate chemical transformation. The extent of rearrangement, *i.e.*, 2,1-hydride shift and 2,1-phenyl shift, was calculated from the product composition and the deuterium distribution in the each product. The results are summarized in Table 3 and illustrated in Scheme 2.

*Partial Solvolysis and the Analysis of Unchanged Brosylate for the DMA Solvolysis of **1c** and **1c**-2-*d. Previously, we have demonstrated that 4-*t*-butylcyclohexyl tosylate undergoes rearrangement of the type *cis*$\rightleftarrows$*trans* during the solvolysis in phenol–benzene,[20] acetic acid,[21] 60% (v/v) acetone–water,[21] and NMA solvent.[16] From these results, it is anticipated that the rearrangement of **1c** from *threo* to *erythro* configuration may also occur during the DMA solvolysis. Accordingly, the half-life solvolysis of **1c** or **1c**-2-*d* has been carried out in the absence and the presence of added pyridinium brosylate at 75.0 °C and then the unchanged brosylate was isolated. The recovered brosylate was converted into the corresponding alcohol keeping the stereochemical integrity by the use of sodium–naphthalene reagent in tetrahydrofuran at −78 °C. The alcohol was analyzed to determine its isomer composition and/or deuterium distribution by means of gas chromatography and ^{1}H NMR spectroscopy. As expected, it was disclosed that *threo* brosylate **1c** rearranges to *erythro* brosylate (**13**) during the solvolysis. The results are summarized in Table 4.

Kinetic Isotope Effect. In order to obtain information on the transition-state structure for the DMA solvolysis of **1c**, the isotope effect on the DMA solvolysis rate of **1c** by deuteration of C(2) position was examined at 75.0 °C. Such examination has been also made on the other carboxamide solvolyses in DMA, NMA, and NMF. These results are tabulated in Table 5 together with data pertinent to appropriate systems. The β-effect ($k_H/k_{\beta-D}$) of 1.93 (DMA solvolysis) appears to be comparable to the values reported for solvolyses of the systems[22–24] with the tertiary β-hydrogen.

Table 5. Summary of isotope effect for solvolysis of secondary alkyl sulfonates bearing tertiary β-hydrogen[a)]

Substrate	Solvent (T/°C)	$k_H/k_{\beta\text{-D}}$	Olefin Yield %[b)]	Ref.
threo-1-Methyl-2-phenylpropyl OBs	DMA (75)	1.93	83	this work
	DMF (75)	1.67	—	this work
	NMA (75)	1.63	62	this work
	NMF (75)	1.41	—	this work
cis-2-Phenylcyclopentyl OTs	AcOH (50)	2.07	96	22
threo-2-Cyclohexyl-1-methylpropyl OTs	AcOH (25)	1.87	54[c)]	23
1,2-Dimethylpropyl OTs	AcOH (25)	2.26	70[d)]	24

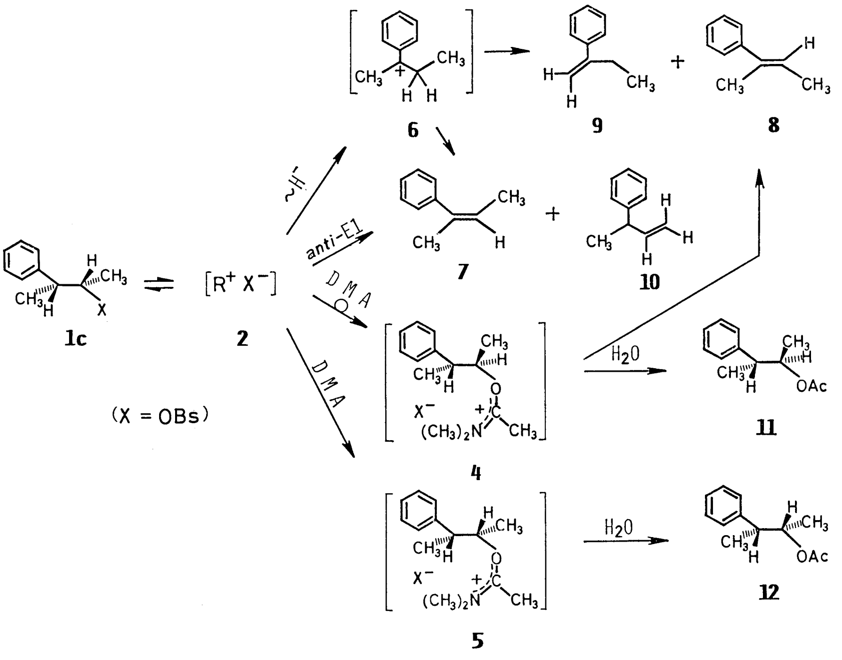
a) Effect by substituting the tertiary β-hydrogen. b) Data for the unlabeled substrate. c) At 35 °C. d) At 75 °C.

Discussion

Possible Reaction Scheme Drawn on the Basis of the Product Distribution and Effect of Water Content on It for DMA Solvolysis of ***1c***. The yields of the (Z)-2-olefin **7** and 1-butenes, **9** and **10**, are virtually unchanged even with the increase in the water content (Fig. 2). In contrast, the yield, though much less, of (E)-2-butene **8** decreases with the increase in water content, but becomes actually invariant at the water concentration higher than 0.15 mol/dm^3. On the other hand, the yield of the *erythro*-acetate **11** increases complementing the decrease in the yield of (E)-2-butene **8**, and it also becomes constant (Fig. 2), although the increase in the acetate **11** yield can not completely compensate the (E)-olefin **8** yield.

From these features of the yield variation caused by increase in water content, the following reaction pathway can be depicted as one of the simplest reaction schemes: a) the (Z)-olefin **7** and 1-butene **10** are formed from the tight ion-pair **2**, b) the *erythro*-acetate **11** can be produced by the reaction of water with *erythro*-imidatonium ion **4**, partially compensating the decrease in the yield of the (E)-2-butene **8**, c) thus the (E)-2-butene **8** comes actually from the *erythro*-imidatonium ion **4**, but a part of it can be formed through a rearranged cation (**6**) which is formed after 2,1-hydride shift of the tight ion-pair 2, d) the 1-butene **9** can also be produced from the rearranged cation **6**, and e) the *threo*-acetate **12**, although in very low yield, is derived from the *threo*-imidatonium ion **5**. These pathways are illustrated in Scheme 3, which are essentially the same as those depicted in Scheme 1.

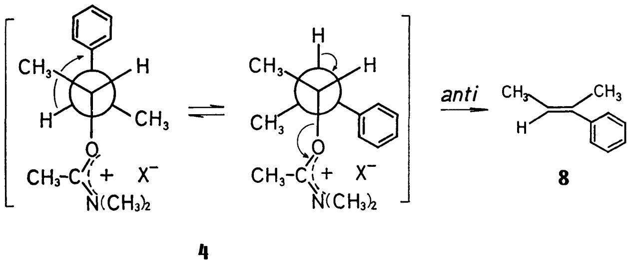
The formation of conjugated terminal olefin **9** suggests the occurrence of 2,1-hydride shift to produce tertiary benzylic cation **6**. Cram and Sahyun[25)] have demonstrated that the acetolysis of a tertiary benzylic system, *i.e.*, 1-methyl-1-phenylpropyl chloride, affords the olefins in 94% yield which consist of (Z)-olefin **7**, (E)-olefin **8**, and 1-butene **9** in the ratio 9 : 68 : 23. If the same ratio for Saytzeff orientation could be expected on the reaction of benzylic cation **6** in the solvolysis of **1c** in DMA containing 0.155 mol/dm^3 of water, the yields of **7** and **8** can be predicted to be 1.4% and 10.6%, respectively, based



Scheme 3.

on the observed yield (3.6%) of **9** (Table 2; $[H_2O]=0.155\ mol/dm^3$). Since the observed yield of (*E*)-olefin **8** (10.1%) is in line with the predicted value (10.6%), most of the (*E*)-olefin **8** should be derived from the benzylic cation **6** (Scheme 3). Obviously, most of (*Z*)-olefin **7** stems from the tight ion-pair **2**, since the yield of **7** is far greater than the expected value (1.4%) from the cation **6**.

Stereochemistry of E1 Reaction. When stereochemistry of the *E*1 reaction was compared with the cyclic systems, in which elimination takes place in *syn*-fashion,[1,16,17] the remarkable contrast was observed. Namely, the formation of (*Z*)-olefin **7** should be ascribed to *anti*-*E*1 reaction from the tight ion-pair **2**; the (*E*)-olefin formation from the imidatonium ion **4** should also be attributed to *anti*-elimination (Scheme 4).



Scheme 4.

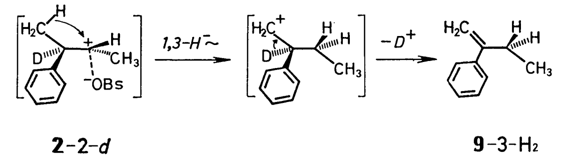
In the solvolysis of cyclic substrates,[1,17] which bear no β-hydrogens antiperiplanar to the leaving group, the *syn*-elimination was predominant. However, the tight ion-pair derived from open-chain compound **1c** can rotate easily to afford the conformers capable of both *syn*- and *anti*-eliminations. In the case of solvolysis of 1-methylpropyl-2-*d* tosylate in a dipolar aprotic solvent, *i.e.*, nitrobenzene, Skell and Hall[26] have demonstrated that it gives predominantly *syn*-elimination product. In contrast, the DMA solvolysis of **1c** afforded overwhelmingly *anti*-elimination product **7**. Thus, this feature seems to be characteristic of DMA solvolysis of the open-chain system. Further scrutinies are required to explain such contrasting stereochemical results.

Occurrence of 2,1-Phenyl Shift in the Tight Ion-pair 2. Appearance of the label at C(3) positions of the olefins **7** and **8**, or at C(1) positions of the acetates **11** and **12** (Table 3 or Scheme 2) clearly indicates that 2,1-phenyl shift occurs not only during the acetolysis with k_Δ process, but also actually *in the DMA solvolysis of 100% k_s process.*

It is notable that the isotopic scrambling in the retained acetate **12** is far from complete equilibration (Table 3) for the DMA solvolysis. Consequently, the formation of this product can not be ascribed to intervention of a symmetrical intermediate expected for the phenonium ion pathway. Although Harris *et al.*[6a] have suggested that even the deactivated substrates of a series of ring substituted 2-phenylethyl system undergo a small, almost undetectable amount of aryl participation (Fk_Δ), the present result rules out such a possibility so far as the DMA solvolysis of **1c** is concerned.

Based on the dual mechanism ($k_\Delta+k_s$) of solvolysis of β-arylalkyl system,[6] the inverted acetate should be produced by k_s pathway without any scrambling, unless the starting material has first undergone the k_Δ ionization at first and subsequently internal return to give a scrambled substrate. The DMA solvolysis of **1c** has already turned out to have no k_Δ process but 100% k_s pathway as is shown in Fig. 1 and mentioned above. Therefore, the scrambling of the isotope in the inverted acetate **11** can not be compatible with the previously proposed k_s process without the scrambling.[6]

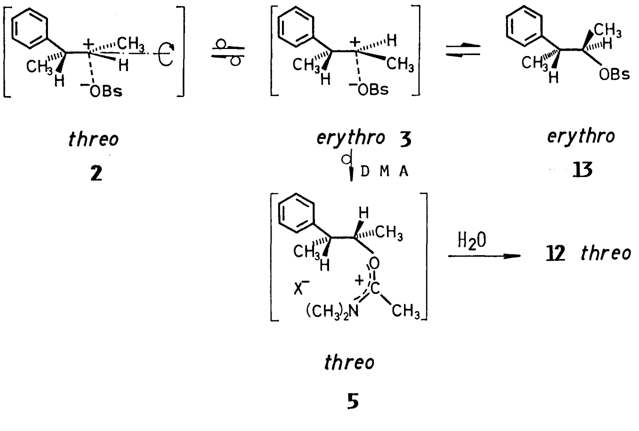
The extent of rearrangement of the DMA solvolysis and the acetolysis was calculated from the data in Table 3 and Scheme 2, to be 22% and 47%, respectively. Thus, DMA solvent much more suppresses the rearrangement accompanied the solvolytic reaction of the brosylate **1c**-2-*d* than does acetic acid as solvent. For the formation of 2-phenyl-1-butene **9**-3-H_2 (Table 3), 3,1-hydride shift and the subsequent deuteron elimination is conceivable (Scheme 5).



Scheme 5.

Possible Double Inversion Course for the Formation of Retained Acetate 12. As is shown in Table 4, it was revealed that *threo* brosylate **1c** rearranges to *erythro* brosylate (**13**) to a substantial extent (5.9%) during the half-life solvolysis of **1c** in DMA solvent. Furthermore, when the similar analysis has been conducted for the solvolysis in the presence of two-fold excess of pyridinium brosylate, the essentially same result was obtained (Table 4), indicating that the *threo*-*erythro* interconversion is caused intramolecularly by the rotation of C(1)–C(2) bond at the stage of the tight ion-pair intermediate **2** (Scheme 6). Such crossover by an internal rotation in the tight ion-pair has also been suggested by Cram and Knight[27] and by Collins *et al.*[28]

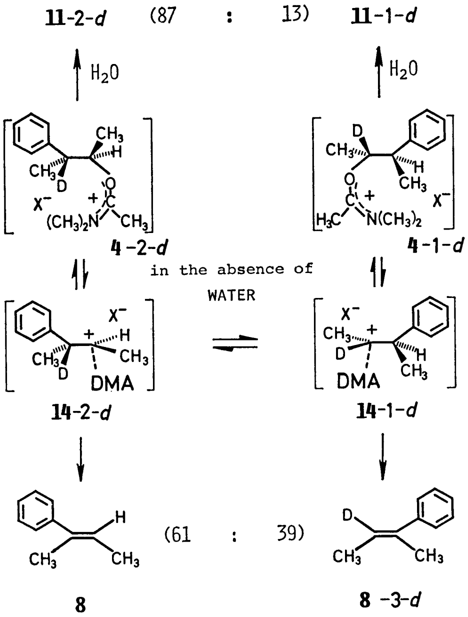
On the basis of Scheme 6, it is deduced that the formation of the retained acetate **12** in the DMA solvolysis of **1c** should be ascribed, at least partly,



Scheme 6.

to the double inversion course; *erythro*-type ion-pair intermediate (**3**) should intervene between *threo*-type ion pair intermediate **2** and *threo*-type imidatonium ion **5** (Scheme 3).

*The Formation of (*E*)-Olefin 8 from* [erythro-*R-DMA*]$^+$-*OBs*$^-$. As mentioned in the foregoing section (Scheme 4), in completely dried DMA, [*erythro*-R-DMA]$^+$OBs$^-$ **4** undergoes *anti*-elimination to give the (*E*)-olefin **8**. The yield of the (*E*)-olefin **8** (8.6% in the wet solvolysis (Table 3)) was increased to 26.7% in the dry solvolysis (Table 3), whereas *erythro*-acetate **11** was reduced from 21% to trace amount under dried conditions. The amounts of the (*E*)-olefin **8** arising from [*erythro*-R-DMA]$^+$OBs$^-$ **4**, therefore, can be calculated to be 18.1%(=26.7−8.6%). If [*erythro*-R-DMA]$^+$OBs$^-$ **4** undergoes *anti*-elimination keeping the same isotopic distribution as that in the *erythro*-acetate **11** (Table 3), the deuterium content at C(3) position of (*E*)-olefin **8** produced can be estimated to be about 20%.[29] However, as is indicated in Table 3, it actually amounts to 38%. This result suggests that [*erythro*-R-DMA]$^+$OBs$^-$ **4** must undergo further 2,1-phenyl shift before it is transformed to (*E*)-olefin **8**. The following scheme can be drawn to account for the situation (Scheme 7), and this scheme appears to be essentially the same as that proposed previously to explain the observed chemical behavior of imidatonium ion derived from *exo*-2-norbornyl cation.[30]



Scheme 7.

Nature of the k_s Pathway. Brown and Kim[5e] have made a detailed comparison of the characteristics of the k_s pathway in secondary *β*-arylalkyl solvolysis with the corresponding characteristics of primary *β*-arylalkyl solvolysis in terms of ΔS^*, secondary isotope effect, *ρ*-value, lyate ion effect, or hydride shift. They have noted on the basis of these features that no evidence for strong nucleophilic solvent participation in the secondary k_s process could be detected and these were considered to lend support to an S_N1 mechanism. The present findings as regards ΔS^* value (Table 1), *ρ*-value (Fig. 1), the cocurrences of 2,1-hydride as well as 2,1-phenyl shift and of intramolecular *threo-erythro* interconversion of the brosylate **1c** (Table 4), or no effect of added pyridine on the rate (*vide supra*), are in line with the implications pointed out by Brown and Kim.[5e]

An additional mechanistic aspect could be drawn on closer inspection of the data for the kinetic isotope effects (Table 5) and the product distributions (Tables 2 and 3), as in the following. First, the olefins arising from the process involving 2,1-hydride shift are not in large amount (Tables 2 and 3), probably suggesting that the relatively large *β*-deuterium isotope effect for the DMA solvolysis of **1c** (Table 5) can not be ascribed to hydrogen participation.[23,24] Secondly, although the olefins arising from *anti*-elimination is predominant, its yield is not sufficiently reduced by C(2)-deuteration, clearly indicating that the intervention of *E*2 process can be eliminated from the present reaction: the yield of (*Z*)-olefin **7** is 64.7% for **1c** and is 54.6% for **1c**-2-*d* (Tables 2 and 3). Thus the isotope effect for the DMA solvolysis of **1c** should be predominently associated with a specific transition-state structure of the reaction. Thirdly, when the isotope effects for the solvolysis of **1c**-2-*d* in the four carboxamide solvents (NMF, NMA, DMF, and DMA) are compared with the yields of (*Z*)-olefin **7** in the corresponding reactions (Table 6), the larger isotope effect is accompanied with the increased yield of the (*Z*)-olefin **7**. This may indicate that the magnitude of kinetic isotope effect for the carboxamide solvolysis of **1c** could be correlated to the degree of hyperconjugative stabilization[14,22] of the transition state with antiperiplanar conformation, from which (*Z*)-2-phenyl-2-butene **7** is formed. The larger isotope effect probably means the more stabilization of antiperiplanar transition state which, in turn, results in the more (*Z*)-olefin **7**.

As regards the relatively high *β*-deuterium isotope effect in the acetolysis of *cis*-2-phenylcyclopentyl tosylate (Table 5), Kim and Brown[22] have recently suggested that it may be the result of the combined effects of hyperconjugative destabilization of the transition state, leading to tight ion-pair intermediate, and of destabilization of the subsequent transition state, leading to tertiary benzylic cation, by the difficulty

TABLE 6. COMPARISON BETWEEN KINETIC ISOTOPE EFFECT AND AMOUNT OF *anti*-ELIMINATION PRODUCT FOR THE CARBOXAMIDE SOLVOLYSES OF **1c**-2-*d* AT 75 °C

Amide	$k_H/k_{\beta-D}$ [a]	Yield % of (*Z*)-olefin **7**[b]
DMA	1.93±0.01	54.9
DMF	1.67±0.01	43.5
NMA	1.63±0.02	43.0
NMF	1.41±0.01	35.5

a) The k_H values for DMF, NMA, and NMF solvolyses were 4.79, 18.1, and 38.5 (10^{-5} s^{-1}), respectively; for the DMA solvolysis, see Table 1. b) Data for the labeled substrate.

of loosening a C–D bond compared to a C–H bond.

In conclusion, all the results presented above can be explained by the mechanism involving the tight ion-pair intermediate **2** which undergores intramolecular processes, such as *anti*-*E*1 reaction, phenyl or hydride shift, and *threo-erythro* interconversion, competitively with the solvent capture leading to the imidatonium ion **4**. These rearrangements require that the site of the carbonium center opposite to the leaving group should not be shielded by solvent molecule at the stage of the tight ion-pair intermediate **2**, and this, in turn, suggests that the reaction may proceed without any kinetically significant involvement of nucleophilic solvent assistence.[6h]

Experimental

Melting points determined on a Yamato Model MP-1 apparatus were uncorrected. NMR spectra were recorded in $CDCl_3$ at 60 MHz on a Hitachi R-24 spectrometer or at 100 MHz on a JEOL JNM-MH 100 or JEOL JNM-FX 100 instrument. Infrared spectra were taken on a Hitachi EPI-S2 spectrometer. Both analytical and preparative GLC's were performed on a Hitachi K-53 gas chromatograph equipped with a thermal conductivity detector. The following columns were used: A, 3 m×3 mm 5% Benton 34+5% DIDP on 60—80 mesh Neopak 1A; B, 3 m×3 mm 10% PEG 6000 on 60—80 mesh Chromosorb W (NAW). Silicic acid powder (Wakogel C-200) was employed for column chromatography. For the alumina column, Merck neutral alumina (activity 1) was used.

Materials and Solvents. *N*,*N*-Dimethylacetamide (DMA) of commercial grade was purified in the same manner as described in the previous paper.[1] $NaBD_4$ (97.0 D-atom %) was supplied from CEA. Ether, diglyme, THF, and pentane used for reaction medium or recrystallization were distilled over sodium–benzophenone ketyl before use. Boron trifluoride etherate was distilled over CaH_2. Pyridine was distilled over BaO. All other solvents and reagents were of reagent grade and liquid materials were distilled before use.

*(*E*)-2-Aryl-2-butenes.* These olefins were prepared in the same manner as reported by Brown and Kim.[5e] Treatment of 2-butanone with arylmagnesium bromide (except for *p*-nitrophenyl derivative) gave 2-aryl-2-butanol which was dehydrated to a mixture of (*Z*)- and (*E*)-2-aryl-2-butenes and 2-aryl-1-butene according to the procedure of Garbisch[31] except for *p*-methoxyphenyl derivative for which dehydration was carried out by the use of $POCl_3$–pyridine mixture (0 °C—room temp, 24 h). The olefin mixture was subjected to fractional distillation by the use of a spinning band column and fractions containing gas chromatographically pure (*E*)-2-aryl-2-butene component were collected.

threo-*3-Aryl-2-butanols.* Various *threo*-3-aryl-2-butanols were prepared from corresponding (*E*)-2-aryl-2-butenes by hydroboration-oxidation reaction following the reported method.[5e]

threo-*2-Aryl-1-methylpropyl Brosylates.* These substrates were synthesized from the corresponding alcohols in the usual manner.[32] The melting points of the various brosylates were 100—101 (**1a**), 97—98 (**1b**), 94—95 (**1c**), 91—93 (**1d**), 69.5—71.5 (**1e**), and 50—51 °C (**1f**) (lit, 97.5—98.5 (**1a**),[33] 97—98 (**1b**),[5e] 93—93 (**1c**),[3] 94—95 (**1c**),[5e] 68.5—69.5 (**1d**),[5e,34] 91.5—92.5 (**1e**),[5e,34] and 50—51 °C (**1f**)[5e]).

threo-*3-(*p*-Nitrophenyl)-2-butanol and Its Brosylate.* *threo*-3-(*p*-Nitrophenyl)-2-butanol was prepared from the parent phenyl derivative similarly to the method reported for the preparation of *cis*-2-(*p*-nitrophenyl)cyclopentanol;[22] *threo*-3-Phenyl-2-butanol (3.1 g, 20.6 mmo) was treated with acetic anhydride (24 cm^3) and pyridine (48 cm^3) at room temp overnight. Workup gave acetate in 95% yield. The acetate was dissolved in a mixture of acetic acid (7 cm^3) and acetic anhydride (10 cm^3) and the resulting solution was cooled to 0 °C. To the solution was added a solution of 90% nitric acid (2 cm^3) in acetic acid (5 cm^3) under stirring at 0 °C and the mixture was stirred for 2 h at 0 °C and overnight at room temp. The mixture was poured on ice–water (100 cm^3) and extracted several times with ether. The ether solutions were washed successively with 10% K_2CO_3 and water, and dried (Na_2SO_4). Evaporation of the ether gave *threo*-1-methyl-2-(*p*-nitrophenyl)propyl acetate in 70% yield (3.3 g). The acetate was dissolved in methanol containing 0.5 mol/dm^3 HCl (43 cm^3) and the resulting solution was heated under reflux for 8 h. After workup, *threo*-3-(*p*-nitrophenyl)-2-butanol was distilled to afford practically pure sample (2.7 g, 98% yield).

The brosylate **1g** was synthesized from this alcohol in the usual manner.[32] **1g**: mp 104—105 °C; NMR (60 MHz) δ=1.25 (d, 3H, CH_3), 1.32 (d, 3H, CH_3), 3.0 (quintet, 1H, C(2)-H), 4.74 (quintet, 1H, C(1)-H), 7.4 (d, 2H, Ar-H), 7.5 (s, 4H, Ar-H), and 8.0 ppm (d, 2H, Ar-H); IR (KBr); 1520 (NO_2), 1350 (SO_2), 1185, and 1170 cm^{-1} (SO_2).

Found: C, 46.50; H, 3.71%. Calcd for $C_{16}H_{16}O_5NSBr$: C, 46.39; H, 3.89%.

threo-*3-Phenyl-2-butan-3-d-2-ol and Its Brosylate* **1c**-*2*-d. Deuterium at C(2) position was introduced by deuterioboration of (*E*)-2-phenyl-2-butene. Deuterioboration–oxidation was carried out according to the standard procedure.[35] Diborane-d_6 was generated externally from $NaBD_4$ and borontrifluoride etherate in diglyme and was supplied into THF solution of the olefin. After workup, the labeled alcohol was purified by column chromatography (alumina) to give pure alcohol in 90% yield.

Brosylate **1c**-2-*d* was prepared from this alcohol in the usual manner.[32] **1c**-2-*d*: mp 93—94 °C (lit,[5e] 93—94 °C for unlabeled sample). ^1H (100 MHz) and ^{13}C (25 MHz) NMR spectra of **1c**-2-*d* indicated an isotopic purity of 97% and the absence of deuterium scrambling throughout its synthesis.

Product Analysis. A reaction mixture for product study was prepared by the same method as described in the previous paper:[1] [ROBs]=0.075 mol/dm^3; [C_5H_5N]=0.077 mol/dm^3 (in an ampoule). The sealed ampoule was then kept at desired temperature for ten half-lives. The contents of the ampoule were poured on ice-water and extracted with pentane–ether mixture. The pentane–ether solution was washed several times with water, dried ($MgSO_4$), and condensed to 1—2 cm^3 by the use of 30-cm distillation column packed with glass helices. The condensed solution was subjected to GLC on column A. An excellent separation was effected on the column for all the products except for (*Z*)-2-phenyl-2-butene **7** and 3-phenyl-1-butene **10** which were identical in their retention times. The yields of (**7**+**10**), **8**, **9**, **11**, **12**, *erythro*-3-phenyl-2-butanol, and *threo*-3-phenyl-2-butanol were calculated from GLC's peak areas, calibrating based on molar response ratios. The mixture of (**7**+**10**) was isolated by means of preparative GLC and their composition was analyzed from the integral intensities of NMR (100 MHz in the Fourier transform mode) signals of methyl protons for the respective olefins **7** and **10**.

Partial Solvolysis and Isolation of Unchanged Brosylate. The brosylate recovered from half-life solvolysis of **1c** or **1c**-2-*d* in DMA solvent was isolated from the reaction mixture by repeated recrystallization at −50 °C (ether–pentane). Colorless crystalline brosylate was obtained easily in 98% yield based on the theoretical amount. The brosylate was kept under high vacuum (0.05 mmHg) at room temperature overnight. ^{1}H NMR spectrum (100 MHz) of the sample exhibited no sign of contamination with the solvolysis products.

Cleavage Reaction of the Recovered Brosylate with Sodium–Naphthalene.[36] A mixture of naphthalene (0.49 g, 3.67 mmol), sodium (0.088 g, 3.67 mmol) cut in small pieces, and THF (12.5 cm^3) was stirred at room temp for 2 h to result in a dark-green solution of sodium–naphthalene anion radical, and then, was cooled to −78 °C. To this solution was added the brosylate (0.226 g, 0.61 mmol), recovered from half-life solvolysis of **1c**-2-*d* in DMA solvent, in THF (3 cm^3) by the use of a syringe through a septum. Within a minute, a critical color changeocc urred (from dark green to reddish black). The excess of reagent was quenched by the addition of THF–water (1 : 1, 5 cm^3). Workup followed by column chromatography (silicic acid, 20 g) afforded a diastereomeric mixture of 3-phenyl-2-butanol in 80% yield: column was eluted successively with benzene and CH_2Cl_2, and the mixture was collected from the fractions eluted with CH_2Cl_2. The mixture was subjected to preparative GLC (column B) which provided *threo*- and *erythro*-3-phenyl-2-butanols without mutual contamination. Deuterium distribution in each alcohol was determined by means of ^{1}H NMR spectroscopy as described below.

Isotopic Distribution Analysis. The deuterium distribution analysis of the solvolysis products was carried out by means of ^{1}H NMR spectroscopy (100 MHz) in the Fourier transform mode. A sample for NMR assay was prepared under dry nitrogen in order to avoid contamination with moisture. The combined use of column chromatography and preparative GLC, and, in some cases, an appropriate chemical transformation, provided the compounds that meet the purpose of the determination of isotopic distribution.

Although the separation of the (*Z*)-olefin **7** and nonconjugated terminal olefin **10** could not be effected on GLC, all the NMR signals due to the both olefins **7** and **10** were advantageously well-resolved. The isotopic distribution in **7** and **10** was, therefore, determined from the NMR spectrum of the mixture which was isolated by means of preparative GLC. For the (*Z*)-olefin **7** a decrease in the integral intensity of the olefinic proton signal was measured. The partial labeling at C(3) position was easily verified by the observation that the C(4)-protons (methyl) gave clean doublet and singlet signals when C(1)-protons (methyl) were irradiated.

As for the 3-phenyl-1-butene **10**, integral intensities of the benzylic proton and internal vinylic proton were measured and a relative intensity of the respective signals to that of methyl protons was calculated. The methyl proton signal, consisted of doublet and triplet, and complicated multiplet of the terminal vinylic proton signals indicated that deuterium was situated at both C(2) and C(3) positions of the olefin **10**.

With regard to 2-phenyl-1-butene **9**, relative integral intensity of the methylene protons (C(3)) to that of methyl or olefinic protons was determined. The methyl signal consisted of "doublet of sharp triplets" and clean triplet. The former is considered to be due to the presence of adjoining –CHD– group to which the methyl protons are coupled and the latter undoubtedly indicates that the methyl protons are involved in spin-spin coupling with the adjoining $-CH_2-$ group. The integral intensity ratio for the olefinic proton *cis* to phenyl, that *trans* to phenyl, and the methyl protons was strictly 1 : 1 : 3. These findings clearly demonstrated that partial deuteron loss, though in small amount, actually occurred during the formation of the olefin **9**.

The deuterium content at C(3) position of the (*E*)-olefin **8** was determined similarly to that described above for the (*Z*)-olefin **7**.

The mixture of diastereomeric acetates **11** and **12** was isolated by column chromatography (silicic acid) and was hydrogenolyzed ($LiAlH_4$) into a mixture of *threo*- and *erythro*-3-phenyl-2-butanols from which each isomer was separated by preparative GLC. Deuterium distribution was determined by measuring the relative integral intensity between the C(2)–H and C(3)–H signals. The partial labeling at both positions was easily observed in splitting pattern of the two methyl signals.

The deuterium distribution in each isomer of the diastereomeric 3-phenyl-2-butanol obtained from the cleavage reaction of the recovered brosylate (*vide supra*) was also determined similarly to the method mentioned above.

The operating parameters employed in ^{1}H NMR spectroscopy in the Fourier transform mode were a spectral width of 1000 Hz, a 45° pulse, pulse repetition of 10 s, and an appropriate number of pulses to provide spectra with almost same S/N ratio for each sample. The integral intensity of each observed nuclei was directly computed on a JEOL 980B computer with SYSTEM Q/D PROGRAM FAFT08/11. The spectra of each unlabeled sample were recorded by the use of above-mentioned parameters and were used in order to calibrate the integral intensity obtained for each labeled sample.

Kinetic Measurements. The procedure was described in the previous paper.[1] In determining the kinetic isotope effect, simultaneous rate measurements of two compounds, the parent and C(2)-deuterated compounds **1c** and **1c**-2-*d*, were carried out. Three individual set of such determinations were conducted.

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