Solvolysis in Carboxamides. VI.[1] Kinetic, Product, and Deuterium Tracer Studies on the *N*,*N*-Dimethylacetamide Solvolysis of *threo*-2-(*p*-Methoxyphenyl)-1-methylpropyl Brosylate. Nature of the k_Δ Pathway

Seiki Saito,* Kenji Doihara, Toshio Moriwake, and Kunio Okamoto**

Department of Synthetics Chemistry, School of Engineering, Okayama University, Tsushima, Okayama 700

***Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606*

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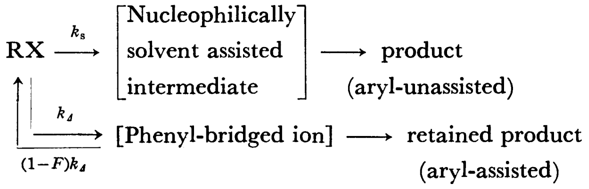
Solvolysis of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl brosylate (**1**) and its deuterium derivative (**1-2-*d***) has been carried out in *N*,*N*-dimethylacetamide (DMA) as solvent at 50.0 and 75.0 °C. Product examination revealed that in the presence of water (0.17 mol/dm^3) the main product is *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl acetate (73% at 50 °C), but in the absence of water (*Z*)-2-(*p*-methoxyphenyl)-2-butene (**5**) (*ca.* 70% at 50 °C). Both of these products are derived from a *threo*-imidatonium ion [*threo*-R-Amide]$^+$ which is produced by DMA capture of the tight ion-pair [R$^+$OBs$^-$] (**2**) from the front-side. A part (*ca.* 14% yield) of the (*Z*)-olefin **5** is directly led from the tight ion-pair **2**. The formation of the olefin **5** can not be explained by intervention of the phenyl-bridged ion. Although the rate of the brosylate **1** exhibits the k_Δ portion deviating upwards from the Hammett plot for a series of *threo*-2-aryl-1-methylpropyl brosylates, the Schleyer's k_Δ-k_s treatment for the rate-(retained)product correlation was unsatisfactory. The classical simple S_N1 mechanism can preferably elucidate the product distribution, including the isotope distribution, without intervention of the phenyl-bridged ion intermediate.

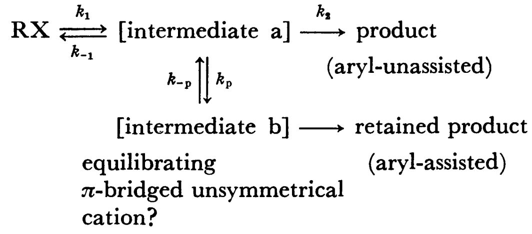
Neighboring β-aryl participation in solvolytic reaction has received considerable attention in recent years.[2] The parent phenyl derivative among a series of substituted 1-methyl-2-phenylpropyl system exhibited remarkable stereospecificity in acetolysis[3] but its rate was unexpectedly slow.[4] This apparent discrepancy has been a starting point of the controversy[2,5] with regard to the role of β-aryl groups and the existence of a phenyl-bridged intermediate in solvolytic reactions.

Schleyer and his collaborators[6] have recently suggested a dual-mechanism in that the solvolysis of β-arylalkyl systems proceeds through aryl-assisted (k_Δ) and/or aryl-unassisted (k_s) pathways; they have divided the observed rate constant (k_t) into discrete Fk_Δ and k_s components, and the Fk_Δ was estimated from the upward deviation from the normal line in Hammett correlation. They have also postulated that the k_Δ pathway prodeeds *via* a phenyl-bridged ion giving a retained product (Scheme 1[6h)]).



Scheme 1.

Although this dissection has been followed in 2-aryl-1-methylpropyl system by Brown and Kim,[7a)] these investigators have proposed another mechanism which postulates prior formation of a tight ion-pair followed by subsequent k_p and k_2 pathways,[7a,b)] which are respectively designated as aryl-assisted and aryl-unassisted pathways (Scheme 2[7a)]). In addition, there still remains an original controversy as regards intervention of the phenyl-bridged ion in the k_Δ pathway.[7b)]



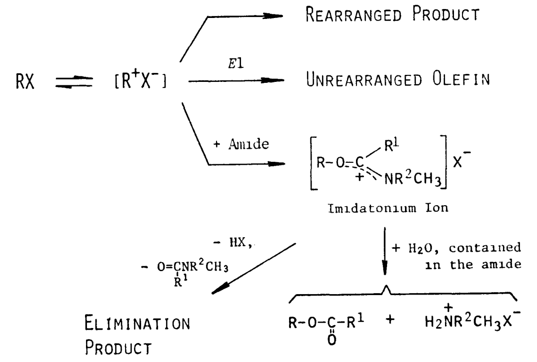
Scheme 2.

In connection with our previous studies,[1,8–11)] which disclosed several characteristics of carboxamide solvolysis, it was tempting to speculate that carboxamide solvolysis serves as a probe to scrutinize the reaction scheme (dual[6h)] or single[7a)]) and to examine the nature of so-called k_Δ pathway, especially as regards the intervention of the phenyl-bridged ion.

In the previous trial[1)] of dissection of the observed rate (k_t) of *N*,*N*-dimethylacetamide (hereafter DMA) solvolysis into k_s and k_Δ components, it has been disclosed that the solvolysis of *threo*-1-methyl-2-phenylpropyl brosylate proceeds by complete (100%) k_s pathway, but the methoxy derivative, *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl brosylate (**1**), predominantly reacts by the k_Δ route. As a model reaction to scrutinize k_Δ process the DMA solvolysis of the methoxyl derivative **1** was selected.

Results and Discussion

Product Distribution in the Presence of Water. In a series of our previous investigation for typical secondary cycloalkyl systems (4-*t*-butylcyclohexyl,[8)] 7β-methylbicyclo[3.3.1]non-3β-yl,[9)] and *exo*-2-norbornyl[11)] systems), it has been revealed that the carboxamide solvolysis proceeds through an intermediate, characterized as a tight ion-pair [R$^+$X$^-$] (classical), and subsequently the intermediate undergoes a variety of processes such as *E*1 deprotonation, solvent capture (formation of an imidatonium ion), and rearrangements (Scheme 3).



Scheme 3.

The unstable imidatonium ion, which otherwise decomposes to give elimination products, can be readily trapped by water to yield the carboxylic ester (Scheme 3); the efficient trapping with sufficient amounts of water has been successfully utilized in the previous works[1,9,11] to estimate the amount of the imidatonium ion and also to investigate the stereochemistry of its formation from the tight ion-pair.

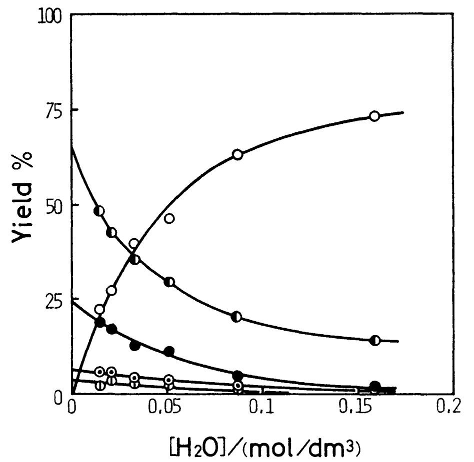
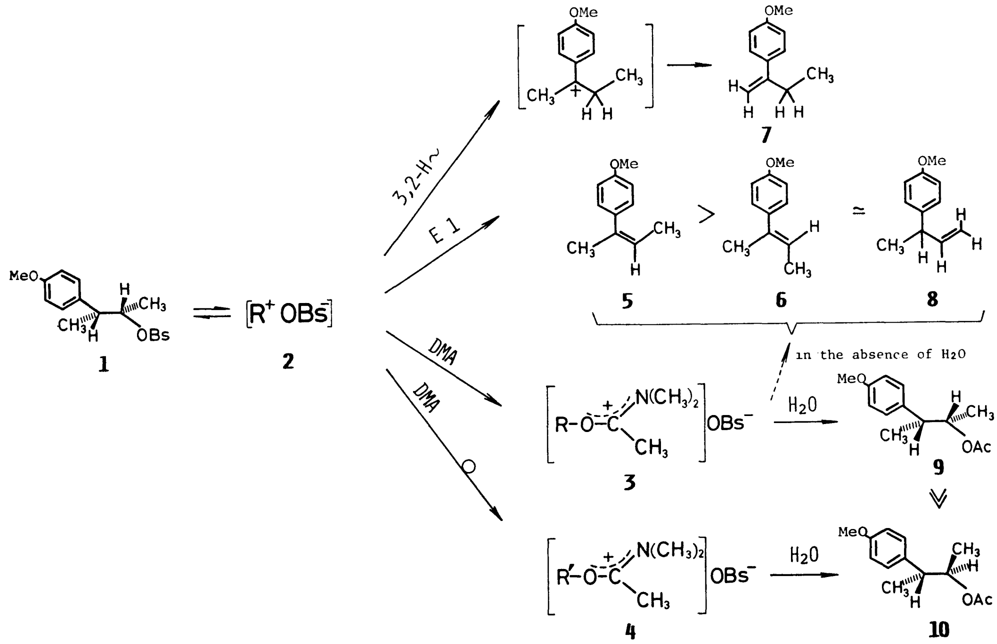


Fig. 1. Effect of water content of DMA on the formations of (*Z*) olefin **5** (◐), (*E*)-olefin **6** (●), 2-(p-MeOC$_6$H$_4$)-1-butene **7** (◉), 3-(p-MeOC$_6$H$_4$)-1-butene **8** (⦶), and *threo*-acetate **9** (○), at 50 °C.

Table 1. Effect of added water on product distribution for the DMA solvolysis of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl brosylate **1**[a)]

T/°C	[H$_2$O]/mol/dm^3	Yield/% Olefin **5**	Olefin **6**	Olefin **7**	Olefin **8**	Ester **9**	Ester **10**	Alcohol **11**	Alcohol **12**
50	0.015	48.2	18.4	5.7	1.9	22.1	2.1	1.5	0.1
	0.021	42.5	17.0	5.8	3.4	27.1	2.4	1.7	0.1
	0.033	35.0	12.6	4.1	2.7	39.9	3.7	1.8	0.2
	0.051	29.5	11.2	3.8	2.3	46.2	3.7	3.1	0.2
	0.087	20.0	4.9	2.0	1.5	63.2	3.5	4.6	0.3
	0.159	14.4	2.2	1.0	0.6	73.1	3.1	5.3	0.3
75	0.170	17.1	5.2	5.1	2.3	60.1	2.6	7.3	0.3

a) [**1**]=0.075 mol/dm^3; [C$_5$H$_5$N]=0.077 mol/dm^3.



Scheme 4.

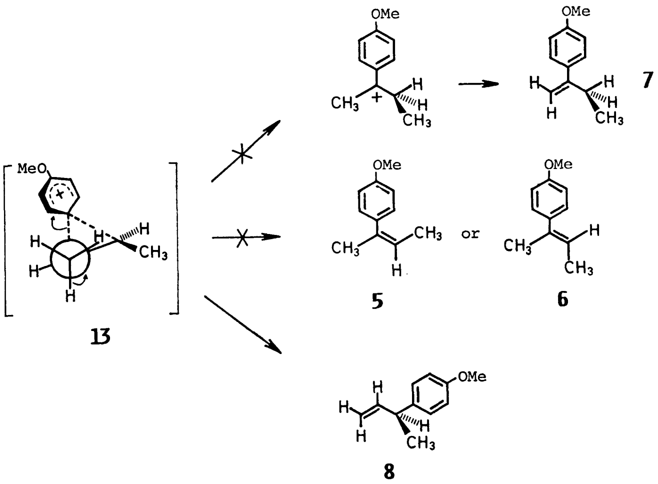
Thus the product distribution was determined in the presence of water, sufficient (0.16—0.17 mol/dm^3) to trap the imidatonium ion at 50.0 and 75.0 °C. The results are summarized in Table 1 and illustrated in Fig. 1 and Scheme 4.

The retained acetate, *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl acetate (**9**), was a major product (60% at 75 °C; 73% at 50 °C), indicating that the most of the tight ion-pair (**2**) is captured by DMA from the retentive site to give a *threo*-imidatonium ion [*threo*-R-Amide]$^+$ (**3**). The rest of the tight ion-pair **2** undergoes 2,1-hydride shift and elimination. It is clear from attenuation of increase in the *threo*-acetate yield (Fig. 1) that 0.16—0.17 mol/dm^3 of water is almost sufficient to convert all imidatonium ion to the acetate.

As another retained product *threo*-3-(*p*-methoxyphenyl)-2-butanol (**11**) was obtained, though in a small amount (7% yield at 75 °C), indicating that the hydrolysis of the *threo*-brosylate **1** also proceeds with predominant retention of configuration (*cf*. the *erythro*-alcohol (**12**) in Table 1).

As regards these retentive pathways, it has been reported that in the acetolysis of various *threo*-2-aryl-1-methylpropyl brosylates the amount of retained product, *i.e.*, the *threo*-acetates, agrees well with the predicted value which was calculated by 100 (Fk_Δ/k_t) provided that the k_Δ pathway leads solely to the retained acetate.[7a)] Furthermore, as shown in a recent tabulation of the rate-(retained)product correlations for β-arylalkyl systems,[12)] satisfactory rate-(retained)product correlation has been observed for acetolysis of many other primary and secondary β-arylalkyl substances.

Therefore, the predominant formation of the retained product might predict a satisfactory rate-(retained)-product correlation in DMA solvolysis. However, the observed amounts of the retentive products (7%+60%, at 75 °C, Table 1) does not agree with the one (83%) calculated by $100(Fk_\Delta/k_t)$ from the Fk_Δ and k_t in the previous work.[1)] This discrepancy implies existence of a mechanism different from the acetolysis and also a need to consider about a reaction pathway which affords the retained product without intervention of a phenyl-bridged ion.



Scheme 5.

Besides the retained substitution products, **9** and **11**, (*Z*)-2-(*p*-methoxyphenyl)-2-butene (**5**), albeit in low yield (17% at 75 °C; 14% at 50 °C), was obtained. This olefin must be derived by *anti*-elimination from the tight ion-pair **2**, competing with DMA capture. Direct formation of the olefin **5** by the *E*2 reaction is less probable in view of the low basicity of DMA. When this olefin is derived from the tight ion-pair **2**, the ion-pair can not have a phenyl-bridged structure, because it has been suggested that the formation of the conjugated olefin such as **5** may be forbidden from the bridged ion **13**, because of the rigid and unfavorable dihedral angle (120°) between the C(1) and C(2) hydrogen and the departing aryl ring (Scheme 5).[13)]

Another minor product, (*E*)-2-(*p*-methoxyphenyl)-2-butene (**6**), can not be derived from the bridged ion **13** either for the same reason (Scheme 5).

A terminal olefin, 2-(*p*-methoxyphenyl)-1-butene (**7**), which must be derived *via* 1-(*p*-methoxyphenyl)-1-methylpropyl cation, a 2,1-hydride shift product, can not obviously be led from the bridged ion **13** (Scheme 5).

The sole olefin, which can be derived from the phenyl-bridged ion **13**, is 3-(*p*-methoxyphenyl)-1-butene (**8**) (Scheme 5). This is actually found in the products, but is in very minor amount (less than 2%).

From these results it is concluded that the tight ion-pair can not be a phenyl-bridged ion, although it affords the retained imidatonium ion **3** and also the

TABLE 2. ISOTOPIC SCRAMBLING OF THE PRODUCTS FOR THE DMA SOLVOLYSIS OF *threo*-2-(*p*-METHOXYPHENYL)-1-METHYLPROPYL-2-*d* BROSYLATE **1**-2-*d*[a)]

Product		Yield/% (Composition/%)[b)] 50 °C	75 °C
Butene:			
(*Z*)-2-(p-$CH_3OC_6H_4$)-2-		12.0	16.0
(3-H: 3-D)	**5**	(52: 48)	(65: 35)
(*E*)-2-(p-$CH_3OC_6H_4$)-2-		1.8	3.7
(3-H: 3-D)	**6**	(57: 43)	(76: 24)
2-(p-$CH_3OC_6H_4$)-1-		0.6	2.4
(3-D,H: 3-H)	**7**	(90: 10)	(62: 38)
3-(p-$CH_3OC_6H_4$)-1-		0.8	3.2
(3-D: 2-D)	**8**	(50: 50)	(50: 50)
Acetate:			
threo-2-(p-$CH_3OC_6H_4$)-1-methyl-		75.8	60.2
propyl (2-D: 1-D)	**9**	(50: 50)	(50: 50)
erythro-2-(p-$CH_3OC_6H_4$)-1-methyl-		3.2	3.5
propyl (2-D: 1-D)	**10**	(49: 51)	(51: 49)
Alcohol:			
threo-3-(p-$CH_3OC_6H_4$)-2-butanol		5.3[c)]	10.3
(3-D: 2-D)	**11**		(54: 46)
erythro-3-(p-$CH_3OC_6H_4$)-2-butanol		0.5[c)]	0.7
(3-D: 2-D)	**12**		(58: 42)

a) [**1**-2-*d*]=0.075 mol/dm^3; [C_5H_5N]=0.077 mol/dm^3; [H_2O]=0.17 mol/dm^3. b) The accuracy for NMR measurement of isotopic content was $\leq$1%; reproducibility=±3%. c) Precise determination of an isotopic distribution was not made: the label would be scrambled more extensively than in the case at 75 °C, in view of the trend found in the other products **5**, **6**, **7**, and **8** at 50 and 75 °C.

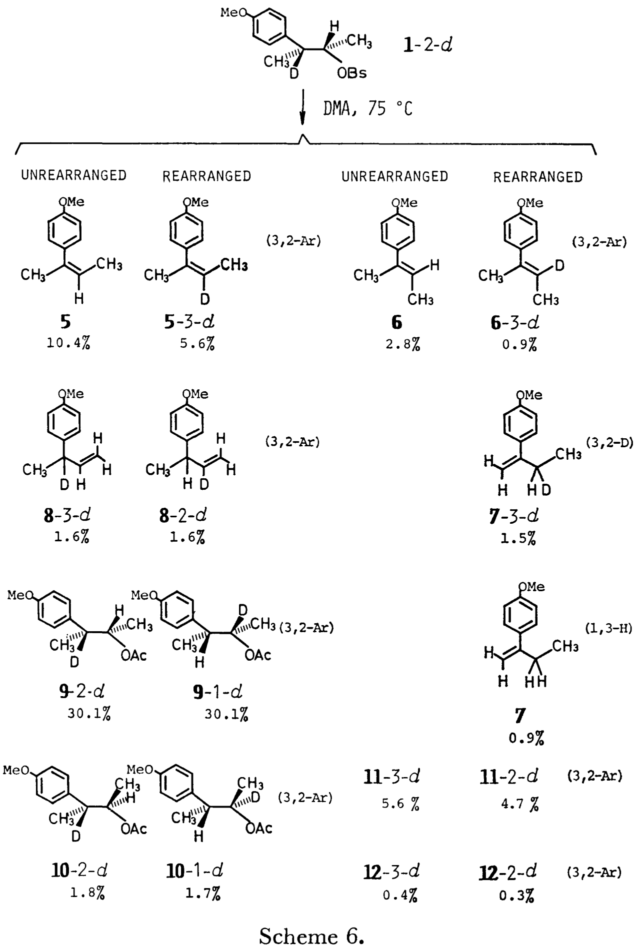
retained alcohol **11**. Possible and the simplest reaction pathways for the formation of these olefins can be depicted as illustrated in Scheme 4 along with those for the imidatonium ion formation and its water trapping pathway.

Product Distribution in the Absence of Water. From variation in the yield at 50 °C (Fig. 1), caused by change in water concentration in DMA, it is indicated that in completely dried DMA the olefins are sole products and among them (*Z*)-2-(*p*-methoxyphenyl)-2-butene (**5**) is a major product (65% yield) along with minor amounts of olefins **6**, **7**, and **8**. Thus it is clear that the imidatonium ion **3**, which gave the retained acetate **9** in the presence of water, can afford mainly the 2-butenes (Saytzeff products) as the final product in the absence of water.

As mentioned above, in the presence of water (0.16 mol/dm^3) the small amounts (3.8% in composite yield) of olefins **6**, **7**, and **8** were produced besides the olefin **5**. However, in the absence of water a fair amounts (*ca.* 30% in composite yield) of these olefins have been obtained. Consequently, most of these olefins (30%—3.8%=26.2% in composite yield) must have come from the imidatonium ion **3** (Fig. 1).

The (*Z*)-olefin **5** was produced in 14% yield from the tight ion-pair **2** in the presence of water (Table 1), but in the absence of water it should be led also from the imidatonium ion **3** in about 51% (*ca.* 65%—14%) yield.

Among these olefins only **8** (*ca.* 3% yield) can be derived from the phenyl-bridged ion. Therefore in the course of the olefin formation from the *threo*-imidatonium ion **3** a possibility of intervention of the phenyl-bridged ion is mostly ruled out.



Scheme 6.

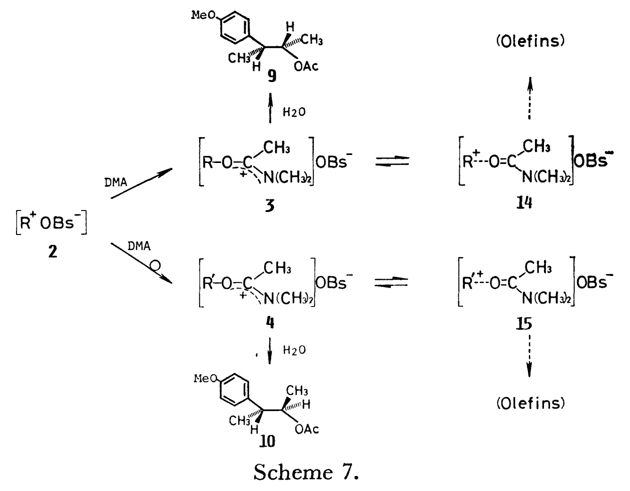
Deuterium Distribution in the Products. In order to examine the reaction pathways thoroughly, the deuterium scrambling in the products **5**—**12**, which were isolated from the wet DMA solvolysis mixture of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl-2-*d* brosylate (**1**-2-*d*), was examined by the use of previously reported ^{1}H NMR spectroscopic method.[1] The results are summarized in Table 2 and illustrated in Scheme 6.

The rearrangement in the product amounts to 50% (complete scrambling) for the acetates **9** and **10** (64% in composite yield), but for the elimination products (**5**, **6**, and **7**, except for **8**) and the hydrolysis products (**11** and **12**) it does not reach complete scrambling. The incomplete scrambling in the elimination and the hydrolysis clearly indicates that the tight ion-pair **2** does not have such symmetrical structure as a phenyl-bridged ion structure.

When the scrambling in the tight ion-pair **2** is so incomplete, the scrambling in the imidatonium ion **3** should also be incomplete, because the imidatonium ion is a primary product from the ion-pair **2** as illustrated in Scheme 4. This indicates in turn that the scrambling in the acetate **9** would not be complete. However, it is not the case.

Thus, the complete scrambling in the acetate **9** implies that it must occur in the process of the hydrolysis of the imidatonium ion **3**. Since the hydrolysis does not proceed on the carbenium ion center of the imidatonium ion **3** but on the carbonyl carbon, it seems difficult to find a reasonable explanation for the scrambling in the imidatonium-ion hydrolysis. However, as one of possible explanations, it might be helpful to consider about a hidden scrambling process during the hydrolysis as illustrated in Scheme 7.

Since in the absence of water the imidatonium ion **3** can give rise to the olefins, these olefins should be produced *via* a new ionized intermediate **14** (Scheme 7). This ionization process might be hidden in the presence of water, because the rate of hydrolysis might overwhelmingly exceed the elimination rate in spite of rapid equilibration between the imidatonium ion **3** and the



Scheme 7.

new ionized intermediate **14**. Conceivably, the hidden ionization would bring about the complete scrambling in the acetate **9**. As mentioned above, most of the olefins formed from the imidatonium ion **3** (in the absence of water) can not be derived from a phenyl-bridged ion. This indicates, consequently, that the intermediate **14** does not have the phenyl-bridged ion structure either.

Furthermore, it is notable that the inverted *erythro* acetate **10**, albeit in very low yield (3% at 50 °C and 2% at 75 °C), also undergoes complete scrabling of deuterium at C(2) and C(3) at 50 °C. The inverted acetate **10** can not be led from the *threo*-phenyl-bridged ion. Therefore, when we follow the reaction schemes shown in Scheme 1, it must be derived *via* k_s route[6h] starting from the *threo*-brosylate **1**. If it is derived *via* k_s route, complete scrambling in the *erythro* acetate **10** is possible only when the scrambling in the unchanged *threo*-brosylate **1-2-*d*** is complete at an early stage of the solvolysis. However, when unchanged brosylate was reclaimed at a half-life, only 30% of deuterium was found at C(2). Consequently, the formation of the *erythro*-acetate **10** *via* k_s route would be ruled out. The rear-side attack of DMA on the tight ion-pair **2** could explain the formation of completely scrambled *erythro*-acetate **10**, if we assume a rapid equilibration between **4** and **15** (Scheme 7). The cross-over between *threo* and *erythro* open carbenium ions in the tight ion-pair **2** or the intermediates **14** and **15** is conceivable, but it is not clear since in the reclaimed brosylate **1** scarecely was contained the *erythro* brosylate.

In conclusion, so far as the DMA solvolysis of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl brosylate is concerned, the intervention of the bridged ion is mostly improbable and the discrete k_Δ-k_s dual mechanism does not give a satisfactory explanation for the rate-(retained)product correlation but the usual S_N1 mechanism, *i.e.*, the prior formation of a tight ion-pair intermediate followed by various subsequent routes such as 2,1-aryl shift, 2,1-hydride shift, *anti*-elimination, and DMA capture, can account for the product and deuterium distributions. For elucidation of the excessive rate enhancement by methoxyphenyl or by the aryl participation, an examination of the linear free-energy relationship, especially reactivity-selectivity correlation, may served as a new probe and this is the subject of the succeeding paper.

Experimental

Melting points determined on a Yamato Model MP-1 apparatus were uncorrected. NMR spectra were recorded on either a Hitachi R-24, JEOL JNM-MH 100, or JEOL JNM-FX 100 instrument, and spectral data were obtained in $CDCl_3$ solution. Both analytical and preparative GLC's were conducted on a Hitachi K-53 gas chromatograph attached with a thermal conductivity detector by the use of helium as carrier gas. The following column was used: 3 m × 3 mm 10% PEG 6000 on 60—80 mesh Chromosorb W (NAW).

Materials. DMA was purified in the identical manner as described in the previous paper.[9] $NaBD_4$ (97.0 D-atom %) was supplied from CEA. Ether, THF, diglyme, and pentane, used as reaction medium or solvent for recrystallization, were distilled from sodium–benzophenone ketyl before use. Reagent grade chemicals were used without further purification unless otherwise noted.

threo-3-(p-Methoxyphenyl)-2-butanol-3-d and Its Brosylate ***1-2-d***.

Deuterium at C(3) position was introduced by deuterioboration of (*E*)-2-(*p*-methoxyphenyl)-2-butene prepared in the same manner as reported.[1] Deuterioboration–oxidation was carried out according to the published method.[14] Diborane-d_6 was generated externally from $NaBD_4$ and boron trifluoride etherate in diglyme and introduced into THF solution of the olefin. The deuterated alcohol was obtained in 83% yield after the purification by column chromatography (Al_2O_3). The brosylate **1-2-*d*** was synthesized from this alcohol in the usual manner[15] in 87% yield. **1-2-*d***: mp 100—101 °C (lit,[16] 97.5—98.5 °C for the unlabeled sample); NMR (100 MHz) δ=1.19 (3H, s, C(4)H_3). 1.30 (3H, d, C(1)H_3), 3.79 (3H, s, OCH_3), 4.70 (1H, quartet, C(2)H), 6.88 (4H, d of d, Ar–H), and 7.55 ppm (4H, s, Ar–H). ^{1}H and ^{13}C NMR spectra showed the absence of deuterium scrambling during the synthesis and an isotopic purity of 97%.

Product Analysis. The method employed was identical with that used in the preceding work.[1] Unlike the parent phenyl derivative, the acetates **9** and **10**, obtained from the DMA solvolysis of **1** or **1-2-*d***, could not be separated on GLC. Therefore, the ratio (**9**: **10**) was determined by means of GLC with the corresponding alcohols which was derived from the esters by hydrogenolysis with $LiAlH_4$ in ether: the ester mixture was isolated from the product mixture by column chromatography (SiO_2).

Partial Solvolysis and Isolation of Unchanged Brosylate. The brosylate recovered from half-life solvolysis of **1-2-*d*** in DMA solvent was isolated from the reaction mixture by repeated recrystallization from ether–pentane at −78 °C. Colorless crystalline brosylate was obtained almost quantitatively based on theoretical amount. The sample was dried by keeping under high vacuum over P_2O_5 at room temperature overnight. ^{1}H NMR spectrum (100 MHz) of the sample exhibited no sign of contamination with the solvolysis products and also of an existence of *erythro*-isomer.

Deuterium Distribution Analysis. The deuterium distribution was determined by means of ^{1}H NMR spectroscopy (100 MHz) in the Fourier transform mode. The operating parameters employed in NMR works were identical with those reported in the preceding paper.[1] Analytical procedures and sample preparations were performed in the same manner as described in the paper,[1] except for the sample of the acetate **9** or **10**.

The mixture of the acetates **9** and **10** was isolated by column chromatography (SiO_2) and was hydrogenolyzed ($LiAlH_4$ in ether) into the corresponding mixture of alcohols from which each isomer was separated by preparative GLC. Each isomeric alcohol was transformed again into the corresponding acetate **9** or **10** in the usual manner (acetic anhydride–pyridine) in order to avoid an overlapping of NMR signals due to *O*-methyl and C(1)–H protons.

Kinetic Measurements. All kinetic runs were carried out in the same way as described in the previous papers.[1,11]

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