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Solvolysis in Carboxamides. IV.9)
Solvolytic Elimination of *exo*-2-Norbornyl Arenesulfonates in Carboxamides. Kinetic, Product, and Deuterium Tracer Studies

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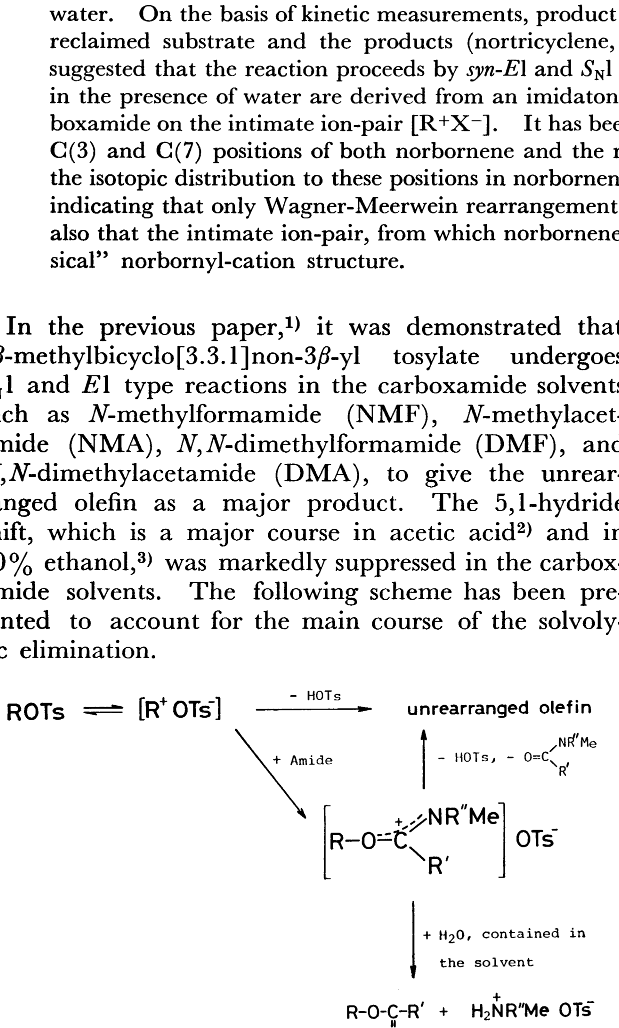
Solvolysis of *exo*-2-norbornyl arenesulfonates (RX: X=OTs (**1a**), $-OSO_2C_6H_4$-*p*-OCH_3, $-OSO_2C_6H_5$, and OBs) and the deuterium labeled tosylates (**1a**-3-*endo-d*, **1a**-3-*exo-d*, and **1a**-3,3-d_2) has been carried out in four carboxamides (*N*-methylformamide, *N*-methylacetamide, *N*,*N*-dimethylformamide, and *N*,*N*-dimethylacetamide (DMA) at 25—100 °C. The solvolysis has also been conducted in the solvents containing 0.01—0.2 mol/dm^3 water. On the basis of kinetic measurements, product analyses, and the examination of isotopic distribution in the reclaimed substrate and the products (nortricyclene, norbornene, and *exo*-norbornyl carboxylates) it has been suggested that the reaction proceeds by *syn-E*1 and S_N1 mechanisms, and that the carboxylates which are produced in the presence of water are derived from an imidatonium ion [R-Amide]$^+$, which is formed by the attack of carboxamide on the intimate ion-pair [R^+X^-]. It has been observed that the isotopic scrambling occurs only between C(3) and C(7) positions of both norbornene and the reclaimed **1a**-3-*endo-d* in DMA solvolysis at 75 °C, and that the isotopic distribution to these positions in norbornene is 57:43 at 10% completion and reaches 50:50 at half-life, indicating that only Wagner-Meerwein rearrangement is predominant in the course of norbornene formation, and also that the intimate ion-pair, from which norbornene is formed, is unsymmetrical and most probably with "classical" norbornyl-cation structure.

In the previous paper,1) it was demonstrated that 7*β*-methylbicyclo[3.3.1]non-3*β*-yl tosylate undergoes S_N1 and *E*1 type reactions in the carboxamide solvents such as *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N*,*N*-dimethylformamide (DMF), and *N*,*N*-dimethylacetamide (DMA), to give the unrearranged olefin as a major product. The 5,1-hydride shift, which is a major course in acetic acid2) and in 80% ethanol,3) was markedly suppressed in the carboxamide solvents. The following scheme has been presented to account for the main course of the solvolytic elimination.



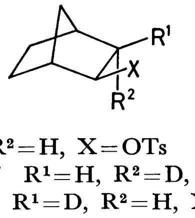
Scheme 1.

The predominant formation of the unrearranged olefin in the carboxamide solvolysis, as compared with other solvolyses,2,3) was reasonably ascribed to the acceleration of *syn-E*1 process by the leaving tosylate anion, because the basicity of the tosylate anion is expected to increase in such non-hydroxylic solvents owing to very weak hydrogen-bonding ability of these carboxamides.1)

Thus, one of the principal characteristics of the carboxamide solvolysis of secondary cycloalkyl tosylates is that the carboxamides suppress the formation of rearranged products even when the substrate has a structure prone to rearrangement. Therefore, it is of interest to explore the generality of this phenomenon by the use of the *exo*-2-norbornyl system, because the 2-norbornyl cation, generated both in solvolytic conditions4) and in stable ion conditions,5) easily undergoes three types of rearrangement, *i.e.*, Wagner-Meerwein, 6,2-hydride, and 3,2-hydride shifts.

These processes take place, however, to regenerate the identical structure with that of the starting ion (automerization6) or degenerated rearrangement7)). Consequently, we selected *exo*-2-norbornyl tosylate labeled at the 3-position (**1a**-3-*endo-d*, **1a**-3-*exo-d*, and **1a**-3,3-d_2) to follow automerization.

In this paper, we report on a) the rates and products of the solvolysis of several *exo*-2-norbornyl *p*-substituted arenesulfonates (**1a**—**d**) in NMF, NMA, DMF, and DMA, b) effects of added water on the product distributions, and c) deuterium distributions of the products in the solvolyses of the tosylate labeled at C(3). We also discuss the generality of the mechanism (Scheme 1) and the structural problem of the norbornyl ion intermediate, since it remains as a controversial problem



1a $R^1=R^2=H$, X=OTs
1a-3-*endo-d* $R^1=H$, $R^2=D$, X=OTs
1a-3-*exo-d* $R^1=D$, $R^2=H$, X=OTs
1a-3,3-d_2 $R^1=R^2=D$, X=OTs
1b $R^1=R^2=H$, X=*p*-MeO-$C_6H_4SO_3$
1c $R^1=R^2=H$, X=$C_6H_5SO_3$
1d $R^1=R^2=H$, X=OBs

TABLE 1. KINETIC DATA FOR THE SOLVOLYSIS OF *exo*-2-NORBORNYL TOSYLATE **1a** IN VARIOUS CARBOXAMIDES[a)]

	Amide			
	DMA	DMF	NMA	NMF
$k_1/(10^{-5}\ s^{-1})$:				
Temp/°C				
100	21.6±0.4			
75	1.99±0.01	7.34±0.10	83.1±0.5	
50		0.493±0.005	5.15±0.01	30.6±0.1
33.3				3.79±0.04
25[b)]	0.00494	0.0201	0.197	1.21
$\Delta H^*/(4.184\ kJ/mol)$:[c)]	24.1±0.3	23.7±0.2	24.3±0.1	24.1±0.2
$\Delta S^*/(4.184\ J/(K\ mol))$:[c)]	−11.1±0.7	−9.8±0.4	−3.0±0.2	−0.1±0.4

a) $[\mathbf{1a}]=0.075\ mol/dm^3$; $[C_5H_5N]=0.077\ mol/dm^3$; $[H_2O]=0.003$ (for DMA or DMF), 0.01 (for NMA), or 0.02−0.03 (for NMF) mol/dm^3. b) Extrapolated from data at other temperatures. c) At 25 °C.

and still is a basic problem of organic chemistry toward which active effort continues both experimentally and theoretically.[8)]

Results and Discussion

Solvolysis Rates of exo-*2-Norbornyl Arenesulfonates in Carboxamides.* The rates of solvolysis of **1a**—**d** in the carboxamides were determined titrimetrically by the use of the same method as described in the previous paper.[1)] A good first-order behavior was observed for all the kinetic runs over two to three half-lives. The results, along with the thermodynamic parameters, are tabulated in Table 1 for **1a** and in Table 2 for **1b**—**d**.

The following findings present unambiguous evidence which demonstrates that the solvolysis proceeds *via* a typical S_N1 or $E1$ mechanism. First, pyridine, added to neutralize the liberated arenesulfonic acids, did not alter the rates. Secondly, a satisfactory linear free-energy relationship was observed when log k_1 values of **1a** were plotted against those for 2-adamantyl tosylate in carboxamides[9)] and a number of other solvents (Fig. 1). Since 2-adamantyl tosylate has a mechanistic feature of S_N1 substrate,[10)] it is a suitable model substrate for the examination of the S_N1 character of other secondary substrates. The slope (0.864) of the least-squares line is larger than those (0.55—0.78)[11)] for other secondary systems. Furthermore, the magnitude (0.83)[12)] of the Grunwald-Winstein *m* value is also larger than those (0.4—0.7) for the solvolysis of usual secondary substrates[13)] and is comparable to that (0.87)[14)] for 2-adamantyl tosylate. Thirdly, at 5% completion of the solvolysis of **1a**-3-*endo-d* in DMA the recovered tosylate was incorporated with *exo*-2-norbornyl-7-*anti-d* tosylate (25%), which must be formed *via* an ionization and a subsequent return step (*vide infra*).

*Products of the Solvolysis of **1a**—**d** in the Carboxamides.* As expected from the Scheme 1, the products in the solvolysis of **1a**—**d** in the carboxamides were elimination products, nortricyclene and norbornene. If water is contained in the amides, the substitution products, *exo*- and *endo*-norbornyl carboxylates were found as the additional products (Scheme 2).

TABLE 2. PRODUCTS AND RATES FOR THE SOLVOLYSIS OF *exo*-2-NORBORNYL *p*-X-BENZENESULFONATES IN THE CARBOXAMIDES AT 75 °C[a)]

Amide	X	k_1 / $10^{-5}\ s^{-1}$	Yield/%[b)] 2	3	4[c)]	5[c)]
DMA	OCH_3	1.04	85.7	13.2	0.8	0.3
	CH_3	1.99	87.0	12.2	0.6	0.2
	H	4.78	89.5	10.0	0.3	0.2
	Br	31.2	91.6	7.5	0.6	0.3
DMF	OCH_3	4.73	86.6	9.5	3.0	0.9
	CH_3	7.34	89.1	7.8	2.1	1.0
	H	17.7	89.7	5.5	3.3	1.1
	Br	88.4[d)]	92.2	3.7	3.0	1.1
NMA	OCH_3	51.8	92.1	3.6	4.1	0.2
	CH_3	83.1[d)]	93.2	3.0	3.5	0.3
	H	203[d)]	92.8	1.9	4.4	0.2
	Br	378[d)]	92.0	1.4	6.2	0.4
NMF[e)]	OCH_3	237[d)]	94.3	1.7	3.9	0.1
	CH_3	499[d)]	91.3	1.1	7.3	0.3
	H	971[d)]	88.5	0.7	10.3	0.3
	Br	1830[d)]	90.4	0.4	9.0	0.2

a) $[ROSO_2C_6H_4\text{-}p\text{-}X]=0.075\ mol/dm^3$; $[C_5H_5N]=0.077\ mol/dm^3$; $[H_2O]=0.003$ (for DMA or DMF), 0.01 (for NMA), or 0.02—0.03 (for NMF) mol/dm^3. b) The averages of two or three determinations, with reproducibility of ±3%, relatively. c) Acetate for DMA and NMA, and formate for DMF and NMF. d) Extrapolated from data at other temperatures. e) The amounts of the substrates were three times as much as those for other amides.

The compositions of the products were determined by the use of GLC and ^1H NMR spectroscopy. The yield of a mixture of *exo*- and *endo*-norbornyl esters was assayed by means of GLC. The epimeric ratio was determined also by means of GLC analysis after conversion of the ester mixture to corresponding norbornanol mixture by lithium aluminum hydride. The

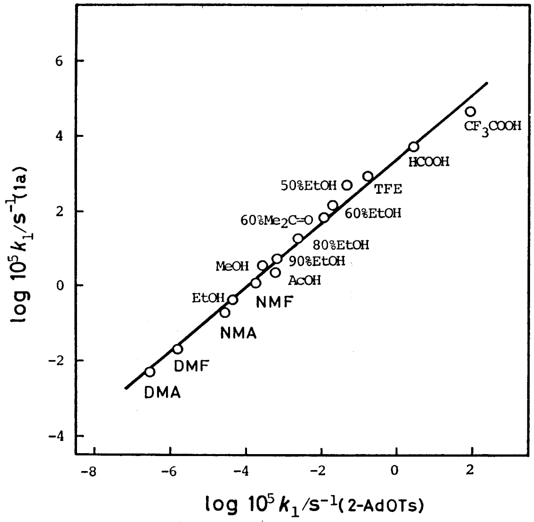
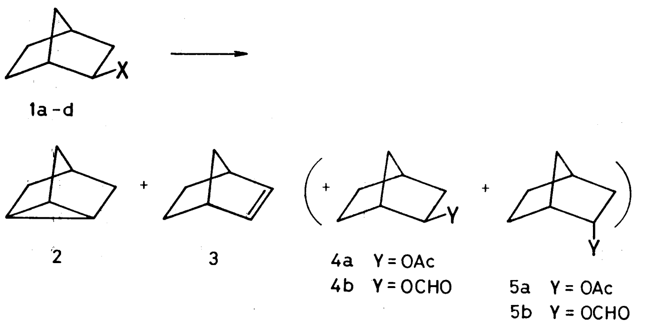


Fig. 1. A linear free-energy relationship between $\log k_1$(**1a**) and $\log k_1$(2-adamantyl tosylate) in various solvents at 25 °C: slope: 0.864, correlation coefficient: 0.994, and standard deviation: 0.22. For the rate constants of 2-adamantyl tosylate in representative solvents other than the amides, see (a) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976). (b) H. C. Brown, "The Nonclassical Ion Problem," Plenum Press, New York, N. Y. (1977), p. 193, and Ref. 10. For the rate constants of **1a** in representative solvents other than the amides, 90, 60, and 50% aqueous ethanols, and 60% aqueous acetone, see reference (b).



Scheme 2.

yield of norbornene was determined by measuring the integrated intensity of NMR signals of olefinic protons relative to that of the methyl protons of anisole (internal marker). The results of the product analysis are summarized in Table 2.

As illustrated in Scheme 1, the esters may be formed by the reaction of an imidatonium ion[15] with water, which is contained in the carboxamides. In this connection, the effect of water content on the product distribution was examined for the solvolysis of **1a** in DMA and in DMF in the presence of various amounts of water. The results are tabulated in Table 3 and illustrated in Figs. 2-1 and 2-2.

In completely dry DMA or DMF nortricyclene and norbornene were sole products, and there was no longer obtained any esters (Fig. 2), indicating that the esters are not a primary solvolysis product in DMA or in DMF.

TABLE 3. EFFECTS OF ADDED H_2O ON PRODUCT DISTRIBUTION FOR *exo*-2-NORBORNYL TOSYLATE **1a** IN DMA AND DMF AT 75 °C[a)]

Amide	$[H_2O]$ mol/dm^3	Yield/%[b)] **2**	**3**	**4**[d)]	**5**[d)]
DMA	0.0030[c)]	87.1	12.1	0.6	0.2
	0.0074	83.1	12.6	2.7	0.6
	0.0163	80.1	11.6	7.4	0.9
	0.0252	76.1	11.6	11.8	0.5
	0.0474	68.5	11.0	20.0	0.5
	0.0918	59.3	9.8	30.4	0.5
	0.120	55.3	9.9	34.3	0.5
	0.181	49.4	9.4	40.8	0.3
DMF	0.0030[c)]	89.2	7.7	2.1	1.0
	0.040	47.8	6.4	45.3	0.5
	0.077	28.8	4.7	66.2	0.3
	0.185	11.8	4.0	84.0	0.2

a) [**1a**]=0.075 mol/dm^3; $[C_5H_5N]$=0.077 mol/dm^3. b) Trace amounts of 2-norbornanol was detected on GLC (≤0.1%). c) Remaining water in the amides after purification. d) See footnote (c) in Table 2.

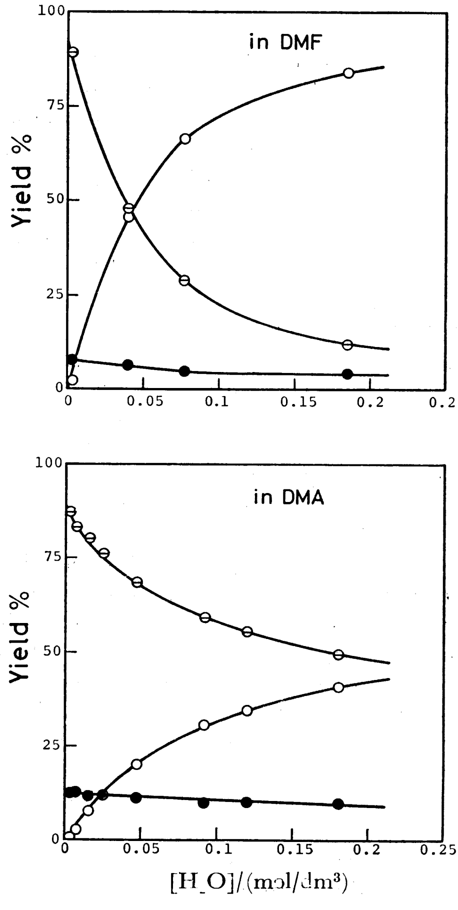
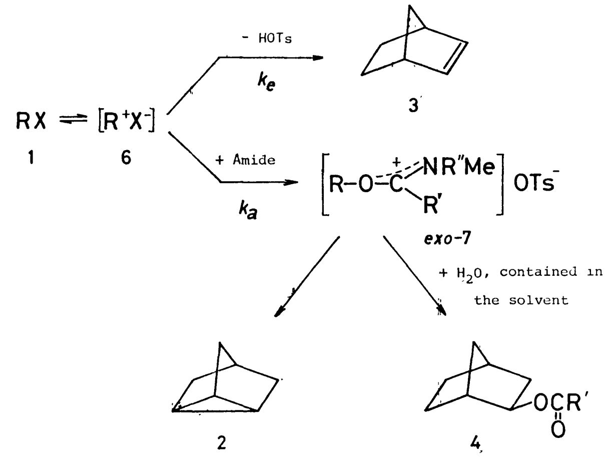


Fig. 2. Effect of water content of DMA(bottom) and of DMF(upper) on the formation of norbornene **3** (●), *exo*-ester **4** (○), and nortricyclene **2** (⊖).

The yield of norbornene was not much affected by the water content of DMA or of DMF (*vide infra*). The yield of nortricyclene, however, decreased with an increase in water content of DMA and of DMF, and the yield of *exo*-norbornyl acetate or formate increased complementing the decrease in the yield of nortricyclene (Figs. 2-1 and 2-2). Therefore, these results indicate that the direct products from the intimate ion-pair $[R^+X^-]$ are norbornene and an imidatonium ion $[R\text{-Amide}]^+$. The latter is so unstable that it would be rapidly converted to nortricyclene, otherwise it would be hydrolyzed by the water in the amide solvent; this is illustrated in Scheme 3.



Scheme 3.

When log k_1 values were plotted against the logarithms of the ratio (%**2**+%**4**): %**3**, a reactivity-selectivity linear relation[16] was observed; this linear relation was established for each carboxamide solvent (Fig. 3). This also indicates that norbornene and the imidatonium ion stem from a single intermediate, *i.e.*, an intimate ion-pair $[R^+X^-]$.

This mechanism is essentially the same as that depicted in Scheme 1 for the carboxamide solvolysis of bicyclo[3.3.1]nonyl system.

syn-*E1 Mechanism for the Formation of Norbornene.* The formation of norbornene depends on the nature of both the leaving group and the solvent. Thus, the norbornene yield increases in the order **1b** (MeO) > **1a** (Me) > **1c**(H) > **1d** (Br) in any carboxamide solvent (Table 2), the sequence fitting in with the order of the increase in the electron-releasing nature of the *para*-substituent in the respective leaving groups. Furthermore, the yield of norbornene also increased in the solvent sequence DMA>DMF>NMA>NMF for each substrate (Table 2), similarly to the order observed in the yield of unrearranged olefin in the case of bicyclo[3.3.1]nonyl system.[1]) This sequence may be explained in terms of the change in the basicity of the leaving group anion which is affected by the hydrogen-bonding ability (NMF>NMA>DMF>DMA)[1]) of the respective carboxamides. These trends in the yield of norbornene suggest that a *syn-E*1 reaction occurs in the norbornene forming step, and that the leaving group anion acts as a base.

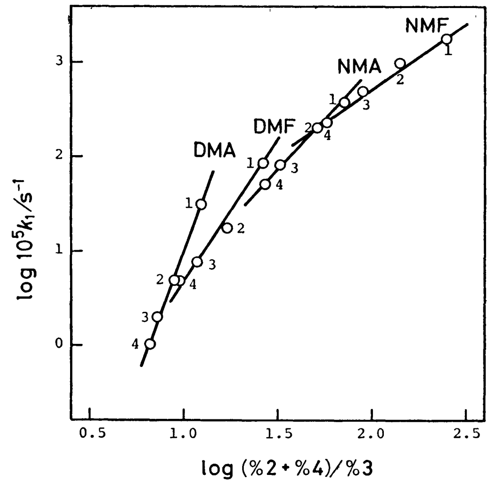
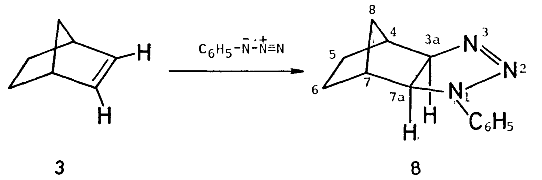


Fig. 3. Linear reactivity-selectivity relationships between log k_1 and log (%**2**+%**4**)/%**3** for the solvolysis of **1a**—**d** in the carboxamide solvents at 75 °C: 1= **1d** (Br); 2=**1c** (H); 3=**1a** (CH_3); 4=**1b** (OCH_3).

In order to confirm this, the stereochemistry of the *E*1 reaction was examined on the solvolysis of **1a**-3-*exo-d* and **1a**-3-*endo-d* in DMA at 75 °C. The norbornene was converted into norbornene–phenyl azide adduct (**8**) by 1,3-dipolar cycloaddition reaction of phenyl azide to norbornene,[17]) because of the ease in separation and purification of small amounts of norbornene (Scheme 4).



Scheme 4.

The adduct **8** was analyzed by ^{13}C NMR spectroscopy in order to obtain the information on the rearrangements during solvolysis by determining the carbon bearing a deuterium atom which shows –CD– triplet (see Experimental). ^{13}C chemical shifts for the adduct **8** were assigned from the multiplicities of the individual nuclei in the off-resonance decoupled spectra and from comparison with the spectra of other substituted norbornanes.[18]) Spectral assignments of the ^{13}C NMR are given in Table 4, together with those for the other norbornane derivatives.

In the case of **1a**-3-*exo-d*, the spectrum of **8** derived from norbornene exhibited –CD– triplet only at 31.9 ppm, indicating the presence of deuterium at C(8) of the adduct **8**. On the other hand, the spectrum of **8** obtained in the case of **1a**-3-*endo-d* showed three triplets (–CD–) at 0.3 ppm upfield from C(3a), C(7a), and C(8) signals. These results clearly indicate that the leaving anion abstracts exclusively *syn-β*-hydrogen atom (or deuterium atom) of the intimate ion-pair intermediate **6**; they also demonstrate that the formation of the ion-pair is attended by the Wagner-Meerwein rearrangement (Table 5, *vide infra*).

Cram and Sahyun,[19a]) Cocivera and Winstein,[19b]) Skell and Hall,[19c]) and Kim and Brown[19d]) have emphasized the importance of the nature of the counter ion and its possible assistance to the proton abstraction in the intimate ion-pair.

In order to know a quantitative relationship between the rate, k_e, of norbornene forming step and the leaving

TABLE 4. ^{13}C CHEMICAL SHIFTS OF NORTRICYCLENE, *exo*-2-SUBSTITUTED NORBORNYL DERIVATIVES, AND ADDUCT **8**

Compound	Chemical shift$^{a,b)}$								
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	CH$_3$	C=O
Nortricyclene$^{c)}$	9.7	9.7	32.9	29.3	32.9	9.7	32.9		
Acetate	41.4	77.6	39.6	35.4	28.2	24.4	35.3	21.3	170.6
Formate$^{d)}$	41.6	77.2	39.6	35.5	28.2	24.3	35.3		160.6
Tosylate	42.0	85.3	39.5	35.1	27.7	23.8	34.9	21.5	
	C-7	C-7a	C-3a	C-4	C-5	C-6	C-8		
Adduct **8**$^{e)}$	40.2*	60.3	86.4	41.5*	25.7†	25.0†	32.2		

a) Chemical shifts are expressed in ppm downfield from Me$_4$Si (in CDCl$_3$ except for the adduct **8** (CD$_2$Cl$_2$)). b) Signals marked *, †, may be interchangeable in the column where they appear. c) See Ref. 18a. d) See Ref. 18c. e) The numbering is shown in Scheme 4.

group structure, a linear relationship between log k_e and the Hammett σ value of the *para*-substituent in the leaving group was examined. The log k_e values were estimated from the product distribution (Table 2) using Eqs. 1 and 2, where the magnitude of k_a[Amide] is a constant in the respective carboxamide solvents. The plot of log %**3**/(%**2**+%**4**) against the σ value is illustrated in Fig. 4.

$$\%\mathbf{3}/\%\mathbf{7} = \%\mathbf{3}/(\%\mathbf{2}+\%\mathbf{4}) = k_e/k_a[\text{Amide}] \qquad (1)$$

$$\log k_e = \log \%\mathbf{3}/(\%\mathbf{2}+\%\mathbf{4}) + \log k_a[\text{Amide}] \qquad (2)$$

Good linear relations, with negative ρ values, -0.54—-1.2, were observed for the series of carboxamides. These linear relations also suggest that in the *E*1 process the leaving group anion intramolecularly abstracts the C(3) proton at the stage of the intimate ion-pair intermediate **6**.

Wagner-Meerwein Rearrangement in the Intimate Ion-Pair and 6,2-Hydride Shift in the Imidatonium Ion. The solvolyses of **1a**-3-*endo*-*d* in DMA, DMF, and NMF were carried out at 75 °C and the deuterium distribution of *exo*-norbornyl carboxylate, norbornene, and nortricyclene were determined by means of ^{13}C and, in some cases, ^{1}H NMR spectroscopies in the Fourier transform mode (see Experimental). The results of the deuterium analyses of the products are tabulated in Table 5 and also illustrated in Scheme 5.

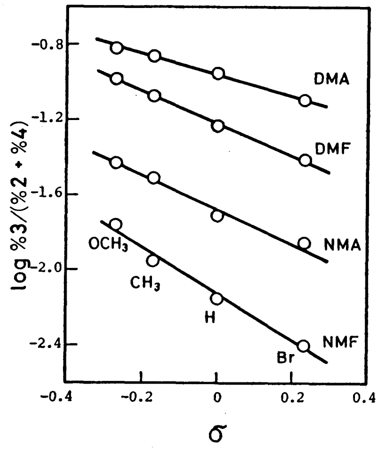
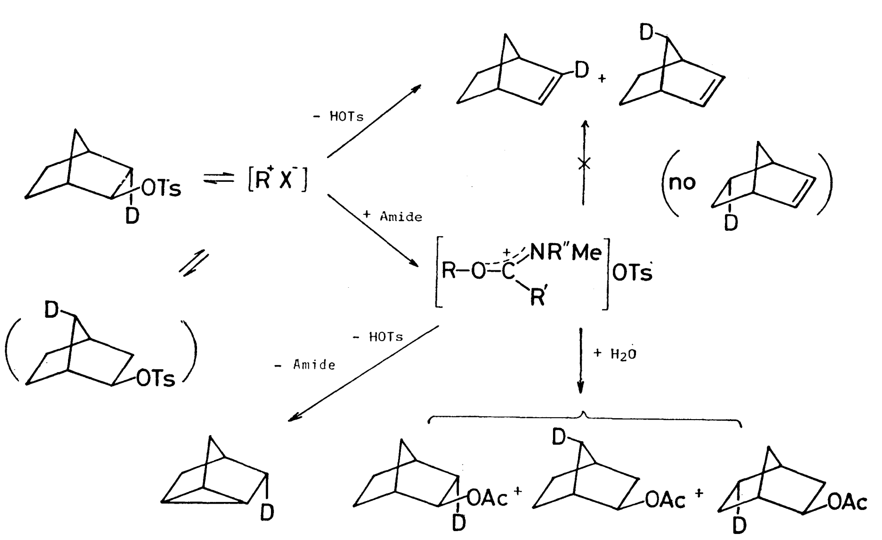


Fig. 4. Linear free-energy relationships between log %**3**/(%**2**+%**4**) and σ for the solvolysis of **1a**—**d** in the carboxamide solvents at 75 °C: $\rho = -0.54$, -0.86, -0.86, and -1.2, respectively for DMA, DMF, NMA, and NMF.

In norbornene the deuterium at *endo*-position of C(3) of **1a**-3-*endo*-*d* scrambled at the C(3) and C(7) positions, whereas in the *exo*-norbornyl ester (acetate or formate) the deuterium scrambled to C(5) position besides C(3) and C(7) positions.

In addition, when the deuterium distribution in the



Scheme 5.

TABLE 5. ISOTOPE DISTRIBUTIONS OF THE PRODUCTS IN DMA, DMF, OR NMF SOLVOLYSIS OF **1a**-3-*endo-d*, **1a**-3-*exo-d*, AND **1a**-3,3-d_2, AT 75 °C[a)]

Compound	Amide	$[H_2O]$ mol/dm^3	Product	Yield %	Deuterium, %[b)] C-3	C-5	C-7
1a-3-*endo-d*	DMA	0.04	**2**	70.3	100		
			3[c)]	11.3	44	0	56
			4a[d,h)]	18.0	41	23	39
	DMA	0.20	**4a**[e,h)]	42.0	43	12	43
	DMF	0.04	**4b**[f,h)]	45.0	46	5	47
	NMF	0.15	**2**	20.3	100		
			3[c,i)]	0.7	48	0	52
			4b[g,h)]	79.0	49	0	49
1a-3-*exo-d*	DMA	0.003	**3**[c)]	11.6	0	0	63
1a-3,3-d_2	DMA	0.003	**2**	87.0	100		

a) $[ROTs]=0.075$ mol/dm^3; $[C_5H_5N]=0.077$ mol/dm^3. b) The percentages of deuterium at the carbons other than C(3), C(5), and C(7) are below the limit of the accuracy (<1%); reproducibility = ±3%. c) Calculated from data of the adduct **8**. d) Contaminated with 2.7% of *endo*-isomer. e) Contaminated with 0.9% of *endo*-isomer. f) Contaminated with 0.4% of *endo*-isomer. g) Contaminated with 0.2% of *endo*-isomer. h) ^{13}C signals of *endo*-isomer do not overlap with those of *exo*-isomer. i) Determined by means of ^1H NMR; the spectrum of the corresponding adduct **8** is identical with that obtained from DMA solvolysis.

TABLE 6. CHANGE IN DEUTERIUM DISTRIBUTIONS OF THE TOSYLATE IN THE COURSE OF THE SOLVOLYSIS OF **1a**-3-*endo-d* IN DMA AT 75 °C[a)]

%Reaction[b)]	Deuterium, %[c)] C-3	C-5	C-7
5	75	0	25
10	66	0	34
25	50	0	50
50	51	0	49
90	53	0	47

a) $[ROTs]=0.075$ mol/dm^3; $[C_5H_5N]=0.077$ mol/dm^3; $[H_2O]=0.003$ mol/dm^3. b) Calculated from the reaction time by the use of the rate constant $k_1=1.69\times 10^{-5}\ s^{-1}$. c) The percentages of deuterium at the carbons other than C(3), C(5), and C(7) are below the limit of the accuracy (< 1%); reproducibility = ±3%.

unchanged tosylate was examined in the course of the solvolysis of **1a**-3-*endo-d* in DMA, the deuterium was detected at C(3) and C(7) positions, but no deuterium was found at C(5) position. This is summarized in Table 6.

Since the scrambling of the C(3) deuterium to C(7) position must be caused by the Wagner-Meerwein rearrangement and the appearance of deuterium at C(5) position must be caused by 6,2-hydride shift, it is concluded that only the Wagner-Meerwein rearrangement attends the formation of the intimate ion-pair intermediate (Scheme 5) and that 6,2-hydride shift takes place at the stage of the subsequent reaction of the imidatonium ion (Scheme 5). Furthermore, it is deduced that the imidatonium ion can not return to the intimate ion-pair. If such a return course is probable, the deuterium should be located at C(5) positions of norbornene and of the unchanged tosylate. This, however, is not the case (Tables 5 and 6). Similarly, since no deuterium was found at C(5) of norbornene, it is deduced that the imidatonium ion can not give rise to norbornene.

This absence of the 6,2-hydride shift at the stage of the intimate ion-pair may be ascribed to an increase in the solvent capture caused by the relatively high nucleophilicity of carboxamides, and also to acceleration in *syn-E*1 as mentioned above. Such accelerations of both of the subsequent reactions are expected to decrease the life-time of the intimate ion-pair, thereby suppressing the 6,2-hydride shift.

The 6,2-hydride shift, when it occurs in the imidatonium ion, is suppressed in the order of DMF>DMA (Table 5). In addition the increase in the water content of NMF and DMA also suppresses the 6,2-hydride shift in the ester product. Especially, in NMF no 6,2-hydride shift was found in **4b**[20)] when the solvolysis was carried out in the presence of 0.15 mol/dm^3 of water. These are summarized in Table 7. These trends clearly indicate that the 6,2-hydride shift competes with the hydrolysis of the imidatonium ion [R-Amide]$^+$, which is originally formed without any 6,2-hydride shift.

TABLE 7. DISTRIBUTION % OF DEUTERIUM FOR ESTERS AS A FUNCTION OF WATER CONTENT IN THE CARBOXAMIDE SOLVOLYSIS OF **1a**-3-*endo-d* AT 75 °C[a)]

Amide	$[H_2O]$ mol/dm^3	Product[b)]	Deuterium, %[c)] C-3	C-5	C-7
DMA	0.04	**4a**	41	23	39
	0.20	**4a**	43	12	43
NMF	0.15	**4b**	49	0	49

a) See footnote (a) in Table 5. b) See footnote (d), (e), (g), and (h) in Table 5. c) The percentages of deuterium at the carbons other than C(3), C(5), and C(7) are below the limit of the accuracy (< 1%); reproducibility = ±3%.

Examination of 3,2-Hydride Shift in the Intimate Ion-Pair and in the Imidatonium Ion Intermediate. Roberts and his collaborators[21] have demonstrated that the 6,2-hydride shift is highly competitive with solvent capture of the 2-norbornyl cation and that the intrusion of the 3,2-hydride shift is much more pronounced in the less nucleophilic solvent such as formic acid. Lee and Lam[22] have suggested that even in acetic acid the 3,2-hydride shift occurs to a significant extent prior to the attack by solvent on the cation. Under the stable ion conditions, it has also been demonstrated that both 3,2- and 6,2-hydride shifts attend the formation of the 2-norbornyl cation.[23]

Thus, we examined by the use of **1a**-3,3-d_2 whether the 3,2-hydride shift actually occurs in this solvolysis or not. When the solvolysis was carried out in DMA solvent at 75 °C, and then isolated nortricyclene was subjected to ^{13}C NMR analysis, the spectrum showed a single $-CD_2-$ signal (quintet) centered at 32.3 ppm, 0.6 ppm upfield from C(3), C(5), or C(7) signal of nortricyclene (Table 4), but no sign of another quintet or triplet. This result unequivocally indicates that neither 3-*exo*- nor 3-*endo*-deuterium has migrated from C(3) to C(2) position and that the 3,2-hydride shift never attends the formation of nortricyclene. This means that no 3,2-hydride shift occurs in the stage of the intimate ion-pair.

The absence of deuterium at the C(2) position in the *exo*-norbornyl ester (acetate or formate) (Table 5) also shows that the 3,2-hydride shift does not occur in the course of the formation of these esters in DMA or in DMF.

Structure of the Ion-Pair Intermediate and the Reaction Pathway for the Formation of Deuterium Labeled Norbornene. The deuterium distributions in the norbornene and in the unchanged tosylate were determined at intervals in the course of the solvolysis of **1a**-3-*endo-d* in DMA at 75 °C; the results are tabulated in Tables 8 and 6, respectively. Since no deuterium was detected at C(5) positions of norbornene and of the unchanged tosylate, it is obvious, as mentioned above, that merely the Wagner-Meerwein rearrangement competes with the *syn-E*1 elimination and with the solvent capture.

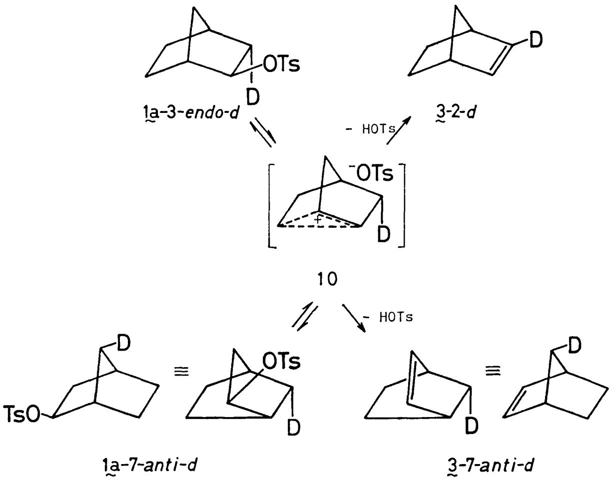
TABLE 8. CHANGE IN DEUTERIUM DISTRIBUTIONS OF NORBORNENE IN THE COURSE OF SOLVOLYSIS OF **1a**-3-*endo-d* IN DMA AT 75 °C[a)]

%Reaction[b)]	Deuterium, %[c,d)]		
	C-3	C-5	C-7
10	57	0	43
25	54	0	46
50	50	0	50
100	44	0	56

a) [ROTs] = 0.075 mol/dm^3; [C_5H_5N] = 0.077 mol/dm^3; [H_2O] = 0.003 mol/dm^3. b) Calculated from the reaction time by use of the rate constant: $k_1 = 1.69 \times 10^{-5}$ s^{-1}. c) The percentages of deuterium at the carbons other than C(3), C(5), and C(7) are below the limit of the accuracy (< 1%); reproducibility = ±3%. d) Calculated from data of the adduct **8**.

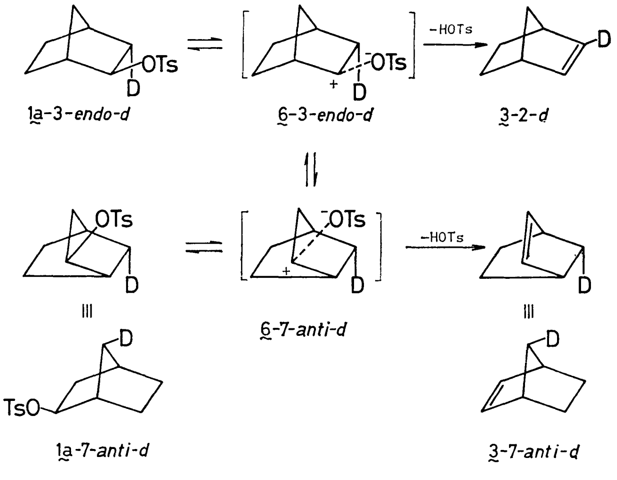
The structural problem of this intimate ion-pair has been long debated[8)] and it is pertinent to discuss it in the light of the change of the deuterium distribution in norbornene in the progress of the solvolysis.

When the intimate ion-pair has a non-classical structure (**10**) depicted in Scheme 6, it would give rise to **1a**-7-*anti-d* and norbornene, **3**-2-*d* and **3**-7-*d*, by an internal return and by *syn-E*1 pathway, respectively. In addition, the tosylate **1a**-7-*anti-d* can also afford the intimate ion-pair which has the structure identical with that from the starting tosylate **1a**-3-*endo-d*. In other words, there is a single structure (non-classical) **10** in the course of the norbornene formation from both **1a**-3-*endo-d* and **1a**-7-*anti-d*. Consequently, the ratio of norbornene **3**-2-*d* and **3**-7-*anti-d* should be invariant regardless the degree of conversion of the tosylate, even if the ratio of the tosylate **1a**-3-*endo-d* and **1a**-7-*anti-d* varies as the solvolysis proceeds (see Scheme 6).



Scheme 6.

On the other hand, if the intermediate exists as an equilibrium mixture of the classical ions **6**-3-*endo-d* and **6**-7-*anti-d*, and in addition, if the *syn-E*1 elimination can compete with the Wagner-Meerwein rearrangement between these ions, the ratio of norbornene **3**-2-*d* and **3**-7-*anti-d* would vary as the elimination progresses (Scheme 7).



Scheme 7.

Since the deuterium distribution in the norbornene varies as the reaction proceeds in DMA, as is shown in Table 8, it is clear that the structure of the intimate ion-pair can not be expressed by the non-classical ion **10**, but by the classical ion **6**, in so far as the norbornene is produced strictly from the intimate ion-pair.

The deuterium content at C(3) of the tosylate decreases from 100 to 50% at 25% completion of the solvolysis, and then increases to 53% at 90% completion (Table 6). Meanwhile, the deuterium content at C(7) of norbornene increases from 50 to 56% as the reaction proceeds from 50 to 100% completion. The slight accumulation of deuterium at C(3) of **1a**-3-*endo-d* and that at C(7) of **3**-7-*anti-d* may be ascribed to the possible slight sluggishness in the rate of solvolysis of **1a**-3-*endo-d* as compared with **1a**-7-*anti-d*. In fact the secondary isotope effect of **1a**-3-*endo-d* amounts to 1.18± 0.02 in DMA at 75 °C.[24] However, the accumulation of deuterium at C(7) of norbornene at 100% reaction appears to be too high to be ascribed to the possible secondary isotope effect, even if the experimental error (±3%) is taken into account. This point will be subjected to a more detailed study with precision.

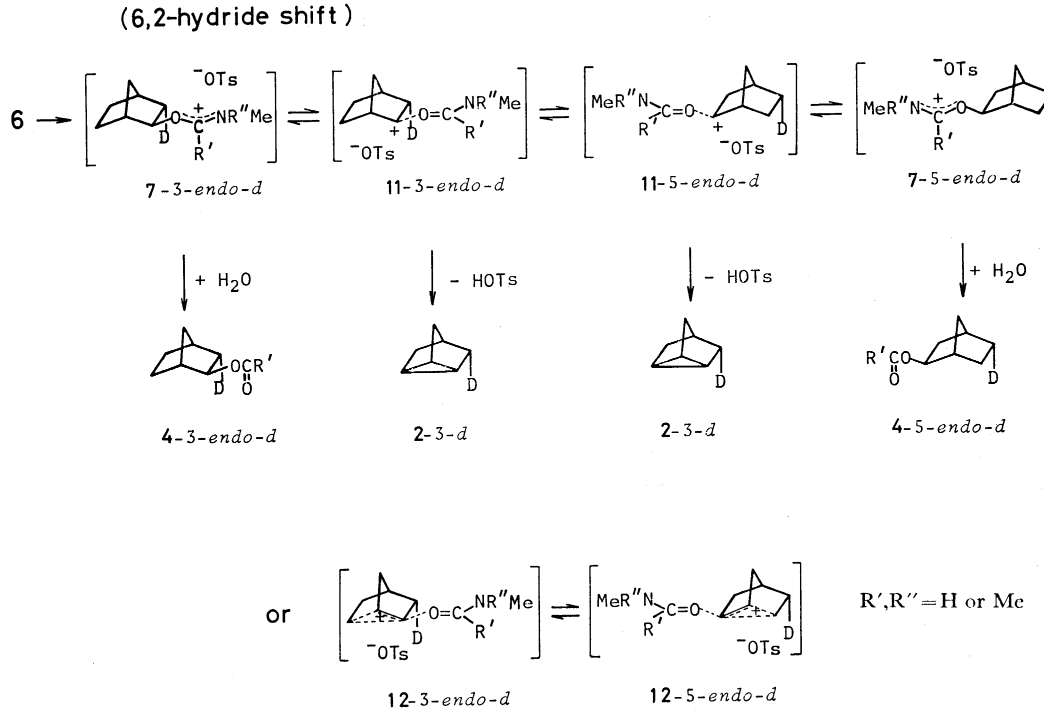
The Formation of exo-*2-Norbornyl-5-*d *Carboxylates and Nortricyclene.* The C(5) positions of *exo*-2-norbornyl esters contain appreciable amounts of deuterium, as it is shown in Table 5. This indicates that the *exo*-imidatonium ion **7**-3-*endo-d* easily rearranges to the **7**-5-*endo-d* ion by the 6,2-hydride shift. Since the classical intermediates **11**-3-*endo-d* and **11**-5-*endo-d* (Scheme 8) give rise to the identical nortricyclene, **2**-3-*d*, we can not obtain more detailed information about the mechanistic insights. Therefore, the possibility of 6,2-hydride shift *via* non-classical structure, **12**-3-*endo-d*,[25] can not be ruled out in the γ-elimination of the *exo*-imidatonium ion **7**.

It is not clear at the present stage of our knowledge why the *exo*-imidatonium ion can easily afford nortricyclene, and why the *exo*-imidatonium ion easily undergoes 6,2-hydride shift.

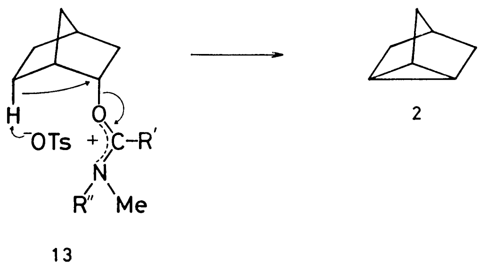
The Formation of endo-*2-Norbornyl Carboxylates.* Small amounts of *endo*-norbornyl acetate or formate, **5a** (≤0.9%) or **5b** (≤1.1%), were produced in the solvolysis of **1a**—**d** in the carboxamide solvents as it is shown in Tables 2 and 3. However, these are in substantial amounts as compared with the result of acetolysis of *exo*-norbornyl brosylate **1d** (0.02%),[26] and also in comparison with the amounts of *exo*-2-norbornyl carboxylates (Table 2). The formation of *endo*-norbornyl esters obviously indicates that the *endo*-imidatonium ion is actually formed in the course of solvolysis. This *endo*-imidatonium ion most probably is formed from the intimate ion-pair with a classical norbornyl ion structure, since it is rather difficult that the *endo* product is formed from a non-classical norbornyl ion.

The C(6) hydrogen of the *endo*-imidatonium ion **13** may be easily abstracted in a cyclic fashion, as depicted in Scheme 9, to give rise to nortricyclene. Peeters and Anteunis[27] have proposed similar cyclic mechanism for solvolytic dehydrobromination of 2-methyl-2-pentyl bromide in DMF at the imidatonium ion stage.

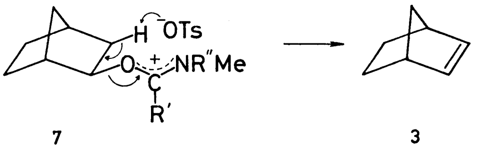
A Possible Norbornene Formation from exo-*Imidatonium Ion.* The possibility that norbornene is formed through the *exo*-imidatonium ion **7**, as depicted in Scheme 10, may not be ruled out. Thus the slight decrease in the yield of norbornene with an increase in water content (Fig. 2) might be attributable to the intrusion of this process. However, as mentioned above, it is clear that at the stage of the imidatonium ion the deuterium scrambles to C(5) position as the result of the 6,2-hydride shift. Therefore, if the elimination occurs by the pathway depicted in Scheme



Scheme 8.



Scheme 9.



Scheme 10.

10, norbornene labeled at C(5) position would be formed; however, this is not the case (Table 5 and Scheme 5). Thus, only the decrease in the basicity of the tosylate anion, due to the increase in the water content, can explain the decrease in the yield of norbornene (Fig. 2).

Experimental

All the melting points are uncorrected. NMR spectra were measured with a Hitachi R-24 (60 MHz) or JEOL JMN MH-100 (100 MHz) instruments. Tetramethylsilane was used as an internal standard in $CDCl_3$ unless otherwise noted. IR spectra were obtained with Hitachi EPI-S2 spectrometer, only the major absorptions being cited. GLC analysis was performed with a Hitachi K-53 gas chromatograph fitted with TCD and a 3 m column (i.d.=3 mm) packed with PEG 6000 on Chromosorb W.

Materials. The four carboxamides were purified by the same method described in the previous paper.[1] Norbornene oxide,[28] *exo*-2-norbornanol,[29] norcamphor,[29] phenyl azide,[30] $(n\text{-Bu})_4NOAc$,[31] trifluoroacetic acid-*d*,[32] *p*-methoxybenzenesulfonyl chloride,[33] and 1-adamantyl bromide[34] were prepared following the published methods. Reagent grade chemicals were used without further purification unless otherwise mentioned. Norbornene was commercial product purified by sublimation.

*exo-2-Norbornyl Arenesulfonates **1a—d**.* The *exo*-alcohol was converted into the corresponding sulfonates in the usual manner.[35] Tosylate **1a**: mp 54.5—55.5 °C (lit, mp 53—54 °C,[4] 53.7—54.6 °C[36]). Brosylate **1d**: mp 55.5—57 °C (lit,[4] mp 55.3—57 °C). Benzenesulfonate **1c** could not be crystallized and was purified by being settled as an oil repeatedly from pentane solution at −30 °C: IR (neat); 1360 (SO_2), 1190 (SO_2), 1100 (Ar–S), and 875—960 cm^{-1} (five max, S–O–C): NMR (60 MHz) δ=0.8—1.75 (m, 8H), 2.3 (broad s, 2H, bridge head CH), 4.36 (t, 1H, $CHOSO_2$), and 7.25—8.0 ppm (m, 5H, Ar–H).

Found: C, 61.93; H, 6.28%. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39%.

p-Methoxybenzenesulfonate **1b**: mp 47.5—49 °C; IR (KBr); 1356 (SO_2), 1263 (Ar–O–C), 1190 (SO_2), 1170, 1100 (Ar–S), and 875—960 cm^{-1} (five max, S–O–C); NMR (60 MHz) δ=0.8—1.8 (m, 8H), 2.30 (broad s, 2H, bridge head CH), 3.88 (s, 3H, OCH_3), 4.41 (t, 1H, $CHOSO_2$), 6.98 (d, 2H, Ar–H), and 7.81 ppm (d, 2H, Ar–H).

Found: C, 59.65; H, 6.38%. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43%.

*exo-2-Norbornanol-3-endo-d and Its Tosylate **1a**-3-endo-d.* *endo*-3-Deuterium was introduced by the $LiAlD_4$ reduction of norbornene oxide.[37,38] A solution of $LiAlD_4$ (99.5% D, 3.0 g) and norbornene oxide[28] (7.3 g) in DME (distilled from Na–benzophenone ketyl, 250 cm^3) was heated at 100—105 °C for 28 h. After the mixture had been cooled in an ice bath, a mixture of THF–H_2O (1:1, v/v, 200 cm^3) was added slowly, and then K_2CO_3 was added to separate water layer. An organic layer was dried ($MgSO_4$), concentrated (Vigreux column), and the residual oil was distilled to give *endo-3-d* alcohol (6.0 g, 80% yield): bp 178—179 °C. Sublimed sample of the alcohol was subjected to ^1H NMR (100 MHz) spectroscopic analysis to show an isotopic purity of 99%. The alcohol was converted into the tosylate in the usual manner.[35] **1a**-3-*endo-d*: mp 54—55 °C; NMR (60 MHz) δ=0.85—1.75 (m, 7H), 2.3 (broad s, 2H, bridge head CH), 2.43 (s, 3H, Ar–CH_3), 4.34 (s, 1H, CHOTs), 7.34 (d, 2H, Ar–H), and 7.78 ppm (d, 2H, Ar–H). ^{13}C NMR spectrum of the tosylate indicated the absence of deuterium scrambling during its preparation.

*exo-2-Norbornanol-3-exo-d and Its Tosylate **1a**-3-exo-d.* *exo*-3-Deuterium was introduced by deuterioboration of norbornene.[37,39] Deuterioboration–oxidation was carried out according to the standard procedure including external generation of diborane-d_6.[39] The 3-*exo-d* alcohol was obtained in 80% yield. ^1H NMR (100 MHz) analysis showed an isotopic purity of 97%. Tosylate **1a**-3-*exo-d* was synthesized from this alcohol in the usual manner.[35] **1a**-3-*exo-d*: mp 54—55 °C; NMR (60 MHz) δ=0.85—1.75 (m, 7H), 2.27 (broad s, 2H, bridge head CH), 2.43 (s, 3H, Ar–CH_3), 4.45 (d, 1H, J=6.2 Hz, CHOTs), 7.32 (d, 2H, Ar–H), and 7.79 ppm (d, 2H, Ar–H). ^{13}C NMR spectrum of the tosylate showed the absence of deuterium scrambling throughout its synthesis.

*exo-2-Norbornanol-3,3-d_2 and Its Tosylate **1a**-3,3-d_2.* Norcamphor-3,3-d_2 was prepared by the method of Schaefer *et al.*[40] in 70% yield: bp 168—169 °C. ^1H NMR (100 MHz) analysis showed an isotopic purity of 97.7%. Reduction of the ketone with $LiAl(OCH_3)_3H$ in THF afforded the *endo*-alcohol stereoselectively[41] (98%) in 94% yield. Then, the alcohol was converted into the brosylate in the usual manner,[35] which was then partially solvolyzed in AcOH–NaOAc for 2 h at 45 °C. The usual work-up and recrystallization from pentane at −30 °C gave *endo*-2-norbornyl-3,3-d_2 brosylate in 70% yield based on the *endo*-alcohol. The brosylate was subjected to S_N2 reaction with $(n\text{-Bu})_4NOAc$[31] in benzene (reflux, 3 h),[37] furnishing *exo*-2-acetate-3,3-d_2 in 98% yield after Kugelrohr distillation. Reduction of the acetate with $LiAlH_4$ gave *exo*-2-norbornanol-3,3-d_2 in 90% yield. ^{13}C NMR analysis showed the absence of deuterium scrambling during the procedures. Tosylate **1a**-3,3-d_2 was prepared in the usual manner:[35] mp 53.5—54.5 °C; NMR (60 MHz) δ=0.87—1.75 (m, 6H), 2.30 (broad s, 2H, bridge head CH), 2.43 (s, 3H, Ar–CH_3), 4.44 (s, 1H, CHOTs), 7.32 (d, 2H, Ar–H), and 7.78 ppm (d, 2H, Ar–H).

Product Analysis. Arenesulfonate (2—3 mmol) was weighed into an ampoule (dried in an oven), which was then repeatedly evacuated and filled with dry nitrogen. A desired amount of solvent was introduced to attain the concentration of the substrate to be 0.075 mol/dm^3 with a syringe through a septum and then pyridine (3% excess) was added in the same manner as above. The ampoule was then sealed under nitrogen and kept at 75 °C for ten half-lives. The ampoule was opened and weighed amounts of anisole was added to the mixture. The resulting solution was poured into ice-water and extracted with pentane. The pentane solution was washed several times with water, dried ($MgSO_4$), and concentrated carefully by the use of 30-cm column packed with glass helices to *ca.* 1 cm^3. A part of the condensed pentane solution was transferred into an NMR tube with a syringe and the sample was repeatedly scanned over the respective regions for olefinic protons of norbornene **3** and O–CH_3 protons of anisole ten times at 30 s intervals. The ratio of the peak area of CH=CH to O–CH_3 was calculated as an average of these scans. The yield calculated from the ratio was reproducible relatively to ±3% or less on repeated runs.

Another part of the pentane solution was analyzed for nortricyclene **2**, norbornene **3**, and esters **4** and **5** by means of GLC.

The remaining pentane solution was combined with that used for NMR assay, concentrated, and the residue was chromatographed over SiO_2, being eluted successively with pentane, pentane–CH_2Cl_2 (8 : 2, v/v), and CH_2Cl_2. The CH_2Cl_2 fractions afforded the ester (**4**+**5**) which was reduced with $LiAlH_4$ in ether to give norbornanol, epimeric composition of which was analyzed by means of GLC (80 °C).

Preparation of Norbornene–Phenyl Azide Adduct. Norbornene **3** obtained from partial or complete solvolysis of **1a**-3-*endo-d* or **1a**-3-*exo-d* was converted into the adduct with phenyl azide[30] (1-phenyl-4,7-methano-3a,4,5,6,7,7a-hexahydrobenzotriazole, **8**) by the method described by Huisgen *et al.*[17] for the sake of easy separation and purification of small amounts (~mg) of norbornene **3** from the solvolysis products without loss and scrambling of deuterium.[42] A typical run is described in the followings.

Tosylate **1a**-3-*endo-d* (2 g) was solvolyzed in DMA for 0.5 half-lives in the same manner as described above. A mixture of nortricyclene **2**, norbornene **3**, the acetates **4** and **5**, and unchanged tosylates was obtained as a pentane solution after the usual work-up. The mixture was passed through an SiO_2 column and the column was eluted with additional pentane. To the combined pentane solution was added dry benzene (0.25 cm^3) and the mixture was concentrated carefully through a column packed with glass helices to *ca.* 1 cm^3. Then, phenyl azide[30] (0.02 cm^3) was added to the condensate and the resulting solution was allowed to stand at room temperature for three days. The volatile components were removed under reduced pressure to give yellow crystalline residue which was recrystallized from hexane to furnish the adduct as fine needles (0.02 g), mp 100—101 °C (lit,[17] mp 100—101 °C, unlabeled adduct **8**).

Separation of Nortricyclene. Tosylate **1a**-3,3-d_2 (0.5 g) was solvolyzed in DMA at 75 °C for ten half-lives. A condensed pentane solution was obtained in the same manner as described above. The solution was then treated with *m*-chloroperbenzoic acid in CH_2Cl_2 (slight excess to norbornene **3**) at 0 °C for 1 h. The mixture was washed with 10% Na_2CO_3, dried ($MgSO_4$), and concentrated by use of 30-cm column packed with glass helices. The residue was chromatographed over SiO_2 (5 g), being eluted with pentane (30 cm^3). The pentane solution was again concentrated through the column and the residue was allowed to stand open to the atmosphere at room temperature for 30 min to give crystalline nortricyclene **2**, which was then separated and purified by sublimation.

Separation of Unchanged Tosylate. The tosylate recovered from partial solvolysis was separated from pentane solution by repeated recrystallization at −30 °C. Colorless crystalline tosylate was obtained, which was kept under high vacuum at room temperature overnight.

^{13}C NMR Spectra. Chemical Shift Determinations. ^{13}C spectra were determined on a JEOL JMN FX-100 spectrometer operated at 25.05 MHz and equipped with JEOL JEC 980B computer (8K) in the Fourier transform mode. All ^{13}C chemical shifts are reported relative to tetramethylsilane in $CDCl_3$ or in CD_2Cl_2.

Spectral assignments were made easily from the multiplicities of the individual nuclei in the off-resonance decoupled spectra and from comparisons with the chemical shifts reported for other substituted norbornanes.[18] The chemical shifts of nortricyclene[18a] and the formate[18c] were available in the literature and our data were satisfactorily consistent with those reported.

Quantitative Intensity Measurements. For the deuterium distribution analysis, the proton-decoupled spectra of nortricyclene **2**, the esters **4a** and **4b**, the adduct **8**, and recovered tosylate were recorded at spectral widths of 2000, 2500, 3000, and 1000 Hz, respectively, by use of a 90° pulse and a pulse repetition of 30 s. A 180°-τ-90° pulse sequence[43] was used to demonstrate that 30 s delay was comparable to $5T_1$ for each of the observed nuclei. A pulse repetition of 60 s was also used to determine more definitely the nuclei labeled by deuterium atom. To circumvent the potential source of error on quantitative analysis,[44] the NOE suppressed gated decoupling technique[45] was used and each spectrum was compared with calibration spectra taken for unlabeled sample, employing unaffected carbon signals such as $\underline{C}H_3$-COO, $-\underline{C}(6)H_2-$, and Ar–$\underline{C}H_3$, respectively for **4a**, **4b** and **8**, and **1a**, as an internal calibration.

For the acetate **4a** deuterium distribution analysis was carried out as follows. The spectrum of an unlabeled sample in $CDCl_3$ was recorded by use of the operating parameters as indicated above. The ratio of the peak area of each observed nuclei to that of $\underline{C}H_3COO$ was directly computed on a JEOL 980B computer with SYSTEM Q/D PROGRAM FAFT08/11. The spectrum of a deuterated sample was then recorded in the identical manner as used in the case of the unlabeled sample. The ratio of the peak area of each observed nuclei so that of $\underline{C}H_3COO$ was measured in the same method as described above. A decrease in the intensity of $-CH_2-$ signals was calculated from the each ratio obtained.

The deuterium distribution analysis of the adduct **8** obtained from the partial solyolysis of low %reaction (≤50%) was carried out by means of ^1H NMR spectroscopy in the Fourier transform mode. Since the ^{13}C spectrum of the adduct **8**, obtained from the solvolysis of **1a**-3-*endo-d* in DMA (100% reaction), has indicated that the deuterium is located at C(3) and C(7) positions of norbornene skeleton, a decrease in the peak area of well-resolved C(3a)- and C(7a)-proton signals was measured. The ratio of the peak area of the concerned protons to that of the bridge head protons was directly obtained by the same method as described for the ^{13}C intensity measurement, which was compared with the corresponding ratio for the unlabeled sample. The operating parameters employed were a spectral width of 1000 Hz, a 45° pulse, pulse repetition of 10 s, and 10—200 pulses, to provide almost same S/N ratio for each sample.

Kinetic Measurements. Solvolysis rates for **1a**—**d** and specifically-labeled tosylates in the carboxmaides were determined in the same manner as described in the previous paper,[1] by the use of KOH (in EtOH) titrant and Thymol Blue–phenolphthalein indicator.

Except for the case of NMA, an experimental infinity titer was in excess of the theoretical one, in proportion to the amounts of the carboxylic acid which was produced by an acid-catalyzed hydrolysis of the amide solvent. The solvent hydrolysis is caused by contaminated water even after rigorous purification of the amide. In all cases, however, $\log a/(a-x)$ -t plots gave straight lines with intercept at an origin even when the excessive infinity titer was employed to calculate $a/(a-x)$ values. In fact, there have been obtained essentially the same rate constants for the solvolysis of **1a**—**d** in the amides containing various amounts of water, although the infinity titers were in the range of 1.1—1.65 times the theoretical titer.

Another control experiment was carried out; the rate constant obtained by the acid-base titration method, infinity titer being in excess, was the same as that obtained by the Volhard method within an experimental error for the solvolysis of 1-adamantyl bromide in the amides.

Rate constants listed in Tables 1 and 2 are the data calculated from experimental infinity titers without correction for the excess because the above-mentioned findings do not require the correction for the excess.

The rates of solvolysis of **1a** in aqueous ethanol and in aqueous acetone were determined titrimetrically in a usual manner.

Control Experiments. All the products were stable under the conditions employed in the present study. It was found that the presence of pyridinium tosylate, acetic acid, formic acid, or pyridine in equimolar amounts to the substrates did not alter the respective yields of the solvolysis products.

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