Solvolysis in Carboxamides. II.[4] Solvolytic Elimination of 7β-Methylbicyclo[3.3.1]non-3β-yl Tosylate in Carboxamides†

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(Received May 13, 1977)

Solvolysis of 7β-methylbicyclo[3.3.1]non-3β-yl tosylate (**1**) was carried out in a series of carboxamides, *N*-methylformamide (NMF), *N*-methylacetamide (NMA), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA), as solvents. The rate (k_1, first-order rate constant) of **1** decreases in the order NMF>NMA>DMF>DMA, a linear free-energy relationship being found between the rates of **1** and those of 1-adamantyl tosylate in acetic acid and 80% ethanol as well as the carboxamides. The products consist of olefin (⩾96%) (*exo*-7-methylbicyclo[3.3.1]non-2-ene (**4**) and 3-methylbicyclo[3.3.1]non-2-ene (**5**)) and small amounts of esters (acetates or formates, ⩽4%). The content of rearranged olefin **5** is considerably less than that of acetolysis (55%) and ethanolysis (55%), decreasing in the order NMF (34%)>NMA(22%)>DMF(13%)>DMA(9%). A linear reactivity-selectivity relationship holds between log k_1 and log (%**5**/%**4**) for the four carboxamide solvents. The observed kinetic isotope effect ($k_H/k_D=1.01\pm0.03$) for 7α-deuterium-tagged derivative (**1**-7α-*d*) in NMF indicates that the σ(C(7)–H)-assisted ionization process for the solvolysis of **1** in the amides is absent. The results are in line with the stepwise mechanism which involves the formation of an intimate ion-pair intermediate followed by competitive processes such as 1,5-hydride shift, *syn*-E1 reaction, and nucleophilic substitution by the amide molecules. Substitution by the amide molecule leads to the formation of a cationic imidate, the hydrolysis of which affords the carboxylic esters. It is proposed that the *syn*-E1 process *via* an intimate ion-pair intermediate is affected by the tosylate anion reactivity in each amide solvent and suppressed by the hydrogen bonding of the each amide with the tosylate anion.

The occurrence of intramolecular hydride shift in S_N1 solvolysis has been demonstrated in various secondary alkyl or cycloalkyl systems.[1] As regards 7β-methylbicyclo[3.3.1]non-3β-yl tosylate (**1**), Eakin *et al.*[2] observed that acetolysis of **1** is accompanied by significant 1,5-transannular hydride shift (55%). They reported that the hydrogen migration occurs after the rate-determining step, on the basis of the absence of a detectable kinetic isotope effect with regard to 7α-deuterium-tagged substrate (**1**-7α-*d*).

Stéhelin *et al.*[3] observed by use of Taft-Hammett treatment that solvolysis of 7β-substituted (CH_3OCH_2–, CH_3OCO–, and NC–) derivatives and **1** is accelerated when it is accompanied by hydride migration from C(7) to C(3), concluding that there is σ(C(7)–H) participation in the rate-determining step of the ethanolysis. Thus, both the stepwise mechanism, involving the formation of an ion-pair intermediate followed by subsequent processes, and the partially or fully concerted mechanism have been proposed.

In the course of our study on the characteristics of carboxamides as an S_N1 solvolysis solvent, it was shown[4] that the solvolysis of *trans*-4-*t*-butylcyclohexyl tosylate in *N*-methylacetamide (NMA) proceeds with markedly suppressed 1,2-hydride shift as compared with acetolysis[5] and phenolysis,[6] giving exclusively unrearranged olefin. From this finding it has been suggested that intramolecular elimination by the leaving tosylate anion in the intimate ion-pair intermediate is markedly accelerated in NMA solvent.

In the present system **1**, the tosyloxy group is oriented in an equatorial position as in the case of *trans*-4-*t*-butylcyclohexyl system. Thus, it is of interest to examine whether solvolysis of **1** in carboxamide solvents proceeds with suppression of 1,5-hydride shift as compared with acetolysis[2] and ethanolysis.[3] It is also interesting to see whether the solvolysis proceeds with σ(C(7)–H) participation or not. We have studied the solvolysis of **1** in carboxamides, *N*-methylformamide (NMF), *N,N*-dimethylformamide (DMF), and *N,N*-dimethylacetamide (DMA), in addition to NMA.

Results and Discussion

Solvolytic Elimination Rates of 7β-Methylbicyclo[3.3.1]non-3β-yl Tosylate **1**. Solvolysis rates of **1** were determined in four carboxamides (NMF, NMA, DMF, and DMA) at two or three temperatures by the usual titrimetric method. Good first-order behavior was observed for all the kinetic runs over two to three half-lives both in the absence and the presence of pyridine added as a neutralizing agent for the liberated *p*-toluenesulfonic acid. Absence of the effect of added pyridine on the rate indicates that the solvolysis proceeds by the typical S_N1-type mechanism. The rate constants and thermodynamic parameters are given in Table 1. The solvolysis rates for **1** decrease in the sequence NMF>NMA>DMF>DMA in line with the trend observed for 1-adamantyl tosylate.[7]

A good linear relation has been observed in a plot of log k_1 (25 °C) for **1** *vs.* log k_1 (25 °C) for 1-adamantyl tosylate, when the solvolysis rates are compared for a series of solvents, such as 80% ethanol,[3,8] acetic acid,[2,8] NMF,[7] NMA,[7] DMF,[7] and DMA[7] (Fig. 1). The magnitude of the Grunwald-Winstein *m* value[9] (0.53) is comparable to those (0.4—0.7) known for the solvolysis of the usual secondary substrates.[10]

Deuterium Isotope Effects in the Solvolysis of 7α-Deuterium-Tagged Substrate **1**-7α-d *in NMF*. If transannular

† Presented in part at the 29th (Hiroshima, October, 1973) and 32nd (Tokyo, April, 1975) National Meetings of the Chemical Society of Japan.

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Table 1. Kinetic data for the solvolysis of 7β-methylbicyclo[3.3.1]non-3β-yl tosylate (**1**) in various carboxamides

Amide	$k_1/(10^{-5}\,s^{-1})$[b]			$\Delta H^{\neq}$[c]	$\Delta S^{\neq}$[c]
	25 °C	35 °C	50 °C	4.184 KJ/mol	4.184 J/(K mol)
DMA	0.114	0.515	3.77	26.2±0.3	2.2±0.8
DMF	0.218	0.949	5.83	24.5±0.7	−2.0±1.7
NMA	1.08	4.24	—	24.4±0.7	0.6±1.7
NMF	3.20	12.4	—	24.1±0.8	1.8±1.9

a) $[ROTs]_0=0.05$ mol/dm³. The rate constants obtained in the presence of equimolar amount of pyridine were essentially the same as those in its absence. b) Mean deviation for k_1 is ±3.6%. c) Probable errors are quoted.

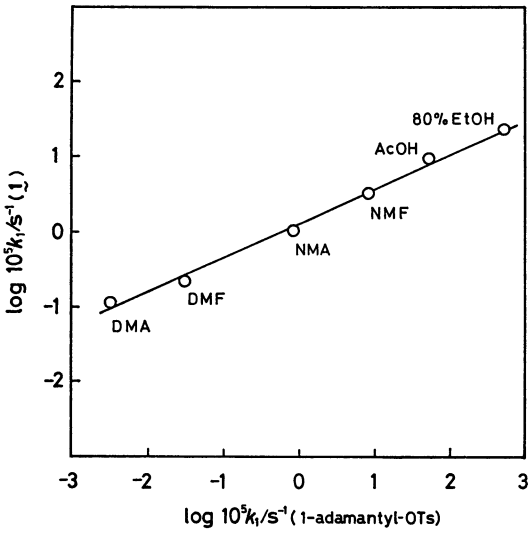


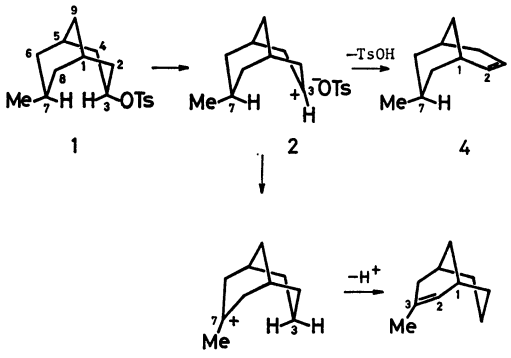
Fig. 1. A linear free-energy relationship between log k_1 (**1**) and log k_1(1-adamantyl tosylate) at 25 °C.

C–H bond breaking (σ-participation) is involved in the rate-determining step, a positive kinetic isotope effect ($k_H/k_D>1$) should be observed upon replacement of the migrating hydrogen atom by a deuterium atom. Thus, the rate of solvolysis of 7α-deuterium-tagged substrate **1**-7α-*d* was determined, using NMF as a solvent. NMF was selected for the reason that a maximal yield of the rearranged olefin (3-methylbicyclo[3.3.1]non-2-ene (**5**)) was observed in the case of NMF as a solvent (*vide infra*). The observed value $k_H/k_D=1.01\pm0.03$, indicates that the solvolysis of **1** proceeds without σ(C(7)–H) participation in NMF.

Elimination Products of the Solvolysis of ***1*** *in the Carboxamides.* In acetic acid[2] and 80% aqueous ethanol[3] the solvolysis product is exclusively a mixture of *exo*-7-methylbicyclo[3.3.1]non-2-ene (**4**) and **5** (**4**: **5**=45: 55). The latter is supposed to be derived from a carbenium ion intermediate (**3**) produced by a transannular C(7)–C(3) hydride shift from the intimate ion-pair intermediate (**2**) of solvolysis (Scheme 1).

It has been accepted that the tosylate **1** has predominantly a twin chair conformation.[11] In this conformation the intermolecular *anti*-elimination is sterically less favored because of the equatorial position of the tosyloxy group, the proton abstraction in this elimination thus being intramolecularly caused by the tosylate anion.

The results of GLC analysis of the solvolysis products



Scheme 1.

indicate that the major product in a series of carboxamide solvolysis is an olefin mixture of **4** and **5**. However, in contrast to the results of acetolysis[2] and ethanolysis,[3] the yield of **5** is much lower and decreases in the order NMF>NMA>DMF>DMA (Table 2). In other words, the hydride shift is suppressed in the carboxamide solvents in the sequence DMA>DMF>NMA>NMF.

Thus, the suppression of hydride shift seems to be a general feature of the carboxamide solvent, since such

Table 2. Products for the solvolysis of 7β-methylbicyclo[3.3.1]non-3β-yl tosylate (**1**) in various carboxamides

Solvent[c]	t/°C	Yield/%[b]				
		Olefin		Ester		ROH[f]
		4	**5**	3α	3β	
DMA	35	90.0	9.3	0.3	0.4	0.1
DMF	35	84.1	13.0	1.5	1.0	0.0[g]
NMA	35	74.3	22.0	1.6	1.5	0.6
NMF	35	66.0	33.6	0.0[g]	0.0[g]	0.5
AcOH[h]	25	44	55	—	1	—
80% EtOH[i]	25	45	55	—	—	0

a) $[\mathbf{1}]_0=0.05$ mol/dm³. [pyridine]=0.0535 mol/dm³. b) Average of two independent experiments. c) Water contents for carboxamides are ≤0.03 mol/dm³. d) Inverted acetate for DMA and NMA, and formate for DMF and NMF. e) Retained acetate for DMA and NMA, and formate for DMF and NMF. f) 7-Methylbicyclo[3.3.1]-nonan-3-ol; isomer compositions were not determined. g) Trace amount of these compounds were detected on GLC. h) Ref. 2. i) Ref. 3.

phenomenon has also been observed in the solvolysis of 4-*t*-butylcyclohexyl tosylate in NMA.[4] Possible causes for such a suppression might be a) specific solvation from the rear side of the carbenium ion **2** by the nucleophilic carboxamide molecule (negative end of dipole) and/or b) the enhancement of the rate of deprotonation in the intimate ion-pair intermediate **2** due to an increase in the basicity of the leaving tosylate anion in such a solvent as carboxamides. However, judging from the steric disadvantage for the carboxamide molecule to achieve such a solvation toward the U-shaped cationic intermediate **2**, cause a) seems less likely.

The basicity of the leaving tosylate anion in the carboxamide solvents would be the reverse of the hydrogen bonding order (NMF>NMA>DMF>DMA),[12] being in line with the observed solvent sequence for the suppression of rearrangement.

The acceleration of intramolecular *syn*-elimination in E1 reaction has been observed in the elimination of 1-methylpropyl-2-*d* tosylate in a dipolar aprotic solvent, *i.e.* nitrobenzene.[13] Kim and Brown[14] proposed that the leaving group anion can in principle attack β-hydrogen in the stage of tight ion-pair formation to give elimination products. The process leading to the unrearranged olefin **4** (**2**→**4** in Scheme 1) in the present study appears to be close to the one they proposed.

A reactivity-selectivity linear relation[15] has been observed between the rates and the composition of olefin **4** and **5**, when log k_1 values in NMF, NMA, DMF, and DMA are plotted against the logarithms of the ratio %**5**: %**4** (Fig. 2), indicating that both elimination products stem from a single intermediate **2** as depicted in Scheme 1.[16]

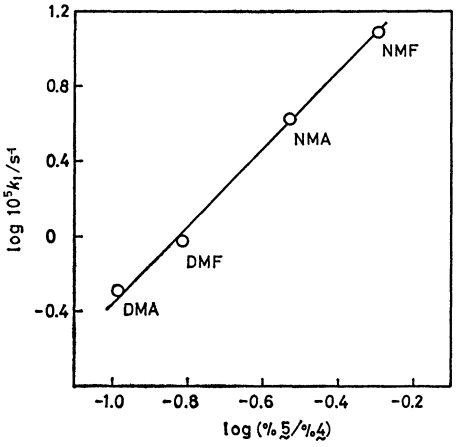


Fig. 2. Linear reactivity-selectivity relationship between log k_1 and log(%**5**/%**4**) for the carboxamide solvent.

Substitution Products of the Solvolysis of ***1*** *in the Carboxamides.* Besides the elimination products, formation of small amounts (≤3%) of ester (acetate or formate) was observed (Table 2). Since the carboxamide solvent used for the solvolysis study is usually contaminated with water (*ca.* 0.003 mol/dm³ or less) even after rigorous purification, the esters seem to be produced by the hydrolysis of an *N*-protonated (as to NMF or NMA) or *N*-methylated (as to DMF or DMA) imidate ester (**6**)[17] which might be derived from the ion-pair intermediate **2** (Scheme 2, *vide infra*). In fact, an examination of the ester yield in DMF with various water contents indicates (Fig. 3, *vide infra*) that no formate is obtained in a completely dried DMF. It is known that a protonated or methylated imidate ester similar to **6** can be rapidly hydrolyzed.[18]

Small amounts of bicyclic alcohol (≤0.7%) are also produced by the hydrolysis of **1** with water contained in the carboxamide solvent.

Effects of Added Water on the Product Distribution in the Solvolysis of ***1*** *in DMF.* GLC product analysis were carried out on the solvolysis of **1** in DMF in the presence of various amounts of water (0.003—0.519 mol/dm³). With an increase in the water content, the yield of the formate increases from zero and reaches a maximum value (7.3%), accompanied by a decrease in the yield of unrearranged olefin **4** from 85.8 to 79.5% (Table 3), whereas the yield of rearranged olefin **5** remains unchanged throughout the whole range of water concentration.

Table 3. Effects of added water on the product distribution for the solvolysis of 7β-methylbicyclo[3.3.1]non-3β-yl tosylate (**1**) in DMF at 35 °C[a]

$[H_2O]$[b] mol/dm³	Yield/% Olefin **4**	Olefin **5**	Ester 3α[c]	Ester 3β[d]	ROH[e]
0.003	85.8	12.8	0.2	0.7	0.5
0.019	84.6	12.5	1.6	1.3	0.0
0.036	83.4	12.9	2.4	1.3	0.0
0.068	82.3	12.6	3.8	1.2	0.0
0.126	80.4	12.7	5.6	1.1	0.2
0.519	79.5	12.7	6.7	0.6	0.5

a) $[ROTs]_0=0.08$ mol/dm³. [pyridine]=0.084 mol/dm³. b) Desired amount of water was added except for the first run, in which the $[H_2O]$ was determined by means of the Karl-Fischer titration. c) Inverted formate. d) Retained formate. e) 3-ol; isomer compositions were not determined.

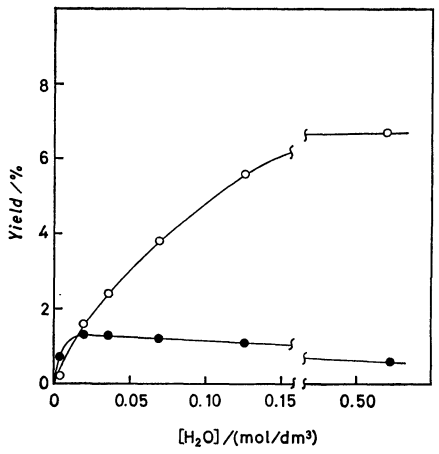
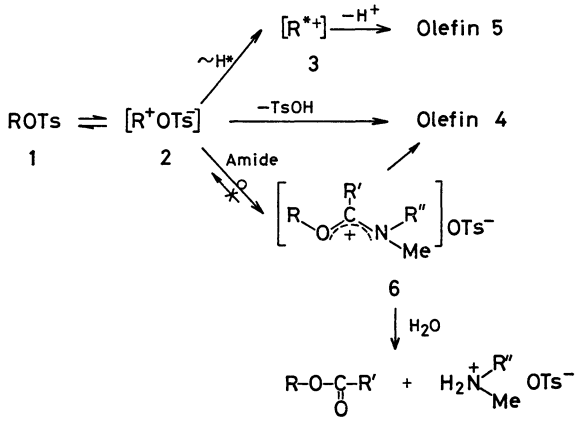


Fig. 3. Effect of added water content in DMF on the formation of 3α- (○) and 3β-formates (●).

The fact that the change in water content affects the yield of unrearranged olefin **4** as well as the yield of the formate suggests that cationic imidate **6** is produced even in the absence of water to form olefin **4**, not returning to the intimate ion-pair intermediate **2**. If such a return course is probable, a decrease in the yield of the olefin **5** would be observed with an increase in the water content. However, this is not the case (Table 3). The probable reaction pathways are shown in Scheme 2.



Scheme 2. (R′=H or Me; R″=H or Me)

The yields of the 3β-formate are less than 1.3%, while the yields of 3α-formate continuously increase with an increase in the water content up to 6.7% (Table 3 and Fig. 3). The latter is most probably formed through the usual inversion course in the reaction sequence as shown in Scheme 2. The course of the formation of 3β-formate remains open for further examination, though it is in low yields and might not represent a major feature of the solvolysis.

In conclusion, the solvolysis of **1** in the carboxamide solvents proceeds *via* the initially-formed intimate ion-pair intermediate **2** upon which the transannular 1,5-hydride shift, *syn*-El reaction, and nucleophilic displacement by the carboxamide molecule occur competitively (Scheme 2). The mechanism is essentially in line with Graham's conclusion.[2]

Experimental

All the melting points are uncorrected. NMR spectra were measured with a Hitachi R-24 instrument, tetramethylsilane being used as an internal standard, IR spectra with a Hitachi 215 or EPI-S2 spectrometer, only the major absorption being cited, and mass spectra with a Hitachi RMS-4 mass spectrometer at 70 eV, the molecular ion being cited. For GLC analysis, a Hitachi K-53 gas chromatograph fitted with a flame ionization detector was used with a 3 m column (i.d. =3 mm) packed with Carbowax 20M or PEG 6000 on Chromosorb W.

Purification of Carboxamides. All the carboxamides used in this study were purified as follows. A reagent grade material was dried for three days over molecular sieves (Type 4A). It was distilled under reduced pressure in the presence of concd H_2SO_4 and the distillate was allowed to stand over CaO or CaH_2 (except for NMF) for several hours. The liquid was transferred to a distillation flask using a large-bore, double ended needle under a positive pressure of nitrogen and distilled under reduced pressure in a dry nitrogen system. The purified carboxamide was stored in an amber bottle with a septum closure under dry nitrogen. In use, a syringe needle is pushed through the septum to gain access to the carboxamides. Titration with Karl Fischer reagent indicates that the water content of the carboxamide is less than 0.003 mol/dm³.

Synthesis of the Substrate ***1***. The synthesis of **1** was reported by Eakin *et al.*[2,19] without any details of the preparation or properties of the substances.

1-Hydroxy-7β-methylbicyclo[3.3.1]nonan-3-one ***(7)***: The procedure is essentially the same as that of Macrosson *et al.*[20] To a stirred solution of NaOMe in MeOH (Na; 0.4 g, MeOH; 30 cm³) was added a mixture of 5-methyl-2-cyclohexen-1-one[21] (1.9 g) and ethyl acetoacetate (2.7 g). After the solution had been heated under reflux for 72 h, a solution of KOH (2.6 g) in water (7.6 cm³) was added, heating under reflux being continued for 12 h. The methanolic solution was concentrated by rotoevaporation. The organic layer was taken up in CH_2Cl_2 and the organic extracts were washed with 5% aq HCl, saturated aq $NaHCO_3$, and saturated aq NaCl. The CH_2Cl_2 solution was dried (Na_2SO_4), concentrated, and recrystallized from CCl_4–hexane, giving 1.95 g (68%) of the hydroxy ketone **7**: mp 79—80 °C; IR (KBr) 3300 (OH) and 1702 cm⁻¹ (C=O); NMR ($CDCl_3$) δ=0.86 (d, 3H, J=4.4 Hz, CH_3), 1.03—2.23 (m, 12H), and 2.59 ppm (s, 1H, exchangeable with D_2O); MS, *m/e* 168. (Found: C, 71.15; H, 9.41%).

1-Bromo-7β-methylbicyclo[3.3.1]nonan-3-one ***(8)***: To a stirred solution of **7** (1.96 g) in dry ether (15 cm³) was added freshly distilled PBr_3 (1.11 g) and the resulting solution was heated under reflux for 30 min. The ether solution was washed with cold water, dried (Na_2SO_4), concentrated, and recrystallized from hexane, giving 2.38 g (88%) of bromo ketone **8**: mp 64.5—65.4 °C; IR (CCl_4) 1718 cm⁻¹ (C=O); NMR ($CDCl_3$) δ=0.86 (d, 3H, J=3.6 Hz, CH_3), 1.0—2.8 (m, 10H), and 3.06 ppm (s, 2H, C(Br)–CH_2–CO).

7β-Methylbicyclo[3.3.1]nonan-3-one ***(9)***: A mixture of **8** (2.1 g), $(n\text{-Bu})_3SnH$ (5.48 g), AIBN (2.07 g), and dry toluene (60 cm³) was heated at 60—65 °C for 4 h. After removal of toluene by rotoevaporation, the residue was treated with hexane and filtered. The filtrate was concentrated and distilled (100 °C/67 Pa) to give crude ketone, from which 1.2 g (87%) of ketone **9** was isolated by means of preparative TLC (alumina PF_{254}, Merck) using hexane–CH_2Cl_2 (19: 1, v/v) as a developing agent: mp 54—54.5 °C (lit,[22] mp 57—58 °C); IR (CCl_4) 1710 cm⁻¹ (C=O); NMR ($CDCl_3$) δ=0.83 (d, 3H, J=5 Hz, CH_3) and 1.1—2.7 ppm (m, 13H).

7β-Methylbicyclo[3.3.1]nonan-3β-ol ***(10)***: Lithium (0.334 g) was dissolved in NH_3 (l) (80 cm³) and to this solution was added a solution of **9** (1.5 g) in dry THF (30 cm³). After being stirred for 30 min, dry EtOH (6.8 cm³) was added and the mixture was stirred until the blue color disappeared. The usual work-up afforded 1.27 g (84%) of the alcohol: mp 69—76 °C. It was found convenient to convert the alcohol into the corresponding formate for separation of the 3α- and 3β-epimers. This was done by treatment of the alcohol with large excess of acetic formic anhydride in pyridine (12 h at room temp). The formate was isolated after the usual work-up as a pale yellow oil (1.45 g) which was recrystallized from ether at −78 °C to give 1.38 g (94%) of 3β-formate (**11**): mp 37—38 °C; IR (neat) 1728 (C=O) and 1185 cm⁻¹ (C–O–C); NMR ($CDCl_3$) δ=0.85 (d, 3H, J=5.8 Hz, CH_3), 1.0—2.3 (m, 13H), 5.56 (nine-line m, 1H, C<u>H</u>(OCHO)), and 7.99 ppm (s, 1H, CHO).

Found: C, 72.77; H, 9.73%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

Pure 3β-alcohol **10** was obtained by the hydrogenolysis of

11 with $LiAlH_4$ in 98% yield: mp 76—78.5 °C (lit,[22] mp 72—75 °C); IR (CCl_4) 3620 (OH), 3300 (OH), and 988 cm^{-1} (C–O); NMR ($CDCl_3$) δ=0.84 (d, 3H, J=5 Hz, CH_3), 1.0—2.5 (m, 14H), and 4.34 ppm (nine-line m, 1H, C<u>H</u>(OH)); MS, *m/e* 154.

7β-Methylbicyclo[3.3.1]non-3β-yl Tosylate ***1***: The compound was prepared from **10** following the method of Stéhelin *et al.*[22] Spectroscopic data for **1** were identical with those reported:[3,22] mp 63.5 °C (dec) (lit,[3,22] mp 64 °C (dec)).

7β-Methylbicyclo[3.3.1]nonan-3α-ol (12).[2] To s atirred solution of $NaBH_4$ (1.5 g) in MeOH (20 cm^3) was added a solution of **9** (1.35 g) in MeOH (60 cm^3) and the resulting mixture was stirred for 15 h at room temp. After the usual work-up, sublimation of the residue *in vacuo* afforded 1.2 g (88%) of an alcohol. GLC assay for the corresponding acetate showed that the alcohol consists of **10** and **12** in the ratio 13: 87. 3α-Alcohol **12** was isolated conventionally from the mixture by fractional crystallization from hexane in 26% yield (based on **9**): mp 66.5—68.5 °C; IR (CCl_4) 3620 (OH), 3300 (OH), and 983 cm^{-1} (C–O): NMR ($CDCl_3$) δ=0.85 (d, 3H, J=6.6 Hz, CH_3), 0.6—2.5 (m, 14H), and 3.92 ppm (distorted m, 1H, C<u>H</u>(OH)); MS, *m/e* 154. (Found: C, 77.53; H, 11.54%).

exo-*7-Methylbicyclo[3.3.1]non-2-ene* ***4***.[2,3] Dehydration of **12** with $POCl_3$ and pyridine afforded olefin **4** in 72% yield: bp 80 °C (bath temp)/427 Pa; IR (neat) 3005 (=C–H) and 1650 cm^{-1} (C=C); NMR ($CDCl_3$) δ=0.83 (d, 3H, J=6 Hz, CH_3), 0.9—2.7 (m, 11H), and 5.70 ppm (m, 2H, CH=CH).

3-Methylbicyclo[3.3.1]non-2-ene ***5***.[2,3] The olefin was separated from a mixture of **4** and **5**, obtained by treating **4** with boiling formic acid,[23] by means of preparative GLC, and used as an authentic sample for GLC assay.

*7β-Methylbicyclo[3.3.1]non-3β-yl-7α-*d *Tosylate* ***1-7α-d***.[2] The compound was prepared according to the reported methods.[2,22] 7-Methylenebicyclo[3.3.1]nonan-3-one obtained by fragmentation of 1,3-dibromoadamantane[24] was reduced with $LiAlD_4$ in ether.[25] By chromatography over neutral alumina (Merck Al_2O_3, 90), pure 7-methylenebicyclo[3.3.1]nonan-3β-ol-3α-*d* was obtained as a minor reduced product (15%). The alcohol was treated with concd H_2SO_4 in MeOH (1: 1, v/v) at room temp for 3 min[2] to furnish the ketone (**9**-7α-*d*), from which **1**-7α-*d* was derived by the method described for the preparation of **1** (*vide supra*): mp 63.5 °C (dec); NMR ($CDCl_3$) δ=0.83 (s, 3H, CH_3–C(7)), 1.0—2.3 (m, 12H), 2.43 (s, 3H, aryl CH_3), 5.20 (nine-line m, 1H, CH(OTs)), and 7.53 ppm (m, 4H, aryl H).

The Acetates of ***10*** *and* ***12****, and the Formate of* ***12***. The acetates were prepared by the usual method (acetic anhydride–pyridine) and the formate was prepared by the same method as described above. They were used as authentic sample for GLC assay.

Spectral Data for 3β-Acetate: IR (CCl_4) 1730 (C=O) and 1022 cm^{-1} (C–O); NMR ($CDCl_3$) δ=0.85 (d, 3H, J=5.2 Hz, CH_3–C(7)), 1.0—2.3 (m, 13H), 2.0 (s, 3H, CH_3CO), and 5.43 ppm (nine-line m, 1H, C<u>H</u>(OAc)).

Spectral Data for the 3α-Acetate: IR (CCl_4) 1730 (C=O) and 1029 cm^{-1} (C–O); NMR ($CDCl_3$) δ=0.86 (d, 3H, J=6 Hz, CH_3–C(7)), 0.7—2.5 (m, 13H), 1.98 (s, 3H, CH_3CO), and 4.98 ppm (distorted m, 1H, C<u>H</u>(OAc)).

Spectral Data for the 3α-Formate: IR (CCl_4) 1728 (C=O) and 1180 cm^{-1} (C–O); NMR ($CDCl_3$) δ=0.87 (d, 3H. J=6 Hz, CH_3), 0.7—2.6 (m, 13H), 5.12 (distorted m, 1H, C<u>H</u>(OCHO)), and 8.01 ppm (s, 1H, CHO).

Found: C, 72.48; H, 9.73%. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95%.

Kinetic Measurement. Rates in carboxamides for **1** were determined titrimetrically by the usual sealed-ampoule technique. In a typical experiment, 13 ampoules each containing *ca.* 1.1 cm^3 of the solution were prepared. They were sealed after being flashed with nitrogen. An aliquot (1 cm^3) of the reaction mixture was pipetted from each ampoule after quenching thermally and titrated with standardized (n-Bu)$_4$NOH (in 2-propanol–MeOH; 3: 1, v/v) or with KOH (in EtOH) solution, using Thymol Blue or Thymol Blue–phenolphthalein mixed indicator, respectively. The rate constants were calculated by means of a linear least-squares fit of the integrated form of the first-order rate equation. All the rate constants are the average values of at least two independent determinations.

Product Analysis. Tosylate **1** (100 mg) was weighed into an ampoule which was repeatedly evacuated and filled with dry nitrogen. A septum is placed over the opening, and a solvent (*ca.* 6.5 cm^3) was introduced with a dried syringe, followed by addition of pyridine (0.028 cm^3) with a dried micro syringe through the septum. The ampoule was then sealed under nitrogen and kept at the desired temperature for ten half-lives. The mixture was poured into water (50 cm^3) and extracted with ether (15 cm^3, three times). The combined ether solution was washed with water, 5% aq HCl, saturated aq $NaHCO_3$, and saturated aq NaCl. After being dried (Na_2SO_4), the ether solution was carefully concentrated by use of a 30-cm column packed with glass helix to *ca.* 1—2 cm^3. The condensed ether solution was subjected to GLC assay.

The products from the solvolysis of **1** in the carboxamides were identified by their retention times on GLC. Separation was achieved at 70 °C for olefins (**4** and **5**) and at 140 °C for esters (3α- and 3β-acetates or formates).

The authers wish to express their thanks to Mr. Masami Inaba for measurement of the mass spectra, and to Messrs. Eiichiro Amano and Tadashi Hanafusa for the microanalysis.

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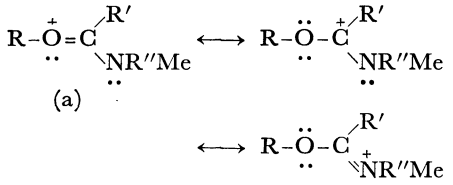

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