THE JOURNAL OF Organic Chemistry®

VOLUME 38, NUMBER 5 | MARCH 9, 1973

Solvolysis of 7-Substituted Bicyclo[3.3.1]non-3-yl Tosylates. A Kinetic Proof of σ(C–H) Participation

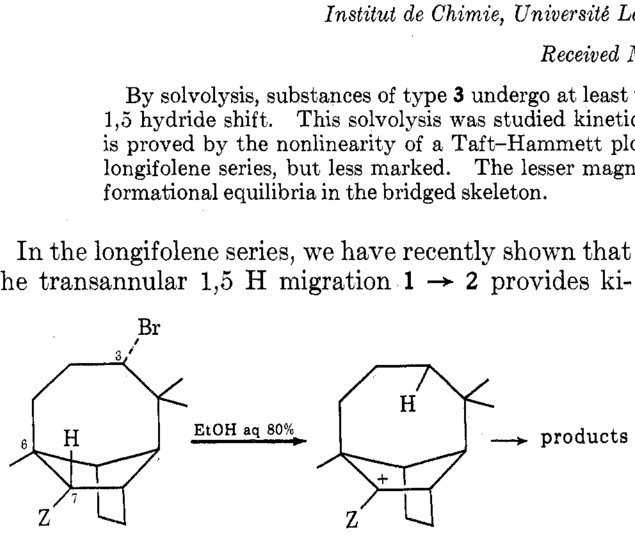
LILIANE STÉHELIN, LEONIDAS KANELLIAS, AND GUY OURISSON*

Institut de Chimie, Université Louis Pasteur, Strasbourg-67, France[1]

Received March 2, 1972

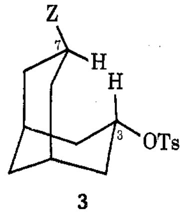
By solvolysis, substances of type **3** undergo at least in part (depending upon the nature of the substituent Z) a 1,5 hydride shift. This solvolysis was studied kinetically. A transannular σ(C–H) participation to ionization is proved by the nonlinearity of a Taft–Hammett plot; this is analogous to results obtained previously in the longifolene series, but less marked. The lesser magnitude of this participation appears to be linked with conformational equilibria in the bridged skeleton.

In the longifolene series, we have recently shown that the transannular 1,5 H migration **1** → **2** provides kinetic assistance to the ionization of the C–Br bond.[2] This was demonstrated by studying the solvolysis of a series of derivatives of type **1**, with Z varying from electron-attracting groups such as CN to electron-releasing groups such as CH_3.



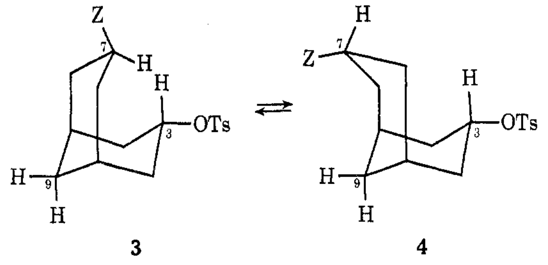
1 **2**

We now describe a similar study in a less exotic system than that of longifolene, with bicyclo[3.3.1]nonane derivatives **3**. As we shall see, the results obtained in the first series have been confirmed; yet they are quantitatively less striking here; and this will form the basis of the concluding discussion.



3

The ring system of bicyclo[3.3.1]nonane is structurally very closely related to that of longifolene. In longifolene derivatives, C-3 and C-7 are only 3.17 Å apart;[3] in the bicyclo[3.3.1]nonane derivatives, C-3 and C-7 are also in van der Waals contact.[4] This leads to two consequences, in both series: any $sp^3 \rightarrow sp^2$ change at C-3, such as that resulting from the solvolysis, will be favored, and the short C-3–C-7 distance favors transannular hydride 1,5 shifts, as is well known in both series.[5–7] However, while longifolene derivatives are practically constrained to one conformation, bicyclo[3.3.1]nonane derivatives can display some conformational mobility. One extreme case would be the chair–boat equilibrium **3** → **4**, but this may be the source of even more severe steric interactions, between Z and C-9.



3 **4**

It is therefore more probable that the rings are only flattened.[8] Anyway, this implies that, in the series **3**,

---

(1) Laboratory associated with the National Center of Scientific Research (France).

(2) L. Stéhelin, J. Lhomme, and G. Ourisson, *J. Amer. Chem. Soc.*, **93**, 1650 (1971).

(3) J. Cl. Thierry and R. Weiss, *Tetrahedron Lett.*, 2663 (1969).

(4) (a) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc. C*, 1844 (1965); (b) N. C. Webb and M. R. Becker, *J. Chem. Soc. B*, 1317 (1967); (c) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, **47**, 695 (1964); (d) J. Laszlo, *Recl. Trav. Chim. Pays-Bas*, **84**, 251 (1965).

(5) D. Helmlinger and G. Ourisson, *Justus Liebigs Ann. Chem.*, **686**, 19 (1965).

(6) (a) R. A. Appleton and S. H. Graham, *Chem. Commun.*, 297 (1965); (b) R. A. Appleton, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, **23**, 805 (1967); (c) W. A. Ayer, and K. Piers, *Chem. Commun.*, 541 (1965); H. Dugas, R. A. Ellison, Z. Valenta, K. Wiesner and C. M. Wong, *Tetrahedron Lett.*, 1279 (1965).

(7) (a) M. A. Eakin, J. Martin, and W. Parker, *Chem. Commun.*, 298 (1968); (b) M. A. Eakin, J. Martin, W. Parker, C. Egan, and S. H. Graham, *Chem. Commun.*, 337 (1968).

(8) M. R. Vegar and R. J. Wells, *Tetrahedron Lett.*, 2847 (1971).

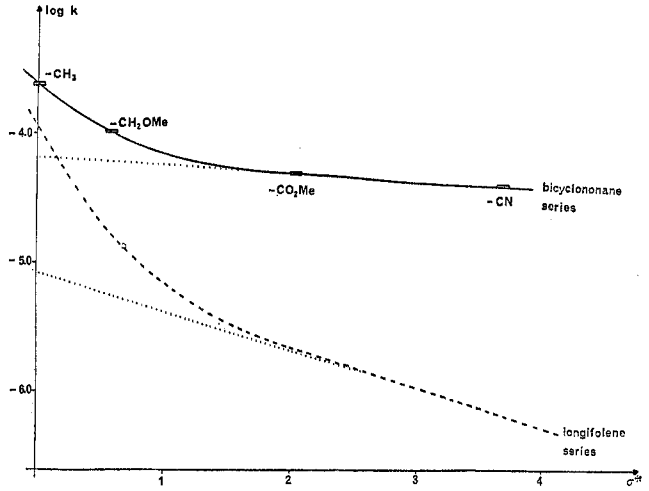


Figure 1.

the distance C-3–C-7 is less rigidly held to the van der Waals contact, and transannular hydride shifts may be less favored. Furthermore, any kinetic consequence of the H assistance to solvolysis in derivatives such as **3** should be weaker than in the longifolene series.

By methods discussed below, we have prepared the four derivatives **3**, Z = CN, CO_2CH_3, CH_2OCH_3, and CH_3. By analogy with our results in the longifolene series, we should expect to observe *no* hydride shift in the first two cases, with electron-attracting groups, and therefore we should expect to get, by solvolysis, exclusively the Δ^2 substances. By contrast, with Z = CH_2OCH_3 or CH_3, one should expect to get some H transfer, and to obtain a mixture of Δ^2 and Δ^6 isomers, as was already known in the case Z = CH_3.[7b] This is indeed confirmed by experiment (Table I). We have therefore studied the kinetics of solvolysis of the four substances **3**, and analyzed the results in a Taft–Hammett plot.[9] Table II summarizes the kinetic results in aqueous ethanol at 25°.

TABLE I

	Solvolysis Products	
Starting material 3	Without H shift	With H shift
OTs(C-3), CN(C-7)	Δ^2, CN(C-7): 100%	
OTs(C-3), CO_2CH_3(C-7)	Δ^2, CO_2CH_3(C-7): 100%	
OTs(C-3), CH_2OCH_3-(C-7)	Δ^2, CH_2OCH_3(C-7): 90%	Δ^6, CH_2OCH_3(C-7): 10%
OTs(C-3), CH_3(C-7)	Δ^2, CH_3(C-7): 45%	Δ^6, CH_3(C-7): 55%

TABLE II

Z	σ*	k, sec⁻¹
CN	+3.64	$(3.92 \pm 0.04)\ 10^{-5}$
CO_2CH_3	+2.00	$(4.89 \pm 0.07)\ 10^{-5}$
CH_2OCH_3	+0.52	$(1.04 \pm 0.02)\ 10^{-4}$
CH_3	0	$(2.28 \pm 0.02)\ 10^{-4}$

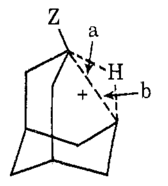
The plot log $k = f(\sigma^*)$ is clearly nonlinear (Figure 1). We have reproduced on the same plot the results previously obtained with longifolene derivatives.

It can be seen that, in the bicyclo[3.3.1]nonane series, (1) the slope for the reaction *without* H migration ($\rho_I^* \sim -0.06$) is less steep than in the longifolene series ($\rho_I^* \sim -0.3$); (2) the deviation from ρ_I^* accompanying the reaction with hydride shift is less marked than in the longifolene series; k_{CH_3} is only four times larger than k extrapolated for a linear plot, instead of 15 times in the longifolene series.

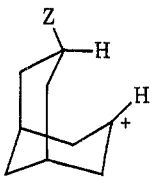
The first observation is in agreement with what can be expected for a system more flexible than that of longifolene: any increase of the distance C-3–C-7 should lead to a decrease of the influence, by a field inductive effect, of the Z group (leading to a lesser influence of the nature of Z on the rate of solvolysis, and therefore to a less steep curve).

The lesser deviation of linearity may be due only to the lesser propensity of H-7 to migrate: in the longifolene series, it is an exo nucleofuge in a bicyclo[2.2.1]heptane system, and furthermore the transition $sp^3 \rightarrow sp^2$ eliminates, on C-7, the eclipsing of the methyl at C-6 and of Z at C-7. So, the near-quantitative hydride migration, as observed in the longifolene series, is far from being reached in the bicyclo[3.3.1]nonane series (Table I).

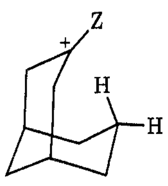
The interpretations given in our study of longifolene derivatives hold also in this case, as well as their ambiguity: the phenomenon of H assistance appears to be compatible with the intervention of a nonclassical ion **5** as the first intermediate, or of the transannular ion **6** derived from an intramolecular S_N2 reaction by the σ(C–H) bond, or from an intimate rearranged ion pair.



5



6



7

It is not possible to choose between these two hypotheses by comparing the rates and the product distribution. By extrapolating the linear portion of the curve to σ* = 0, one obtains a "theoretical" k_{CH_3}, which would correspond to solvolysis without migration. This "theoretical" k_{CH_3} is one-fourth of the observed k_{CH_3}, which would lead to a "theoretical" distribution of products of one-fourth without and three-fourths with H migration, instead of the observed distribution (45% without and 55% with H migration).

This discrepancy would be easily explained by an asymmetric opening of the nonclassical ion **5**, collapsing competitively by cleavage a (for 55%) and by cleavage b (for 20%). However, the second hypothesis would also be compatible with the observed facts: the classical ion **6**, kinetically formed, could be equilibrated with the isomeric ion **7**, in a subsequent step; the relative collapse rate of ions **6** and **7** would then have to be similar to that postulated for the competitive cleavages of **5**.

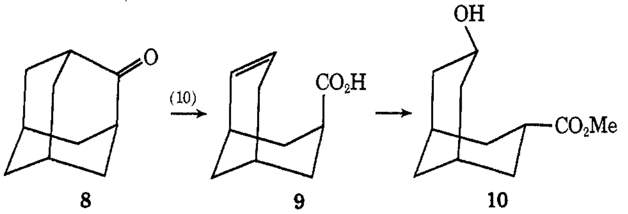
Our results can therefore not help to define the structure of the first intermediate in the solvolysis of the products studied. However, they demonstrate clearly the effect of the migration of H to increase the rate of solvolysis at the site, across the ring, toward which H migrates. σ(C–H) assistance to solvolysis can now be taken as a general phenomenon, and this is

---

[9] (a) Reference 2; see ref 14, 15, and 16a therein. (b) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556. (c) For a recent example in the phenyl participation problem, see H. C. Brown and C.-J. Kim, *J. Amer. Chem. Soc.*, **93**, 5765 (1971).

why we are now extending this study to 9,9-dimethyl derivatives of the series **3**, which should be conformationally blocked, and for which we therefore predict a closer similarity with the longifolene series.

Synthesis of the Substrates.—The substrates selected for the study require a convenient precursor with the exo,exo configuration of the substituents at C-3 and C-7. Such a precursor was found in the exo,exo hydroxy ester **10**, obtained from adamantanone **8** *via* the



unsaturated endo ester **9**. Charts I and II summarize the reactions giving the four substances used for the kinetic study; these reactions are described in the Experimental Section.

Chart I

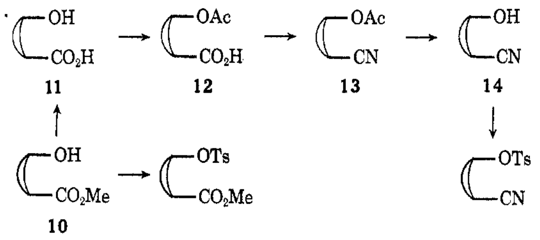
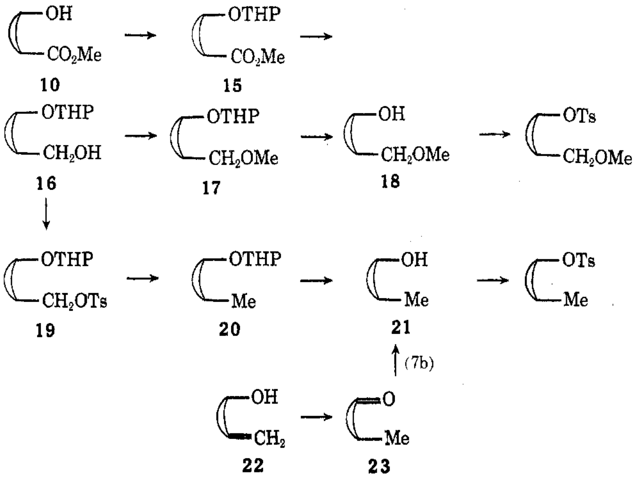


Chart II



Experimental Section

The following instruments were used: melting points, Reichert heating stage and microscope; infrared spectra (ir), Beckman IR-8A spectrophotometer; nuclear magnetic resonance spectra (nmr), Varian A-60, tetramethylsilane as internal reference; mass spectra, Thomson-Houston THN-208 double focusing spectrometer, direct inlet, 70 eV; gas chromatography, Aerograph Hy-Fi 600. Microanalyses were run by the Strasbourg Division of the Service Central of Microanalyse of CNRS.

***endo*-7-Carboxybicyclo[3.3.1]non-3-Ene (9) (3-Ene, *endo*-7-CO_2H).**—Adamantanone **8** (2 g) was dissolved in methanesulfonic acid (50 ml), and sodium azide (1.3 g) was added in small portions at 0° over 30 min. After the reaction was allowed to stand for 1 hr, the solution was poured onto ice and neutralized with a 5% aqueous sodium hydroxide solution. When the mixture was clearly alkaline, extra pellets of sodium hydroxide were added to make the medium strongly basic. The solution was stirred for 2 hr and then acidified with concentrated hydrochloric acid. Extraction by the usual method gave crude white crystals of the unsaturated acid **9** (2 g, 91%), recrystallizable from cyclohexane and identified by comparison with an authentic sample.

7-Carbomethoxybicyclo[3.3.1]nonan-3-ol (10) (3-OH, 7-CO_2CH_3).—The methyl ester of **9** (30.4 g) was dissolved in a solution of sodium methoxide in methanol (15 g of sodium in 1300 ml of methanol). Freshly distilled hexamethylphosphotriamide (HMPT) (270 ml) was added and the mixture was refluxed under nitrogen for 20 hr. After it was cooled and acidified with 1 *N* aqueous hydrochloric acid, the mixture was extracted in the normal way to give a crude liquid product (23.2 g) whose nmr spectrum showed it to be a mixture of acid and ester, both 7-exo. The yield was 82%. The crude product was esterified with boron trifluoride etherate in methanol to provide the 7-exo unsaturated ester, which was purified by sublimation and then submitted to hydroboration (see below): bp 58° (0.5 mm); ir ($CHCl_3$) 1730 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 5.77 (m, 2, HC=CH), 3.65 (s, 3, CO_2CH_3); mass spectrum *m/e* 180, 165, 148, 121.

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.98; H, 8.93.

A solution of diborane in tetrahydrofuran was prepared by the method of Zweifel and Brown.[11] The 7-exo unsaturated ester (0.5 g) was dissolved in tetrahydrofuran (11 ml), freshly distilled from lithium aluminum hydride. The apparatus was carefully purged with nitrogen. Then a solution of diborane in tetrahydrofuran (1.75 ml of 0.6 *M* solution) was slowly added *with continuous shaking* from a syringe. The reaction mixture was left to stir for 1 hr at room temperature and then 3 *N* aqueous sodium hydroxide (1.75 ml) was cautiously added, followed by hydrogen peroxide (30%, 1.75 ml), the reaction mixture being maintained at room temperature. The mixture was left to stir for 1 hr, and then most of the tetrahydrofuran was evaporated off under reduced pressure, and, after saturation of the aqueous phase with sodium chloride, extraction was carried out in the usual way. The crude product was a very viscous liquid (0.485 g, 88%), identified by nmr as a 55:45 mixture of 3-hydroxy ester **10** and corresponding 2-hydroxy ester.

Note that the molecular ratio ester/diborane is 3:1; from the volume of water necessary to destroy the excess diborane, it can be calculated that 1 mol of diborane reacts with 4 mol of ester. If too much diborane is added, the ester is reduced to a hydroxy compound. The stirring must be vigorous and the nitrogen flow not too violent to prevent entrainment of the diborane.

The 3-hydroxy ester **10** was separated from the 2-hydroxy ester by chromatography on neutral alumina (Woelm, activity II) by eluting with mixtures of increasing polarity of ethyl acetate in benzene, and then recrystallized from petroleum ether (bp 30–60°): mp 74–75°; ir ($CHCl_3$) 3600, 3440 (OH), 1725 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 4.28 (m, 1, CHOH), 3.65 (s, 3, CO_2CH_3); mass spectrum *m/e* 198, 180, 167, 166, 139,

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.61; H, 9.15.

The 2-hydroxy ester was characterized as follows: bp 100° (0.01 mm); ir ($CHCl_3$) 3600, 3420, (OH), 1720 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 3.88 (m, 1, CHOH), 3.65 (s, 3, CO_2CH_3); mass spectrum *m/e* 198, 180, 166, 138.

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.60; H, 9.06.

The 2-hydroxy ester (0.1 g) was readily dehydrated in anhydrous pyridine (4 ml); phosphorus oxychloride (0.2 ml) was added and the reaction was left for 20 hr at room temperature. A crude product was obtained (0.075 g, 82%), identified by nmr as the 7-*exo*-unsaturated ester.

7-Cyano-3-hydroxybicyclo[3.3.1]nonane (14) (3-OH; 7-CN). A. Hydroxy Acid 11 (3-OH; 7-COOH).—Saponification of the hydroxy ester **10** in the usual way (potassium hydroxide in

---

(10) (a) M. A. McKervey, personal communication, 1970; (b) D. J. Raber, G. J. Kane, and P. v. R. Schleyer, *Tetrahedron Lett.*, 4117 (1970).

[11] G. Zweifel and H. C. Brown, "Organic Reactions," Vol. 13, Wiley, New York, N. Y., 1962, p 33.

TABLE III

Product	Mp, °C	Ir ($CHCl_3$), cm^{-1}	Nmr ($CDCl_3$), δ	Mass spectrum Calcd	Mass spectrum Found
3 (Z = CN)	102–103	2240 (CN)	4.93 (m, 1, CHOTs)	$C_{17}H_{21}O_3NS$ M^+ 319	319, 172, 147
3 (Z = CO_2CH_3)	72–73	1730 (ester C=O)	5.14 (m, 1, CHOTs) 3.66 (s, 3, CH_3CO_2)	$C_{18}H_{24}O_5S$ M^+ 352	352, 180, 172 148
3 (Z = CH_2OCH_3)	67–68		5.20 (m, 1, CHOTs) 3.30 (s, 3, CH_3OCH_2) 3.11 (d, 2, J = 5 Hz, CH_2OCH_3)	$C_{18}H_{26}O_4S$ M^+ 338	338, 172, 166, 121
3 (Z = CH_3)	64 dec		5.23 (m, 1, CHOTs) 0.83 (d, 3, J = 5 Hz, CH_3CH)	$C_{17}H_{24}O_3S$ M^+ 308	$(TsOH)^+$ 172 dec

methanol) gave the hydroxy acid **11** (98.5%), slightly soluble in ether and almost insoluble in chloroform: ir (KBr) 3420 (OH), 1700 cm^{-1} (acid C=O); nmr (CH_3OD) δ 4.24 (m, 1, CHOH).

B. Acetoxy Acid 12 (3-OAc; 7-COOH).—The hydroxy acid **11** was treated with acetic anhydride in pyridine in the usual way to give the acetoxy acid **12** (85%) (under no circumstances should methanol be used to destroy excess acetic anhydride, which is sufficient to esterify the acid function): ir ($CHCl_3$) 1720 (ester C=O), 1700 cm^{-1} (acid C=O); nmr ($CDCl_3$) δ 5.37 (m, 1, CHOAc), 2.09 (s, 3, CH_3CO_2).

C. Acetoxy Nitrile 13 (3-OAc; 7-CN).—The acetoxy acid **12** (2.5 g) was dissolved in anhydrous benzene (140 ml) and freshly distilled thionyl chloride (2.5 ml) was added. After refluxing for 4 hr followed by evaporation to dryness under reduced pressure, the residue was taken up again in benzene (150 ml) and saturated with ammonia. The solution was evaporated to dryness again and the residue was dissolved in anhydrous ether (70 ml) and filtered to remove the precipitated ammonium chloride. The product was added to a solution of phosphorus oxychloride (5 ml) in anhydrous ether (70 ml) with anhydrous pyridine (20 ml) and refluxed overnight. Excess phosphorus oxychloride was destroyed by the addition of water at 0°. Extraction in the usual way gave a crude, viscous product (2.15 g, 94%), the acetoxy nitrile **13**: ir ($CHCl_3$) 2240 (CN), 1720 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 5.37 (m, 1, CHOAc), 2.09 (s 3, CH_3CO_2).

D. Hydroxy Nitrile 14 (3-OH; 7-CN).—Saponification of the acetoxy nitrile **13** in the usual way (potassium hydroxide in methanol) gave the hydroxy nitrile **14** (71%), recrystallizable from petroleum ether: mp 108–109°; ir ($CHCl_3$) 3590, 3420 (OH), 2240 cm^{-1} (CN); nmr ($CDCl_3$) δ 4.13 (m, 1, CHOH); mass spectrum m/e 165, 147, 120.

Anal. Calcd for $C_{10}H_{15}ON$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.34; H, 9.17; N, 8.72.

7-Methoxymethylbicyclo[3.3.1]nonan-3-ol (18) (3-OH; 7-CH_2OCH_3). A. Ether Ester 15 (3-OTHP; 7-CH_2OCH_3).—Dihydropyran (1.4 ml) was added to a solution of the hydroxy ester **10** (2.58 g) in anhydrous benzene (10 ml), followed by several rigorously dried crystals of *p*-toluenesulfonic acid. After the reaction was complete a few crystals of sodium bicarbonate were added. When the benzene and excess dihydropyran were evaporated off the tetrahydropyranyl derivative **15** was obtained as a viscous liquid (3.6 g, 98%): ir ($CHCl_3$) 1720 cm^{-1} (ester C=O); nmr ($CDCl_3$) δ 4.32 (m, 1, CHOTHP), 3.65 (s, 3, CH_3CO_2).

B. Hydroxy Ether 16 (3-OTHP; 7-CH_2OH).—Usual reduction of the ether ester **15** with lithium aluminum hydride in refluxing ether gave the hydroxy ether **16** (90%): ir ($CHCl_3$) 3610, 3420 cm^{-1} (OH); nmr ($CDCl_3$) δ 4.32 (m, 1, CHOTHP), 3.38.

C. Diether 17 (3-OTHP; 7-CH_2OCH_3).—The hydroxy ether **16** (1.4 g) was dissolved in 1,2-dimethoxyethane (28 ml) containing methyl iodide (1.4 ml). Sodium hydride (2.74 g) in a 50% dispersion in paraffin oil was added at 0° and the reaction mixture was stirred at room temperature. Excess sodium hydride was cautiously destroyed by the addition of water, at 0°, and the mixture was extracted in the usual way, saturating the aqueous phase with sodium chloride. A liquid volatile product (2.51 g, 77%) was obtained which was a mixture of the diether **17** and paraffin oil: nmr ($CDCl_3$) δ 4.28 (m, 1, CHOTHP), 3.30 (s, 3, CH_3OCH_2), 3.11 (d, 2, J = 5 Hz, CH_2OCH_3).

D. Hydroxy Ether 18 (3-OH; 7-CH_2OCH_3).—Treatment of the diether **17**, dissolved in acetone, with a 5% solution of perchloric acid in water gave the hydroxy ether **18** (90%): mp (*p*-nitrobenzoate) 81–82°; ir ($CHCl_3$) 3600, 3420 cm^{-1} (OH); nmr ($CDCl_3$) δ 4.32 (m, 1, CHCH), 3.28 (s, 3, CH_3OCH_2), 3.11 (d, 2, J = 5 Hz, CH_2OCH_3); mass spectrum m/e 184, 166, 152, 139.

Anal. (*p*-nitrobenzoate). Calcd for $C_{18}H_{23}O_5N$: C, 64.85; H, 6.95; N, 4.20. Found: C, 64.86; H, 6.89; N, 4.41.

7-Methylbicyclo[3.3.1]nonan-3-ol (21) (3-OH; 7-CH_3). A. Tosylate Ether 19 (3-OTHP; 7-CH_2OTs).—Usual treatment of the hydroxy ether **16** with *p*-toluenesulfonyl chloride in anhydrous pyridine gave the ether tosylate **19** (92%): nmr ($CDCl_3$) δ 3.76 (d, 2, J = 6 Hz, CH_2OTs), 2.45 (s, 3, CH_3PhS).

B. Alcohol 21 (3-OH; 7-CH_3).—Usual reduction of the ether tosylate **19** with lithium aluminum hydride in ether gave the alcohol **21** (95%): mp 72–75°; ir ($CHCl_3$) 3600, 3420 cm^{-1} (OH); nmr ($CDCl_3$) δ 4.13 (m, 1, CHOH), 8.33 (d, 3, J = 5 Hz, CH_3CH); mass spectrum m/e 154, 136, 121.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.35; H, 11.57.

The tosylates of the derivatives **14**, **10**, and **18**, and **21** were all prepared by a method identical with that described for the preparation of the tosylate **19**. The physical characteristics of these tosylates are shown in Table III.

Kinetics.—Each solvolysis was carried out with nine titrations at appropriate time intervals. The 80% aqueous ethanol was prepared by the addition, at 20°, of 1 volume of distilled water to 4 volumes of freshly distilled absolute ethanol. The substance studied was ground in an agate mortar, weighed in a graduated 50-ml flask (0.5 or 0.25 mmol was weighed to ±0.1 mg), and then rapidly dissolved at room temperature by stirring. For each derivative studied, 50 ml of the solution, prepared as above, was placed in the thermostat bath (Colora ultrathermostat, ±0.1°). When temperature equilibrium at 25° had been reached, a 5-ml sample was withdrawn using a pipette and titrated. Seven samplings of the remaining solution were thus titrated at appropriate time intervals (the seventh at about 85% degree of completion of reaction). The remaining solution was left in the thermostat for at least 10 times the reaction half-life so as to measure the "experimental infinity." Each titration used a 0.01 *M* solution of sodium methoxide in methanol (standardized with a solution of potassium hydrogen phthalate). The indicator used was *p*-bromothymol blue, at the point of turning blue. A Manostat–Greiner micrometric buret was used, giving an accuracy of 0.001 ml. The products of the solvolytic reactions were determined by examination of 0.1 *M* solutions which had either been heated or allowed to stand for 10 times the reaction half-life, in the presence of 1 equiv of sodium carbonate.

For the derivative **3** (Z = CH_3) the kinetics were determined also by following the reaction in ultraviolet.[12] Results from both methods (titration and spectrography) were consistent.

The solvolysis products in the bicyclo[3.3.1]nonane series are very volatile. As we had only small quantities of starting

---

[12] C. G. Swain and C. R. Morgan, *J. Org. Chem.*, **29**, 2097 (1964).

TABLE IV

Starting material	Solvolysis product (registry no.)	Nmr ($CDCl_3$), δ	Mass spectrum Calcd	Mass spectrum Found
3 (Z = CN)	Δ², CN(C-7) (37741-58-5)	5.80 (m, 2, HC=CH)	$C_{10}H_{13}N$ M^+ 147	147, 120
3 (Z = CO_2CH_3)	Δ², CO_2CH_3(C-7)	5.76 (m, 2, HC=CH) 3.63 (s, 1, CO_2CH_3)	$C_{11}H_{16}O_2$ M^+ 180	180, 165, 148, 121, 120
3 (Z = CH_2OCH_3)	Δ², CH_2OCH_3(C-7) (37741-60-9)	5.71 (m, 2, HC=CH) 3.28 (s, 3, CH_3OCH_2) 3.17 (d, 2, J = 6 Hz, CH_2OCH_3)	$C_{11}H_{18}O$ M^+ 166	166, 124
	Δ⁶, CH_2OCH_3(C-7) (37741-61-0)	5.48[a] (m, 1, HC=C–)		
3 (Z = CH_3)	Δ², CH_3(C-7) (2721-44-0)	5.73 (m, 2, HC=CH) 0.82 (d, 3, J = 6 Hz, CH_3)	$C_{10}H_{16}$ M^+ 136	136, 121
	Δ⁶, CH_3(C-7) (2721-36-0)	5.40 (m, 1, HC=C–) 1.67 (s, 3, CH_3)		

[a] The nmr signal of this hydrogen is too weak to be assigned an unambiguous shift value; the shift (δ 5.48), here indicated, is compatible with the homolog multiplet on the solvolysis product of **3** (Z = CH_3).

materials, the solvolyses for preparative purposes were run with solutions 0.1 *M* in 80% aqueous acetone, in the presence of sodium carbonate, to avoid a thermodynamic equilibrium between the products of the reaction. Evaporation of the reaction mixture was easier than with aqueous ethanol, so that quantitative extraction of the reaction products was facilitated. Aqueous acetone is slightly less nucleophilic and less ionizing than 80% aqueous ethanol.[13]

We checked by vpc that the same products were obtained as those from solvolyses 0.01 *M* run in aqueous ethanol in the presence of sodium carbonate. The ratio of product without H shift/product with H shift was determined by a direct vpc evaluation of the crude product of such solvolyses. Table IV gives the nmr and mass spectral data of the products of those solvolyses studied.

Registry No.—**3** (Z = CN), 37741-64-3; **3** (Z = CO_2CH_3), 37731-04-7; **3** (Z = CH_2OCH_3), 37731-05-8; **3** (Z = CH_3), 19912-54-0; **8**, 700-58-3; **9**, 21932-98-9; **9** *exo*-methyl ester, 37741-59-6; **10**, 37731-09-2; **11**, 37731-10-5; **12**, 37731-11-6; **13**, 37731-12-7; **14**, 37731-13-8; **15**, 37731-14-9; **16**, 37731-15-0; **17**, 37731-14-9; **18**, 37731-17-2; **18** *p*-nitrobenzoate, 37731-18-3; **19**, 37731-19-4; **21**, 37741-57-4; 7-carbomethoxybicyclo[3.3.1]nonan-2-ol, 37731-21-8.

Acknowledgment.—We thank Dr. M. A. McKervey (Belfast) for a generous gift of the unsaturated acid **9**.

---

[13] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962.

Solvolysis of 9,9-Dimethylbicyclo[3.3.1]non-3-yl Tosylate. Enhancement of σ (C–H) Participation by Steric Blocking

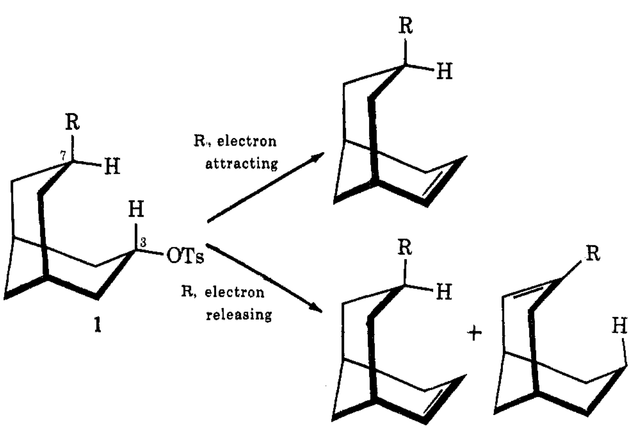
LILIANE STÉHELIN, LEONIDAS KANELLIAS, AND GUY OURISSON*

Laboratoire associé au CNRS, Institut de Chimie, Université Louis Pasteur, Strasbourg-67, France

Received September 6, 1972

7,9,9-Trimethylbicyclo[3.3.1]non-3-yl tosylate (**2**, R = CH_3) undergoes solvolysis with quantitative 7–3 hydride transfer. The rate of solvolysis of **2** (R = CH_3) is four times higher than that of the lower homolog **1** (R = CH_3). This is interpreted by an anchoring of the conformation of both rings of **2** in a chair form, ensuring favorable geometry for H transfer.

We have recently shown that transannular H migrations accompanying solvolysis can produce a rate enhancement in the longifolene series[1] and in the bicyclo[3.3.1]nonane series.[2] In this last series, for instance, solvolysis of 7-substituted bicyclononyl tosylates **1** has been shown, by a Taft–Hammett treatment,[3] to be accelerated when it is accompanied by hydride migration from C-7 to C-3; there is a σ(C–H) participation in the step determining the rate of solvolysis.



However, in the bicyclononane series, this kinetic effect is less marked than in the longifolene series, and

---

[1] L. Stéhelin, J. Lhomme, and G. Ourisson, *J. Amer. Chem. Soc.*, **93**, 1650 (1971).

[2] L. Stéhelin, L. Kanellias, and G. Ourisson, *J. Org. Chem.*, **38**, 847 (1973).

[3] (a) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 556; (b) A. Streitwieser, Jr., *J. Amer. Chem. Soc.*, **78**, 4935 (1956); "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962, pp 122, 146; (c) C. J. Lancelot, J. J. Harper, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4294 (1969); (d) P. G. Gassman, J. L. Marshall, J. G. Macmillan, and J. M. Hornback, *ibid.*, **91**, 4282 (1969).