11. Electrophilic Additions to Strained Bridgehead Olefins. Estimation of Strain by Comparison with the Solvolysis of Bridgehead Bromides[1]

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(4. X. 76)

Summary

The addition of water, acetic acid, and hydrogen bromide to the strained bridgehead olefins bicyclo[3.3.1]-1(2)-nonene (**1**), bicyclo[4.2.1]-1(8)-nonene (**2**), and bicyclo[4.2.1]-1(2)-nonene (**3**) gives exclusively the bridgehead alcohols, acetates, and bromides, respectively. The reaction rate constants for the addition of acetic acid to the bridgehead olefins **1**, **2** and **3**, and the solvolysis rates for the related 1-bromobicyclo[3.3.1]nonane (**4**) and 1-bromobicyclo[4.2.1]nonane (**5**) were measured. A comparison of the activation enthalpies of these two reactions gives an estimate of relative strain of the bridgehead double bond. The strain in the bicyclo[4.2.1]nonenes **2** and **3** is similar to that in *trans*-cyclooctene (8–9 kcal/mol).

Introduction. – The strain inherent in the double bond of bridgehead olefins such as the bicyclononenes **1**, **2** and **3** [1] should lead to an enhanced reactivity in addition reactions compared to other, unstrained trisubstituted olefins. Indeed, as shown by *Wiseman* [2] and *Marshall* [3], bicyclo[3.3.1]-1(2)-nonene (**1**) reacts extremely fast with electrophilic reagents, *e.g.* acetic acid, water or alcohol in the presence of an acid catalyst, bromine, osmium tetroxide, peracid, and diborane. A reaction was also observed with the nucleophilic reagents methyllithium and phenyllithium, with the dipolarophile diazomethane, and with some dienes yielding *Diels-Alder* adducts.


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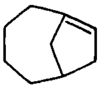
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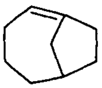
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Recently *Kresge et al.* [4] published a study on the kinetics and mechanism of the acid catalysed hydration of the strained bridgehead olefins bicyclo[3.3.1]-1(2)-nonene (**1**) and bicyclo[4.2.1]-1(8)-nonene (**2**). They showed that these compounds react by the

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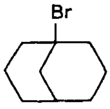
[1] Taken in part from the 'Habilitationsschrift' of *K. B. Becker*, Basel 1976.

mechanism now known to apply to the hydration of simple unstrained olefins, namely slow protonation of the double bond at the secondary carbon atom followed by rapid hydration of the bridgehead carbenium ion thus formed. Based on deuterium isotope effects, *Brønsted* coefficients, and relative rate constants, conclusions concerning the transition state of protonation and the strain in the bridgehead olefins were drawn. These results will be discussed together with our own work (*vide infra*).

Strain is defined as the enthalpy difference between the bridgehead olefin and a hypothetic olefin containing a π-bond without twist and out-of-plane deformation of the substituents, but with an identical bicyclic arrangement of the σ-bonds2). Experimentally this strain might be approximated by the difference of the enthalpies of hydrogenation of bicyclo[3.3.1]-1(2)-nonene (**1**) and bicyclo[3.3.1]-2-nonene.

The reaction enthalpy for the addition of acetic acid to **1** has been measured by *Lesko & Turner* [6]. From this experimental figure and an estimated reaction enthalpy for a model compound containing an unstrained trisubstituted double bond, a strain of 12 kcal/mol was calculated for the bridgehead double bond in **1**, compared to 9.2 kcal/mol for the double bond in *trans*-cyclooctene. Calculations of the strain and geometry of the bridgehead double bond have been made using a newly developed forcefield method for alkenes by *Allinger* [7]. For **1** a dihedral angle of 138° was found resulting in a strain of 12.85 kcal/mol. Similar calculations are reported for the two bicyclo[4.2.1]nonenes **2** and **3** [8].

Goal of the work presented here was a comparative study of the three isomeric bridgehead olefins bicyclo[3.3.1]-1(2)-nonene (**1**), bicyclo[4.2.1]-1(8)-nonene (**2**), and bicyclo[4.2.1]-1(2)-nonene (**3**) in electrophilic addition reactions. A comparison of the activation parameters for the addition of acetic acid to the bridgehead olefins with the activation parameters for the solvolysis of the corresponding bromides 1-bromobicyclo[3.3.1]nonane (**4**) and 1-bromobicyclo[4.2.1]nonane (**5**) should eventually lead to an estimate of strain for the bridgehead double bond.



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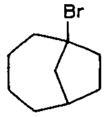

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The electrophilic addition of HX. – The olefins **1**, **2** and **3** reacted with aqueous acetone in the presence of catalytic amounts of perchloric acid at room temperature to give quantitatively3) the bridgehead alcohols **6** and **7**, respectively. The structures of 1-bicyclo[3.3.1]nonanol (**6**) [9] and 1-bicyclo[4.2.1]nonanol (**7**) [10] were confirmed by comparison with authentic samples.

Remarkably, a reaction of the bridgehead olefins **1**, **2** and **3** with acetic acid took place without catalysis by mineral acid. The olefin **1** yielded 1-bicyclo[3.3.1]nonyl acetate (**8**) as the only product3) within minutes at room temperature. The olefins **2** and

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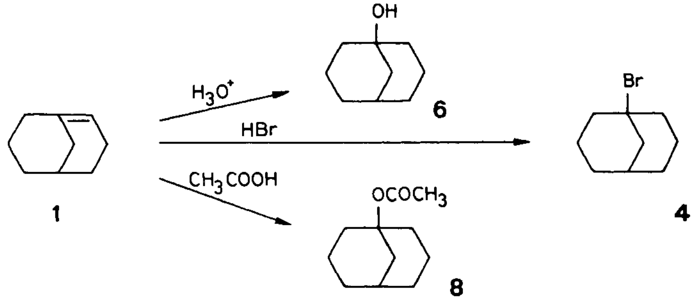
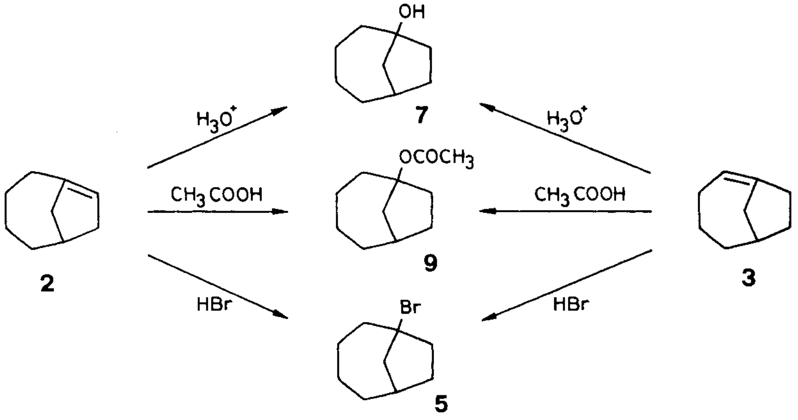
2) For an extensive discussion of strain see [5].

3 gave 1-bicyclo[4.2.1]nonyl acetate (**9**)[3] analogously, however, the reaction was slow at room temperature. Unstrained trisubstituted olefins do not react with acetic acid alone, but non-catalysed addition is observed in refluxing acetic acid with other strained olefins, namely with norbornadiene [11], bicyclo[2.1.1]-2-hexene [12], *trans*-cyclooctene [13], and the annulated bridgehead olefin bicyclo[3.3.0]-1(2)-octene [14] accompanied by partial isomerization of the double bond.





The olefins **1**, **2** and **3** reacted with hydrogen bromide in ethyl ether or aqueous concentrated hydrobromic acid to yield 1-bromobicyclo[3.3.1]nonane (**4**) and 1-bromobicyclo[4.2.1]nonane (**5**), respectively. Bromide **4** had been prepared previously by bromination of the bicyclic hydrocarbon [15]. The synthesis of **5** by HBr-addition to bridgehead olefin **2** represents a direct access to this hitherto unknown compound.

Protonation of the bridgehead olefins **1**, **2** and **3** always leads to the tertiary carbenium ions **10** and **11**, respectively. This regiospecificity is in accordance with *Markownikoff*'s rule, however, it is surprising because the bridgehead ions **10** and **11** cannot adopt the ideal trigonal planar conformation and therefore retain some strain of the original double bond [16].

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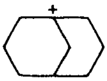
[3] More than 99% (GLC.)



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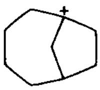

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Reaction rate of the addition of acetic acid. - The reaction rates of the addition of acetic acid to the bridgehead olefins **1**, **2** and **3** were measured with the aid of gas liquid chromatography (GLC.). After a given time at a given temperature, 0.1M solutions of the olefins in acetic acid containing an internal standard were diluted with a ten-fold excess of pentane and stirred with saturated aqueous sodium carbonate to neutralize the acid. The pentane solutions were analysed with GLC. This work-up proved to be unnecessary with the olefins **2** and **3** which gave the same results on analysing the solutions in acetic acid directly. The decrease of the olefin concentration was equal to the increase of the acetate concentration within the error limit of the GLC. method, and showed good correlation with a first order reaction, *i.e.* $d[X]/dt = k[X]$ for at least three half lives. The reaction rate constant k and the activation parameters were calculated from the change in acetate concentration. The results are compiled in Table 1.

The solvolysis of bridgehead bromides. - The reaction rate constants for the solvolysis of 1-bromobicyclo[3.3.1]nonane (**4**) and 1-bromobicyclo[4.2.1]nonane (**5**) were measured conductometrically in 80 vol.-% ethanol. The reaction rate was first order in bromide and showed no dependence on the concentration of added base. The reaction rate constants at four temperatures and the activation parameters are listed in Table 2. Our measurements show good agreement with the results of *Schleyer* [15] for bromide **4**. For comparison the reaction rate constants for *t*-butyl bromide (**12**) [17], 1-bromoadamantane (**13**) [18], and 1-bromobicyclo[2.2.2]octane (**14**) [19] are shown in Table 2. 1-Bromobicyclo[4.2.1]nonane (**5**) reacts *ca.* 10 times slower than 1-bromo-[3.3.1]nonane (**4**) and 1000 times slower than *t*-butyl bromide (**12**).

The products obtained on solvolysis of the bromides **4** and **5** in 80 vol.-% ethanol were the bridgehead alcohols **6** and **7**, and the corresponding ethyl ethers. The solvolysis therefore proceeded without rearrangement of the bridgehead carbenium ions **10** and **11**, respectively.

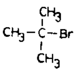
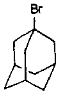
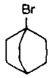
Discussion. - The experimental determination of the activation parameters for the addition of acetic acid to the bridgehead olefins allows an estimation of strain of the bridgehead double bond in **1**, **2** and **3**. The bicyclo[4.2.1]nonenes **2** and **3** may be compared directly with each other because the protonation leads to the same intermediate, the carbenium ion **11**. It is generally assumed that in endothermic carbenium ion forming reactions the intermediate carbenium ion resembles the transition state by which it is generated, a reasoning based on the *Hammond* postulate [20]. The difference of activation enthalpies $\Delta H^{\neq}$ for the reaction of **2** and **3** with acetic acid should therefore be a good approximation of the ground state enthalpy difference between the two isomers. On this basis **3** with the double bond in the seven-membered

Table 1. *Reaction rate constants (RRC.) and activation parameters of the addition of acetic acid in 0.1* M *solution*

	°C	RRC. (s^{-1})	k_{rel}	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (cal/mol · degree)
1	17.0	$1.16 \cdot 10^{-3}$			
	25.0	$2.36 \cdot 10^{-3}$			
	33.0	$4.39 \cdot 10^{-3}$			
	25a)	$2.32 \cdot 10^{-3}$	275	14.1	−23
2	40.0	$3.62 \cdot 10^{-5}$			
	50.0	$1.04 \cdot 10^{-4}$			
	60.0	$2.17 \cdot 10^{-4}$			
	25a)	$8.43 \cdot 10^{-6}$	1	17.9	−22
3	30.0	$5.32 \cdot 10^{-5}$			
	40.0	$1.51 \cdot 10^{-4}$			
	50.0	$3.37 \cdot 10^{-4}$			
	25a)	$3.33 \cdot 10^{-5}$	3.95	17.3	−21

a) Extrapolated.

Table 2. *Reaction rate constants (RRC.) and activation parameters of the solvolysis in 80 vol.-% ethanol*

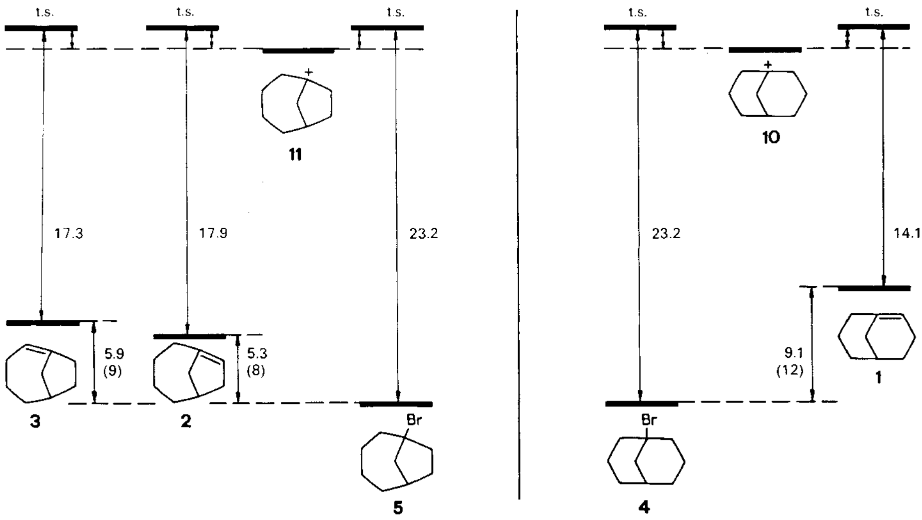
	°C	RRC. (s^{-1})	k_{rel}	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (cal/mol · degree)
4	50.0	$9.46 \cdot 10^{-5}$			
	60.0	$2.87 \cdot 10^{-4}$			
	70.0	$8.37 \cdot 10^{-4}$			
	80.0	$2.24 \cdot 10^{-3}$			
	25a)	$4.19 \cdot 10^{-6}$	$1.2 \cdot 10^{-2}$	23.2	−5.1
	25a) [15]	$3.53 \cdot 10^{-6}$		23.9	−3.2
5	70.0	$6.85 \cdot 10^{-5}$			
	80.0	$1.90 \cdot 10^{-4}$			
	90.0	$4.84 \cdot 10^{-4}$			
	100.0	$1.15 \cdot 10^{-3}$			
	25a)	$3.52 \cdot 10^{-7}$	$1.0 \cdot 10^{-3}$	23.2	−10.1
 $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br$ **12**	25a) [17]	$3.58 \cdot 10^{-4}$	1	21.5	−2.3
 **13**	25a) [18]	$4.38 \cdot 10^{-7}$	$1.2 \cdot 10^{-3}$	22.6	−12.0
 **14**	25a) [19]	$9.99 \cdot 10^{-11}$	$2.8 \cdot 10^{-7}$	26.2	−16.6

a) Extrapolated.

ring is more strained by 0.6 kcal/mol than isomer **2** with the double bond in the five-membered ring.

The bicyclo[4.2.1]nonenes **2** and **3** cannot be compared directly with bicyclo-[3.3.1]-1(2)-nonene (**1**), because two different carbenium ions, **10** and **11**, are formed on protonation. The latter may be similarly strained as their corresponding hydrocarbons [21], but a better comparison is obtained *via* the bridgehead bromides **4** and **5** as saturated reference compounds. The *Hammond* postulate again leads to the well founded hypothesis that the activation enthalpy for the solvolysis of the bromides **4** and **5** is a good approximation for the enthalpy difference between the bromide and the corresponding carbenium ion, the same carbenium ion that is formed on protonation of the bridgehead olefins **1**, and **2** and **3**, respectively. The difference of the activation enthalpies of both reactions (see *Scheme*) is therefore a measure of the strain in the bridgehead olefins, and corresponds to the enthalpy difference between the bridgehead olefin and the related bridgehead bromide.

Scheme. *Estimation of strain in bridgehead olefins by comparison of the activation enthalpies* $\Delta H^{\neq}$ *of the addition of acetic acid to the olefins and the solvolysis of bridgehead bromides*



t.s. = transition state
The enthalpy is given in kcal/mol. The numbers in brackets are absolute values of strain (see text).

Based on this comparison, the double bond in **1** is found to be more strained by *ca.* 4 kcal/mol than the double bond in **2**. Combined with the absolute value of strain in **1** of 12 kcal/mol [6], the strain in bicyclo[4.2.1]-1(8)-nonene (**2**) is 8 kcal/mol, and 9 kcal/mol in bicyclo[4.2.1]-1(2)-nonene (**3**). These two olefins are therefore similarly strained as the parent *trans*-cyclooctene (9 kcal/mol [6] [7]).

Above calculations heavily rely on the assumption that the transition state resembles the bridgehead carbenium ion. *Chiang, Kresge & Wiseman* [4] in their discussion of the hydration of bridgehead olefin **1** came to the conclusion that the transition state of protonation occurs somewhat earlier along the reaction coordinate, and that proton transfer is not as far advanced as it is in the case of simple unstrained olefins. Their conclusions are based on the low *Brønsted* exponent $\alpha = 0.67$ for general acid catalysis and on a deuterium isotope effect $k_{H^+}/k_{D^+} = 2.5$ (2.1 for bicyclo-[4.2.1]-1(8)-nonene (**2**)) for the hydration by the hydronium ion H_3O^+, compared to $k_{H^+}/k_{D^+} = 1.5$ for the unstrained olefin 2-methylpropene.

In the addition reaction of acetic acid to the bridgehead olefins **1**, **2** and **3** the activation enthalpy is 14, 17 and 18 kcal/mol, respectively, *i.e.* still sufficiently large to justify the application of the *Hammond* postulate on endothermic reactions. If indeed the transition state occurs earlier on the reaction coordinate, the enthalpy differences remain comparatively small and should cancel each other to a great extent. The above reasoning therefore remains valid.

No obvious dependence of strain on the ring size containing the double bond is found in the series of methylene-bridged *trans*-cyclooctenes. The results presented here contradict the statement of *Wiseman* [22], who concluded that bicyclo[4.2.1]-1(8)-nonene (**2**) is more strained than isomer **3** based on the percent composition of the two isomers obtained upon *Hofmann* elimination of 1-bicyclo[4.2.1]nonyl-trimethyl-ammonium hydroxide.

Financial support from *Ciba-Geigy AG* is greatfully acknowledged. I thank Prof. *C. A. Grob* for his encouragement and continuous interest in this work.

Experimental part

General remarks. See [14].

1-Bicyclo[*3.3.1*]*nonanol* (**6**). 50 mg (0.41 mmol) of bicyclo[3.3.1]-1(2)-nonene (**1**) were dissolved in 80% aqueous acetone (5 ml) and treated with one drop of 60% perchloric acid. After 5 min all of the olefin had reacted and a single alcohol had been formed to more than 99% by GLC. (Carbowax 20 M or PPE). The solution in acetone was diluted with ethyl ether, washed with 2N $NaHCO_3$ and water, dried over $MgSO_4$, and the solvent distilled off over a *Vigreux* column. The sublimation of the residue at 85°/14 Torr gave 42 mg (73%) of **6**, m.p. 167–172°, identical with the alcohol obtained upon solvolysis of bicyclo[3.3.0]octyl-methyl *p*-toluenesulfonate in aqueous acetone [9]. After repeated sublimation: white crystals, m.p. 178–180° ([9]: 182.5–184°). – IR. (CCl_4): 3620, 3400 (OH), 2930, 1087, 930. – ^{1}H-NMR. (CCl_4): 1.2–2.0 (*m*, 14H, 7 CH_2); 2.0–2.4 (*m*, 1H, CH); 2.3 (*s*, 1H, OH).

$C_9H_{16}O$ (140.23) Calc. C 77.09 H 11.50% Found C 76.88 H 11.29%

1-Bicyclo[*4.2.1*]*nonanol* (**7**). 121 mg (0.99 mmol) of bicyclo[4.2.1]-1(8)-nonene (**2**) were dissolved in 80% aqueous acetone (5 ml) containing one drop of 60% perchloric acid, and kept at RT. for 24 h under nitrogen. A single alcohol was formed in 99% yield by GLC. Work-up as above and sublimation at 90°/12 Torr gave 109 mg (78%) of **7**, m.p. 102–107°, identical with the alcohol obtained upon hydration of bicyclo[4.2.1]-1(2)-nonene (**3**) or solvolysis of bicyclo[4.2.0]octyl-methyl *p*-toluenesulfonate in aqueous acetone [10]. After repeated sublimations: white crystals, m.p. 112–114° ([10]: 129–131°). – IR. (CCl_4): 3620, 3400 (OH), 2925, 1078, 1045, 970, 932, 908. – ^{1}H-NMR. (CCl_4): 1.0–2.0 (*m*, 14H, 7 CH_2); 1.75 (*s*, 1H, OH); 2.1–2.5 (*m*, 1H, CH).

$C_9H_{16}O$ (140.23) Calc. C 77.09 H 11.50% Found C 76.81 H 11.54%

1-Bicyclo[*3.3.1*]*nonyl acetate* (**8**). 380 mg (3.11 mmol) of bicyclo[3.3.1]-1(2)-nonene (**1**) were dissolved in acetic acid (5 ml) under nitrogen. After 30 min, the solution was diluted with water and extracted with pentane. The extract, containing more than 99% of a single acetate by GLC. (Carbowax 20 M or SE-52), was washed with 2N Na_2CO_3 and water, and dried over $MgSO_4$. The distillation in a bulb tube at 130°/12 Torr gave 490 mg (86%) of **8**, m.p. 25–27°. – IR. (film): 2960, 1742 (C=O), 1458, 1363, 1252, 1230, 1060, 1020, 985, 953, 849. – ^{1}H-NMR. (CCl_4): 1.3–1.9 (*m*, 11H, CH_2); 1.87 (*s*, 3H, CH_3); 1.9–2.5 (*m*, 4H, CH, CH_2). – MS. (*m/e*): no M^+, 140 (M^+-42, 10), 97 (100).

$C_{11}H_{18}O_2$ (182.26) Calc. C 72.49 H 9.96% Found C 72.37 H 9.96%

The reduction of acetate **8** with lithiumaluminiumhydride in ethyl ether gave 96% of 1-bicyclo[3.3.1]nonanol (**6**), m.p. 165–170°, identical with the product described above.

1-Bicyclo[4.2.1]nonyl acetate (**9**). 230 mg (1.88 mmol) of bicyclo[4.2.1]-1(8)-nonene (**2**) were dissolved in acetic acid (5 ml) and warmed to 60° for 20 h under nitrogen. Work-up as above gave 290 mg (84%) of the acetate **9** as a colourless oil. – IR. (film): 2920, 1735 (C=O), 1450, 1362, 1248, 1217, 1075, 1043, 1018. – NMR. (CCl_4): 1.2–2.5 (*m*, 15H, 7 CH_2 and 1 CH); 1.90 (*s*, 3H, CH_3). – MS. (*m/e*): no M^+, 140 (M^+-42, 12), 83 (100).

$C_{11}H_{18}O_2$ (182.26) Calc. C 72.49 H 9.96% Found C 72.77 H 10.10%

Acetate **9** was identical with the addition product of acetic acid to bicyclo[4.2.1]-1(2)-nonene (**3**) and with the acetate obtained upon acetolysis of bicyclo[4.2.0]octyl-methyl *p*-toluenesulfonate [10]. The reduction of the acetate **9** with lithiumaluminiumhydride in ethyl ether gave 90% of 1-bicyclo[4.2.1]nonanol (**7**), m.p. 108–112° (see above).

1-Bromobicyclo[3.3.1]nonane (**4**). 88 mg (0.72 mmol) of bicyclo[3.3.1]-1(2)-nonene (**1**) in ethyl ether (2 ml) were added to a saturated solution of hydrogen bromide in ethyl ether (5 ml) at 0° under nitrogen. After 30 min the solution was diluted with pentane, washed with 2N $NaHCO_3$ and water, and dried over $MgSO_4$. The analysis by GLC. (SE-52) showed a single bromide contaminated with *ca.* 5% of 1-bicyclo[3.3.1]nonanol (**6**). Chromatography on silica gel with petroleum ether followed by sublimation at 110°/12 Torr gave 109 mg (75%) of **4**, m.p. 50–52° ([15]: 52–53°). – IR.(CCl_4): 2930, 1448, 1135, 1108, 1040, 949, 648. – ^{1}H-NMR. (CCl_4): 1.0–2.6 (*m*). – MS. (*m/e*): no M^+, 123 (M^+-Br, 91), 81 (100), 79 (90).

1-Bromobicyclo[4.2.1]nonane (**5**) was prepared as described above for bromide **4**, either from bicyclo[4.2.1]-1(8)-nonene (**2**) or from bicyclo[4.2.1]-1(2)-nonene (**3**). The distillation in a bulb tube at 110°/12 Torr gave 84% of bromide **5** as a colourless oil. – IR. (film): 2930, 1465, 1220, 984, 946, 922, 837, 788. – ^{1}H-NMR. (CCl_4): 1.0–2.6 (*m*). – MS. (*m/e*): no M^+, 187 (17), 185 (11), 123 (M^+-Br, 42), 83 (100).

$C_9H_{15}Br$ (203.14) Calc. C 53.21 H 7.44 Br 39.34% Found C 53.42 H 7.51 Br 39.71%

Reaction rate of the addition of acetic acid to the bridgehead olefins **1**, **2** *and* **3**. 0.20 ml of acetic acid (*Merck*, *pro analysi*) were flushed with nitrogen and pre-warmed for at least 10 min in a thermostat with a temp. deviation of ± 0.02°. 5 µl of a mixture of bicyclo[3.3.1]-1(2)-nonene (**1**; 0.020 mmol) and tridecane as an internal standard were injected through a septum to the stirred acetic acid under nitrogen. After a given time, the reaction was quenched by the addition of 2 ml of pentane. The acid was neutralized by rapid stirring with saturated aqueous carbonate, and the pentane solution analysed by GLC. (SE-52 2.5%, 110°). The decrease of the olefin concentration was equal to the increase of the acetate concentration. Less than 0.3% of unknown side products were observed. The reproducibility of the work-up method and GLC. analysis (± 1%) was tested with pure olefin, pure acetate, and mixtures of known composition. It was shown that quenching with pentane slowed down the addition reaction of acetic acid by more than a factor of 1000. The reaction rate constants were calculated by linear regression from 25 measurements of % acetate formed in function of time within 3 half-lives [23]. The correlation coefficient for a first order reaction was *ca.* 0.998, the standard deviation ± 5%.

The addition reaction of acetic acid to the less reactive olefins bicyclo[4.2.1]-1(8)-nonene (**2**) and bicyclo[4.2.1]-1(2)-nonene (**3**) could be analysed without prior neutralization of the acid. 13.5 µl of a mixture of olefin **2** or **3** (0.050 mmol) and tridecane were injected into 0.50 ml of acetic acid under nitrogen. Samples were analysed by GLC. at regular time intervals. Less than 1.0% of unknown side products were observed. The correlation coefficient for a first order reaction was better than 0.999, and the standard deviation within ± 2%. The reaction rate constants calculated from 3–4 different runs were within ± 8% in the worst case.

Reaction rate of the solvolysis of bromides **4** *and* **5** *in 80 vol.-% ethanol.* 80 vol.-% ethanol (d_{22}^{22} 0.8518) was prepared from 2795 g of abs. ethanol and 887.4 g of bidistilled water. The reaction rate constants were determined by a conductometric method [24] in a pressure cell with platinum electrodes. The concentration of the bromides was $1.0 \cdot 10^{-3}$M, and the reaction was followed for three half-lives. A slight acceleration of the solvolysis rate due to a normal salt effect was observed when the reaction was conducted in the presence of 1.2 or 4.0 equiv. of triethylamine. The standard deviation for a single run was *ca.* ± 0.3%, and the reaction rates of 4–7 runs at the same temp. were within ± 1% except in one case (± 3%).

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