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SYNTHESES OF BICYCLIC 1,2-DIOLS VIA THE RING-EXPANSION OF BRIDGEHEAD ALDEHYDES OF BICYCLO[3.2.1]OCTANE AND BICYCLONONANES WITH BENZOYL TRIFLATE

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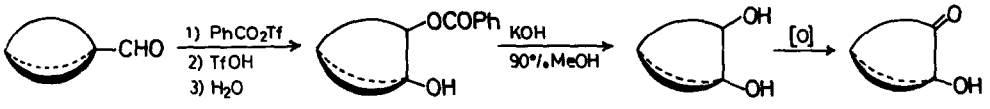
Abstract - Bridgehead aldehydes of bicyclo[3.2.1]octane (**11a**), bicyclo-[3.3.1]nonane (**12a**), and bicyclo[3.2.2]nonane (**13a**) have been subjected to acylative ring-expansion by using benzoyl trifluoromethanesulfonate (triflate) to give mixtures of two or three bicyclic 1,2-diol monobenzoates containing the hydroxyl group on the bridgehead carbon. Control experiments have shown that the reaction is kinetically controlled. The direction of the ring-expansion has been found to be predictable by comparing the strain energies calculated by molecular mechanics of the parent hydrocarbons corresponding to the produced diol monobenzoates. The major monobenzoates, easily isolated in practical yields by crystallization or column chromatography, have been converted to the corresponding diols, and their structures determined. For synthetic purposes, **11a** gives bicyclo[3.3.1]nonane-1,endo-2-diol (**27**), and **12a** the endo and exo isomers of bicyclo[4.3.1]decane-1,2-diol (**33** and **35**, respectively). From **13a** is furnished bicyclo[4.2.2]decane-1,2-diol (**42**). Diols **27**, **33**, and **42** are conveniently oxidized to the corresponding ketols by using silver carbonate in 50 - 80% yields. The oxidation of diol **35** to 1-hydroxybicyclo[4.3.1]decan-2-one (**34**) failed under similar conditions, but it was achieved by the Corey oxidation by using dimethylsulfide - chlorine complex.

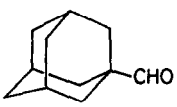
Bicycloalkanediols containing the hydroxyl groups on the bridgehead and the vicinal position are potentially useful starting materials leading to vicinally bifunctional, bicyclic compounds. Recently, we reported that the acylative ring-expansion of various bridgehead aldehydes with benzoyl trifluoromethanesulfonate (triflate) gives 1,2-diol monobenzoates in good yields.[1] The monobenzoates are readily saponified to 1,2-diols (Scheme 1).[1,2] Some diols were converted to the corresponding ketols, which were successfully used for the synthesis of the substrates generating α-keto cations in solvolysis.[3]



Scheme 1

Besides this method of Scheme 1, four processes have been reported, to our knowledge, on the synthesis of some limited bicyclic 1,2-diols. Wiseman reported the oxidation of a bridgehead olefin, bicyclo[3.3.1]non-1-ene, with osmium tetroxide.[4] McKervey obtained 1,2-adamantanediol starting from protoadamantan-4-one ethylene ketal.[5] Eaton beautifully applied acyloin-like coupling to the preparation of the diol intermediate leading to pentaprismane.[6] Recently, Hua synthesized a bicyclic 1,2-diol by demethylation of the corresponding bridgehead monomethyl ether.[7] At the present stage, however, the scope and generality of these methods remain to be clarified. Accordingly, we wished to investigate the present reaction (Scheme 1) more extensively.

In the previous work we described that the acylative ring-expansion of the bridgehead aldehydes of adamantane (**1**), noradamantane (**2**), bicyclo[2.2.2]octane (**3**), 7,7-dimethylbicyclo-[2.2.1]heptane (**4**), and bicyclo[2.2.1]heptane (**5**) furnish the diol monobenzoates **6**, **7**, **8**, **9**, and **10**, respectively, in good yields.[1] In these cases the direction of the ring-expansion was self-evident for the aldehydes with C_{3v} symmetry (**1** and **3**), or it was easily predictable for the cases containing a highly strained C-C bond (**2**, **4**, and **5**).



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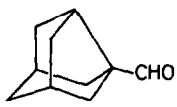

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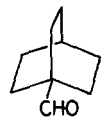

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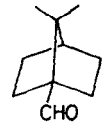

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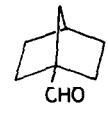

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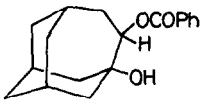

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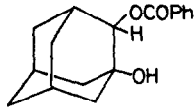

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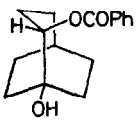

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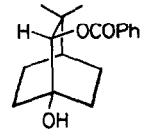

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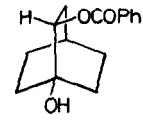

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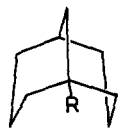
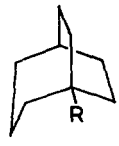
In the present work the reaction was extended to bicyclo[3.2.1]octane-, bicyclo[3.3.1]-nonane-, and bicyclo[3.2.2]nonane- 1-carbaldehydes (**11a**, **12a**, and **13a**, respectively) which were expected to give rather complex mixtures of diol monobenzoates. Fortunately, isolation of major products was relatively easily attained by crystallization and/or column chromatography, providing a convenient route to various bicyclic vicinal diols. We herein describe the characterization of the products and their conversion to diols. The oxidation of the diols to the corresponding ketols is also described.



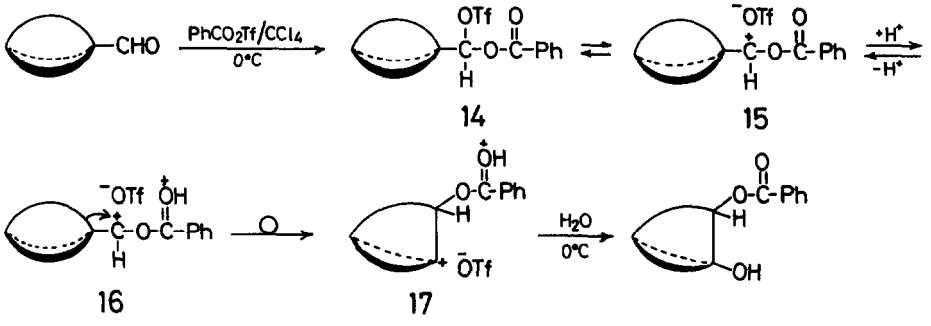


R = CHO	11a	12a	13a
R = CH_2OH	11b	12b	13b
R = CO_2H	11c	12c	13c

RESULTS AND DISCUSSION

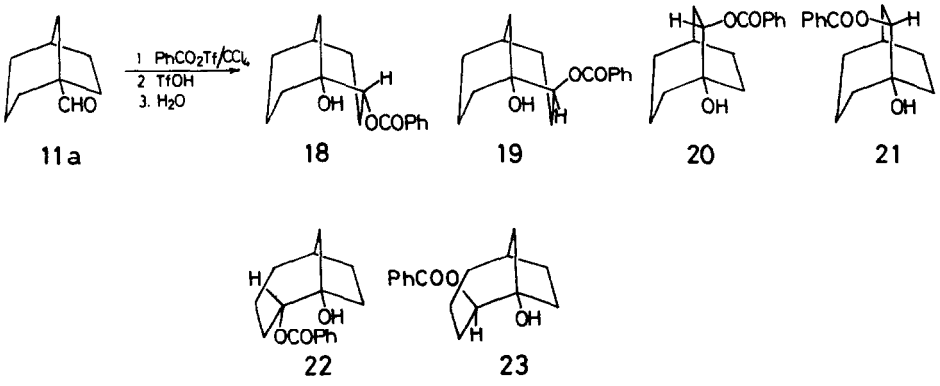
Synthesis of Aldehydes **11a**, **12a**, and **13a**. All the aldehydes were obtained from the corresponding known carboxylic acids **11c**,[8] **12c**,[9] and **13c**,[10] via lithium aluminum hydride (LAH) reduction followed by pyridinium chlorochromate (PCC) oxidation[11] in overall yields of 80-90%. Since these aldehydes were unstable to air, the crude aldehydes were used immediately after being prepared.

Mechanism and General Procedure for Acylative Ring-Expansion of the Aldehydes. As previously described,[1,2] the reaction proceeds following Scheme 2 via the rapid nucleophilic attack of the aldehyde oxygen to benzoyl triflate giving a benzoate-triflate **14** in carbon tetrachloride at 0°C. Addition of three equiv of trifluoromethanesulfonic acid (triflic acid) causes rearrangement of **14** which is presumably in equilibrium with ionized species **15**. Perhaps, the protonated dication **16** is so unstable that this rearranges to the bridgehead cation (dication) **17**, where the two cationic centers are more separated than in **16**. Addition of water at 0°C yields diol monobenzoates. A strong acid is indispensable to cause the ring-expansion as demonstrated in the case of **13a** (vide infra).

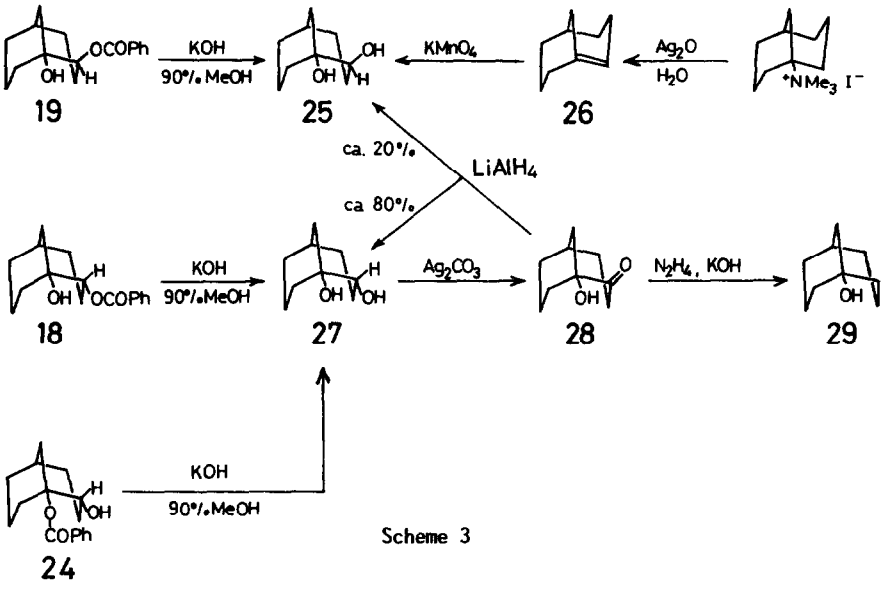


Scheme 2

Acylative Ring-Expansion of Bicyclo[3.2.1]octane-1-carbaldehyde (**11a**). This aldehyde was presumed to give six diol monobenzoates **18** - **23** in principle. However, HPLC analyses on the crude product exhibited only three components in a ratio 81:11:8. Crystallization followed by MPLC of the crystallization residue afforded the three products in 64%, 6.2%, and 4.2% yields. These products were identified as **18**, **24** (an unexpected product; Scheme 3), and **19**, respectively, as shown in Scheme 3.



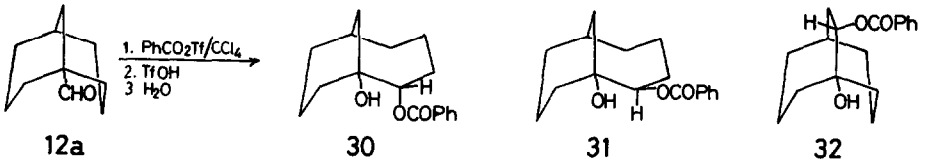
The diol obtained from **19** by saponification showed a ^{13}C NMR spectrum identical with that of bicyclo[3.3.1]nonane-1,exo-2-diol (**25**)[4] which was prepared by permanganate oxidation[12] of bicyclo[3.3.1]non-1-ene (**26**). The major monobenzoate **18** was saponified to diol **27**, which was then oxidized with silver carbonate on celite[13] to give ketol **28** in a two-step yield of 44%. The Wolff-Kishner reduction of **28** under Huang-Minlon conditions[14] afforded bicyclo[3.3.1]nonan-1-ol (**29**). LAH reduction of **28** furnished diols **25** and **27** in an approximate ratio 1:4 as determined by ^{13}C NMR. Thus, the structures of **18**, **19**, and corresponding diols **27** and **25** were unequivocally determined.



Scheme 3

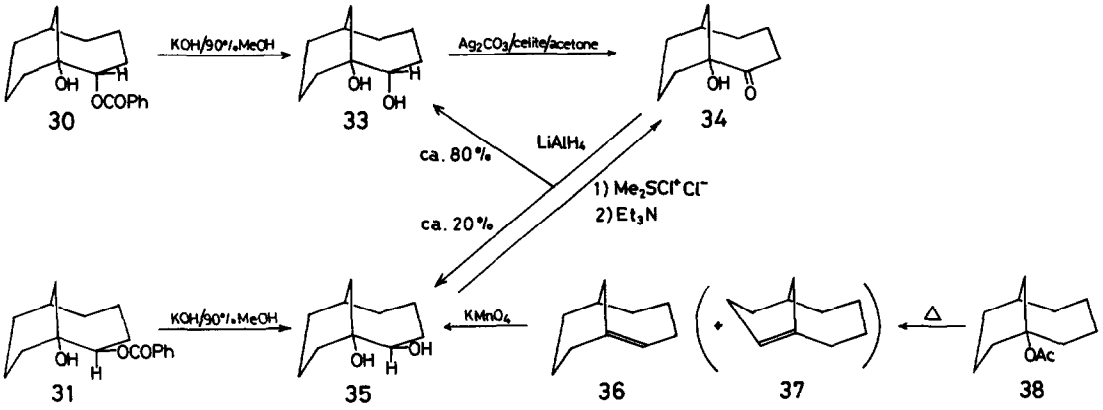
The structure of unexpected endo-2-hydroxybicyclo[3.3.1]non-1-yl benzoate (**24**) was elucidated from the ^{13}C NMR signals at 87.3 (s) and at 73.7 (d) ppm. For comparison, **18** showed the signals at 69.8 (s) and at 79.8 (d) ppm. The other skeletal carbons of the two monobenzoates exhibited similar spectrum patterns. Finally, **24** gave **27** on saponification. Presumably, **24** was formed from **18** (or the corresponding bridgehead carbocation) via intramolecular ester interchange under strongly acidic conditions.

Acylative Ring-Expansion of Bicyclo[3.3.1]nonane-1-carbaldehyde (**12a**). This aldehyde is expected to give the diol monobenzoates **30**, **31**, and **32**, but separation of the crude product by MPLC gave the endo and exo isomers of 1-hydroxybicyclo[4.3.1]dec-2-yl benzoate (**30** and **31**, respectively) in 34% and 42% yields, respectively. No trace amount of **32** was detected.



The structures of **30** and **31** were determined following Scheme 4. Saponification of **30** to diol **33**, followed by silver carbonate oxidation afforded ketol **34** in a two-step yield of 81%. The diol **35** was obtained from **31**. Reduction of **34** with LAH gave a mixture containing diols **33** and

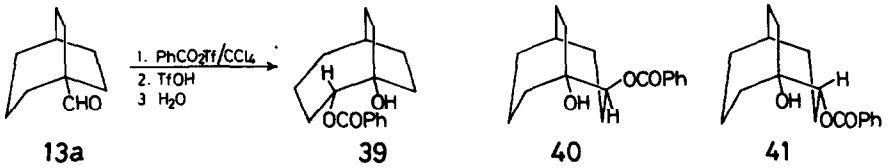
35 in an approximate ratio 4:1 as estimated from ^{13}C NMR spectra, indicating that 33 and 35 possess the same carbon skeleton. On the other hand, the structure of 35 was elucidated from its ^{13}C NMR spectrum which was identical with that of diol 35 unambiguously synthesized from bicyclo[4.3.1]dec-1-ene (36) by permanganate oxidation[12]. The bridgehead olefin 36 was prepared as a mixture with bicyclo[4.3.1]dec-1(9)-ene (37) by thermal elimination[15] of bicyclo[4.3.1]-dec-1-yl acetate (38).



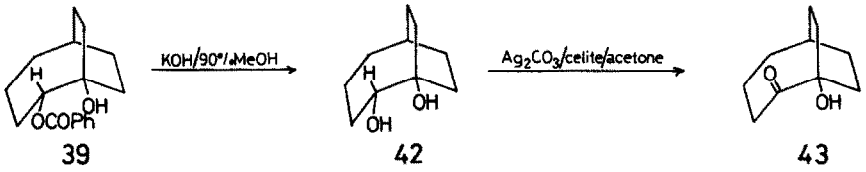
Scheme 4

In contrast to the successful oxidation of 33 to 34 with silver carbonate, 35 gave 34 in a yield as low as 12%. The major product obtained in 32% yield was an unidentified unstable aldehyde which was presumed to arise due to C-C bond cleavage of the 1,2-diol unit of 35. However, application of the Corey oxidation by using dimethyl sulfide - chlorine complex[16] afforded 34 in 45% yield.

Acylative Ring-Expansion of Bicyclo[3.2.2]nonane-1-carbaldehyde (13a). Aldehyde 13a is presumed to yield diol monobenzoates 39, 40, and 41. Actually, the three products, 1-hydroxy-bicyclo[4.2.2]dec-2-yl benzoate (39), 1-hydroxybicyclo[3.3.2]dec-exo- and endo-2-yl benzoates (40 and 41, respectively), were formed, with a ratio between 39, 40, and 41 being 71:19:10, as determined by ^{13}C NMR and HPLC for the crude product. Unfortunately, difficulties were encountered in completely separating 39 and 41 from each other either by MPLC or by HPLC; however, separation by MPLC followed by one recrystallization of a mixture of 39 and 41 afforded 39 of 94% purity in 39% yield based on 13a. A further recrystallization increased the purity to 97%. Purification of 41 failed, and this was obtained as a 1:1 mixture with 39 in the recrystallization residue. Isolation of pure 40 was only successful by using HPLC.



Structural determination was arrived at by working similarly to the preceding description (Scheme 5). Saponification of **39** to diol **42** followed by silver carbonate oxidation afforded ketol **43** in a two-step yield of 70%. The symmetric structure of **43** was unequivocally shown by ^{13}C NMR.

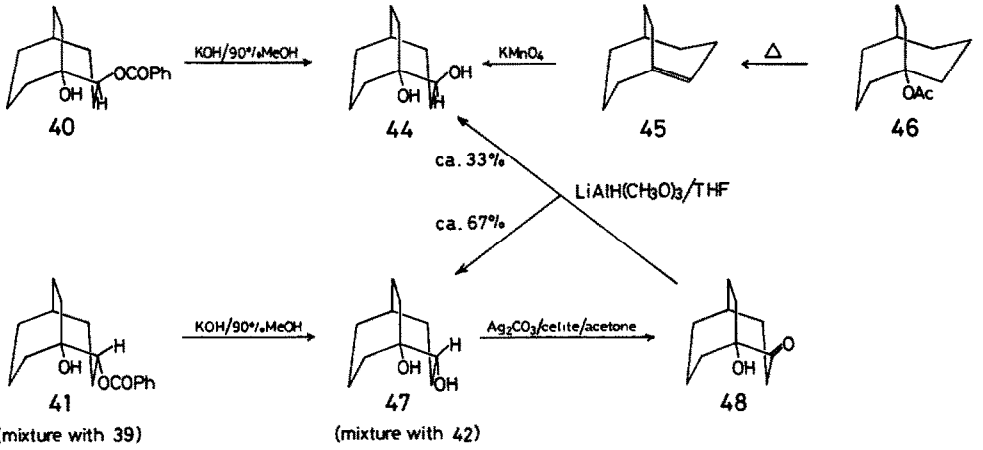


Scheme 5

Saponification of pure **40** gave a diol whose ^{13}C NMR spectrum was identical with that of diol **44** prepared from bicyclo[3.3.2]dec-1-ene (**45**) by permanganate oxidation[12] (Scheme 6). The bridgehead olefin **45** was obtained by thermal elimination[15] of bicyclo[3.3.2]dec-1-yl acetate (**46**).

When the crystallization residue containing **39** and **41** in ca. 1:1 was saponified and the resulting diol mixture (**42** and **47**) oxidized with silver carbonate, a mixture of ketols **43** and **48** was obtained (Scheme 6). These ketols were easily separated from each other by MPLC.

Reduction of ketol **48** with lithium trimethoxyaluminohydride in THF[17] afforded a mixture of diols **47** and **44** in a ratio of ca. 2:1 (Scheme 6). In this way the structures of monobenzoates **39**, **40**, **41**, and respective diols **42**, **44**, and **47** were unequivocally determined. In cases where ketols **43** and/or **48** are required, a mixture containing **39**, **40**, and **41** can be subjected to saponification and the diol mixture directly oxidized to give a mixture of ketols **43** and **48**, which can easily be separated by MPLC.



Scheme 6

Requirement of a Strong Acid in Ring-Expansion. As previously described,[1] the present ring-expansion reaction requires the presence of a strong acid. With a view to test the effect of various acids on the yields of diol monobenzoates, bicyclo[3.2.2]nonane-1-carbaldehyde (**13a**) was subjected to the reaction in the absence and presence of three molar equiv of a strong acid. As the acids were employed fluorosulfonic acid and 98% sulfuric acid, besides abovementioned triflic acid. As shown in Table 1, the distribution of the three monobenzoates **39**, **40**, and **41**

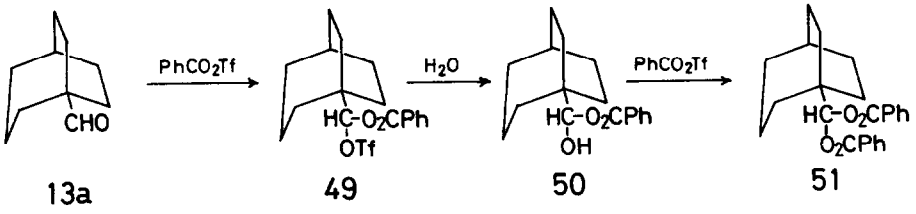
as determined by ^{13}C NMR was essentially unchanged. In contrast, the combined yield of the monobenzoates markedly increased in the order, none < 98% sulfuric acid < fluorosulfonic acid < triflic acid.

Table 1. Distributions and Combined Yields of Diol Monobenzoates **39**, **40**, and **41** from bicyclo[3.2.2]nonane-1-carbaldehyde (**13a**)

strong acid[a]	distribution of monobenzoate/%[b]			combined yield/%[c]
	39	**40**	**41**	
none	64	21	15	18
98% H_2SO_4	71	20	9	52
FSO_3H	73	18	9	66
CF_3SO_3H	71	19	10	79

a) Three molar equivalent based on **13a**. b) Determined by ^{13}C NMR.
c) The combined yield of **39**, **40**, and **41**.

The major product in the absence of strong acids was an acylal of **13a**, (bicyclo[3.2.2]non-1-yl)methane-1,1-diyl dibenzoate (**51**). The structure of **51** was determined from the ^{13}C NMR signals showing the symmetric structure and the presence of methine carbon (d, δ 95.1 ppm), and the ^1H NMR spectrum consistent with the structure. The acylal **51** was also detected in small amounts by TLC when fluorosulfonic acid or sulfuric acid was employed, but the use of triflic acid completely eliminated its formation. Probably, **51** resulted from benzoylation of a short-lived intermediate **50** which would arise from **49** on addition of water. Apparently, triflic acid facilitates the rearrangement of **14** to **17** (Scheme 2).



13a **49** **50** **51**

Evidence for Kinetic-Control Nature of the Acylative Ring-Expansion. In order to examine whether the isomeric diol monobenzoates are formed following kinetic or thermodynamic control, each of monobenzoates **31** and **39** was treated in carbon tetrachloride in the presence of 3 equiv of triflic acid and 1.5 equiv of triflic anhydride at 0°C. After usual work-up, the starting monobenzoate was recovered quantitatively, as revealed by the ^{13}C NMR spectra. This shows that the present acylative ring-expansion is a kinetically controlled process.

Prediction of the Direction of Ring-Expansion Based on Strain Energies of Intermediates and Products. The present ring-expansion reaction is kinetically controlled. Therefore, the product distribution is expected to be principally determined by the stability of carbocation **17** which is irreversibly generated from **16** (Scheme 2). Recently, Müller and his coworkers calculated steric energies of various bridgehead carbocations by Allinger's force-field which was modified for calculation of carbocations, and showed that the 1-bicyclo[3.3.1]nonyl cation is more stable than the 1-bicyclo[3.2.2]nonyl cation by 6 kcal mol^{-1}.[18] If we neglect the effect of the benzoyloxy group on the C(2) position on the relative stability of the carbocations, the calculation is in harmony with our observation that any trace amount of **20** or **21** was not detected in the product. Unfortunately, the steric energy of the 1-bicyclo[4.2.1]nonyl cation has not been reported.

Müller reported that bicyclo[3.3.1]nonane is also more stable than bicyclo[3.2.2]nonane by 6 kcal mol^{-1}.[18] Thus, the relative stability of the parent hydrocarbons coincides with that of the bridgehead carbocations. This suggests that the strain energies of the parent hydrocarbons may be employed to evaluate the relative stabilities of the relevant bridgehead carbocations, if the ring size is great enough to make the cationic center planar without much strain. In other words, for practical purposes the product distribution may be predicted by comparing the stabilities of the parent hydrocarbons corresponding to the diol monobenzoates, again by neglecting the effects of the benzoyloxy and hydroxy groups.

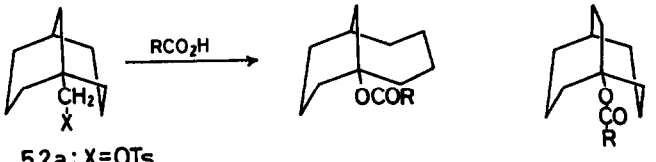
Maier and Schleyer[19] calculated strain energies of a number of bicycloalkanes by using MM1 program[20]. In Table 2 are summarized the possible monobenzoates which would arise from aldehydes **11a**, **12a**, and **13a**, and the strain energies of saturated parent hydrocarbons corresponding to the monobenzoates in their most stable conformations. The strain energies of Table 2 suggest that **18** and **19** are more stable than **20** - **23** by 6 - 7 kcal mol^{-1}. Actually, only **18** and **19** were formed, although **24** was also produced, perhaps via intramolecular ester interchange. Similarly, **30** and **31** which are supposed to be more stable than **32** by 6 kcal mol^{-1} were the products isolated. In contrast, **39** and **40** (or **41**) are supposed to be of similar stability: indeed, all the three products were formed. Although more examples are required for generalization of the present predictions, the direction of the ring-expansion of **11a**, **12a**, and **13a** are nicely explained in terms of the strain energies of the products. For rationalization of the exo:endo product ratios, more rigorous calculations are required.

Table 2. Possible Monobenzoates and Strain Energies of the Corresponding Parent Hydrocarbons

starting aldehyde	monobenzoate and strain energy[a] of parent hydrocarbon in parenthesis		
11a	**18**, **19** (9.04)	**20**, **21** (14.92)	**22**, **23** (15.88)
12a	**30**, **31** (14.64)	**32** (20.50)	
13a	**39** (20.35)	**40**, **41** (20.50)	

a) In kcal mol^{-1}; ref. 19.

The present reaction resembles the solvolysis of (1-bicycloalkyl)methyl arenesulfonates or the Koch-Haaf carboxylation of (1-bicycloalkyl)methanol in that ring-expansion products are obtained. Graham and Jonas reported the solvolysis of (1-bicyclo[3.3.1]nonyl)methyl tosylate (**52a**) and brosylate (**52b**) in acetic acid, formic acid, and trifluoroacetic acid in the presence or absence of buffer.[21] In many cases, they obtained bicyclo[4.3.1]dec-1-yl derivative **53** alone, but only the acetolysis of **52a** buffered with sodium acetate afforded **54** as the major product.[21] They postulated different ionic intermediates in the solvolysis of **52a** and **52b**.

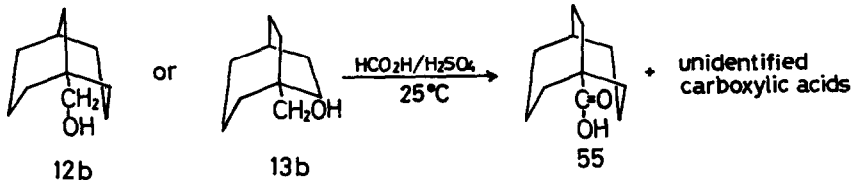


52a; X=OTs
52b; X=OBs

53

54

Rüchardt and coworkers reported the Koch-Haaf carboxylation of **12b** and **13b** by using formic acid in sulfuric acid.[10] In the both cases they isolated bicyclo[3.3.2]decane-1-carboxylic acid **(55)** in 64% (from **12b**) or 20% (from **13b**). Notably, the major product **55** obtained from **12b** is supposed to be more strained than the other expected product, bicyclo[4.3.1]decane-1-carboxylic acid (vide supra). Thus, the results of solvolysis and the Koch-Haaf reaction do not wholly in harmony with the present results. Although the diversity in the product may be attributed to different characteristics of carbocation intermediates under different conditions, the present acylative ring-expansion appears to reflect most closely the stability of intermediate carbocations.



EXPERIMENTAL

M.p.s and b.p.s are uncorrected. Elemental analyses were performed by the Microanalytical Center, Kyoto University. ^{1}H NMR spectra were recorded with a Hitachi R-24 (60 MHz) or a JEOL FX90 (90 MHz) instrument. ^{13}C NMR spectra were measured with a JEOL FX90 (22.5 MHz) or a JEOL FX100 (25 MHz) instrument. IR spectra were obtained on a Hitachi 215 spectrophotometer.

Materials. All reagents were of reagent-grade quality except when otherwise noted. Bicyclo[3.2.1]octane-1-carboxylic acid **(11c)**,[8] bicyclo[3.3.1]nonane-1-carboxylic acid **(12c)**,[9] bicyclo[3.2.2]nonane-1-carboxylic acid **(13c)**,[10] and bicyclo[3.3.1]non-1-ene **(26)**[4] were prepared following reported methods. Benzoyl triflate[22] was prepared by the method of Brown and Koreeda. Silver carbonate on celite containing ca. 48wt% Ag_2CO_3 was prepared following the literature method.[13] Dichloromethane and carbon tetrachloride were refluxed over P_2O_5 and distilled. Tetrahydrofuran was dried over Molecular Sieves 5A and distilled from $LiAlH_4$. Triethylamine was distilled from KOH.

Bridgehead Methanols **11b, 12b, and 13b**. The bridgehead methanols were prepared by $LiAlH_4$ reduction of the corresponding carboxylic acids in THF. A typical procedure follows. To $LiAlH_4$ (2.43 g, 64.0 mmol) in THF (50 ml) was added bicyclo[3.2.1]octane-1-carboxylic acid **(11c)** (7.59 g, 49.2 mmol) in THF (40 ml) under nitrogen over 35 min and then the reaction mixture heated at reflux for 2 h. Excess $LiAlH_4$ and alkoxides were decomposed by slowly adding water (2.4 ml), 15% NaOH (2.4 ml), and water (7.2 ml) in this sequence. White precipitates were filtered and thoroughly washed with THF. The filtrate was dried ($MgSO_4$) and evaporated to give **11b** (7.22 g) as a colorless viscous liq in 100% yield. An analytical sample was obtained by distillation; b.p. 71 - 72°C/1mmHg; m.p. 31 - 33°C; IR (CCl_4) 3640 m, 3350 br, 1450 m, 1020 m cm^{-1}; ^{1}H NMR (CCl_4) δ 0.8 - 2.4 (br, 13 H), 3.23 (s, 2 H), 3.5 (br, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 45.5 (C); 35.6 (CH); 19.3, 28.9, 31.0, 32.2, 34.5, 41.2, 70.8 (CH_2). Found: C, 77.34; H, 11.79. Calc for $C_9H_{16}O$: C, 77.09; H, 11.50%. **12b** and **13b** were obtained from **12c** and **13c**, respectively, in a similar manner. **12b**; viscous liq (lit.[21] b.p. 82°C/0.5 mmHg). **13b**; m.p. 40 - 42°C; IR (CCl_4) 3650 m, 3400 br, 1460 m, 1070 m, 1035 m, 1020 m cm^{-1}; ^{1}H NMR (CCl_4) δ 0.7 - 2.7 (br, 15 H), 3.00 (s, 2 H), 3.6 (br, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 31.0 (C); 28.8 (CH); 22.1, 25.6, 27.9, 35.8, 36.6, 73.7 (CH_2). **13b** has been reported,[10] but no spectral data given.

Bridgehead Aldehydes **11a, 12a, and 13a**. These aldehydes were prepared by PCC oxidation[11] of the corresponding methanols **11b, 12b,** and **13b** in 89 - 93% yields in the manner described for **1** - **5**.[1] Since the aldehydes were unstable in air, they were used immediately after being prepared without further purification. ^{13}C NMR spectra showed the purities of higher than 95%. **11a**[4]; semisolid; ^{13}C NMR ($CDCl_3$) δ 54.6 (C); 35.6 (CH); 18.2, 28.6, 29.4, 30.3, 31.6, 40.1 (CH_2); 204.9 (C=O). **12a**; waxy solid; ^{13}C NMR ($CDCl_3$) δ 44.3 (C); 27.1 (CH); 20.9, 29.7, 30.3, 33.4 (CH_2); 206.0 (C=O). **13a**; m.p. 70.5 - 72.5°C; ^{13}C NMR ($CDCl_3$) δ 46.3 (C); 28.0 (CH); 21.0, 24.3, 24.8, 32.9, 34.7 (CH_2); 204.0 (C=O).

Acylative Ring-Expansion of Bicyclo[3.2.1]octane-1-carbaldehyde **(11a)**. The procedure is essentially similar to that previously described.[1] To a magnetically stirred solution of benzoyl triflate (5.8 ml, 35 mmol) in CCl_4 (27 ml) cooled 0°C under nitrogen was added a

solution of crude **11a** (3.88 g, 28.1 mmol) in CCl_4 (15 ml) over 9 min. After stirring for 20 min at 0°C, triflic acid (7.4 ml, 84 mmol) was slowly added. Ice-cold water (16 ml) was added dropwise over 9 min and then stirring continued for 25 min at 0°C. Water (80 ml) and ether (160 ml) were added. The organic layer was washed with saturated $NaHCO_3$ (4 x 70 ml), saturated NaCl (75 ml), and dried ($MgSO_4$). Evaporation of the solvent afforded a brown solid (7.71 g). An HPLC analysis of the crude product by using a μ-Porasil column (8 mm x 30 cm) and hexane - ether (3:1) showed endo-2-hydroxybicyclo[3.3.1]non-1-yl benzoate **(24)**, 1-hydroxybicyclo[3.3.1]non-exo-2-yl benzoate **(19)**, and 1-hydroxybicyclo[3.3.1]non-endo-2-yl benzoate **(18)** in a ratio 11:8:81, which eluted in this order. Recrystallization of the crude product from hexane - benzene gave **18** as pale brown crystals (4.26 g) in 59% yield. MPLC over SiO_2 (hexane - ether) of the crystallization residue furnished **24** (0.45 g; 6.2%), **19** (0.31 g; 4.2%), and **18** (0.39 g; 5.3%). The total yield of **18** was 64%. **18**; m.p. 106.5 - 107.0°C; IR (CCl_4) 3600 w, 3470 br, 1720 s, 1270 s, 1110 s, 710 s cm^{-1}; ^1H NMR (CCl_4) δ 1.2 - 2.3 (br, 13 H), 2.47 (s, 1 H, -OH), 4.97 (t, 1 H, J = 8.5 Hz), 7.2 - 8.1 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 70.3 (C); 30.9, 80.1 (CH); 22.1, 28.5, 29.2, 29.8, 33.5, 41.5 (CH_2); 128.0, 129.4, 130.3, 132.6, 166.3 (PhCO). Found: C, 73.86; H, 7.74. Calc for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%. **19**; oil; IR (CCl_4) 3610 w, 3430 br, 1720 s, 1270 s, 1100 s, 710 s cm^{-1}; ^1H NMR (CCl_4) δ 0.7 - 2.2 (br, 13 H), 2.37 (s, 1 H, -OH), 4.97 (s, 1 H), 7.1 - 8.0 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 69.3 (C); 30.7, 77.0 (CH); 21.9, 25.6, 28.1, 29.5, 35.3, 36.6 (CH_2); 127.8, 129.1, 130.2, 132.3, 165.5 (PhCO). Found: C, 74.00; H, 8.03. Calc for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%. **24**; oil; IR (CCl_4) 3430 br, 1710 m, 1690 s, 1290 s, 1125 m, 1070 m, 710 s cm^{-1}; ^1H NMR (CCl_4) δ 0.9 - 2.8 (br, 13 H), 4.12 (br s, 1 H, -OH) [overlapped with δ 4.07 (t, 1 H, J = 8.5 Hz)], 7.2 - 8.0 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 87.3 (C); 30.5, 73.7 (CH); 21.5, 28.6, 28.8, 29.0, 30.9, 37.7 (CH_2); 127.8, 129.2, 130.8, 132.4, 166.4 (PhCO). Found: C, 73.04; H, 7.81. Calc for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74%.

Bicyclo[3.3.1]nonane-1,exo-2-diol **(25)** by Saponification of **19**. A solution of **19** (277 mg, 1.06 mmol) and KOH (181 mg, 2.7 mmol) in 90% MeOH was heated at reflux for 3 h. After most of the methanol had been evaporated, $CHCl_3$ (7 ml) and water (0.5 ml) were added. The aqueous layer was extracted with $CHCl_3$ (3 x 5 ml). The combined extracts were dried ($MgSO_4$) and evaporated to give a pale brown solid (153 mg). Recrystallization from hexane - benzene afforded **25** (132 mg; 80%) as white crystals. An analytical sample was provided by sublimation at 50 - 80°C/2 mmHg and further recrystallization; m.p. 216 - 220°C (lit.[4] 219 - 221°C); IR ($CHCl_3$) 3560 m, 3420 br, 1450 m, 1080 m, 1045 m, 1020 m, 980 m, 920m cm^{-1}; ^1H NMR δ 1.1 - 2.3 (m, 13 H), 2.81 (s, 2 H, -OH), 3.67 (br s, 1 H, width at half height 6.5 Hz); ^{13}C NMR ($CDCl_3$) δ 71.1 (C); 31.3, 73.3 (CH); 22.4, 25.2, 29.6, 29.8, 35.7, 35.7 (CH_2). The ^{13}C NMR spectrum was superimposable with that for **25** prepared by permanganate oxidation of bicyclo[3.3.1]non-1-ene **(26)**.

Bicyclo[3.3.1]nonane-1,exo-2-diol **(25)** from Bicyclo[3.3.1]non-1-ene **(26)**. The oxidation was conducted by using $KMnO_4$[12] in the place of OsO_4[4]. To a vigorously stirred solution of **26** (154 mg, 1.26 mmol) in t-BuOH (12 ml), water (2.5 ml), and ice (6 g) chilled in an ice-salt bath was added a cold solution of $KMnO_4$ (295 mg, 1.87 mmol) and NaOH (95 mg, 2.4 mmol) in water (20 ml) all at once and then the mixture stirred for 30 min. After concentration by simple distillation, the residue was extracted with CH_2Cl_2 (3 x 15 ml), the combined extract dried ($MgSO_4$), and evaporated to afford crude **25** (49 mg; 25%). The ^{13}C NMR spectrum was superimposable with that for **25** obtained by saponification of **19**.

Bicyclo[3.3.1]nonane-1,endo-2-diol **(27)** by Saponification of **18**. A solution of **18** (1.10 g, 8.07 mmol) and KOH (1.23 g, 18.7 mmol) in 90% MeOH (45 ml) was refluxed for 3 h. After most of the methanol had been evaporated, $CHCl_3$ (30 ml) and water (3 ml) were added. The aqueous layer was extracted with $CHCl_3$ (2 x 8 ml). The combined extracts were dried ($MgSO_4$) and then evaporated to give a pale brown solid. Recrystallization from hexane - benzene afforded **27** (1.05 g,; 83%) as needles; m.p. 228.0 - 228.5°C; IR ($CHCl_3$) 3590 m, 3430 br, 1450 w, 1460 w, 1050 s, 995 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 - 2.3 (br, 13 H), 3.23 (s, 2 H, -OH), 3.65 (t, 1 H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 72.1 (C); 31.3, 77.1 (CH); 22.0, 29.6, 30.0, 30.8, 32.2, 41.2 (CH_2). Found: C, 69.05; H, 10.60. Calc for $C_9H_{16}O_2$: C, 69.19; H, 10.32%.

Bicyclo[3.3.1]nonane-1,endo-2-diol **(27)** by Saponification of **24**. Saponification of **24** (89 mg, 0.34 mmol) in the manner described for **18** afforded **27** (29 mg) in 55% yield after sublimation at 50 - 80°C/2 mmHg; m.p. 223.5 - 226.0°C. IR, ^1H NMR, and ^{13}C NMR spectra were superimposable with those of **27** obtained from **18**.

1-Hydroxybicyclo[3.3.1]nonan-2-one **(28)** by Oxidation of **27**. To a suspension of Ag_2CO_3 - celite[13] (28.2 g) in acetone (300 ml) was added a solution of **27** (981 mg, 6.23 mmol) in acetone (40 ml) under reflux and then reflux was continued for 17 h under protection from moisture. Filtration of black precipitates followed by evaporation of the acetone afforded yellowish semisolid. MPLC over SiO_2 (hexane - ether 1:1) furnished **28** (509 mg; 53%) as white crystals. An analytical sample was obtained by recrystallization from pentane; m.p. 148.5 - 149.0°C; IR (CCl_4) 3500 m, 1700 s, 1450 m, 1380 m, 1240 m, 1120 s, 1100 s, 995 m, 940 m cm^{-1}; ^1H NMR (CCl_4) 1.5 - 2.7 (br, 13 H), 3.71 (s, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 75.2 (C); 30.3 (CH); 21.6, 29.9, 30.0, 36.2, 38.4, 41.1 (CH_2); 213.5 (C=O). Found: C, 69.54; H, 9.17. Calc for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

Wolff-Kishner Reduction of 1-Hydroxybicyclo[3.3.1]nonan-2-one (28) to Bicyclo[3.3.1]nonan-1-ol (29). Following Huang-Minlon modification,[14] a mixture of **28** (101 mg, 0.655 mmol), KOH (130 mg, 1.97 mmol), and hydrazine hydrate (0.095 ml, 2.0 mmol) in triethylene glycol (1.0 ml) was refluxed for 40 min and then the temperature of the oil bath raised to 200°C, while low boiling substances were distilled off. The residue was extracted with pentane to give **29** (10 mg; 11%). An analytical sample was obtained by recrystallization from pentane; m.p. 181.5 - 183.5°C (lit.[23] 182.5 - 184.0°C). A mixture with authentic **29**[23] did not show any m.p. depression. The IR spectrum was identical with that of authentic **29**.

Lithium Aluminum Hydride Reduction of 1-Hydroxybicyclo[3.3.1]nonan-2-one (28). Ketol **28** (100 mg, 0.648 mmol) was reduced with $LiAlH_4$ (34 mg, 0.90 mmol) in ether at 25°C to give a mixture (103 mg; 100%) containing diols **25** and **27** in an approximate ratio 1:4 as determined by ^{13}C NMR.

Acylative Ring-Expansion of Bicyclo[3.3.1]nonane-1-carbaldehyde (12a). The ring-expansion was conducted in a manner similar to that described for **11a**. From 1.78 g (11.7 mmol) of **12a** and 3.5 ml (20.8 mmol) of benzoyl triflate was obtained 4.99 g of brown solid. MPLC over SiO_2 (hexane - ether) afforded 1-hydroxybicyclo[4.3.1]dec-exo-2-yl benzoate (**31**) (1.10 g; 34%) and the endo isomer (**30**) (1.35 g; 42%) in this sequence. **30**; m.p. 134.0 - 135.0°C (from diisopropyl ether); IR (CCl_4) 3600 m, 3500 br, 1720 s, 1450 m, 1270 s, 1110 s, 710 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 - 2.6 (br, 15 H), 2.40 (br s, 1 H, -OH), 4.91 (dd, 1 H, J = 5.0, 10.0 Hz), 7.2 - 8.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 73.1 (C); 28.4, 82.7, (CH); 19.6, 21.2, 30.7, 31.4, 32.4, 33.3, 37.1 (CH_2); 128.0, 129.4, 130.3, 132.7, 166.2 (PhCO). Found: C, 74.44; H, 8.17. Calc for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%. **31**; m.p. 100.0 - 101.5°C (from hexane); IR (CCl_4) 3600 m, 3425 br, 1720 s, 1450 m, 1270 s, 1110 s, 705 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.0 - 2.5 (br, 15 H), 2.37 (br s, 1 H, -OH), 5.10 (br d, 1 H, J = 4.0 Hz), 7.1 - 8.2 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 72.3 (C); 28.0, 78.7 (CH); 19.0, 19.3, 29.5, 30.9, 32.0, 35.2, 36.2 (CH_2); 127.9, 129.2, 130.2, 132.4, 165.4 (PhCO). Found: C, 74.44; H, 8.15. Calc for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%.

Bicyclo[4.3.1]decane-1,endo-2-diol (33) by Saponification of 30. The procedure was essentially similar to that described for **19**. Saponification of **30** (1.16 g, 4.22 mmol) with KOH (0.75 g, 13 mmol) in 90% MeOH (26 ml) at reflux for 3.5 h followed by sublimation of the crude product at 130°C/1 mmHg afforded **33** (657 mg; 92%); m.p. 161.0 - 162.5°C (sealed tube) (from benzene); IR ($CHCl_3$) 3580 m, 3430 br, 1455 m, 1465 m, 1040 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7 - 2.6 (br, 17 H), 3.30 (dd, 1 H, J = 5.0, 10.0 Hz); ^{13}C NMR ($CDCl_3$) δ 74.2 (C); 28.7, 80.3 (CH); 19.5, 21.6, 30.8, 31.8, 32.8, 32.9, 37.2 (CH_2). Found: C, 70.32; 10.92. Calc for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

Bicyclo[4.3.1]decane-1,exo-2-diol (35) by Saponification of 31. The procedure was essentially similar to that described for **19**. Saponification of **31** (902 mg, 3.29 mmol) with KOH (0.53 g, 9.5 mmol) in 90% MeOH (20 ml) at reflux for 3.5 h followed by sublimation of the crude product at 115°C/1 mmHg afforded **35** (467 mg; 83%) as a waxy solid; m.p. 165.0 - 166.5°C (sealed tube) (from hexane); IR ($CHCl_3$) 3550 m, 3420 br, 1460 m, 1450 m, 1060 s, 1025 m cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9 - 2.4 (br, 15 H), 2.6 (br, 2 H, -OH), 3.60 (br, 1 H); ^{13}C NMR ($CDCl_3$) δ 73.5 (C); 28.5, 74.7 (CH); 18.5, 19.7, 31.3, 31.8, 32.0, 34.6, 37.0 (CH_2). Found: C, 70.26; 10.67. Calc for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

1-Hydroxybicyclo[4.3.1]decan-2-one (34) by Oxidation of 33. To a stirred suspension of Ag_2CO_3 - celite (18 g) in acetone (200 ml) was added a solution of **33** (657 mg, 3.86 mmol) in acetone (30 ml) under reflux and then reflux was continued for 30 min under protection from moisture. Filtration of black precipitates followed by evaporation of the acetone afforded yellowish semisolid (764 mg). MPLC over SiO_2 (hexane - ether) furnished **34** (571 mg; 88%) as white crystals. An analytical sample was obtained by recrystallization from pentane; m.p. 122.0 - 123.0°C; IR (CCl_4) 3570 m, 3475 br, 1690 s, 1460 m, 1075 m, 1060 s cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.2 - 3.1 (m, 15 H), 3.69 (s, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 76.5 (C); 30.7 (CH); 21.5, 22.1, 30.1, 35.3, 36.6, 37.7, 42.3 (CH_2); 217.5 (C=O). Found: C, 70.62; H, 9.73. Calc for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. The unsatisfactory C% is due to hygroscopic nature of **34**.

1-Hydroxybicyclo[4.3.1]decan-2-one (34) by Oxidation of 35. The literature procedure[6,16] was followed. To a solution of Cl_2 (13 mmol) in CH_2Cl_2 (14 ml) under argon was added Me_2S (1.7 g, 27 mmol) over 10 min with stirring, while the temperature was kept at -23°C - -10°C by cooling in a dry ice-CCl_4 bath. The cooling bath was replaced with an ice-water bath and then stirring continued for 10 min. The solution was again cooled to -23°C and powdered diol **35** (205 mg, 1.20 mmol) was added. The mixture was stirred at -23°C for 3 h and then Et_3N (2.72 g, 26.8 mmol) in CH_2Cl_2 (16 ml) was added over 10 min at -23°C - -10°C. After stirring for 10 min at -23°C the mixture was allowed to warm to room temperature. The mixture containing white precipitates was poured into dry ether (50 ml) and the precipitates were filtered off. Evaporation of the solvent afforded an orange oil, which on MPLC over SiO_2 (hexane - ether) gave **34** (90 mg; 45%) as a pale yellow semisolid. The ^{13}C NMR spectrum was superimposable with that of **34** obtained by Ag_2CO_3 oxidation of **33**.

Attempted Oxidation of Bicyclo[4.3.1]decane-1,exo-2-diol (35) with Silver Carbonate. To a stirred suspension of Ag_2CO_3 -celite[13] (4.39 g) in acetone (50 ml) was added a solution of **35** (163 mg, 0.957 mmol) in acetone (7 ml) under reflux and then reflux was continued for 35 min

under protection from moisture. Filtration of black precipitates followed by evaporation of the acetone afforded yellowish semisolid (164 mg). MPLC over SiO_2 (hexane - ether) furnished **34** (25 mg; 12%) and an unidentified liquid keto aldehyde (47 mg; 29%), possibly, 4-(3-oxocyclohexyl)butanal, in this sequence. The keto aldehyde showed following spectral data; IR (CCl_4) 2710 m, 1730 s, 1710 s cm^{-1}; ^1H NMR (CCl_4) δ 1.0 - 2.6 (m, 15 H), 9.67 (t, 1 H, J = 1.5 Hz); ^{13}C NMR ($CDCl_3$) δ 19.1, 25.1, 31.0, 35.8, 38.7, 41.4, 43.7, 47.9, 202.0, 211.5.

Bicyclo[4.3.1]dec-1-yl Acetate (38). Following the procedure of Graham and Jonas,[21] a solution of bicyclo[4.3.1]dec-1-yl tosylate (m.p. 74.0 - 75.0°C; lit.[21] 75 - 76°C) (2.80 g, 9.08 mmol) and NaOAc (894 mg, 10.9 mmol) in AcOH (91 ml) was refluxed for 10 h. After usual work-up, **38** of 97% purity (0.65 g; 36%) was obtained as an oil by MPLC (SiO_2; hexane-ether 99:1); ^{13}C NMR ($CDCl_3$) δ 84.4 (C); 30.3 (CH); 20.5, 24.4, 27.0, 30.2, 34.9, 36.7, 38.2, 38.6 (CH_2); 21.8 (CH_3); 169.1 (C=O).

Bicyclo[4.3.1]dec-1-ene (36) by Pyrolysis of 38. The acetate **38** (342 mg, 1.74 mmol) in a simple distillation apparatus was heated by means of a small flame, while a slow stream of nigrogen was passed through the vapor phase. The distillate was dissolved in pentane and the solution washed with aq $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the pentane furnished a mixture (211 mg) of two bridgehead olefins in an approximate ratio 2:1 and ca. 13% of unchanged **38** as determined by ^{13}C and ^1H NMR. The major and minor olefins were assigned to **36** and **37**, respectively, from integration of the respective triplet signals at δ 5.31 with J = 6.7 Hz (lit.[24] δ 5.27, J = 6 Hz) and at δ 5.59 with J = 5.7 Hz (lit.[24] δ 5.55, J = 5.5 Hz). The ^{13}C NMR ($CDCl_3$) δ values for olefinic carbons were 118.4 (CH) and 141.7 (C) for **36** and 125.3 (CH) and 141.7 (C) for **37**.

Bicyclo[4.3.1]decane-1,exo-2-diol (35) from 36. The mixture (211 mg) containing the bridgehead olefins **36** (117 mg), **37** (58 mg), and acetate **38** (36 mg) was subjected to permanganate oxidation[12] following the procedure described for the oxidation of **26**. Oxidation by using $KMnO_4$ (367 mg, 2.32 mmol) and NaOH (77 mg, 1.9 mmol) in aq t-BuOH followed by MPLC (SiO_2, hexane - ether) afforded a mixture (39 mg) containing diol **35** and most probably bicyclo[4.3.1]decane-1,exo-9-diol in an approximate ratio 2:1 as determined by ^{13}C NMR. The ^{13}C NMR signals of the major component were superimposable with those of **35** prepared by saponification of **31**.

Lthium Aluminum Hydride Reduction of 1-Hydroxybicyclo[4.3.1]decan-2-one (34). Ketol **34** (84 mg, 0.50 mmol) was reduced with $LiAlH_4$ (58 mg, 1.5 mmol) in THF at 25°C to give a mixture (79 mg; 92%) containing diols **33** and **35** in an approximate ratio 4:1 as determined by ^{13}C NMR.

Acylative Ring-Expansion of Bicyclo[3.2.2]nonane-1-carbaldehyde (13a) by Using Triflic Acid as a Strong Acid. The ring-expansion was conducted similarly to that described for **11a**. To benzoyl triflate (4.7 ml, 28 mmol) in CCl_4 (23 ml) were added **13a** (3.30 g, 21.7 mmol) in CCl_4 (18 ml) and then triflic acid (6.1 ml, 69 mmol) while the temperature was kept below 10°C. After cold water (13 ml) had been added, the mixture was worked up as described for the reaction of **11a** to afford brown solid (5.53 g), which was found by HPLC (μ-Porasil, 8 mm x 30 cm, hexane - ether) to contain **39**, **40**, and **41** in a ratio 71:19:10. The mixture was separated by MPLC (SiO_2, hexane - ether) into two fractions, the first fraction (4.12 g) containing **39**, **40**, and **41** in 80:9:11 and the second one (0.64 g) containing **39** and **40** in 13:87. One recrystallization of the solid from the first fraction gave **39** (2.36 g) of 94% purity. Two recrystallizations afforded **39** (1.50 g) of 98% purity in 25% yield. From the mixture of **39** and **40** from the above second fraction of MPLC was obtained **40** (0.11 g) in 2% yield by HPLC (μ-Porasil, 8 mm x 30 cm, hexane - ether) followed by recrystallization from hexane - benzene. Monobenzoate **41** could not be isolated by our hands, but obtained as a mixture containing **39** and **41** in 1:1. **39**; m.p. 114.0 - 115.0°C; IR (CCl_4) 3600 w, 3500 br, 1720 s, 1450 m, 1315 m, 1270 s, 1180 m, 1110 m, 1070 m, 1030 m, 710 s cm^{-1}; ^1H NMR (CCl_4) δ 1.3 - 2.5 (br, 16 H); 4.90 (br t, 1 H, J = 5 Hz); 7.2 - 8.1 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 72.9 (C); 26.8, 80.5 (CH); 19.9, 24.3, 24.9, 27.9, 29.0, 31.0, 36.2 (CH_2); 127.8, 129.2, 130.2, 132.4, 165.7 (PhCO). Found: C, 74.57, H, 8.23. Calc for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%. **40**; m.p. 75.0 - 76.0°C; IR (CCl_4) 3610 w, 3500 br, 1720 s, 1450 m, 1315 m, 1270 s, 1180 m, 1120 m, 1070 m, 1030 m, 710 s cm^{-1}; ^1H NMR (CCl_4) δ 1.1 - 2.9 (br, 16 H), 5.17 (t, 1 H, J = 4.0 Hz); 7.0 - 8.3 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 77.0 (C); 32.1, 82.5 (CH); 21.9, 25.4, 26.7, 29.0, 29.6, 33.2, 38.6 (CH_2); 128.0, 129.2, 132.5, 130.4, 166.1 (PhCO). Found: C, 74.71; H, 8.33. Calc for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%. **41**; ^{13}C NMR ($CDCl_3$) δ 76.0 (C); 27.3, 82.8 (CH); 21.1, 26.5, 26.8, 31.5, 35.3, 36.9 (CH_2) (one methylene missing due to overlapping); 127.8, 129.2, 132.4, 130.2, 165.7 (PhCO).

Acylative Ring-Expansion of Bicyclo[3.2.2]nonane-1-carbaldehyde (13a) by Using Fluorosulfonic Acid or Sulfuric Acid as a Strong Acid. To benzoyl triflate (0.66 ml, 3.9 mmol) in CCl_4 (3 ml) were added **13a** (457 mg, 3.00 mmol) in CCl_4 (3 ml) and then fluorosulfonic acid (0.55 ml, 9.6 mmol) or 98% sulfuric acid (0.51 ml, 9.6 mmol), while the temperature was kept below 10°C. After water (2.0 ml) had been added, the mixture was worked up as described for the reaction of **11a**. A mixture of diol monobenzoates **39**, **40**, and **41** was obtained by MPLC (SiO_2, hexane - ether) and their percentages composition were determined by ^{13}C NMR. The combined yield of **39**, **40**, and **41** was 66% or 52% for the use of fluorosulfonic acid or 98% sulfuric acid, respectively.

Acylative Ring-Expansion of Bicyclo[3.2.2]nonane-1-carbaldehyde (**13a**) without a Strong Acid. To benzoyl triflate (0.62 ml, 3.7 mmol) in CCl_4 (3 ml) were added **13a** (430 mg, 2.82 mmol) in CCl_4 (3 ml) at 0°C and then water (2.0 ml). The mixture was worked up as described for the reaction of **11a**, and then the fraction containing (bicyclo[3.2.2]non-1-yl)methane-1,1-diyl dibenzoate (**51**) (360 mg; 47%) and that containing **39**, **40**, and **41** (combined yield 138 mg; 18%) were collected by MPLC (SiO_2, hexane - ether) in this sequence. **51**; m.p. 124.5 - 126.0°C; IR (CCl_4) 3060 w, 1740 s, 1600 w, 1450 m, 1270 s, 1255 s, 1240 s, 1055 s, 1020 s, 975 s, 705 s cm^{-1}; ^1H NMR (CCl_4) δ 1.3 - 2.0 (br, 15 H), 6.87 (s, 1 H), 7.2 - 8.1 (m, 10 H); ^{13}C NMR ($CDCl_3$) 39.5 (C); 28.1, 95.1 (CH); 21.5, 24.7, 26.1, 33.5, 35.4 (CH_2); 128.0, 129.2, 129.5, 133.0, 164.2 (PhCO). Found: C, 76.25; H, 6.72. Calc for $C_{24}H_{26}O_4$: C, 76.17; H, 6.92%.

Bicyclo[4.2.2]decane-1,2-diol (**42**) by Saponification of **39**. The procedure was essentially similar to that described for **18**. Saponification of **39** (400 mg, 1.46 mmol) with KOH (255 mg, 4.54 mmol) in 90% MeOH (10 ml) at reflux for 3.5 h afforded essentially pure **42** (262 mg; 100%). An analytical sample was obtained by recrystallization from hexane - benzene; m.p. 217 - 220°C; IR (CCl_4) 3400 br, 1470 m, 1450 m, 1040 m, 1010 m cm^{-1}; ^1H NMR (CCl_4) δ 0.7 - 2.3 (br, 15 H), 3.37 (br, 1 H), 3.67 (s, 2 H, -OH); ^{13}C NMR ($CDCl_3$) δ 74.2 (C); 27.0, 78.0 (CH); 20.3, 24.6, 25.1, 26.3, 31.3, 31.9, 36.8 (CH_2). Found: C, 70.10; H, 10.83. Calc for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

Bicyclo[3.3.2]decane-1,exo-2-diol (**44**) by Saponification of **40**. The procedure was essentially similar to that described for **18**. Saponification of **40** (122 mg, 0.445 mmol) with KOH (75 mg, 1.34 mmol) in 90% MeOH (3 ml) at reflux for 2 h afforded essentially pure **44** (77 mg; 100%). An analytical sample was obtained by recrystallization from hexane - benzene; m.p. 236 - 238°C; ^{13}C NMR ($CDCl_3$) δ 77.9 (C); 32.0, 77.5 (CH); 21.3, 26.6, 27.8, 28.4, 30.8, 32.1, 39.5 (CH_2). Found: C, 69.88; H, 10.73. Calc for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66%.

Bicyclo[3.3.2]decane-1,endo-2-diol (**47**) in a Mixture with **42**. The procedure was essentially similar to that described for **18**. Saponification of a 1:1 mixture (430 mg) of **39** and **41** with KOH (260 mg, 4.7 mmol) in 90% MeOH (10 ml) at reflux for 3 h afforded a solid mixture (284 mg) of **42** and **47**. ^{13}C NMR ($CDCl_3$) δ values for **47** were obtained by subtracting the signals due to **42** from the spectrum; 77.1 (C); 26.8, 79.2 (CH); 22.0, 28.8, 29.3, 29.9, 31.5, 34.8, 35.5 (CH_2).

1-Hydroxybicyclo[4.2.2]decan-2-one (**43**) and 1-Hydroxybicyclo[3.3.2]decan-2-one (**48**) by Oxidation of a Mixture of **42**, **44**, and **47**. To a stirred suspension of Ag_2CO_3 - celite[13] (43 g) in acetone (570 ml) was added a mixture of **42**, **44**, and **47** (71:19:10) (1.63 g, 9.56 mmol) under reflux and then reflux continued for 1 h under protection from moisture. Filtration of black precipitates followed by evaporation of the acetone afforded off-white oil (1.90 g). MPLC (SiO_2, hexane - ether) furnished **43** (686 mg) and **48** (400 mg) as white crystals in 43% and 25% yields, respectively, based on **42** and **44** plus **47**. **43**; m.p. 147.0 - 147.5°C; IR (CCl_4) 3490 m, 1685 s, 1470 m, 1450 m, 1380 m, 1300 m, 1260 m, 1080 s cm^{-1}; ^1H NMR (CCl_4) δ 1.2 - 2.9 (br, 15 H); 4.0 (s, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 76.3 (C); 26.6 (CH); 21.8, 24.2, 30.7, 36.7, 40.6 (CH_2); 215.0 (C=O). Found: C, 70.22; H, 9.67. Calc for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59%. The unsatisfactory C% is due to hygroscopic nature of **43**. **48**; m.p. 140 - 145°C; IR (CCl_4) 3500 br, 1685 s, 1460 m, 1445 m, 1380 m, 1200 m, 1060 s, 1040 s cm^{-1}; ^1H NMR (CCl_4) δ 1.2 - 2.8 (br, 15 H), 3.4 (s, 1 H, -OH); ^{13}C NMR ($CDCl_3$) δ 80.6 (C); 31.6 (CH); 21.2, 26.1, 27.0, 33.7, 33.7, 39.4, 41.1 (CH_2); 217.4 (C=O): 2,2,2-trifluoroethanesulfonate; m.p. 67.5 - 68.5°C; IR (CCl_4) 1710 s, 1385 s, 1320 s, 1275 s, 1260 s, 1180 s, 1135 s, 1095 s, 910 s cm^{-1}; ^1H NMR (CCl_4) δ 1.0 - 3.0 (br, 15 H), 3.93 (q, 2 H, J = 4.0 Hz); ^{13}C NMR ($CDCl_3$) δ 98.8 (C); 31.3 (CH); 18.7, 25.5, 25.7, 34.7, 34.9, 40.0, 40.7, 55.3 (q, J = 32.9 Hz) (CH_2); 121.1 (q, J = 277 Hz, CF_3); 211.4 (C=O). Found: C, 45.59; H, 5.56. Calc for $C_{12}H_{17}F_3O_4S$: C, 45.86; H, 5.45%.

1-Hydroxybicyclo[3.3.2]decan-2-one (**48**) by Oxidation of a Mixture of **42** and **47**. A mixture (239 mg) of **42** and **47** (approximately 1:1) was oxidized with Ag_2CO_3 - celite[13] (12.7 g) in acetone (94 ml) at reflux for 3 h. Filtration of black precipitates followed by evaporation of the acetone gave a yellowish semisolid (220 mg). MPLC over SiO_2 (hexane - ether) afforded **43** (30 mg) and **48** (30 mg). The ^{13}C NMR spectrum of the latter was superimposable with that of **48** obtained in the Ag_2CO_3 oxidation of a mixture of **42**, **44**, and **47**.

Bicyclo[3.3.2]dec-1-ene (**45**) by Pyrolysis of **46**. Bicyclo[3.3.2]dec-1-yl acetate (**46**) (550 mg, 2.80 mmol), which was obtained by separation from a mixture with bicyclo[3.3.2]decan-1-ol,[9] was heated with a free flame in a simple distillation apparatus under a slow stream of nitrogen. The distillate was dissolved in pentane and the solution washed with aq $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the pentane afforded a mixture (193 mg) of **45** and **46** (90:10 by ^{13}C NMR) as a semisolid; ^1H NMR (CCl_4) δ 5.57 (dd, J = 10.0, 6.0 Hz); ^{13}C NMR ($CDCl_3$) δ 142.6 (C); 31.1, 127.4 (CH); 25.7, 26.0, 27.2, 27.3, 33.1, 39.0, 39.4 (CH_2).

Bicyclo[3.3.2]decane-1,exo-2-diol (**44**) from **45**. The crude bridgehead olefin **45** (153 mg) was subjected to permanganate oxidation[12] following the procedure described for the oxidation of **26**. Oxidation by using $KMnO_4$ (267 mg, 1.69 mmol) and NaOH (57 mg, 1.43 mmol) in aq t-BuOH followed by purification over silica gel afforded a semisolid (21 mg) whose ^{13}C NMR spectrum was superimposable with that of **44** obtained by saponification of diol monobenzoate **40**.

Lithium Trimethoxyaluminohydride Reduction of 1-Hydroxybicyclo[3.3.2]decan-2-one (**48**). Ketol **48** (140 mg, 0.83 mmol) was reduced with $LiAlH(CH_3O)_3$[17] (2.08 mmol) in THF (5.7 ml) at 0°C for 1 h to give a white solid (138 mg) containing diols **44** and **47** in an approximate ratio 1:3 as determined by ^{13}C NMR.

Control Experiments for the Acylative Ring-Expansion. To a solution of 1-hydroxybicyclo-[4.3.1]dec-exo-2-yl benzoate (**31**) (179 mg, 0.652 mmol) in CCl_4 (2.2 ml) was added a mixture of triflic anhydride (0.17 ml, 1.0 mmol) and triflic acid (0.27 ml, 3.1 mmol) at 3 - 6°C. After the dark brown solution consisting of two phases had been stirred for 10 min, cold water (0.51 ml) was added over 3 min. To the resulting mixture were added water (2.5 ml) and ether (20 ml), and then the organic layer was worked up in a usual manner to give a yellow solid (179 mg). The ^{13}C NMR spectrum of the recovered solid was superimposable with that of **31**, no signals of endo isomer **30** being detected. A similar control experiment for 1-hydroxybicyclo[4.2.2]dec-2-yl benzoate (**39**) showed no isomerization to 1-hydroxybicyclo[3.3.2]dec-2-yl benzoates (**40** and **41**).

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