157. Acid-Catalyzed Rearrangements of 5,6-*exo*-Epoxy-7-oxabicyclo[2.2.1]hept-2-yl Derivatives. Migratory Aptitudes of Acyl *vs.* Alkyl Groups in *Wagner-Meerwein* Transpositions[1])

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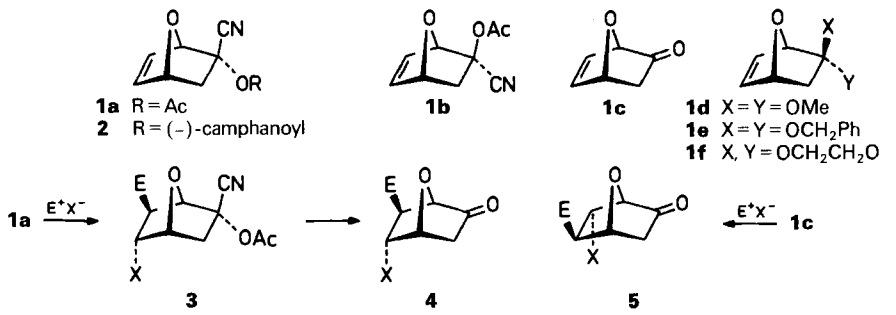
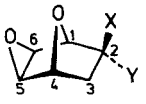
In the presence of HSO_3F/Ac_2O in CH_2Cl_2, 2-*exo*- and 2-*endo*-cyano-5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]hept-2-yl acetates (**6a, b**) gave products derived from the epoxide-ring opening and a 1,2-shift of the unsubstituted alkyl group (σ bond C(3)–C(4)). In contrast, under similar conditions, the 5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]heptan-2-one (**6c**) gave 5-oxo-2-oxabicyclo[2.2.1]heptane-3,7-diyl diacetates **20** and **21** arising from the 1,2-shift of the acyl group. Acid treatment of 5,6-*exo*-epoxy-2,2-dimethoxy-7-oxabicyclo[2.2.1]heptane (**6d**) and of 5,6-*exo*-epoxy-2,2-bis(benzyloxy)-7-oxabicyclo[2.2.1]heptane (**6e**) gave minor products arising from epoxide-ring opening and the 1,2-shift of σ bond C(3)–C(4) and major products (**25, 29**) arising from the 1,3-shift of a methoxy and benzyloxy group, respectively. Under similar conditions, 5,6-*exo*-epoxy-2,2-ethylenedioxy-7-oxabicyclo[2.2.1]heptane (**6f**) gave 1,1-(ethylenedioxy)-2-(2-furyl)ethyl acetate (**32**, major) and a minor produt **33** arising from the 1,2-shift of σ bond C(3)–C(4). The following order of migratory aptitudes for 1,2-shifts toward electron-deficient centers has been established: acyl > alkyl > alkyl α-substituted with inductive electron-withdrawing groups. This order is valid for competitive *Wagner-Meerwein* rearrangements involving equilibria between carbocation intermediates with similar exothermicities.

Introduction. – Derivatives of 7-oxabicyclo[2.2.1]heptane have been used as starting materials in the synthesis of natural products and compounds of biological interest [2] [3]. Some derivatives have also been shown to exhibit antitumor [4] and antiinflammatory activity [5]. We have shown that the 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives (+)-**1b**, (+)-**1c**, and (+)-**2** can be readily obtained optically pure [6] [7].



[1]) *For a preliminary communication, see* [1].



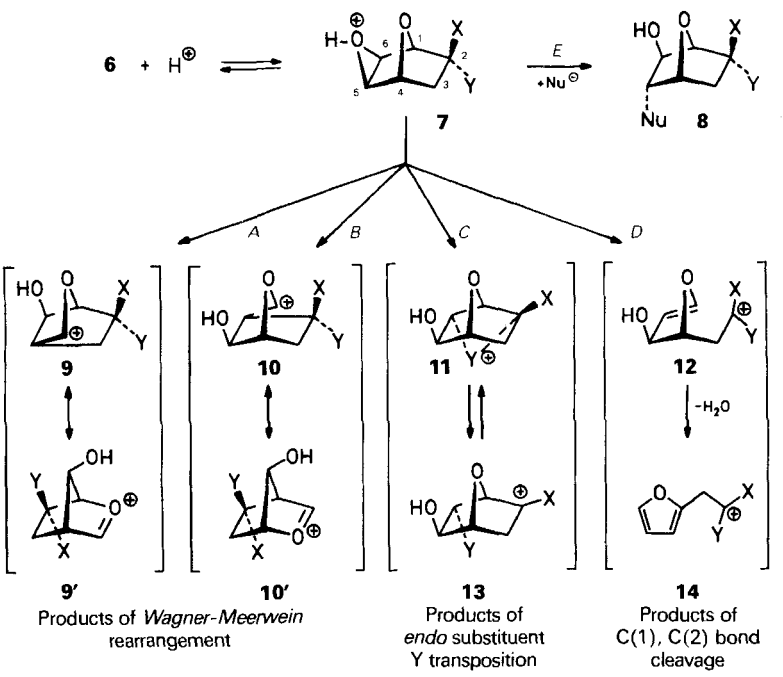
6

a X = CN, Y = OAc
b X = OAC, Y = CN
c X, Y = =O
d X = Y = OMe
e X = Y = OCH_2Ph
f X, Y = OCH_2CH_2O
g X = CN, Y = OH
h X = OH, Y = CN

Because of their bicyclic structure, the C=C bond of 7-oxabicyclo[2.2.1]hept-5-en-2-yl compounds reacts preferentially onto its *exo* face, thus ensuring good stereoselectivity [8–10]. The regioselectivity of electrophilic additions of bicyclo[2.2.*n*]alk-5-en-2-yl derivatives depends on the nature of the substituents at C(2) [11]. For instance, while the CN and OAc groups in **1a** play the role of electron-withdrawing substituents, giving exclusively the corresponding adducts **3** with E^+X^-, the carbonyl group in **1c** acts as an electron-donating substituent (because of a favourable hyperconjugative interaction involving the n electrons of the carbonyl function [11]) and leads to the formation of adducts **5**, under conditions of kinetic control [10]. Adducts **3** can be transformed into ketones **4**, regioisomeric with **5**. The centre α to the carbonyl group in **4** and **5** can be substituted with high stereoselectivity and the products transformed into a variety of compounds, including sugar derivatives such as L-daunosamine [2a]. Since the optically pure **1b**, **1c**, and **2** can be readily substituted at C(3), C(5), and C(6), they possess the same stereochemical information as hexoses and, therefore, can be viewed as 'naked sugars' [2a].

We report here our studies on the reactions of acids toward 5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]hept-2-yl derivatives **6** derived from the racemic olefins **1a–e**. *A priori*, the five paths *A–E* giving **8** or involving the cations **9–14** as shown in *Scheme 1* are

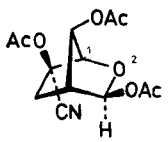
Scheme 1



possible for the reaction of the protonated epoxides **7**. We shall show that the selectivity observed strongly depends on the nature of the substituents X and Y at C(2). Conditions have been found under which the acid treatment of the epoxides **6** gives selectively new polysubstituted cyclopentyl or 7-oxabicyclo[2.2.1]heptyl derivatives that are potentially useful synthetic intermediates, thus valorising our 'naked sugars'.

Results. – ZnI_2-catalyzed *Diels-Alder* addition of furan to 1-cyanovinyl acetate gave a 4:1 mixture **1a**/**1b** [7] which was separated by column chromatography on silica gel and crystallization. On treatment with *m*-chloroperbenzoic acid in $CHCl_3$, the corresponding epoxides **6a** (92%) and **6b** (86%) were obtained. Saponification of **6a** with K_2CO_3 in aqueous MeOH in the presence of formaline afforded the epoxy ketone **6c** (85%). The acetals **1d** (86%), **1e** (85%), and **1f** (96%) were derived from **1c** on treatment with $MeOSiMe_3$, $PhCH_2OSiMe_3$, and $Me_3SiOCH_2CH_2OSiMe_3$, respectively, in the presence of 0.08 equiv. of $CF_3SO_3SiMe_3$ in CH_2Cl_2 [12]. Epoxides **6d** (91%), **6e** (87%), and **6f** (88%) were obtained by oxidizing **1d**, **1e**, and **1f**, respectively, with *m*-chloroperbenzoic acid in $CHCl_3$. The *exo* configuration of the epoxy moiety in **6** was established by the ^{1}H-NMR spectra which showed the absence of vicinal coupling between the bridgehead protons H–C(1), H–C(4) and the epoxide protons H–C(5), H–C(6) [13].

All our attempts to generate unrearranged adducts from epoxides **6a–c** failed. They led either to the recovery of the starting material (*e.g.*: **6a** + conc. HCl (100 equiv.) in $CHCl_3$ at 20°; **6a** + HBr (20 equiv.) in $AcOH/Ac_2O$ at 20°; **6a** + HI/pyridine [14] in $CHCl_3$ at 80° for 34 h; $CF_3SO_3SiMe_3$/lutidine 1:1 in toluene at 115° for 100 h) or to the formation of polymers (*e.g.*: **6a** + $CF_3SO_3SiMe_3$ (1 equiv.) in CH_2Cl_2 at 20°; **6a** + NaN_3 in dimethylformamide at 135° for 6 h [15]). When **6a** was treated with 0.2 equiv. of HSO_3F and 3 equiv. of Ac_2O in CH_2Cl_2 at −25°, the products **15–17** of acetolysis and *Wagner-Meerwein* rearrangement involving migration of the alkyl group (C(3)–C(4) bond; path *A*) were isolated in 43, 11, and 7% yield, respectively, after aqueous ($NaHCO_3$) workup and chromatography on silica gel. Under similar conditions (0.4 equiv. of HSO_3F, 12 equiv. of Ac_2O, CH_2Cl_2, 20°), epoxide **6b** yielded the acylal **18** in 45% isolated yield. It also arises from a *Wagner-Meerwein* rearrangement involving C(3)–C(4) bond migration (path *A*). No other isomeric products could be isolated or detected in the crude reaction mixtures. Products **15–18** are various protected forms of the carba analogue of (±)-lyxose (**19**).



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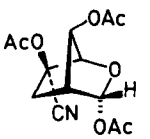

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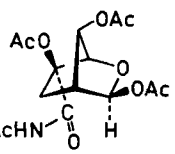

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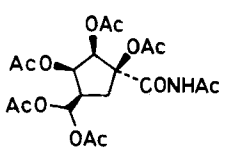

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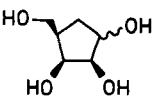

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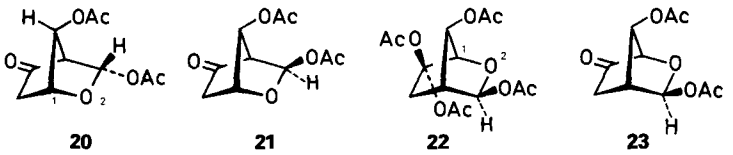
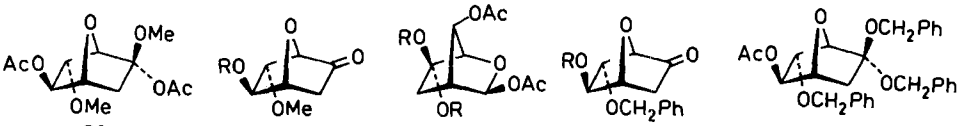
The acid-catalyzed acetolysis of epoxy ketone **6c** (0.4 equiv. of HSO_3F, 6 equiv. of Ac_2O, CH_2Cl_2, −51°) gave as major products **20** (51%) and **21** (8%) resulting from a *Wagner-Meerwein* rearrangement involving the migration of the acyl group (path *B*), and minor amounts of **22** (1%) and **23** (0.4%) resulting from a *Wagner-Meerwein* rearrangement implying alkyl group migration (path *A*). The proportions of products **20**/**21**/**22**/**23**



20 **21** **22** **23**

in the crude reaction mixture did not vary significantly by changing the amount of HSO_3F (0.1 to 0.4 equiv.), the temperature (−51 to −30°), and the reaction time (24–60 h).

Treatment of the dimethyl acetal **6d** with 0.2 equiv. of HSO_3F and 3 equiv. of Ac_2O in CH_2Cl_2 at −78° (12 h) afforded, after aqueous workup ($NaHCO_3$), a mixture of **24**, **25**, and **26** which were separated by column chromatography on silica gel and isolated in 30, 17, and 5% yield, respectively. The major products **24** and **25** arose from 1,3-migration of the *endo*-MeO group (path *C*) and the minor product **26** from the *Wagner-Meerwein* rearrangement involving the migration of the unsubstituted alkyl group (C(3), C(4) bond; path *A*). When the reaction was run at −40°, the acyl methyl acetal **24** was not observed, and ketone **25** was isolated in 55% yield. In the presence of 1 equiv. of CD_3OD, there was no incorporation of a D-atom in **24**–**26**, thus confirming the intramolecular nature of the methoxy-group migration **6d**→**7d**→**11d**→**13d**→**24** + **25**. When **6d** was treated with 0.3 equiv. of HSO_3F and 4 equiv. of MeOH in CH_2Cl_2 at 20° (36 h), the *trans*-disubstituted 7-oxabicyclo[2.2.1]heptan-2-one **27** was obtained and isolated in good yield (83%).

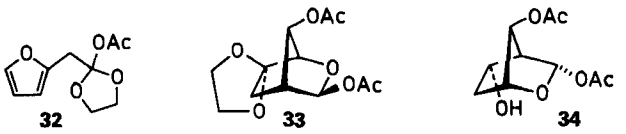


24 **25** R = Ac, **27** R = H **26** R = Me, **30** R = $PhCH_2$ **28** R = H, **29** R = Ac **31**

Under the same conditions, the epoxy ketone **6c** gave first **6d**, and then **27**. Similarly, when the dibenzyl acetal **6e** was treated with 0.6 equiv. of HSO_3F and 8 equiv. of $PhCH_2OH$ in CH_2Cl_2 at 20° (14 h), the corresponding ketone **28** was formed and isolated in 88% yield. Thus, reactions **1c**→**6c**→**27**, **1c**→**1d**→**6d**→**27**, or **1c**→**1e**→**6e**→**28** are efficient methods for introducing two different oxy functions at C(5) and C(6) of 7-oxabicyclo[2.2.1]heptan-2-one in a stereoselective, if not stereospecific, fashion. When the cyano acetates **6a** and **6b** were treated with HSO_3F in $MeOH/CH_2Cl_2$, the corresponding cyanohydrins **6g** and **6h**, respectively, were isolated pure by crystallization in 71 and 64% yield, respectively.

The treatment of the dibenzyl acetal **6e** with 0.5 equiv. of HSO_3F and 8 equiv. of Ac_2O in CH_2Cl_2 at −78° (90 min) gave a mixture from which ketone **29** and the product of acetolysis and rearrangement **30** were isolated in 57 and 7% yield, respectively. In some runs, 1–8% of the dibenzyl acetal **31** were also isolated.

Finally, treatment of the ethylene acetal **6f** with 0.4 equiv. of HSO_3F and 7 equiv. of Ac_2O in CH_2Cl_2 at −50° led to the formation of a mixture of products from which the furan derivative **32** arising from C(1)–C(2) bond cleavage (path *D*) and the product of acetolysis and rearrangement **33** (path *A*) were isolated in 41 and 24% yield, respectively,



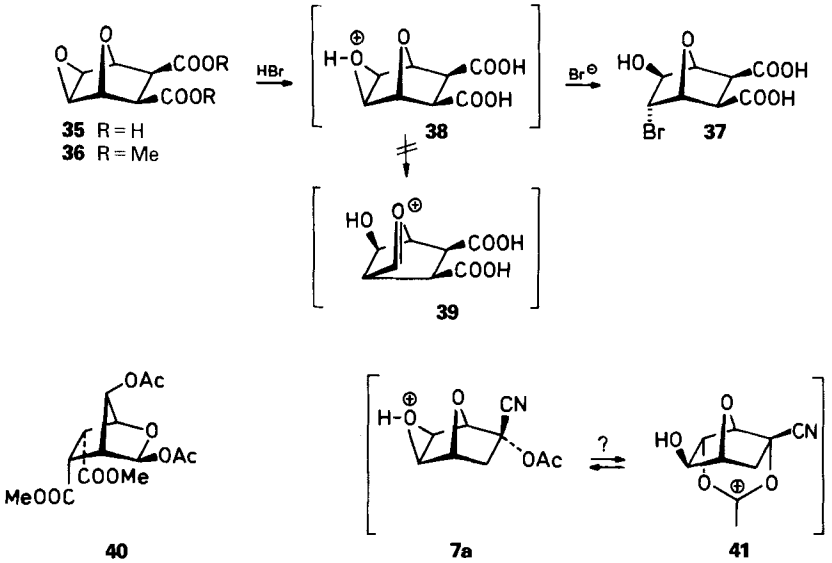
32 33 34

after column chromatography on silica gel. Compound **32** is an uncommon ethylene acetal of the mixed anhydride derived from acetic acid and furane-2-acetic acid [16].

The 360-MHz ^{1}H-NMR spectra of the crude reaction mixtures resulting from the acidic treatment of epoxides **6** did not show signals with significant intensities which could be attributed to other products (apart from a little polymeric material in some runs) than those isolated and presented here. All the new compounds were fully characterized by their elemental analysis and spectral data. The ^{1}H-NMR signals (360 MHz) were attributed unambigously by double-irradiation experiments and nuclear *Overhauser* effect (NOE) measurements. Furthermore, ketone **21** was reduced the *endo*-alcohol **34** whose ^{1}H-NMR spectrum confirmed the structure of **21**. The minor compound **23** obtained in the acid-promoted acetolysis and rearrangement of **6c** was found to be identical to the ketone obtained on hydrogenolysis (H_2, Pd/C) of product **30** obtained by acid-promoted acetolysis and rearrangement of the dibenzyl acetal **6e**.

Discussion. – Epoxides **6** are relatively unreactive toward protic acids and nucleophiles. The 'super acid' HSO_3F was required to induce ring opening of the oxiranes. This lack of reactivity compared with that of the corresponding C-bridged *exo*-epoxybicyclo[2.2.1]heptyl derivatives [17] is attributed to the inductive effect of the bridge O(7) in **6** [18]. *Yur'ev* and *Zefirov* [19] were able to esterify the diacid **35** to **36** in MeOH in the presence of oleum without ring opening of the epoxide *(Scheme 2)*. They also found that

Scheme 2



40 7a 41

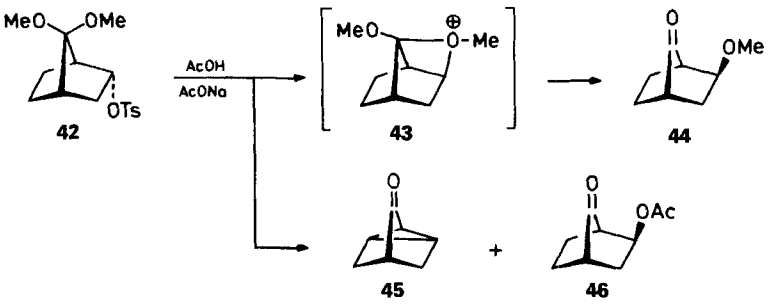
HBr adds to **35** in AcOH to furnish the bromohydrin **37** in 62% yield [20]. The absence of products of *Wagner-Meerwein* rearrangement was a surprise for at least two reasons. First of all, 5,6-epoxybicyclo[2.2.1]hept-2-yl derivatives are known to undergo easily skeletal rearrangement under acidic conditions [17], and secondly, the isomerization of **38** (protonated form of **35**) to the rearranged cationic intermediate **39** is expected to be an exothermic process because of the relatively high stability of the alkoxy-substituted carbenium ion **39** [18a]. Therefore, the relatively high energy barrier associated with the hypothetical rearrangement **38**→**39** must be attributed to the destabilizing effect of the electron-withdrawing COOH groups in **38** [19] [20–23].

In media of lower nucleophilicity than HBr/AcOH, *Wagner-Meerwein* rearrangement of type **38**→**39** are possible. Indeed, when the epoxy diester **36** was treated with H_2SO_4 in Ac_2O at 70°, *Yur'ev* and *Zefirov* isolated the rearranged product of acetolysis **40** in 65% yield [24]. Thus, in the light of these results, the preference of the cyanohydrin acetates **6a** and **6b** to undergo *Wagner-Meerwein* rearrangements with migration of the unsubstituted alkyl group (C(3)–C(4) bond; path *A*) rather than with migration of the substituted alkyl group (C(1)–C(2) bond; path *B*) was to be expected.

It is interesting to note that products resulting from the migration of the *endo*-acetoxy group **6a**→**7a**→**11a**→**13a** (path *C*) were not observed, probably because of the lack of stability of the cyano-substituted 7-oxa-2-norbornyl cation intermediate **13a**. This observation does not exclude, however, the possible formation of an intermediate such as **41** [25]. If equilibrium **7a** ⇄ **41** should exist, it could explain the preference for the 1,2-shift **7a**→**9a** (*Wagner-Meerwein* rearrangement) of the unsubstituted alkyl group. We do not favour the latter hypothesis as nucleophile quenching of **41** would be expected to yield 5,6-disubstituted 7-oxanorbornanes (similar to **24** or **25**) in the reaction mixture from the acid-promoted acetolysis of **6a**. This was not the case[2]). In the acid-promoted ring opening of epoxide **6b**, the *endo*-cyano substituent is not expected to participate, at least not as easily as the *endo*-acetoxy group in **6a**.

As we have seen, even in this case, the 1,2-shift of the unsubstituted alkyl group (path *A*) is the preferred migration.

The preference for the 1,3-migration of an *endo*-alkoxy group (path *C*) in the case of the acetals **6d** and **6e** must be attributed to the relatively high stability of the 2-alkoxy-7-oxabicyclo[2.2.1]hept-2-yl cation intermediates **13d** and **13e**, respectively. A similar rearrangement had been reported for the buffered acetolysis of the dimethyl acetal **42** which



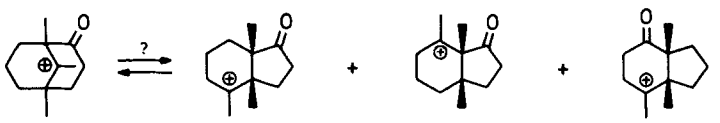
[2]) Products of skeleton rearrangement were also observed in the electrolysis of 7-oxabicyclo[2.2.1]heptane-2-carboxylic acid and derivatives [26].

was shown to afford a 11:20:39 mixture **44**/**45**/**46** [27]. The results were interpreted in terms of formation of the oxonium-ion intermediate **43** (→**44**), analogous to **11d**, competitively with elimination of *p*-toluenesulfonic acid (→**45**) and direct displacement of the tosyloxy by the acetoxy group (→**46**).

In the case of the ethylene acetal **6f**, the 1,3-migration of the *endo*-alkoxy group is prohibited for steric reasons, thus making the bond cleavage **7f**→**12f** the preferred process as **12f**, a dialkoxy-substituted carbenium-ion intermediate is expected to be a relatively stable species. The latter then eliminates 1 equiv. of H_2O, giving **14f** which is then quenched with AcOH or Ac_2O and furnishes the major product **32**.

The minor products **26**, **30**, and **33** of the acid-promoted acetolysis of epoxy acetals **6d**, **6e**, and **6f**, respectively, arose from *Wagner-Meerwein* rearrangements (path *A*) implying migration of the non-substituted alkyl group, in agreement with the hypothesis that, because of the inductive effect of the acetal function, the substituted alkyl group 1,2-shift becomes a less favourable process. If the carbonyl group in epoxy ketone **6c** should be considered as an electron-withdrawing group similar to the acetal functions in **6d**–**f** and the AcO and CN groups in **6a** and **6b**, the acid-promoted rearrangement of **6c** should have given preferentially the products of *Wagner-Meerwein* rearrangement **22** and **23** (path *A*) rather than products **20** and **21** (path *B*), the former arising from 1,2-shift of the alkyl group and the latter from 1,2-shift of the acyl group. Our results demonstrate, on the contrary, that the acyl-group migration is definitively a faster process that the alkyl-group migration.

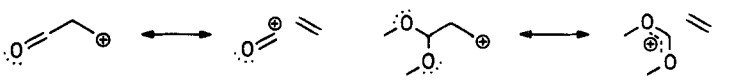
In several carbenium-ion rearrangements, 1,2-shifts of electron-withdrawing group such as RCO [28] [29] or COOR [30] [31] toward electron-deficient centers have been observed. This was possible because alternative migrations of hydride, alkyl, or aryl groups would have led to much less stable carbenium-ion intermediates. Recently, *Gambacorta* and coworkers [32] have shown that acyl- and alkyl-group migrations were competitive processes in the acid-promoted rearrangements of 9-hydroxybicyclo[3.3.1]nonan-2-ones to *cis*-fused hexahydroinden-1-ones. Since the generated cationic intermediates **47**–**50** might have similar stabilities (all are methylcyclohexyl cations perturbed at a remote position by the carbonyl group), it could not be excluded that the proportion of products observed expressed the relative stabilities of **48**, **49**, and **50**



47 **48** **49** **50**

(equilibrium of tertiary carbenium ions) rather than the relative rate of their formation (non-equilibrating ions). This ambiguity does not exist in the case of the acid-promoted acetolysis of epoxy ketone **6c** for the following reason. Both reactions **7c**→**9c** and **7c**→**10c** *(Scheme 1)* are expected to be highly exothermic because of the formation of the stable alkoxy-substituted carbenium ions **9c** and **10c**. Quantum-mechanical calculations (*ab initio* STO 6–31 G*, completely optimized geometries [33]) suggested that **9c** and **10c** have similar stabilities, the oxo group having a smaller differential substituent effect than in 6-oxo- and 5-oxobicyclo[2.2.1]hept-2-yl cations [11b] because of the delocalization of

the positive charge in cations **9**↔**9′** and **10**↔**10′**. Therefore, the competition between *Wagner-Meerwein* rearrangements **7c**→**9c** (path *A*) and **7c**→**10c** (path *B*) depends on the intrinsic migratory aptitude (kinetic effect) of acyl *vs.* alkyl groups. Consequently, the acid-promoted acetolysis of **6c** is unique since it reveals the 'true' migratory aptitudes of acyl *vs.* alkyl groups in an 'energetically unbiased' situation [34] because of the similar exothermicities of reaction **7c**→**9c** and **7c**→**10c**. The facile acyl-group 1,2-shift can be attributed to the electron-donating ability (polarizability) of the C=O function [11] which can be interpreted in terms of the canonical forms **51**↔**52** [35]. It is not obvious, though, why a similar hyperconjugative interaction **53**↔**54** does not dominate the *Wagner-Meerwein* tendencies (path *A vs.* path *B*) in the acetals **1d**–**f**[3])[4])[5]).



51 **52** **53** **54**

Conclusion. – The 5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]hept-2-yl derivatives **6** (epoxides of 'naked sugars') have shown a high versatility in their acid-catalyzed acetolysis. Depending on the nature of the substituents at C(2), the 1,2-shifts (*Wagner-Meerwein* rearrangements) of alkyl groups or acyl groups compete with the 1,3-shifts of the *endo* substituents at C(2) and the C(1)–C(2) σ bond cleavage. Conditions have been found that allow one to transform 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives into carba analogues of lyxose or into polyoxy-substituted 7-oxabicyclo[2.2.1]heptane derivatives in a stereoselective fashion. Finally, we have established the following order of intrinsic migratory aptitudes for 1,2-shifts toward electron-deficient centers: acyl > alkyl > alkyl α-substituted with inductive electron-withdrawing groups. This order is valid for competitive *Wagner-Meerwein* rearrangements involving equilibria between carbocation intermediates with similar exothermicities.

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[3]) In 1962, *Meinwald* and *Cadoff* [36] had already tried to compared the migratory aptitudes of acyl *vs.* alkyl group in the acid-promoted ring-opening of the epoxide in 5,6-*exo*-epoxybicyclo[2.2.1]heptan-2-one. Unfortunately, no product of *Wagner-Meerwein* rearrangement could be observed, the reaction giving mostly products arising from C(1)–C(2) bond cleavage (similar to path *D* and as observed for **6f**→**32**).

[4]) The absence of products resulting from hydride migration is not a surprise if the 7-oxabicyclo[2.2.1]hept-2-yl cations can be considered to have analogous properties, as far as their rearrangements are concerned, with those of bicyclo[2.2.1]hept-2-yl-cation intermediates [37].

[5]) Homoconjugation between the carbonyl group and the carbenium ion should not be a significant phenomenon [11b] [33].

Experimental Part

1. *General.* See [2a] [10]. All reactions were run under N_2 or Ar. Dimethoxyethane (DME) and tetrahydrofuran (THF) were freshly distilled from $LiAlH_4$/NaH. CH_2Cl_2 was distilled from CaH_2, Ac_2O from P_4O_{10}. HSO_3F *(Fluka)* was purified by distillation at 20 Torr and stored in sealed *Pyrex* ampoules. MeOH was distilled from Mg and $PhCH_2OH$ from CaH_2 (20 Torr). Hexamethylphosphoric triamide (HMPT) was distilled from NaH (0.1 Torr). Elution chromatography: *Lobar* system using *Merck Lichroprep Si 60* (40–63 μm), size *B* columns; detection with a differential diffractometer *(Knauer)*. TLC: silica gel; detection by dipping in anisaldehyde (2 ml)/H_2SO_4 (2.5 ml)/AcOH (7 ml)/EtOH (70 ml) followed by heating.

2. *(1*RS,*2*SR,*4*RS,*5*RS,*6*RS*)-2*-exo-*Cyano-5,6-*exo-*epoxy-7-oxabicyclo[2.2.1]hept-2-*endo-*yl Acetate* (**6a**). *m*-Chloroperbenzoic acid (*m*-$ClC_6H_4CO_3H$; 85%, *Fluka;* 16.2 g, 80 mmol) was added portionwise to a stirred soln. of **1a** [7] (13.5 g, 75.4 mmol) in $CHCl_3$ (70 ml). After heating to 40° for 24 h (a precipitate was formed after 30 min), the mixture was poured into AcOEt (300 ml) and washed successively with 40% aq. $NaHSO_3$ soln. (30 ml) and sat. aq. $NaHCO_3$ soln. (60 ml). After drying ($MgSO_4$) and solvent evaporation, the crude **6a** was purified on a short silica-gel column (AcOEt/petroleum ether 1:2) yielding 13.9 g of an oil which crystallized. Recrystallization from AcOEt/petroleum ether gave 12.85 g of colourless crystals, m.p. 119–120°. Concentration of the mother liquor afforded 0.62 g (total yield 92%) of colourless crystals, m.p. 117–119°. IR (KBr): 3095, 3070, 3020, 2980, 2250, 1760, 1445, 1370, 1245, 1230, 1215, 1190, 1055, 1030, 995, 960, 920, 860, 790, 710, 625. ^{1}H-NMR ($CDCl_3$, 80 MHz): 4.97 (*s*, H–C(1)); 4.6 (*d*, ^3J = 5, H–C(4)); 3.4 (br. *s*, H–C(5), H–C(6)); 2.7 (*dd*, ^2J = 14, ^3J = 5, H_{exo}–C(3)); 2.12 (*s*, CH_3CO); 1.85 (*d*, ^2J = 14, H_{endo}–C(3)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 168.9 (*s*); 117.5 (*s*); 78.2 (*dm*, ^1J(C,H) = 175, C(1) or C(4)); 75.1 (*s*, C(2)); 73.9 (*dm*, ^1J(C,H) = 170, C(4) or C(1)); 48.2 (*dm*, ^1J(C,H) = 195, C(6)); 46.1 (*dd*, ^1J(C,H) = 200, ^3J(C,H) = 5, C(5)); 41.1 (*t*, ^1J(C,H) = 140, C(3)); 20.0 (*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 195 (1, $M^{+\cdot}$), 153 (27), 152 (6), 126 (10), 125 (5), 124 (5), 106 (27), 84 (100). Anal. calc. for $C_9H_9NO_4$ (195.173): C 55.39, H 4.65, N 7.18; found: C 55.27, H 4.68, N 7.17.

3. *(1*RS,*2*RS,*4*RS,*5*RS,*6*RS*)-2*-endo-*Cyano-5,6-*exo-*epoxy-7-oxabicyclo[2.2.1]hept-2-*exo-*yl Acetate* (**6b**). *m*-$ClC_6H_4CO_3H$ (85%, 1.8 g, 9 mmol) was added to a soln. of **1b** (obtained by column chromatography of the mother liquor of crystallization of **1a** [7] on silica gel; 1 g, 5.6 mmol) in $CHCl_3$ (7 ml). After heating to 45° for 24 h, the mixture was poured into AcOEt (50 ml) and washed successively with 40% aq. $NaHSO_3$ soln. (10 ml), sat. aq. $NaHCO_3$ soln. (10 ml), and sat. aq. NaCl soln. (10 ml). After drying ($MgSO_4$) and solvent evaporation, the crude epoxide was purified by filtration on a short column of silica gel (AcOEt/petroleum ether 1:2), yielding 990 mg of a white solid. Recrystallization from AcOEt/petroleum ether gave 810 mg, m.p. 174–175°; concentration of the mother liquor gave 130 mg (total yield 86%), m.p. 173–175°, colourless crystals. IR (KBr): 3100, 3090, 2250, 1750, 1440, 1372, 1245, 1212, 1055, 1025, 945, 935, 890, 880, 865. ^{1}H-NMR ($CDCl_3$, 360 MHz): 4.8 (*s*, H–C(1)); 4.67 (*d*, ^3J = 5, H–C(4)); 3.64 (*AB*, ^3J = 3, $\nu_0\delta$ = 74, H–C(5), H–C(6)); 2.46 (*d*, ^2J = 14, H_{endo}–C(3)); 2.31 (*dd*, ^2J = 14, ^3J = 5, H_{exo}–C(3)); 2.15 (*s*, CH_3CO). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 170 (*s*); 116 (*s*); 78.8 (*dm*, ^1J(C,H) = 160), 74.2 (*dm*, ^1J(C,H) = 170, C(1), C(4)); 73.9 (*s*, C(2)); 49.1 (*dm*, ^1J(C,H) = 195, C(5)); 46.1 (*dd*, ^1J(C,H) = 200, ^3J(C,H) = 5, C(6)); 43.1 (*t*, ^1J(C,H) = 135, C(3)); 20.5 (*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 195 (1.3, $M^{+\cdot}$), 153 (27), 152 (5), 126 (9), 125 (5), 124 (3), 106 (27), 84 (100). Anal. calc. for $C_9H_9NO_4$ (195.173): C 55.39, H 4.65, N 7.18; found: C 55.46, J 4.74, N 7.17.

4. *(1*RS,*4*RS,*5*RS,*6*RS*)-5,6-*exo-*Epoxy-7-oxabicyclo[2.2.1]heptan-2-one* (**6c**). To a soln. of **6a** (5 g, 26 mmol) in MeOH (150 ml) cooled to 0°, formaline (40% aq. CH_2O soln.; 4.2 ml, 52 mmol) and a soln. of K_2CO_3 (200 mg, 1.5 mmol) in H_2O (1 ml) were added successively. After stirring at 0° for 30 min, formaline (2 ml) was added and the mixture stirred at 0° for 25 min. After addition of AcOH (0.4 ml, 7 mmol), the mixture was concentrated to 30 ml by evaporation. The mixture was poured into sat. aq. NaCl soln. (30 ml) and extracted with AcOEt (100 ml, 3 times). After drying ($MgSO_4$) and solvent evaporation, the crude **6c** was purified by column chromatography on silica gel (Et_2O/petroleum ether 2:1) yielding first 2.8 g of **6c** (solidifying oil) and then 360 mg (7%) of **6a**. Recrystallization of **6c** from Et_2O/petroleum ether gave 1.93 g (60%) of colourless crystals, m.p. 54–56°. Concentration of the mother liquor yielded 350 mg (11%) of a second crop of crystals, m.p. 55–56°. Evaporation of the latter mother liquor, followed by chromatography and recrystallization gave 260 mg (8%) of colourless crystals, m.p. 55–56° (total yield 79%). IR (KBr): 3070, 3040, 2950, 1730, 1405, 1295, 1225, 1135, 1120, 1015, 915, 855, 785. ^{1}H-NMR ($CDCl_3$, 360 MHz): 4.72 (*d*, ^3J = 5, H–C(4)); 4.29 (br. *s*, H–C(1)); 3.55 (*AB*, ^3J = 3, $\nu_0\delta$ = 45, H–C(5), H–C(6)); 2.45 (*dd*, ^2J = 18, ^3J = 5, H_{exo}–C(3)); 1.97 (*d*, ^2J = 18, H_{endo}–C(3)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 207 (*s*); 76.7 (*dm*, ^1J(C,H) = 170), 73.3 (*dm*, ^1J(C,H) = 172, C(1), C(4)); 50.8 (*dm*, ^1J(C,H) = 196, C(5)); 45.8 (*dd*, ^1J(C,H) = 200, ^3J(C,H) = 5, C(6)); 38.2 (*t*, ^1J(C,H) = 136, C(3)). MS (70 eV): 126 (7, $M^{+\cdot}$), 125 (1), 124 (4), 98 (21), 97 (100). Anal. calc. for $C_6H_6O_3$ (126.110): C 57.15, H 4.80; found: C 57.21, H 4.94.

5. *(1RS,4RS)-5,5-Dimethoxy-7-oxabicyclo[2.2.1]hept-2-ene* (**1d**). Trimethylsilyl trifluoromethanesulfonate ($CF_3SO_3SiMe_3$, 40 µl, 0.2 mmol) was added to a stirred soln. of methoxytrimethylsilane (5.5 ml, 40 mmol) and **1c** [37] (2.05 g, 18.6 mmol) in anh. CH_2Cl_2 (20 ml) cooled to 0°. After stirring at 0° for 40 min and at 20° for 20 min, methoxytrimethylsilane (1.5 ml, 11 mmol) and $CF_3SO_3SiMe_3$ (20 µl, 0.1 mmol) were added. After 1 h at 20°, sat. aq. $NaHCO_3$ soln. (20 ml) was added and the mixture extracted with Et_2O (150 ml). After washing with sat. aq. NaCl soln. (10 ml) and drying ($MgSO_4$), the solvent was evaporated and the residue purified by column chromatography on silica gel (AcOEt/petroleum ether 1:2) and bulb-to-bulb distillation (*Büchi*, 150°/20 Torr), yielding 2.49 g (86%) of colourless oil. IR (film): 3090, 3005, 2940, 2840, 1460, 1440, 1420, 1320, 1295, 1242, 1135, 1120, 1070, 1060, 1030, 990, 910, 890, 865, 795, 755, 705. ^{1}H-NMR ($CDCl_3$, 80 MHz): 6.3 (*ABXY*, ^3J = 6, 2, $\nu_0\delta$ = 8, H–C(2), H–C(3)); 5.0 (br. *d*, ^3J = 5, H–C(1)); 4.72 (br. *s*, H–C(4)); 3.28, 3.17 (2*s*, 2 MeO); 2.0 (*dd*, ^2J = 11.5, ^3J = 5, H_{exo}–C(6)); 1.39 (*d*, ^2J = 11.5, H_{endo}–C(6)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 137.9, 132.8 (2*dm*, ^1J(C,H) = 175, C(2), C(3)); 110.1 (*s*, C(5)); 80.8 (*dm*, ^1J(C,H) = 160), 78.8 (*dm*, ^1J(C,H) = 165, C(1), C(4)); 50.7, 49.7 (2*q*, ^1J(C,H) = 140, 2 MeO); 36.6 (*t*, ^1J(C,H) = 135, C(6)). MS (70 eV): 156 (0.3, $M^{+\cdot}$), 155 (0.2), 140 (1.2), 125 (4.5), 109 (3), 108 (3), 97 (10), 88 (100).

6. *(1RS,4RS)-5,5-Bis(benzyloxy)-7-oxabicyclo[2.2.1]hept-2-ene* (**1e**). $CF_3SO_3SiMe_3$ (100 µl, 0.55 mmol) was added to a soln. of **1c** (2 g, 18 mmol) and (benzyloxy)trimethylsilane (8.5 g, 47 mmol) in CH_2Cl_2 (20 ml) cooled to 4°. After staying at 4° for 3 h, pyridine (1 ml) was added, and the mixture was poured into sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with AcOEt (80 ml, twice). The extract was washed with sat. aq. NaCl soln. (10 ml), dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (Et_2O/petroleum ether 2:3), yielding 5.1 g of **1e**. Crystallization from Et_2O/petroleum ether gave 4.1 g of colourless crystals, m.p. 83–85°. Concentration of the mother liquor gave 0.66 g, m.p. 82–84° (total yield 85%). IR (KBr): 3060, 3030, 3010, 2960, 2920, 2885, 1500, 1455, 1380, 1315, 1295, 1245, 1230, 1180, 1120, 1075, 1055, 1020, 1000, 910, 895, 870, 800. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.25–7.46 (*m*, 10 arom. H); 6.57, 6.47 (2*dd*, ^3J = 4, 2, H–C(2), H–C(3)); 5.08 (br. *d*, ^3J = 5, H–C(1)); 4.94 (br. *s*, H–C(4)); 4.72 (*AB*, ^2J = 12, $\nu_0\delta$ = 18.5, PhCH_2); 4.56 (*AB*, ^2J = 12, $\nu_0\delta$ = 54.7, PhCH_2); 2.24 (*dd*, ^2J = 12, ^3J = 5, H_{exo}–C(6)); 1.65 (*d*, ^2J = 12, H_{endo}–C(6)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 138.3 (*s*, arom. C); 138.0, 133.4 (2*d*, ^1J(C,H) = 175, C(2), C(3)); 137.9 (*s*, arom. C); 128.4, 127.6, 127.4, 127.3 (4*d*, ^1J(C,H) = 160, arom. C); 110.7 (*s*, C(5)); 81.5, 79.0 (2*dm*, ^1J(C,H) = 165, C(1), C(4)); 65.9, 65.0 (2*t*, ^1J(C,H) = 142, 2 PhCH_2); 37.7 (*t*, ^1J(C,H) = 136, C(6)). MS (70 eV): 217 (0.6, $M^{+\cdot}$ – 91), 181 (0.6), 149 (2), 108 (2), 107 (3), 106 (2), 105 (4), 92 (1), 91 (100). Anal. calc. for $C_{20}H_{20}O_3$ (308.375): C 77.90, H 6.54; found: C 77.79, H 6.53.

7. *(Benzyloxy)trimethylsilane* [38]. Benzylic alcohol (55 g, 0.5 mol) was added to a stirred mixture of NaH (55–60% suspension in oil, 24 g, 0.55 mol) and anh. THF (250 ml). After heating under reflux for 16 h, the mixture was cooled to 5°, and chloromethylsilane (88 ml, 0.7 mol) was added slowly under stirring. After the end of the addition, the mixture was heated under reflux for 4 h. The mixture was distilled at normal pressure and then at 20 Torr, yielding 74 g (b.p. 70–100°). After addition of NaH suspension in oil (2 g), the mixture was redistilled at 20 Torr, yielding 65 g (71%) of colourless oil, b.p. 82–83° ([38]: b.p. 90°/19 Torr).

8. *(1RS,4RS)-5,5-Ethylenedioxy-7-oxabicyclo[2.2.1]hept-2-ene* (**1f**). At 0°, 1,2-bis(trimethylsilyloxy)ethane (2.2 ml, 9 mmol) was added to a soln. of **1c** (0.85 g, 7.7 mmol) in anh. CH_2Cl_2 (15 ml). After addition of $CF_3SO_3SiMe_3$ (25 µl) and standing at 0° for 4 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with Et_2O (100 ml). After washing with sat. aq. NaCl soln. (5 ml), drying ($MgSO_4$), and solvent evaporation, the crude **1f** was purified by chromatography on silica gel (Et_2O/petroleum ether 1:2), yielding 1.14 g (96%) of slowly crystallizing, colourless oil, m.p. 47–49° (Et_2O/petroleum ether). IR (KBr): 3100, 3030, 3000, 2900, 1620, 1480, 1450, 1320, 1250, 1130, 1050, 1020, 905, 855, 800, 700. ^{1}H-NMR ($CDCl_3$, 80 MHz): 6.3–6.6 (*m*, H–C(2), H–C(3)); 5.0 (*d*, ^3J = 5, H–C(1)); 4.4 (br. *s*, H–C(4)); 3.7–4.1 (*m*, OCH_2CH_2O); 2.07 (*dd*, ^2J = 12, ^3J = 5, H_{exo}–C(6)); 1.5 (*d*, ^2J = 12, H_{endo}–C(6)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 138.6, 133.1 (2*dm*, ^1J(C,H) = 175, C(2), C(3)); 114.4 (*s*, C(5)); 81.2 (*dd*, ^1J(C,H) = 170, ^3J(C,H) = 8, C(1)); 78.7 (*dm*, ^1J(C,H) = 160, C(4)); 65.1, 64.3 (2*t*, ^1J(C,H) = 150, OCH_2CH_2O); 39.2 (*t*, ^1J(C,H) = 136, C(6)). MS (70 eV): 154 (0.8, $M^{+\cdot}$), 128 (1), 125 (3), 124 (2), 101 (2), 99 (2), 94 (2), 87 (100). Anal. calc. for $C_8H_{10}O_3$ (154.164): C 62.33, H 6.54; found: C 62.29, H 6.58.

9. *(1RS,4RS,5RS,6RS)-5,6-*exo*-Epoxy-2,2-dimethoxy-7-oxabicyclo[2.2.1]heptane* (**6d**). A mixture of *m*-$ClC_6H_4CO_3H$ (85%; 3.4 g, 17 mmol) and **1d** (2.2 g, 14 mmol) in anh. $CHCl_3$ (30 ml) was stirred at 20° for 90 min. The mixture was poured into AcOEt (150 ml) and washed successively with 40% aq. $NaHSO_3$ soln. (10 ml), sat. aq. $NaHCO_3$ soln. (25 ml), and sat. aq. NaCl soln. (10 ml). After drying ($MgSO_4$) and solvent evaporation, the

crude **6d** was purified by chromatography on silica gel (AcOEt/petroleum ether 1:2), yielding 2.3 g of slowly crystallizing, colourless oil. Recrystallization from Et_2O/petroleum ether gave 1.9 g of colourless crystals, m.p. 56–57°. Concentration of the mother liquor gave 0.3 g, m.p. 55–57° (total yield 91%). IR (KBr): 3100, 3070, 2850, 1600, 1575, 1440, 1370, 1315, 1285, 1260, 1170, 1130. ^{1}H-NMR ($CDCl_3$, 80 MHz): 4.45 (*d*, ^3J = 6, H–C(4)); 4.32 (*s*, H–C(1)); 3.42 (*AB*, ^3J = 3.5, $\nu_o\delta$ = 7, H–C(5), H–C(6)); 3.2 (*s*, 2 MeO); 1.9 (*dd*, ^2J = 12, ^3J = 6, H_{exo}–C(3)); 1.55 (*d*, ^2J = 12, H_{endo}–C(3)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 111.7 (*s*, C(2)); 74.8, 73.9 (*2dm*, ^1J(C,H) = 165, C(1), C(4)); 51.4, 49.25 (*2q*, ^1J(C,H) = 144, 2 MeO); 49.7 (*dm*, ^1J(C,H) = 196, C(5)); 47.9 (*dd*, ^1J(C,H) = 200, ^3J(C,H) = 5, C(6)); 37.5 (*t*, ^1J(C,H) = 135, C(3)). MS (70 eV): 172 (11, $M^{+\cdot}$), 143 (17), 141 (25), 127 (11), 111 (25), 57 (100). Anal. calc. for $C_8H_{12}O_4$ (172.179): C 55.81, H 7.02; found: C 55.75, H 7.08.

10. *(1*RS,*4*RS,*5*RS,*6*RS*)-2,2-Bis(benzyloxy)-5,6-*exo*-epoxy-7-oxabicyclo[2.2.1]heptane* (**6e**). A mixture of **1e** (2.68 g, 8.7 mmol) and *m*-$ClC_6H_4CO_3H$ (85%; 1.9 g, 9.4 mmol) in anh. $CHCl_3$ (20 ml) was stirred at 20° for 3 h. AcOEt (120 ml) was added and the mixture washed successively with 10% aq. K_2CO_3 soln. (20 ml, twice) and sat. aq. NaCl soln. (10 ml). After drying ($MgSO_4$) and solvent evaporation, the crude **6e** was purified by column chromatography on silica gel (AcOEt/petroleum ether 1:3), yielding 2.64 g of slowly crystallizing oil. Crystallization from Et_2O/petroleum ether gave 2.1 g of colourless crystals, m.p. 93.5–94.5°. Concentration of the mother liquor afforded 0.34 g (total yield 87%), m.p. 92–94°. IR (KBr): 3070, 3040, 3020, 2960, 2940, 2890, 1590, 1495, 1455, 1380, 1310, 1255, 1220, 1185, 1120, 1095, 1050, 1030, 1000, 890, 855, 760, 705, 695. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.29–7.39 (*m*, 10 H); 4.61 (*AB*, ^2J = 12, $\nu_o\delta$ = 20, PhCH_2); 4.56 (*AB*, ^2J = 12, $\nu_o\delta$ = 9, PhCH_2); 4.5 (*d*, ^3J = 6, H–C(4)); 4.48 (*s*, H–C(1)); 3.57, 3.39 (*2d*, ^3J = 3.3, H–C(5), H–C(6)); 2.14 (*dd*, ^2J = 12.5, ^3J = 6, H_{exo}–C(3)); 1.77 (*d*, ^2J = 12.5, H_{endo}–C(3)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 137.6, 137.3 (*2s*, arom. C); 128.3, 127.7, 127.4, 127.2, 127.1 (*5d*, ^1J(C,H) = 160, arom. C); 112.1 (*s*, C(2)); 75.3, 74.0 (*2dm*, ^1J(C,H) = 165, C(1), C(4)); 66.3, 64.4 (*2t*, ^1J(C,H) = 145, PhCH_2); 49.7 (*dm*, ^1J(C,H) = 200, C(5)); 48.0 (*dd*, ^1J(C,H) = 200, ^3J(C,H) = 5, C(6)); 38.4 (*t*, ^1J(C,H) = 135, C(3)). MS (70 eV): 324 (0.1, $M^{+\cdot}$), 234 (0.6), 233 (4), 133 (2), 127 (2), 117 (5), 107 (6), 92 (45), 91 (100). Anal. calc. for $C_{20}H_{20}O_4$ (324.374): C 74.06, H 6.21; found: C 74.01, H 6.16.

11. *(1*RS,*4*RS,*5*RS,*6*RS*)-5,6-*exo-*Epoxy-2,2-ethylenedioxy-7-oxabicyclo[2.2.1]heptane* (**6f**). A mixture of **1f** (1.06 g, 6.9 mmol) and *m*-$ClC_6H_4CO_3H$ (85%; 1.5 g, 7.4 mmol) in $CHCl_3$ (15 ml) was stirred at 20° for 2 h. After addition of AcOEt (60 ml), the mixture was washed successively with 40% aq. $NaHSO_3$ soln. (10 ml), sat. aq. Na*H*CO_3 soln. (10 ml), and sat. aq. NaCl soln. (10 ml). After drying ($MgSO_4$) and solvent evaporation, the crude **6f** was purified by column chromatography on silica gel (AcOEt/petroleum ether 3:2), yielding 1.08 g (92%) of crystals. Recrystallization from Et_2O/petroleum ether gave 0.88 g (75%) of colourless crystals, m.p. 106.5–107.5°. Concentration of the mother liquor gave 0.15 g (13%) of **6f**, m.p. 105.5–107°. IR (KBr): 3040, 3005, 2970, 2920, 2870, 1480, 1445, 1325, 1260, 1205, 1185, 1145, 1110, 1040, 1025, 990, 940, 925, 860. ^{1}H-NMR ($CDCl_3$, 80 MHz): 4.45 (*d*, ^3J = 5, H–C(4)); 4.02 (*s*, H–C(1)); 3.8–4.1 (*m*, OCH_2CH_2O); 3.45 (*AB*, ^3J = 3.5, $\nu_o\delta$ = 7, H–C(5), H–C(6)); 2.1 (*dd*, ^2J = 13, ^3J = 5, H_{exo}–C(3)); 1.7 (*d*, ^2J = 13, H_{endo}–C(3)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 115.9 (*s*, C(2)); 76.0 (*dm*, ^1J(C,H) = 162), 73.7 (*dm*, ^1J(C,H) = 167, C(1), C(4)); 65.0, 64.5 (*2t*, ^1J(C,H) = 150, OCH_2CH_2O); 49.8 (*dm*, ^1J(C,H) = 200, C(5)); 47.5 (*dd*, ^1J(C,H) = 200, ^3J(C,H) = 5, C(6)); 39.5 (*t*, ^1J(C,H) = 135, C(3)). MS (70 eV): 170 (2.5, $M^{+\cdot}$), 169 (12), 152 (2), 149 (4), 141 (60), 115 (11), 114 (14), 113 (20), 99 (74), 86 (100). Anal. calc. for $C_8H_{10}O_4$ (170.163): C 56.47, H 5.92; found: C 56.63, H 5.97.

12. *Reaction of* **6a** *with* HSO_3F/Ac_2O. Ac_2O (0.5 ml, 5.3 mmol) and then HSO_3F (20 µl, 0.3 mmol) were added to a soln. of **6a** (0.29 g, 1.5 mmol) in anh. CH_2Cl_2 (5 ml) cooled to − 78°. The mixture was allowed to stand at − 25° for 3 h and then was poured into sat. aq. $NaHCO_3$ soln. (5 ml). The mixture was extracted with AcOEt (80 ml). The extract was washed successively with sat. aq. $NaHCO_3$ soln. (10 ml) and sat. aq. NaCl soln. (10 ml). The aq. phases were extracted with AcOEt (50 ml). The org. phases were dried ($MgSO_4$) and evaporated. The residue was separated and purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 2:3), yielding successively 221 mg (50%) of **15**/**16** (4:1), white crystals, 20 mg (7%) of **6a**, m.p. 113–116°, and 32 mg (7%) of **17**, m.p. 200–202°. The mixture **15**/**16** was separated by HPLC (*Zorbax-sil*, 250 × 21 mm; AcOEt/petroleum ether 1:2, 20 ml/min) yielding 35 mg (8%) of **15** and 142 mg (32%) of **16** which were recrystallized from AcOEt/petroleum ether.

*(1*RS,*3*SR,*4*RS,*6*SR,*7*RS*)-6-*endo-*Cyano-2-oxabicyclo[2.2.1]heptane-3-*exo*,6-*exo*,7-*syn*-triyl Triacetate* (**15**). Colourless crystals. M.p. 169–170°. IR (KBr): 3030, 3005, 2980, 2950, 2250, 1765, 1745, 1440, 1370, 1255, 1235, 1220, 1195, 1095, 1040, 1025, 1000, 960, 890, 830. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.0 (*s*, H–C(3)); 4.89 (*d*, ^3J = 1.5, H–C(7)); 4.73 (*s*, H–C(1)); 2.93 (br. *d*, ^3J = 4.5, H–C(4)); 2.43 (*d*, ^2J = 15, H_{endo}–C(5)); 2.23 (*dd*, ^2J = 15, ^3J = 4.5, H_{exo}–C(5)); 2.14, 2.13, 2.07 (*3s*, 3 AcO); NOE's were observed between H–C(3)/H–C(4),

H–C(3)/H_{endo}–C(5), H–C(7)/H–C(1), and H–C(7)/H_{exo}–C(5). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.3, 168.9, 167.9 (3*s*, 3 COO); 115.8 (*s*, CN); 97.4 (*dm*, ^1J(C,H) = 182, C(3)); 80.2 (*d*, ^1J(C,H) = 175), 74.3 (*dd*, ^1J(C,H) = 160, ^3J(C,H) = 10, C(1), C(7)); 71.2 (*t*, ^nJ(C,H) = 7, C(6)); 41.3 (*d*, ^1J(C,H) = 156, C(4)); 37.5 (*t*, ^1J(C,H) = 141, C(5)); 20.9, 20.6, 20.5 (3*q*, ^1J(C,H) = 131, 3 CH_3CO). MS (70 eV): 297 (0.3, $M^{+\cdot}$), 254 (3), 238 (23), 195 (34), 153 (24), 136 (13), 135 (100). Anal. calc. for $C_{13}H_{15}NO_7$ (297.262): C 52.53, H 5.09, N 4.71; found: C 52.71, H 5.09, N 4.85.

*(1*RS,*3*RS,*4*RS,*6*SR,*7*RS*)-6-*endo-*Cyano-2-oxabicyclo[2.2.1]heptane-3-*endo,*6-*exo,*7-*syn-*triyl Triacetate* (**16**). Colourless crystals. M.p. 129–130°. IR (KBr): 3020, 3000, 2950, 1775, 1750, 1440, 1390, 1370, 1320, 1285, 1230, 1210, 1190, 1120, 1080, 1050, 1030, 960, 940, 915, 895, 825. ^{1}H-NMR ($CDCl_3$ 360 MHz): 6.47 (*d*, ^3J = 2.5, H–C(3)); 5.08 (*d*, ^3J = 2, H–C(7)); 4.53 (*s*, H–C(1)); 3.08 (*d*, ^2J = 15, H_{endo}–C(5)); 2.76–2.8 (*m*, H–C(4)); 2.18, 2.16, 2.15 (3*s*, 3 CH_3COO); 2.03 (*dd*, ^2J = 15, ^3J = 4, H_{exo}–C(5)); NOE's were observed between H–C(7)/H–C(1) (7%) and H–C(7)/H_{exo}–C(5) (2%). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.1, 169.6, 167.9 (3*s*, 3 COO); 115.9 (*s*, CN); 96.5 (*dm*, ^1J(C,H) = 184, C(3)); 80.1 (*dd*, ^1J(C,H) = 165, ^3J(C,H) = 5), 77.2 (*dd*, ^1J(C,H) = 160, ^3J(C,H) = 11, C(1), C(7)); 72.2 (*t*, ^nJ(C,H) = 7, C(6)); 41.1 (*d*, ^1J(C,H) = 154, C(4)); 34.0 (*tm*, ^1J(C,H) = 142, C(5)); 20.9, 20.7, 20.6 (3*q*, ^1J(C,H) = 130, 3 CH_3CO). MS (70 eV): 297 (1.5, $M^{+\cdot}$), 255 (1.5), 254 (3), 238 (11), 195 (39), 153 (27), 136 (11), 135 (100). Anal. calc. for $C_{13}H_{15}NO_7$ (297.262): C 52.53, H 5.09, N 4.71; found: C 52.44, H 5.01, N 4.74.

*(1*RS,*3*SR,*4*RS,*6*RS,*7*RS*)-6-*endo-*(N-Acetylcarbamoyl)-2-oxabicyclo[2.2.1]heptane-3-*exo,*6-*exo,*7-*syn-*triyl Triacetate* (**17**). Colourless crystrals. M.p. 203–205°. IR (KBr): 3270, 3030, 3000, 1750, 1740, 1500, 1440, 1370, 1280, 1250, 1220, 1165, 1095, 1050, 1025. ^{1}H-NMR ($CDCl_3$, 360 MHz): 8.81 (*s*, NH); 5.91 (*s*, H–C(3)); 4.99 (*d*, ^3J = 1.5, H–C(7)); 4.55 (br. *s*, H–C(1)); 2.94 (*d*, ^2J = 15, H_{endo}–C(5)); 2.91 (br. *dd*, ^3J(H–C(4), H–C(5)) = 4, ^3J(H–C(4), H–C(7)) = 1.5, H–C(4)); 2.49 (*s*, CH_3CON); 2.13, 2.11, 2.05 (3*s*, 3 CH_3COO); 1.75 (*dd*, ^2J = 15, ^3J = 4, H_{exo}–C(5)); NOE's were observed for NH/H–C(1), H–C(3)/H–C(4), H–C(3)/H_{endo}–C(5), H–C(7)/H–C(1), and H–C(7)/H_{exo}–C(5). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 173.3, 170.5, 169.1, 168.1, 166.0 (5*s*, 5 CO); 97.4 (*dm*, ^1J(C,H) = 180, C(3)); 82 (*s*, C(6)); 81.2 (*dm*, ^1J(C,H) = 170), 76.1 (*dm*, ^1J(C,H) = 160, C(1), C(7)); 42.2 (*dm*, ^1J(C,H) = 160, C(4)); 32.1 (*tm*, ^1J(C,H) = 140, C(5)); 25.2, 20.9, 20.7, 20.6 (4*q*, ^1J(C,H) = 130, 4 CH_3CO). MS (70 eV): 315 (47, $M^{+\cdot}$ – 42), 298 (10), 273 (12), 256 (12), 255 (28), 237 (12), 213 (16), 212 (13), 195 (33), 170 (16), 169 (13), 153 (100). MS (CI, CH_4): 386 ([M + 29]$^+$), 358 ([M +1]$^+$). Anal. calc. for $C_{15}H_{19}NO_9$ (357.313): C 50.42, H 5.36, N 3.92; found: C 50.50, H 5.32, N 3.94.

13. *(1*RS,*2*SR,*3*SR,*4*SR*)-1-(*N-*Acetylcarbamoyl)-4-(diacetoxymethyl)cyclopentane-1,2,3-triyl Triacetate* (**18**). Ac_2O (0.5 ml, 5 mmol) and HSO_3F (15 µl, 0.2 mmol) were added successively to a soln. of **6b** (82 mg, 0.42 mmol) in anh. CH_2Cl_2 (3 ml) cooled to – 50°. After 1 h at – 50°, the mixture was allowed to stand at 0° for 2 h, and then at 20° for 4 h. After pouring into sat. aq. $NaHCO_3$ soln. (10 ml), the mixture was extracted with AcOEt (60 ml). The extract was washed with sat. aq. $NaHCO_3$ soln. (5 ml, twice) then with sat. aq. NaCl soln. (5 ml). The aq. phases were extracted with AcOEt (30 ml). The org. phases were dried ($MgSO_4$), and evaporated. The crude **18** was purified by column chromatography on silica gel (AcOEt/petroleum ether 55:45) yielding 87 mg (45%) of crystals, m.p. 141–143°. Recrystallization from AcOEt/petroleum ether gave pure **18**, colourless crystals, m.p. 143–144°. IR (KBr): 3280, 1770, 1750, 1695, 1485, 1380, 1290, 1240, 1220, 1090, 1045, 1015, 950. ^{1}H-NMR (C_6D_6, 360 MHz): 9.28 (br. *s*, NH); 7.41 (*d*, ^3J(C*H*(OAc)$_2$,H–C(4)) = 9, C*H*(OAc)$_2$); 5.66 (br. *t*, ^3J(H–C(2),H–C(3)) ≈ ^3J(H–C(3),H–C(4)) ≈ 4, H–C(3)); 5.62 (br. *d*, ^3J = 4, H–C(2)); 3.24 (*dd*, ^2J = 15, ^3J = 8, H–C(5) *pro-S**); 2.56–2.65 (*m*, H–C(4)); 2.47 (*d*, ^2J = 15, H–C(5) *pro-R**); 2.40 (*s*, CH_3CON); 1.96, 1.84, 1.80, 1.72, 1.60 (5*s*, 5CH_3COO); NOE's were observed between NH/H–C(2), NH/H–C(5) *pro-S**, C*H*(OAc)$_2$/H–C(5) *pro-R**, and H–C(2)/H–C(4). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 172.5, 169.7, 169.6, 169.4, 169.1, 168.7, 168.2 (7*s*, 7 CO), 88.1 (*dm*, ^1J(C,H) = 180, C*H*(OAc)$_2$); 83.9 (*s*, C(1)); 74.1 (*dm*, ^1J(C,H) = 145), 72.0 (*dm*, ^1J(C,H) = 160, C(2), C(3)); 41.4 (*dm*, ^1J(C,H) = 135, C(4)); 35.1 (*tm*, ^1J(C,H) = 140, C(5)); 25.1, 20.1–20.7 (6*q*, ^1J(C,H) = 130, 6 CH_3CO). MS (70 eV): 417 (5, $M^{+\cdot}$ – 42), 373 (11), 358 (17), 315 (7), 272 (13), 271 (100). MS (CI, CH_4): 488 ([M + 29]$^+$), 460 ([M + 1]$^+$). Anal. calc. for $C_{19}H_{25}NO_{12}$ (459.402): C 49.68, H 5.48, N 3.04; found: C 49.46, H 5.42, N 2.84.

14. *Reaction of* **6c** *with HSO$_3$F/Ac$_2$O.* HSO_3F (34 µl, 0.6 mmol) was added to a soln. of **6c** (191 mg, 1.5 mmol) and Ac_2O (0.8 ml, 8.5 mmol) in anh. CH_2Cl_2 (10 ml) cooled to – 78°. After staying at – 51° for 30 h, the mixture was poured into sat. aq. $NaHCO_3$ soln. (6 ml) and extracted with AcOEt (60 ml). The org. layer was washed with sat. aq. $NaHCO_3$ soln. (8 ml, twice) and than with sat. aq. NaCl soln. (10 ml). The aq. phases were extracted with AcOEt (50 ml). The org. phases were dried ($MgSO_4$) and evaporated giving **20**/**21**/**22**/**23** (100:14:2.5:1; ^{1}H-NMR ($CDCl_3$, 360 MHz)). Chromatography on a column of silicic acid (150 g, AcOEt/petroleum ether 1:1) gave 130 mg (38%) of **20** and a 2nd fraction of 53 mg composed of 24 mg of **20**, 22 mg of **21**, 6 mg of **22**, and 1 mg of **23** (^{1}H-NMR). A 3rd fraction (35 mg) was obtained. It was separated by column chromatography on silica gel (*Lobar*,

size *A*, AcOEt/petroleum ether 3:7) giving 2 mg of **21**, then 25 mg (13%) of **6c**. The 2nd fraction was separated by HPLC (*Zorbax-sil* 250 × 21 mm, 20 ml/min, AcOEt/petroleum ether 1:2) giving 22 mg (6%) of **20** (ret. time 9 min), 18 mg of **21** (ret. time 10.3 min), and 9 mg of **21**/**22**/**23** (ret. time 11 min). Pure **22** was obtained by another HPLC purification of this fraction.

*(1RS,3SR,4SR,7SR)-5-Oxo-2-oxabicyclo[2.2.1]heptane-3-*endo,*7-*syn*-diyl Diacetate* (**20**). Colourless crystals. M.p. 74–76° (AcOEt/petroleum ether). IR (KBr): 3040, 3000, 1775, 1750, 1385, 1340, 1250, 1220, 1180, 1150, 1135, 1055, 1020. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.54 (*d*, ^3J = 3, H–C(3)); 5.1 (*d*, ^3J = 1, H–C(7)); 4.77 (br. *s*, ^3J = 1.3, H–C(1)); 3.1 (*m*, ^3J = 3, 1, H–C(4)); 2.65 (*d*, ^2J = 19, H_{endo}–C(6)); 2.40 (br. *dd*, ^2J = 19, ^3J = 1.3, H_{exo}–C(6)); 2.15, 2.07 (2*s*, 2 AcO); NOE's were observed for H–C(1)/H–C(7), H_{exo}–C(6)/H–C(7), and H–C(1)/H_{endo}–C(6). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 202.5 (*s*, C(5)); 169.8, 169.4 (2*s*, 2 COO); 96.1 (*dt*, ^1J(C,H) = 186, ^3J(C,H) = 8, C(3)); 78.3 (*dm*, ^1J(C,H) = 160), 77.4 (*dm*, ^1J(C,H) = 160, C(1), C(7)); 57.2 (*d*, ^1J(C,H) = 159, C(4)); 45.2 (*td*, ^1J(C,H) = 136, ^3J(C,H) = 3, C(6)); 20.6, 20.4 (2*q*, ^1J(C,H) = 131, 2 CH_3CO). MS (70 eV): 228 (0.3, $M^{+\cdot}$), 200 (4.5), 186 (5), 185 (18), 169 (4), 168 (4), 158 (4), 157 (40), 143 (42), 140 (50), 127 (17), 126 (63), 125 (31), 115 (100). Anal. calc. for $C_{10}H_{12}O_6$ (228.199): C 52.63, H 5.30; found: C 52.57, H 5.29.

*(1RS,3RS,4SR,7SR)-5-Oxo-2-oxabicyclo[2.2.1]heptane-3-*exo,*7-*syn*-diyl Diacetate* (**21**). Colourless crystals. M.p. 83–84° (AcOEt/petroleum ether). IR (KBr): 3060, 3010, 2940, 1765, 1750, 1730, 1390, 1370, 1255, 1220, 1200, 1155, 1130, 1075, 1045, 1015, 995, 975, 950, 915, 870, 825. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.12 (*s*, H–C(3)); 5.02 (*m*, ^3J = 1.8, H–C(7)); 4.98 (*m*, ^3J = 1.7, H–C(1)); 3.34 (*m*, ^3J(H–C(4),H–C(7)) = 1.8, ^4J(H–C(4),H–C(6)) = 0.5, H–C(4)); 2.51 (*d*, ^2J = 19, H_{endo}–C(6)); 2.26 (br. *dd*, ^2J = 19, ^3J = 1.7, ^4J = 0.5, H_{exo}–C(6)); 2.15, 2.09 (2*s*, 2 CH_3CO); NOE's were observed between H–C(3)/H–C(4) (3%), H–C(3)/H_{endo}–C(6) (0.7%), H–C(7)/H_{exo}–C(6) (2%), H–C(1)/H_{endo}–C(6) (1%), H–C(4)/H–C(7), and H–C(1)/H_{exo}–C(6); no NOE could be detected for H–C(4)/H_{exo}–C(6). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 204.5 (*s*, C(5)); 170.3, 169.2 (2*s*, COO); 93.4 (*dt*, ^1J(C,H) = 181, ^3J(C,H) = 7, C(3)); 79.4 (*dm*, ^1J(C,H) = 175), 75.3 (*dd*, ^1J(C,H) = 165, ^nJ(C,H) = 12, C(1), C(7)); 58.9 (*d*, ^1J(C,H) = 161, C(4)); 44.9 (*t*, ^1J(C,H) = 134, C(6)); 21.0, 20.7 (2*q*, ^1J(C,H) = 130, 2 CH_3CO). MS (70 eV): 200 (5.5, $M^{+\cdot}$ – 28), 186 (3), 185 (5), 169 (3), 168 (3), 157 (16), 143 (8), 127 (6), 126 (30), 115 (31), 109 (22), 108 (13), 45 (100). Anal. calc. for $C_{10}H_{12}O_6$ (228.199): C 52.63, H 5.30; found: C 52.65, H 5.36.

*(1RS,3SR,4RS,7RS)-2-Oxabicyclo[2.2.1]heptane-3-*exo,*6,6,7-*syn*-tetrayl Tetraacetate* (**22**). Colourless crystals. M.p. 132–134° (AcOEt/petroleum ether). IR (KBr): 2980, 2940, 1760, 1740, 1410, 1350, 1305, 1200, 1145, 1060, 1035, 1010, 900, 890, 805. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.93 (*s*, H–C(3)); 5.12 (br. *s*, $^4J \approx 1$, H–C(1)); 4.88 (br. *s*, $^3J \approx 1$, H–C(7)); 2.84 (br. *dt*, ^3J = 4.5, $^3J \approx 1$, $^4J \approx 1$, H–C(4)); 2.38 (*dd*, ^2J = 15, ^3J = 4.5, H_{exo}–C(5)); 2.18 (*d*, ^2J = 15, H_{endo}–C(5)); 2.13, 2.09, 2.07 (3*s*, 4 CH_3CO); NOE's were observed between H–C(3)/H–C(4) (3%), H–C(3)/H_{endo}–C(5) (5%), H–C(1)/H–C(7) (3%), H_{exo}–C(5)/H–C(7) (3%), H–C(4)/H_{endo}–C(5) (1%), H–C(4)/H–C(7), and H–C(4)/H_{exo}–C(5); no NOE was detected for H–C(1)/H–C(4) and H–C(1)/H–C(5). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.5, 169.3, 168.6, 167.9 (4*s*, 4 CO); 101.6 (*m*, C(6)); 97.3 (*dm*, ^1J(C,H) = 177, C(3)); 80.3 (*dm*, ^1J(C,H) = 175), 75.1 (*dm*, ^1J(C,H) = 170, C(1) or C(7)); 42.4 (*dm*, ^1J(C,H) = 155, C(4)); 38.3 (*t*, ^1J(C,H) = 139, C(5)); 21.3, 21.1, 21.0, 20.7 (4*q*, ^1J(C,H) = 130, 4 CH_3CO). MS (70 eV): 287 (2, $M^{+\cdot}$ – 43), 271 (3), 200 (4), 185 (14), 169 (19), 127 (12), 126 (43), 115 (5), 112 (12), 109 (8), 108 (34), 103 (12), 98 (28), 97 (61), 45 (100). Anal. calc. for $C_{14}H_{18}O_9$ (330.287): C 50.91, H 5.49; found: C 51.02, H 5.47.

*(1RS,3SR,4RS,7RS)-6-Oxo-2-oxabicyclo[2.2.1]heptane-3-*exo,*7-*syn*-diyl Diacetate* (**23**). A mixture of **30** (23 mg, 0.05 mmol) and 5% Pd/C (10 mg) in AcOEt (2 ml) was pressurized (1 atm) with H_2. After stirring at 20° for 24 h, H_2 was evacuated, replaced by N_2, and the mixture filtered through *Celite*. The solvent was evaporated and the residue purified by column chromatography on silica gel (AcOEt/petroleum ether 1:2, *Lobar*) yielding 12 mg (100%) of a colourless oil. Crystallization from AcOEt/petroleum ether gave 9 mg (75%) of colourless crystals. M.p. 91–92°. IR (KBr): 3040, 2980, 2930, 1765, 1730, 1360, 1245, 1215, 1175, 1130, 1110, 1050, 990, 970, 930, 910, 885, 860, 800. ^{1}H-NMR ($CDCl_3$, 360 MHz): 6.04 (*s*, H–C(3)); 4.87 (*d*, ^3J = 1.6, H–C(7)); 4.38 (*d*, ^4J = 1, H–C(1)); 3.17 (br. *ddd*, ^3J = 4.4, 1.6, ^4J = 1, H–C(4)); 2.43 (*dd*, ^2J = 19, ^3J = 4.4, H_{exo}–C(5)); 2.29 (*d*, ^2J = 19, H_{endo}–C(5)); 2.16, 2.12 (2*s*, 2 CH_3CO); NOE's were observed between H–C(1)/H–C(7), H–C(4)/H–C(7), and H_{exo}–C(5)/H–C(7). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 200.3 (*s*, C(6)); 170.1, 169.4 (2*s*, COO); 97.7 (*dq*, ^1J(C,H) = 180, ^3J(C,H) = 6, C(3)); 82.3 (*dd*, ^1J(C,H) = 175, ^3J(C,H) = 4), 75.3 (*dd*, ^1J(C,H) = 162, ^nJ = 13, C(1), C(7)); 42.8 (*d*, ^1J(C,H) = 155, C(4)); 38.8 (*t*, ^1J(C,H) = 136, C(5)); 20.9, 20.6 (2*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 200 (24, $M^{+\cdot}$ – 28), 169 (6), 157 (6), 140 (6), 129 (6), 127 (5), 126 (6), 115 (10), 112 (11), 98 (29), 97 (26), 96 (12), 85 (12), 82 (13), 81 (29), 80 (21), 70 (68), 45 (100).

The ^{1}H-NMR ($CDCl_3$, 360 MHz) of **23** was superposable with that of the minor compound formed on reaction of **6c** with HSO_3F/Ac_2O.

15. *Reaction of* **6d** *with* HSO_3F/Ac_2O. HSO_3F (30 µl, 0.5 mmol) was added to a soln. of **6d** (450 mg, 2.6 mmol), Ac_2O (0.8 ml, 8.5 mmol), and anh. CH_2Cl_2 (8 ml) cooled to – 78°. After 12 h at – 78°, the mixture was poured into

a sat. aq. $NaHCO_3$ soln. (10 ml) and extracted with AcOEt (100 ml). The extract was washed with sat. aq. $NaHCO_3$ soln. (10 ml), then with sat. aq. NaCl soln. (10 ml). The aq. layers were extracted with AcOEt (50 ml). The combined org. phase was dried and evaporated and the residue purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 2:3) giving 80 mg (15%) of **25** as slowly crystallizing oil, then 36 mg (5%) of **26** as colourless crystals, m.p. 81–82°, 188 mg (26%) of **24** as colourless crystals, m.p. 101–104°, and finally 60 mg (13%) of **6d**.

*(1RS,2RS,4RS,5RS,6SR)-2-*exo*,6-*endo*-Dimethoxy-7-oxabicyclo[2.2.1]-heptane-2-*endo*,5-*exo*-diyl Diacetate* (**24**). Recrystallization from Et_2O/petroleum ether gave 170 mg (24%) of colourless crystals. M.p. 108–109°. IR (KBr): 3000, 2980, 2960, 2920, 2830, 1760, 1735, 1440, 1375, 1365, 1330, 1250, 1235, 1225, 1205, 1185, 1150, 1120, 1070, 1040, 1020, 990, 965, 950, 880, 870. ^{1}H-NMR ($CDCl_3$, 360 MHz): 4.95 (*d*, ^3J = 5, H–C(1)); 4.67 (*d*, ^3J = 3, H–C(5)); 4.43 (br. *d*, ^3J = 6, H–C(4)); 3.79 (br. *ddd*, ^3J = 5, 3, ^4J = 1, H–C(6)); 3.35 (*s*, CH_3O–C(6)); 3.30 (*s*, CH_3O–C(2)); 2.34 (*dd*, ^2J = 13, ^3J = 6, H_{exo}–C(3)); 2.11, 2.02 (2*s*, CH_3CO); 1.90 (*d*, ^2J = 13, H_{endo}–C(3)); NOE's were observed between H–C(4)/H–C(5) (1%), H_{endo}–C(3)/H–C(5) (3%), H–C(5)/CH_3O–C(6) (2%), H–C(6)/CH_3O–C(6) (6%), and H_{exo}–C(3)/CH_3O–C(2) (5%). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.7, 169.3 (2*s*, 2 COO); 107.9 (*s*, C(2)); 86.9 (br. *d*, ^1J(C,H) = 150); 81.2 (*dm*, ^1J(C,H) = 167); 80.3 (br. *d*, ^1J(C,H) = 157); 79.0 (*dm*, ^1J(C,H) = 168); 59.7 (*qd*, ^1J(C,H) = 142, ^3J(C,H) = 5, CH_3O–C(6)); 49.3 (*q*, ^1J(C,H) = 143, CH_3O–C(2)); 38.7 (br. *t*, ^1J(C,H) = 135, C(3)); 20.9, 20.8 (2*q*, ^1J(C,H) = 130, 2 CH_3CO). MS (70 eV): 274 (0.9, M^+), 243 (2.5), 235 (3), 234 (4), 233 (2), 220 (2), 219 (4), 217 (3), 216 (1), 215 (7), 185 (5), 171 (13), 158 (26), 157 (20), 127 (25), 125 (19), 111 (45), 45 (100). Anal. calc. for $C_{12}H_{18}O_7$ (274.267): C 52.55, H 6.61; found: C 52.51, H 6.64.

*(1RS,2RS,3SR,4RS)-3-*endo*-Methoxy-5-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate* (**25**). Recrystallization from AcOEt/petroleum ether gave 68 mg (13%) of colourless crystals. M.p. 37–38°. IR (KBr): 2950, 2840, 1780, 1740, 1380, 1370, 1255, 1230, 1120, 1060, 1025, 990, 890, 870, 790. ^{1}H-NMR ($CDCl_3$, 360 MHz): 4.82 (*d*, ^3J = 1.5, H–C(2)); 4.76 (*dm*, ^3J(H–C(1), H–C(6)) = 7, ^4J(H–C(1),H–C(3)) = 2, ^4J(H–C(1),H–C(4)) = 1, H–C(1)); 4.45 (br. *d*, ^3J(H–C(3),H–C(4)) = 6, ^4J(H–C(4),H–C(6)) = 1.5, H–C(4)); 3.93 (br. *d*, ^3J = 6, 1.5, ^4J = 2, H–C(3)); 3.40 (*s*, MeO); 2.49 (*ddd*, ^2J = 18, ^3J = 7, ^4J = 1.5, H_{exo}–C(6)); 2.20 (*d*, ^2J = 18, H_{endo}–C(6)), 2.13 (*s*, CH_3CO); NOE's were observed between H_{endo}–C(6)/H–C(2), H–C(2)/CH_3O (2%), H–C(4)/CH_3O (1%), and H–C(3)/CH_3O (4%). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 205.9 (*s*, C(5)); 170.3 (*s*, COO); 84.2 (*dm*, ^1J(C,H) = 155); 80.6, 80.1, 79.6 (3*dm*, ^1J(C,H) = 160); 58.5 (*qd*, ^1J(C,H) = 140, ^3J(C,H) = 5, CH_3O); 38.7 (*t*, ^1J(C,H) = 135, C(6)); 20.7 (*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 200 (1.5, M^+), 158 (37), 157 (27), 127 (31), 126 (16), 125 (19), 111 (10), 101 (18), 74 (100). Anal. calc. for $C_9H_{12}O_5$ (200.189): C 54.00, H 6.04; found: C 54.09, H 6.09.

*(1RS,3SR,4RS,7RS)-6,6-Dimethoxy-2-oxabicyclo[2.2.1]heptane-3-*exo*,7-*syn*-diyl Diacetate* (**26**). Recrystallization from Et_2O/petroleum ether gave 26 mg (4%) of colourless crystals. M.p. 104–106°. IR (KBr): 3020, 3000, 2960, 2850, 1745, 1445, 1375, 1325, 1250, 1230, 1130, 1085, 1070, 1050, 1025, 955, 865, 835. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.92 (*s*, H–C(3)); 4.91 (br. *s*, ^3J = 1.5, H–C(7)); 4.37 (br. *s*, ^4J = 1, H–C(1)); 3.25, 3.18 (2*s*, 2 MeO); 2.79 (*m*, ^3J(H–C(4),H–C(5)) = 4.7, ^3J(H–C(4),H–C(7)) = 1.5, ^4J(H–C(1),H–C(4)) = 1, H–C(4)); 2.10, 2.06 (2*s*, 2 CH_3CO); 2.01 (*dd*, ^2J = 13.5, ^3J = 4.7, H_{exo}–C(5)); 1.49 (*d*, ^2J = 13.5, H_{endo}–C(5)). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.6, 169.6 (2*s*, 2 COO); 104 (br. *s*, C(6)); 98.1 (*dq*, ^1J(C,H) = 182, ^3J(C,H) = 6, C(3)); 80.1 (*d*, ^1J(C,H) = 167), 76.1 (*dm*, ^1J(C,H) = 170, C(1), C(7)); 50.4, 48.4 (2*q*, ^1J(C,H) = 143, 2 MeO); 42.8 (*dm*, ^1J(C,H) = 154, C(4)); 34.3 (*t*, ^1J(C,H) = 135, C(5)); 21.1, 20.9 (2*q*, ^1J(C,H) = 130, 2 CH_3CO). MS (70 eV): 274 (0.7, M^+), 244 (2), 243 (15), 219 (3), 218 (11), 217 (5), 216 (18), 215 (100), 183 (8), 172 (5), 155 (48), 143 (12), 141 (22), 127 (26). Anal. calc. for $C_{12}H_{18}O_7$ (274.267): C 52.55, H 6.61; found: C 52.46, H 6.53.

16. *(1RS,4RS,5RS,6SR)-5-*exo*-Hydroxy-6-*endo*-methoxy-7-oxabicyclo[2.2.1]heptan-2-one* (**27**). HSO_3F (0.1 ml, 1.7 mmol) was added to a soln. of **6d** (830 mg, 4.8 mmol), MeOH (1 ml, 25 mmol), and anh. CH_2Cl_2 (20 ml) cooled to 0°. After 36 h at 20°, sat. aq. $NaHCO_3$ soln. (10 ml) was added and the mixture extracted with AcOEt (60 ml, twice). The extract was washed with sat. aq. $NaHCO_3$ soln. (15 ml) and then with sat. aq. NaCl soln. (15 ml). The aq. layers were extracted with AcOEt (60 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by column chromatography on silica gel (AcOEt/petroleum ether 1:1), yielding 634 mg (83%) of a slowly crystallizing oil. Recrystallization from AcOEt/petroleum ether gave an anal. sample. M.p. 55–56°. IR (KBr): 3440, 3000, 2940, 2840, 1770, 1630, 1115, 1080, 1015, 975, 960, 780. ^{1}H-NMR ($CDCl_3$, 80 MHz): 4.62 (*d*, ^3J = 6, H–C(4)); 4.40 (*d*, ^3J = 6, H–C(1)); 3.95 (br. *d*, ^3J = 6, H–C(5)); 3.7 (*d*, ^3J = 6, H–C(6)); 3.3 (*s*, MeO); 2.7 (br. *d*, ^3J(OH,H–C(5)) = 6, OH); 2.45 (*dd*, ^2J = 18, ^3J = 6, H_{exo}–C(3)); 2.0 (*d*, ^2J = 18, H_{endo}–C(3)). The coupling constant ^3J(OH,H–C(5)) is not always detected. ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 207 (*s*, C(2)); 87.05 (*dm*, ^1J(C,H) = 155); 82.7 (*dm*, ^1J(C,H) = 160); 80.4 (*dd*, ^1J(C,H) = 165, ^3J(C,H) = 6); 78.0 (*dm*, ^1J(C,H) = 150); 58.2 (*qd*, ^1J(C,H) = 144, ^3J(C,H) = 4, CH_3O); 38.4 (*t*, ^1J(C,H) = 135, C(3)). MS (70 eV): 126 (20), 85 (100), 84 (42). MS (CI, CH_4): 159 ([M +1]$^+$). Anal. calc. for $C_7H_{10}O_4$ (158.152): C 53.16, H 6.37; found: C 53.17, H 6.24.

17. *(1RS,4RS,5RS,6SR)-6-*endo*-(Benzyloxy)-5-*exo*-hydroxy-7-oxabicyclo[2.2.1]heptan-2-one* (**28**). HSO_3F (40 µl, 0.7 mmol) was added to a soln. of **6e** (380 mg, 1.17 mmol), benzyl alcohol (1 ml, 10 mmol), and anh. CH_2Cl_2 (8 ml) cooled to − 15°. The mixture was allowed to warm up to 20° and stirred overnight, then sat. aq. $NaHCO_3$ soln. (10 ml) was added and the mixture extracted with AcOEt (40 ml, twice). The extract was washed with sat. aq. $NaHCO_3$ soln. (10 ml), then with sat. aq. NaCl soln. (10 ml). The aq. layers were extracted with AcOEt (30 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by column chromatography on silica gel (AcOEt/petroleum ether 1:1), yielding 242 mg (88%) of colourless crystals, m.p. 130–132°. Recrystallization from AcOEt/petroleum ether gave an anal. sample of **28**. M.p. 132.5–133.5°. IR (KBr): 3400, 3030, 2900, 2880, 1780, 1500, 1460, 1400, 1315, 1270, 1230, 1120, 1095, 1075, 1020, 995, 965, 945, 890, 785, 750, 700. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.3–7.4 (*m*, 5H); 4.65 (br. *d*, ^3J = 7, H–C(4)); 4.57 (*AB*, ^2J = 11.4, $\nu_o\delta$ = 39.8, PhCH_2); 4.44 (br. *d*, ^3J = 5, H–C(1)); 4.03 (*d*, ^3J(H–C(5),OH) = 7, H–C(5)); 3.94 (br. *d*, ^3J = 5, H–C(6)); 2.48 (*ddd*, ^2J = 18, ^3J = 7, ^4J = 1.5, H_{exo}–C(3)); 2.3 (br. *d*, ^3J = 7, OH); 2.13 (*d*, ^2J = 18, H_{endo}–C(3)). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 206.9 (*s*, C(2)); 136.6 (*s*, arom. C); 128.4, 128.0 (2*d*, ^1J(C,H) = 160, arom. C); 84.8, 78.5 (2*dm*, ^1J(C,H) = 155); 82.7 (*dm*, ^1J(C,H) = 165); 80.6 (*dd*, ^1J(C,H) = 165, ^3J(C,H) = 5); 72.5 (*tm*, ^1J(C,H) = 144, PhCH_2); 38.4 (*tm*, ^1J(C,H) = 135, C(3)). MS (70 eV): 234 (1.5, $M^{+\cdot}$), 175 (11), 143 (1), 125 (2), 97 (3), 92 (11), 91 (100). Anal. calc. for $C_{13}H_{14}O_4$ (234.250): C 66.66, H 6.02; found: C 66.72, H 6.11.

18. *Reaction of* **6e** *with* HSO_3F/Ac_2O. HSO_3F (30 µl, 0.5 mmol) was added to a soln. of **6e** (340 mg, 1 mmol), Ac_2O (0.7 ml, 7.4 mmol), and anh. CH_2Cl_2 (7 ml) cooled to − 78°. After 90 min at − 78°, the mixture was poured into a sat. aq. $NaHCO_3$ soln. (15 ml) and extracted with AcOEt (40 ml, twice). The extract was washed with sat. aq. $NaHCO_3$ soln. (10 ml), then with sat. aq. NaCl soln. (10 ml). The aq. layers were extracted with AcOEt (40 ml). The combined org. extract was dried ($MgSO_4$) and evaporated and the residue purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 3:7). A 1st fraction contained 2 to 45 mg of **31**. The 2nd fraction (240 mg) was separated by HPLC (*Zorbax-sil*, 250 × 21 mm; 20 ml/min; AcOEt/petroleum ether 13:87) giving 164 mg (57%) of **29** (ret. time 12 min), then 32 mg (7%) of **30** (ret. time 14 min).

*(1RS,2RS,3SR,4RS)-3-*endo*-(Benzyloxy)-5-oxo-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate* (**29**). Crystallization from Et_2O/petroleum ether gave 140 mg (49%) of colourless crystals. M.p. 45–45.5°. IR (KBr): 3070, 3040, 2970, 2880, 1755, 1730, 1440, 1365, 1325, 1255, 1215, 1185, 1145, 1125, 1085, 1065, 955, 880, 785, 740, 695. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.27–7.35 (*m*, 5H); 4.85 (*d*, ^3J(H–C(2),H–C(3)) = 1.1, H–C(2)); 4.76 (*ddd*, ^3J(H–C(1),H–C(6)) = 6.5, ^4J(H–C(1),H–C(3)) = 2, ^4J(H–C(1),H–C(4)) = 1, H–C(1)); 4.61 (*AB*, ^2J = 11.5, $\nu_o\delta$ = 14, PhCH_2); 4.44 (br. *d*, ^3J(H–C(3),H–C(4)) = 5.6, ^4J(H–C(4),H–C(6)) = 1, ^4J = 1, H–C(4)); 4.09 (*ddd*, ^3J = 5.6, 1.1, ^4J = 2, H–C(3)); 2.52 (*ddd*, ^2J = 17.7, ^3J = 6.5, ^4J = 1, H_{exo}–C(6)); 2.23 (*d*, ^2J = 17.7, H_{endo}–C(6)); 2.10 (*s*, CH_3COO). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 206.0 (*s*, C(5)); 170.4 (*s*, COO); 136.6 (*s*, arom. C); 128.5, 128.1, 128.0 (3*d*, ^1J(C,H) = 160, arom. C); 81.8, 80.1 (2*dm*, ^1J(C,H) = 155); 80.6 (*dm*, ^1J(C,H) = 165); 80.3 (*dd*, ^1J(C,H) = 168, ^3J(C,H) = 7); 72.8 (*t*, ^1J(C,H) = 142, PhCH_2); 38.9 (*t*, ^1J(C,H) = 136, C(6)); 20.8 (*q*, ^1J(C,H) = 130, CH_3CO). MS (70 eV): 276 (1, $M^{+\cdot}$), 187 (1), 185 (1), 175 (1), 143 (2), 131 (2), 125 (2), 106 (3), 105 (5), 97 (2), 92 (8), 91 (100). Anal. calc. for $C_{15}H_{16}O_5$ (276.286): C 65.21, H 5.84; found: C 65.25, H 5.87.

*(1RS,3SR,4RS,7RS)-6,6-Bis(benzyloxy)-2-oxabicyclo[2.2.1]heptane-3-*exo*,7-*syn*-diyl Diacetate* (**30**). Recrystallization from Et_2O/petroleum ether gave 26 mg (6%) of colourless crystals. M.p. 125–126°. IR (KBr): 3070, 3040, 3015, 2930, 2880, 1750, 1740, 1370, 1250, 1225, 1155, 1125, 1090, 1065, 1035, 995, 965, 955, 920, 885, 830, 750, 700. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.29–7.39 (*m*, 10H); 6.04 (*s*, H–C(3)); 5.03 (*m*, ^3J(H–C(4),H–C(7)) = 1, H–C(7)); 4.60 (*s*, H–C(1)); 4.59 (*AB*, ^2J = 11, $\nu_o\delta$ = 19, PhCH_2); 4.55 (*AB*, ^2J = 11, $\nu_o\delta$ = 10, PhCH_2); 2.89 (br. *d*, ^3J = 4.5, ^3J = 1, H–C(4)); 2.20 (*dd*, ^2J = 13.5, ^3J = 4.5, H_{exo}–C(5)); 2.13, 2.09 (2*s*, 2 CH_3CO); 1.74 (*d*, ^2J = 13.5, H_{endo}–C(5)). MS (70 eV): 216 (2, $M^{+\cdot}$ − 210), 185 (12), 108 (3), 107 (3), 106 (5), 105 (7), 97 (2), 92 (10), 91 (100). MS (CI, CH_4): 367 ([M − 59]$^+$). Anal. calc. for $C_{24}H_{26}O_7$ (426.462): C 67.59, H 6.14; found: C 67.69, H 6.20.

*(1RS,2RS,3SR,4RS)-3-*endo*,5,5-Tris(benzyloxy)-7-oxabicyclo[2.2.1]hept-2-*exo*-yl Acetate* (**31**). M.p. 108–109° (Et_2O/petroleum ether). IR (KBr): 3090, 3060, 3040, 3010, 2960, 2890, 1730, 1480, 1450, 1365, 1320, 1250, 1190, 1130, 1090, 1075, 1010, 970, 880, 750, 740, 725, 700, 690. ^{1}H-NMR ($CDCl_3$, 360 MHz): 7.22–7.41 (*m*, 15H); 4.84 (*d*, ^3J(H–C(2),H–C(3)) = 2.7, H–C(2)); 4.66, 4.60 (2 *AB*, 2 PhCH_2); 4.62 (*s*, PhCH_2); 4.54 (br. *d*, ^3J(H–C(3),H–C(4)) = 5, H–C(4)); 4.49 (*dd*, ^3J(H–C(1), H–C(6)) = 6.7, ^4J(H–C(1),H–C(3)) = 1.5, H–C(1)); 4.14 (*ddd*, ^3J = 5, 2.7, ^4J = 1.5, H–C(3)); 2.39 (*dd*, ^2J = 13, ^3J = 6.7, H_{exo}–C(6)); 2.10 (*s*, CH_3CO); 2.03 (*d*, ^2J = 13, H_{endo}–C(6)). MS (70 eV): 277 (1.3, $M^{+\cdot}$ − 149), 252 (2), 250 (1), 217 (1), 193 (1), 182 (1), 181 (6), 106 (15), 105 (18), 92 (12), 91 (100). Anal. calc. for $C_{29}H_{30}O_6$ (474.550): C 73.40, H 6.37; found: C 73.49, H 6.33.

19. *Reaction of* **6f** *with* HSO_3F/Ac_2O. HSO_3F (25 µl, 0.4 mmol) was added to a soln. of **6f** (200 mg, 1.2 mmol), Ac_2O (0.8 ml, 8.5 mmol), and anh. CH_2Cl_2 (8 ml) cooled to − 50°. After 3 h at − 50°, the mixture was poured into a sat. aq. $NaHCO_3$ soln. (15 ml) and extracted with AcOEt (70 ml). The extract was washed with sat. aq. $NaHCO_3$

soln. (10 ml), then with sat. aq. NaCl soln. (10 ml). The aq. layers were extracted with AcOEt (50 ml). The combined org. phase was dried ($MgSO_4$) and evaporated and the residue purified by column chromatography on silica gel (*Lobar*, AcOEt/petroleum ether 3:7) yielding 76 mg (31%) of **32**, then 58 mg (18%) of **33**, and finally 47 mg (24%) of **6f**.

1,1-(Ethylenedioxy)-2-(2-furyl)ethyl Acetate (**32**). Oil. IR (film): 3160, 3140, 2870, 1750, 1645, 1605, 1510, 1380, 1340, 1220, 1155, 1075, 1055, 1015, 970, 945, 885, 740. ^{1}H-NMR ($CDCl_3$, 80 MHz): 7.35 (br. *s*, H–C(5)); 6.2–6.4 (*m*, H–C(3), H–C(4)); 4.3 (br. *s*, OCH_2CH_2O); 3.67 (*s*, CH_2–C(2)); 2.0 (*s*, CH_3CO).

On treating **32** (84 mg, 0.4 mmol) with 95% MeOH (4 ml) and LiOH (30 mg, 0.7 mmol) for 10 min at 20°, 49 mg (98%) of furane-2-acetic acid was isolated after extraction. Recrystallization from Et_2O/petroleum ether gave 40 mg (80%) of colourless crystals. M.p. 65–66° ([39]: 67.3–67.5°).

*(1RS,3SR,4RS,7RS)-6,6-(Ethylenedioxy)-2-oxabicyclo[2.2.1]heptane-3-*exo,*7-*syn*-diyl Diacetate* (**33**). Recrystallization from AcOEt/petroleum ether gave 50 mg (16%) of colourless crystals. M.p. 130–131°. IR (KBr): 3010, 2870, 2830, 1750, 1440, 1375, 1335, 1250, 1115, 1090, 1065, 1035, 1015, 980, 945, 905, 850, 835. ^{1}H-NMR ($CDCl_3$, 360 MHz): 5.92 (*s*, H–C(3)); 4.90 (*d*, ^3J(H–C(4),H–C(7)) = 1.6, H–C(7)); 4.12 (br. *s*, H–C(1)); 3.88–4.08 (*m*, OCH_2CH_2O); 2.80 (*m*, ^3J = 5, 1.6, H–C(4)); 2.10, 2.06 (2*s*, $2CH_3CO$); 2.08 (*dd*, ^2J = 14, ^3J = 5, H_{exo}–C(5)); 1.80 (*d*, ^2J = 14, H_{endo}–C(5)); NOE's were observed between H–C(3)/H_{endo}–C(5), H–C(3)/H–C(4), H–C(1)/H–C(7), and H_{exo}–C(5)/H–C(7). ^{13}C-NMR ($CDCl_3$, 15.08 MHz): 170.3, 169.4 (2*s*, COO); 110.4 (*s*, C(6)); 97.8 (*dm*, ^1J(C,H) = 180, C(3)); 80.1 (*dm*, ^1J(C,H) = 160), 75.7 (*dm*, ^1J(C,H) = 164, C(1), C(7)); 65.0 (*t*, ^1J(C,H) = 150, OCH_2CH_2O); 42.1 (*dm*, ^1J(C,H) = 156, C(4)); 36.4 (*dm*, ^1J(C,H) = 137, C(5)); 20.9, 20.6 (2*d*, ^1J(C,H) = 130, 2 CH_3CO). MS (70 eV): 272 (2, $M^{+\cdot}$), 214 (12), 213 (100), 170 (10), 153 (43), 125 (12). Anal. calc. for $C_{12}H_{16}O_7$ (272.251): C 52.94, H 5.92; found: C 52.85, H 5.92.

20. *(1RS,3SR,4SR,5SR,7SR)-5-*endo-*Hydroxy-2-oxabicyclo[2.2.1]heptane-3-*endo,*7-*syn*-diyl Diacetate* (**34**). A soln. of **20** (145 mg, 0.64 mmol) in anh. MeOH (4 ml) was added dropwise to a stirred soln. of $NaBH_4$ (18 mg, 0.5 mmol) in anh. MeOH (3 ml) cooled to – 78°. After stirring at – 78° for 36 h, acetone (0.3 ml) was added and the mixture allowed to warm up to 20°. After addition of sat. aq. NH_4Cl soln. (7 ml), the mixture was extracted with AcOEt (40 ml, 3 times). The extracts were washed with sat. aq. NaCl soln. (5 ml), dried ($MgSO_4$), and evaporated, and the residue was purified by column chromatography on silica gel (*Lobar*, AcOEt), yielding 18 mg (12%) of **20**, then 131 mg of **34**. Purification by HPLC (*Zorbax-sil*, 250 × 21 mm; AcOEt/petroleum ether 7:3, 20 ml/min; ret. time 7 min) gave 102 mg of colourless oil. IR (film): 3460, 2980, 2940, 1735, 1430, 1370, 1240, 1180, 1105, 1070, 1030, 925, 830, 770. ^{1}H-NMR (C_6D_6, 360 MHz): 6.90 (*dd*, ^3J(H–C(3),H–C(4)) = 2.7, ^4J(H–C(3),H–C(5)) = 2, H–C(3)); 4.40 (br. *d*, ^3J(H–C(4),H–C(7)) = 2, H–C(7)); 4.12 (br. *d*, ^3J(H–C(1),H_{exo}–C(6)) = 2.6, H–C(1)); 4.04 (*m*, H–C(5)); 3.2 (*m*, OH); 2.47 (*m*, ^3J(H–C(4),H–C(5)) = 2, ^3J = 2.7, 2, H–C(4)); 1.88 (*dd*, ^2J = 14.5, ^3J(H–C(5),H_{exo}–C(6)) = 10.5, ^3J = 2.6, H_{exo}–C(6)); 1.63 (*dd*, ^2J = 14.5, ^3J(H–C(5),H_{endo}–C(6)) = 5.8, H_{endo}–C(6)); 1.59, 1.49 (2*s*, 2 CH_3CO). ^{13}C-NMR ($CDCl_3$, 90.55 MHz): 170.4, 168.9 (2*s*, 2 COO); 100.4 (*dm*, ^1J(C,H) = 180, C(3)); 79.9 (*dm*, ^1J(C,H) = 170), 77.6 (*dd*, ^1J(C,H) = 155, ^3J(C,H) = 9, C(1), C(7)); 68.5 (*dm*, ^1J(C,H) = 150, C(5)); 46.6 (*d*, ^1J(C,H) = 153, C(4)); 39.2 (*tm*, ^1J(C,H) = 135, C(6)); 21.2, 20.8 (2*q*, ^1J(C,H) = 130, 2 CH_3CO). MS (70 eV): 188 (1.7, $M^{+\cdot}$ – 42), 187 (6), 164 (2.5), 158 (3), 141 (2.5), 127 (4), 126 (3), 115 (4), 110 (15), 82 (22), 81 (54), 60 (27), 53 (85), 45 (100).

21. *(1RS,2RS,4RS,5RS,6RS)-5,6-*exo-*Epoxy-2-*exo-*hydroxy-7-oxabicyclo[2.2.1]heptane-2-*endo-*carbonitrile* (**6h**). HSO_3F (25 µl, 0.4 mmol) was added to a soln. of **6b** (70 mg, 0.36 mmol), MeOH (0.7 ml), and CH_2Cl_2 (5 ml). After 20 days at 20°, sat. aq. $NaHCO_3$ soln. (5 ml) was added and the mixture extracted with AcOEt (40 ml, 3 times). The extract was washed with sat. aq. $NaHCO_3$ soln. (5 ml), then with sat. aq. NaCl soln. (5 ml). The aq. layers were extracted with AcOEt (30 ml). The org. phases were dried ($MgSO_4$) and evaporated. The residue was dissolved in AcOEt/petroleum ether and allowed to stand at – 20°, yielding 35 mg (64%) of colourless crystals. M.p. 115–117°. IR (KBr): 3440, 3385, 3110, 3040, 2250, 1455, 1360, 1305, 1255, 1250, 1230, 1220, 1185, 1120, 1090, 1060, 1020, 930, 860, 800, 735. ^{1}H-NMR (CD_3OD, 80 MHz): 4.64 (*d*, ^3J = 4.5, H–C(4)); 4.44 (*s*, H–C(1)); 3.6 (*AB*, ^3J = 3, $\nu_0\delta$ = 2, H–C(5), H–C(6)); 2.32 (*d*, ^2J = 13, H_{endo}–C(3)); 2.02 (*dd*, ^2J = 13, ^3J = 4.5, H_{exo}–C(3)). MS (70 eV): 153 (2.4, $M^{+\cdot}$), 149 (1), 135 (1), 126 (3), 124 (3), 106 (6), 98 (26), 97 (100). Anal. calc. for $C_7H_7NO_3$ (153.136): C 54.90, H 4.61, N 9.15; found: C 54.76, H 4.63, N 9.09.

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