Selectivity in the ring-expansion and ring-switching reactions of bicyclooxonium ions

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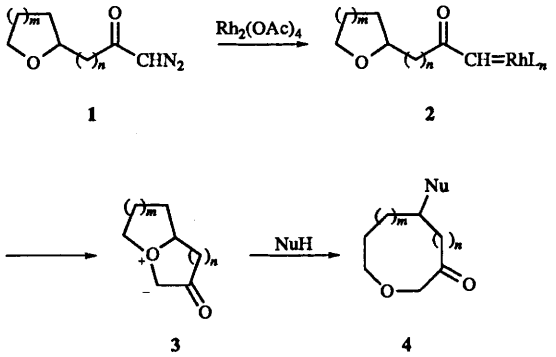
Treatment of ω-(2-oxacycloalkyl)alkyl bromides 5a–e with Ag_2O in the presence of a nucleophile (acetic or trifluoroacetic acid) yielded ring-expanded product 8, ring-switched product 7 or/and non-rearranged product 6. Regioselectivity in the nucleophilic attack on the intermediate bicyclooxonium ions 10 governs the product formation. Bicyclo[*n*.3.0]oxonium ions (*n* = 3, 4, 5) 10a–c, which can be formed from tetrahydrofuranylalkyl bromides 5a–c, underwent nucleophilic attack at the five-membered ring to produce a ring-switched product 7. Only bicyclo[3.3.0] ion 10a can undergo the preferential attack at the bridgehead position releasing ring strain to produce a ring-expanded product 8 in addition to the formation of 7. Similarly, in the reaction of tetrahydropyranylpropyl and oxepanylpropyl bromides 5d,e, initially formed bicyclo[*m* + 2.3.0]oxonium ions (*m* = 2, 3) underwent strain release by cleavage of a five-membered ring resulting in the exclusive formation of non-rearranged products 6d and 6e, respectively. The reason for the observed selectivity is discussed.

Oxonium ions of ethers are less stable than the analogous sulfonium and ammonium ions. However, their instability, which is mainly caused by the high reactivity of carbon–oxygen bond of the ions toward nucleophiles, has been manipulated intentionally for synthetic purposes such as the polymerization of cyclic ethers.[1] Meanwhile, in the total synthesis of natural products possessing medium or large-sized cyclic ether units such as brevetoxins[2] and laurencin,[3] efficient methods for the construction of their cyclic units seem essential. For this purpose, the intramolecular condensation of medium or long chain α,ω-diol derivatives,[4] the reduction of lactones[5] and the Baeyer–Villiger oxidation of cyclic ketones[6] have been investigated.

Recently, we have found a novel method for the preparation of medium- to large-sized cyclic ketoethers, where the intramolecular formation of bicyclooxonium ylides from rhodium(II) β-ketocarbenoids was successfully utilized for the purpose (Scheme 1).[7] It was assumed that, in the presence of an

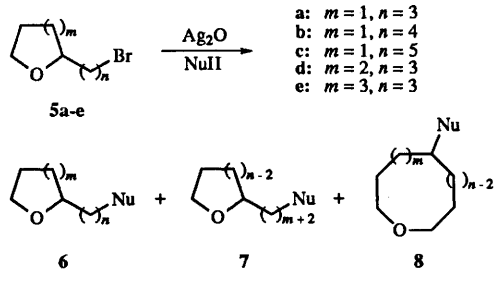


1 2 3 4

Scheme 1

appropriate nucleophile NuH, the ring expansion is governed by the regioselective nucleophilic attack on the bicyclooxonium ion intermediate, which is generated from the corresponding oxonium ylide **3**. It was also assumed that the desired ring expansion could be attained by the relief of strain in the bicyclic ring system. To examine these assumptions, oxonium ylide **3** did not seem to be an appropriate model because the two rings contain different functionalities and, hence, the effect of ring strains cannot be compared on a simple basis.

In the present study, bicyclooxonium ions which do not possess a carbonyl group were generated for the purpose of comparing the effect of ring strain on favouring the ring expansion. To substantiate the formation of bicyclooxonium ions, carbocations or their equivalents were generated at the terminus of an alkyl chain attached to the α-position of a cyclic ether (Scheme 2).



5a-e 6 7 8

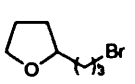
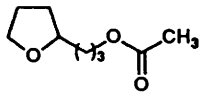
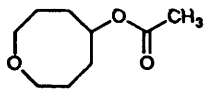
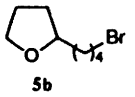
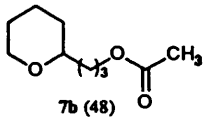
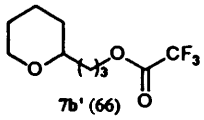
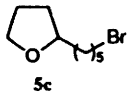
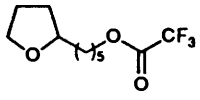
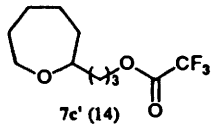
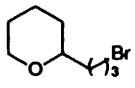
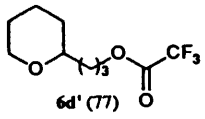
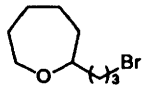
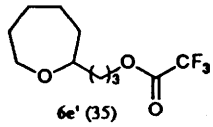
Scheme 2

Results and discussion

Carbocations or their equivalents[8] were generated by the treatment of ω-(2-oxacycloalkyl)alkyl bromides **5a–e** with silver(I) oxide in dichloromethane, acetic acid or trifluoroacetic acid (Scheme 2). Results are summarized in Table 1. Before describing the detail of product formation, it should be noted here that the bicyclooxonium ion **10**, once formed from carbocation **9** or its equivalents in the presence of a nucleophile, will undergo nucleophilic attack at one of three positions *a*, *b* or *c* shown in structure **10** (Scheme 3): (*a*) a position equivalent to the ω-position of **5** leading to non-rearranged product **6**; (*b*) a position leading to ring-switched product **7**; (*c*) a position leading to ring-expanded product **8**. With **5a**, however, which can form a symmetrical ion **10a**, it is difficult to distinguish between positions *a* and *b* without labelling (*vide infra*). Following are the results of the reaction together with a discussion on product variation mainly on the basis of ring-size effects.

Treatment of 3-(tetrahydrofuran-2-yl)propyl bromide **5a** with silver(I) oxide in acetic acid yielded oxocan-5-yl acetate **8a**, a ring-expanded product, together with a minor amount of tetrahydrofuranylpropyl acetate (18–21%) (entries 1 and 2). It should be noted here that both the ring-switched product and

Table 1 Reaction of ω-(2-oxacycloalkyl)alkyl bromides with nucleophiles over silver(I) oxide

Entry	Bromide 5	NuH	Solvent[a]	Non-rearranged 6	Product (yield%) ring-switched 7	Ring-expanded 8
1	 **5a**	CH_3CO_2H	CH_3CO_2H	—	 **7a** (21)	 **8a** (56)
2	**5a**	CH_3CO_2H	CH_2Cl_2	—	**7a** (18)	**8a** (54)
3	 **5b**	CH_3CO_2H	CH_3CO_2H[b]	—	 **7b** (48)	—
4	**5b**	CF_3CO_2H	CF_3CO_2H	—	 **7b'** (66)	—
5	**5b**	CF_3CO_2H	CH_2Cl_2	—	**7b'** (73)	—
6	 **5c**	CF_3CO_2H	CF_3CO_2H	 **6c'** (23)	 **7c'** (14)	—
7	**5c**	CF_3CO_2H	CH_2Cl_2	—	**7c'** (35)	—
8	 **5d**	CF_3CO_2H	CF_3CO_2H	 **6d'** (77)	—	—
9	**5d**	CF_3CO_2H	CH_2Cl_2	**6d'** (75)	—	—
10	 **5e**	CF_3CO_2H	CF_3CO_2H	 **6e'** (35)	—	—
11	**5e**	CF_3CO_2H	CH_2Cl_2	**6e'** (64)	—	—

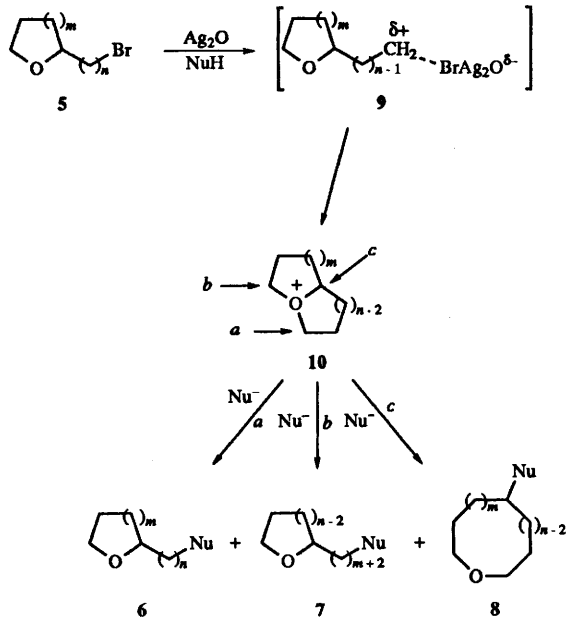
[a] Reaction conditions: at ambient temperatures unless otherwise stated. [b] Under refluxing conditions.

non-rearranged acetolysis product possess the same structure and, without any labels on either the ring or side chain of **5a**, it is difficult to differentiate between the two paths (*vide supra*). However, the following two pieces of experimental evidence support the ring-switching path: (i) in refluxing acetic acid (entry 3) or in trifluoroacetic acid with Ag_2O at room temperature (entries 4 and 5), 4-(tetrahydrofuran-2-yl)butyl bromide **5b** yielded the ring-switched product 3-tetrahydropyran-2-yl)propyl acetate **7b** or trifluoroacetate **7b'** (66–73%), respectively;† (ii) similarly, 5-(tetrahydrofuran-2-yl)pentyl bromide **5c** yielded ring-switched product **7c'** together with **6c'** in trifluoroacetic acid (in acetic acid the reaction was sluggish), but no ring-expanded product (entries 6 and 7).

† The reaction of bromide **5b** was sluggish in comparison with **5a** at room temperature. We presume that the silver-assisted ionization of **5b** to form the bicyclo[4.3.0] ion **10b**, even with an assisted intramolecular attack of the THF oxygen, must be much slower in acetic acid than for **5a** at room temperature, but faster than the acetolysis. In polar solvents such as trifluoroacetic acid, however, the ionization seems to be facilitated.

Therefore, the formation of the bicyclo[*n*.3.0]oxonium ions from tetrahydrofuranyl-C_n-alkyl bromides **5a–c** must be a favourable process at least for the side-chain length of n = 3–5. However, the formation of the bicyclooxonium ion **10c** becomes slow in competition with the acetolysis of **5c** because the formation of a seven-membered ring is unfavourable. In contrast to the behaviour of the tetrahydrofuranyl derivatives, reactions of 3-(tetrahydropyran-2-yl)propyl bromide **5d** and 3-(oxepan-2-yl)propyl bromide **5e** with Ag_2O in trifluoroacetic acid, where the same bicyclooxonium ions as were formed from **5b** and **5c** were supposed to be formed, yielded only non-rearranged products **6d'** and **6e'**, respectively (entries 8, 9, 10 and 11). The results indicate that only (tetrahydrofuran-2-yl)alkyl bromides **5a–c** can yield the ring-expanded product or/and ring-switched products, meaning that a nucleophile can attack either positions *c* or *b* (in **10a**, positions *b* and *a* are equivalent) of the bicyclooxonium ion **10a–c** (m = 1, n = 3,4,5) formed from **5a–c** (Scheme 3).

Two factors seem to control the regioselectivity of the nucleophilic attack on **10**. Firstly there is a steric effect similar to that proposed by Allred and Winstein.[9] They postulated that



Scheme 3

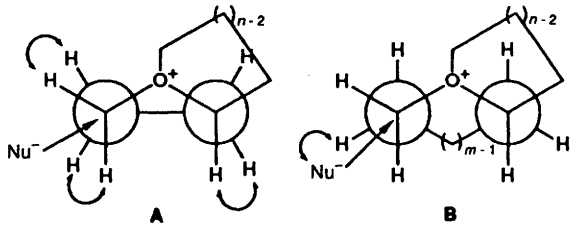


Fig. 1 Steric repulsion between the vicinal hydrogens of tetrahydrofuran ring (**A**, n = 3–5), and between a nucleophile and β-hydrogen in the other ring (**B**, n = 3, m = 2 or 3)

a bicyclo[n.3.0] system can undergo nucleophilic attack at the α-carbon of a THF ring without hindrance from the β-hydrogen atoms, which lie in a nearly eclipsed conformation with α-hydrogen atoms (Fig. 1, type A). On the other hand, when a nucleophile attacks at the α′-position of the other ring which adopts a chair-like conformation, the β′-hydrogen atoms occupy eclipsed positions which hinder the approach of the nucleophile (type B).

The second and major factor must be a strain effect. In bicyclo[n.3.0]oxonium ions, a five-membered ring in which all the vicinal hydrogen atoms lie in a nearly eclipsed conformation has a larger strain than the other ring with a larger size. Accordingly, cleavage of a five-membered ring by nucleophilic attack at either the b or c positions can release more strain energy than attack at other positions.[9] The energy release is maximized by the attack at the c position in the case of the [3.3.0] system, but by attack at the b position (not c) in the cases of the [4.3.0] (m = 1, n = 4) and [5.3.0] (m = 1, n = 5) systems. Therefore, the distribution of products is that ring-expanded and ring-switched products (**8a** and **7a**) were formed from **5a**, ring-switched product **7b** or **7b′** from **5b** and ring-switched product **7c′** and non-rearranged product **6c′** from **5c**. In oxonium ions **10b** and **10c**, the strain at the central bond must be insufficient to undergo cleavage. This may also imply that a partial positive charge can be developed at position c of **10a** whereas it is not significant in other ions and a S_N2 reaction at position b takes place giving the ring-switched product **7**.[10]

The reactions of propyl bromides **5d** and **5e** bearing a cyclic ether larger than tetrahydrofuran were again unequivocal yielding only non-rearranged products **6d′** and **6e′**, respectively (entries 8–11). Exactly the same mechanism must be operating as that proposed for the above-mentioned THF-derivatives. Because their side-chain lengths are C_3, the formation of bicyclo-[4.3.0] or -[5.3.0] ions must be a facile intramolecular process. Then, an exclusive S_N reaction takes place on the five-membered ring of the oxonium ion to give the non-rearranged product **6d′** or **6e′**. Therefore, again, the intramolecular formation of a second five-membered ring of the oxonium ion and subsequent release of the strain by nucleophilic attack is the dominant mechanism.

Conclusion

To summarize, for the formation of 1-oxoniabicyclo[n.3.0]-alkane ions, carbocation precursors such as **5a–c** possessing a tetrahydrofuran ring at **a** terminus or **5d,e**, possessing both a C_3 side chain and an ether ring which has more than five members, seem essential. However, only **5a** which forms a [3.3.0] system can afford ring-expanded product **8a**, while **5b,c** which form bicyclo[n.3.0]oxonium ions **10b,c** (n = 4, 5) afford ring-switched products **7b,c**, and **5d,e** which also form [m + 2.3.0] oxonium ions **10d,e** (m = 2, 3) afford non-rearranged products **6d,e**. In all the reactions reported here, the strain of intermediately formed bicyclic oxonium ion **10** controls the dominant regioselective reaction path.

Experimental

Tetrahydrofuran and dichloromethane were purified by the usual methods[11] and other commercially available chemicals were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were measured on a GE QE-300 spectrometer in $CDCl_3$ solutions using $CHCl_3$ (δ_H 7.26) and $CDCl_3$ (δ_C 77.0) as internal standards. Chemical shifts (δ) are given in ppm and the coupling constants (J) are given in Hz. IR spectra were recorded on a JASCO IR-810 spectrometer. High resolution mass spectra were measured on a Hitachi M-80 spectrometer.

3-(Tetrahydrofuran-2-yl)propyl bromide 5a

Bromide **5a** was prepared according to the reported method.[12]

4-(Tetrahydrofuran-2-yl)butyl bromide 5b[13]

Triphenylphosphine (3.2 g, 12 mmol) and carbon tetrabromide (5.1 g, 15 mmol) were added successively to a solution of 4-(tetrahydrofuran-2-yl)butanol[14] (1.5 g, 10 mmol) in dichloromethane (110 cm^3) at ambient temperature under an Ar atmosphere, and the solution was stirred for 15 min. The solution was washed with aq. sodium hydrogen carbonate, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to flash column chromatography to afford **5b** (1.8 g, 85%); δ_H 1.37–1.63 (5 H, m), 1.80–2.03 (5 H, m), 3.41 (2 H, t, J 6.9), 3.70 (1 H, ddd, J 8.0, 7.5 and 6.6), 3.78 (1 H, m) and 3.85 (1 H, ddd, J 8.0, 7.2 and 6.8); δ_C 24.99, 25.64, 31.31, 32.76, 33.61, 34.70, 67.59 and 78.96; ν_{max}/cm^{-1} (liq. film) 2960, 2940, 2850, 1460, 1080, 730 and 630; m/z (CI) (Found: [M + H]$^+$, 207.0376 and 209.0372. $C_8H_{16}BrO$: requires M, 207.0385 and 209.0365); (Found: C, 46.2; H, 7.6; Br, 38.7. Calc. for $C_8H_{15}BrO$: C, 46.39; H, 7.30; Br, 38.58%).

5-(Tetrahydrofuran-2-yl)pentyl bromide 5c

5-(Tetrahydrofuran-2-yl)pentanol[14] (2.0 g, 13 mmol) was treated by a similar procedure mentioned above for **5b** to yield **5c** (2.6 g, 94%); δ_H 1.38–1.60 (6 H, m), 1.75–1.90 (6 H, m), 3.99 (2 H, t, J 6.8), 3.69 (1 H, dt, J 6.9 and 6.9), 3.76 (1 H, m) and 3.84 (1 H, td, J 6.9 and 6.6); δ_C 25.59, 25.71, 28.25, 31.40, 32.77, 33.86, 35.52, 67.63 and 79.19; ν_{max}/cm^{-1} (liq. film) 2960, 2940, 2850, 1240, 1070, 730 and 640; m/z (CI) (Found: [M + H]$^+$, 221.0544 and 223.0531. $C_9H_{18}BrO$ requires M, 221.0541 and 223.0521); (Found: C, 48.8; H, 8.0; Br, 36.15. Calc. for $C_9H_{17}BrO$: C, 48.88; H, 7.75; Br, 36.13%).

3-(Tetrahydropyran-2-yl)propyl bromide 5d

3-(Tetrahydropyran-2-yl)propanol[15] (2.7 g, 19 mmol) was treated by a similar procedure mentioned above for **5b** to yield **5d** (3.5 g, 89%); δ_H 1.19–1.33 (1 H, m), 1.39–1.63 (6 H, m), 1.77–1.85 (1 H, m), 1.91 (1 H, dquint, *J* 8.1 and 7.2), 2.02 (1 H, dsex, *J* 8.1 and 6.9), 3.24 (1 H, ddd, *J* 12.5, 10.7 and 2.0), 3.42 (1 H, ddd, *J* 13.2, 6.5 and 3.2), 3.42 (1 H, m, containing *J* 12.5) and 3.95 (1 H, ddt, *J* 11.1, 3.9 and 1.9); δ_C 23.46, 26.04, 28.95, 31.92, 34.11, 34.98, 68.44 and 76.86; ν_{max}/cm^{-1} (liq. film) 2930, 2840, 1440, 1090 and 1050; *m/z* (CI) (Found: $[M + H]^+$, 207.0387 and 209.0389. $C_8H_{16}BrO$ requires *M*, 207.0385 and 209.0365); (Found: C, 46.35; H, 7.5; Br, 38.5. Calc. for $C_8H_{15}BrO$: C, 46.39; H, 7.30; Br, 38.58%).

3-(Oxepan-2-yl)propyl bromide 5e

To a solution of tetrahydrofuran (2.5 cm^3) containing 2-allyloxepane[16] (1.1 g, 76 mmol) and $NaBH_4$ (84 mg, 2.2 mmol), were added trifluoroborane–diethyl ether (0.1 cm^3), water (0.5 cm^3) and aq. sodium hydroxide (3 mol dm^{-3}; 0.83 cm^3) successively at 0 °C under an Ar atmosphere. After 10 min, aq. hydrogen peroxide (30%; 0.83 cm^3) was added to the solution. The solution was saturated with sodium chloride, and brine (20 cm^3) was added after which the solution was extracted with ether (4 × 20 cm^3). The organic extracts were dried over $MgSO_4$ and evaporated to give a residue, which was subjected to flash column chromatography to yield crude 3-(oxepan-2-yl)propanol (0.24 g, 39%). This alcohol (0.24 g) was subjected to a similar procedure to that for **5b** to yield **5e** (0.27 g, 79%); δ_H 1.42–1.80 (10 H, m), 1.89 (1 H, dddd, *J* 14.5, 14.5, 7.2 and 6.9), 20.4 (1 H, dddd, *J* 14.5, 14.0, 7.1 and 6.9), 3.40–3.55 (1 H, m), 3.41 (1 H, dt, *J* 9.9 and 6.9), 3.45 (1 H, dt, *J* 9.9 and 6.9) and 3.84 (1 H, tdd, *J* 6.1, 6.0 and 4.7); δ_C 25.77, 26.61, 29.52, 30.97, 34.11, 35.25, 36.15, 68.54 and 78.79; ν_{max}/cm^{-1}(liq. film) 2930, 2850, 1440, 1110 and 650; *m/z* (CI) (Found: $[M + H]^+$, 221.0547 and 223.0502. $C_9H_{18}BrO$ requires *M* 221.0541 and 223.0521); (Found: C, 9.0; H, 8.0; Br, 36.1. Calc. for $C_9H_{17}BrO$: C, 48.88; H, 7.75; Br, 36.13%).

Treatment of ω-(2-oxacycloalkyl)alkyl bromides 5a, 5b, 5c, 5d and 5e with silver(I) oxide in the presence of acetic acid or trifluoroacetic acid

Typical procedure. To a solution of Ag_2O (0.60 g, 2.6 mmol) and acetic acid (0.16 g, 2.6 mmol) or trifluoroacetic acid (0.30 g, 2.6 mmol) in dichloromethane (21 cm^3), or in an excess amount of acetic acid (11 cm^3) or trifluoroacetic acid (11 cm^3), was added **5** (2.6 mmol) dissolved in the same solvent (5 cm^3) at ambient temperature under an Ar atmosphere in the dark. The solution was stirred overnight after which the salt was filtered off and washed with dichloromethane (30 cm^3). The filtrate and washings were combined, washed with aq. sodium hydrogen carbonate, dried over $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to flash column chromatography to afford the corresponding products whose spectroscopic and analytical data are as follows. For product yields, see Table 1.

3-(Tetrahydrofuran-2-yl)propyl acetate 6a and 7a. δ_H 1.40–2.00 (8 H, m), 2.03 (3 H, s), 3.70 (1 H, tt, *J* 7.8 and 6.5), 3.82 (1 H, ddd, *J* 13.5, 10.4 and 7.0) and 4.07 (2 H, td, *J* 6.5 and 0.7); δ_C 20.90, 25.48, 25.63, 31.27, 31.90, 64.40, 67.61, 78.72 and 171.14; ν_{max}/cm^{-1} (liq. film) 2930, 2850, 1730, 1460, 1440, 1370, 1250 and 1100; *m/z* (CI) (Found: $[M + H]^+$, 173.1177. $C_9H_{17}O_3$ requires *M*, 173.1178); (Found: C, 62.9; H, 9.35. Calc. for $C_9H_{16}O_3$: C, 62.77; H, 9.36%).

Oxocan-5-yl acetate 8a. δ_H 1.58–1.90 (8 H, m), 2.00 (3 H, s), 3.48 (2 H, ddd, *J* 12.0, 7.5 and 3.6), 3.71 (2 H, ddd, *J* 12.0, 7.4 and 4.5) and 5.11 (1 H, tt, *J* 8.4 and 3.4); δ_C 21.45, 25.80, 31.17, 69.38, 75.16 and 170.37; ν_{max}/cm^{-1} (liq. film) 2930, 2850, 1730, 1460, 1440, 1370, 1250 and 1100; *m/z* (CI) (Found: $[M + H]^+$, 173.1170. $C_9H_{17}O_3$ requires *M*, 172.9801); (Found: C, 62.6; H, 9.4. Calc. for $C_9H_{16}O_3$: C, 62.77; H, 9.36%).

3-(Tetrahydropyran-2-yl)propyl acetate 7b. δ_H 1.17–1.29 (1 H, m), 1.38–1.82 (9 H, m), 2.01 (3 H, s), 3.21 (1 H, dddd, *J* 10.9, 7.3, 4.9 and 2.4), 3.37 (1 H, td, *J* 11.2 and 3.3), 3.93 (1 H, ddt, *J* 10.9, 4.5 and 1.8) and 4.04 (2 H, t, *J* 6.8); δ_C 20.89, 23.45, 24.69, 26.06, 31.86, 32.78, 64.46, 68.39, 77.15 and 171.06; ν_{max}/cm^{-1}(liq. film) 2930, 2840, 1740, 1240 and 1090; *m/z* (CI) (Found: $[M + H]^+$, 187.1327. $C_{10}H_{19}O_3$ requires *M*, 187.1335); (Found: C, 64.6; H, 10.0. Calc. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%).

3-(Tetrahydropyran-2-yl)propyl trifluoroacetate 7b′ and 6d′. δ_H 1.2–1.3 (1 H, m), 1.40–1.63 (6 H, m), 1.72–1.98 (3 H, m), 3.25 (1 H, dtt, *J* 10.8, 4.8 and 2.4), 3.40 (1 H, ddd, *J* 11.0, 10.8 and 3.4), 3.96 (1 H, ddt, *J* 11.4, 3.6 and 1.7), 4.36 (1 H, dt, *J* 17.4 and 4.2) and 4.36 (1 H, dt, *J* 17.4 and 10.7); δ_C 23.36, 24.39, 25.96, 31.82, 32.29, 68.28, 68.38, 76.91, 114.50 (q, *J* 283.7) and 157.40 (q, *J* 42.0); ν_{max}/cm^{-1}(liq. film) 2940, 2840, 1780, 1440, 1400, 1350, 1220, 1160, 1090, 780 and 730; *m/z* (CI) (Found: $[M + H]^+$, 241.0992. $C_{10}H_{16}O_3F_3$ requires *M*, 241.1065); (Found: C, 49.8; H, 6.2; F, 23.6. Calc. for $C_{10}H_{15}O_3F_3$: C, 50.00; H, 6.29; F, 23.73%).

5-(Tetrahydrofuran-2-yl)pentyl trifluoroacetate 6c′. δ_H 1.36–1.60 (6 H, m), 1.70–2.00 (6 H, m), 3.71 (1 H, ddd, *J* 15.0, 8.1 and 6.9), 3.77 (1 H, m), 3.83 (1 H, ddd, *J* 15.0, 8.1 and 6.9) and 4.33 (1 H, t, *J* 6.6); δ_C 25.37, 25.43, 25.50, 25.73, 27.93, 31.21, 35.31, 67.37, 67.99, 78.93, 114.41 (q, *J* 283.0) and 157.25 (q, *J* 44.8); ν_{max}/cm^{-1}(liq. film) 2940, 2860, 1785, 1350, 1220, 1160, 775 and 730; *m/z* (CI) (Found: $[M + H]^+$, 255.1231. $C_{11}H_{18}O_3F_3$ requires *M*, 255.1208); (Found: C, 51.9; H, 6.9; F, 22.4. Calc. for $C_{11}H_{17}O_3F_3$: C, 51.96; H, 6.74; F, 22.42%).

3-(Oxepan-2-yl)propyl trifluoroacetate 6e′ and 7c′. δ_H 1.40–2.00 (12 H, m), 3.40–3.54 (2 H, m), 3.84 (1 H, ddd, *J* 12.1, 6.2 and 4.5), 4.35 (1 H, dt, *J* 15.3 and 6.8) and 4.38 (1 H, dt, *J* 15.3 and 6.8); δ_C 24.90, 25.69, 26.52, 30.89, 32.59, 36.10, 68.29, 68.59, 78.86, 114.55 (q, *J* 278.9) and 157.40 (q, *J* 43.4); ν_{max}/cm^{-1}(liq. film) 2930, 2850, 1775, 1450, 1150, 790 and 730; *m/z* (CI) (Found: $[M + H]^+$, 255.1193. $C_{11}H_{18}O_3F_3$ requires *M*, 255.1208); (Found: C, 52.1; H, 7.25; F, 20.0. Calc. for $C_{11}H_{17}O_3F_3$: C, 51.97; H, 6.74; F, 22.42%).

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