65. Structurally Biased 2-Fluoroallyl Cations as Generated – or not Generated – in Cyclopropane Ring-opening Reactions[1])

by **Manfred Schlosser** and **Yvonne Bessière**

Institut de Chimie Organique de l'Université, Rue de la Barre 2, CH-1005 Lausanne

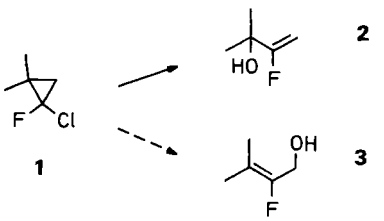
(21.XII.76)

Summary

The silver ion-catalysed ring-opening of 2-*t*-butyl-1-chloro-1-fluoro-2-methylcyclopropane (see *Scheme 2*) gave the expected mixture of primary and tertiary fluoroalkenols, whereas a tricyclic analog (bornane-*spiro*-chlorofluorocyclopropane) (see *Scheme 3*) exclusively underwent a *Wagner/Meerwein* rearrangement upon ionization to lose finally a proton affording a 2-fluoro-1,4-diene.

Surprisingly the hydrolytic ring-opening of 1-chloro-1-fluoro-2,2-dimethylcyclopropane (**1**, see *Scheme 1*) yields 2-fluoro-3-methyl-1-buten-3-ol (**2**) as the principal product, the less branched isomer 2-fluoro-3-methyl-2-buten-1-ol (**3**) being present only as a minor component [1].

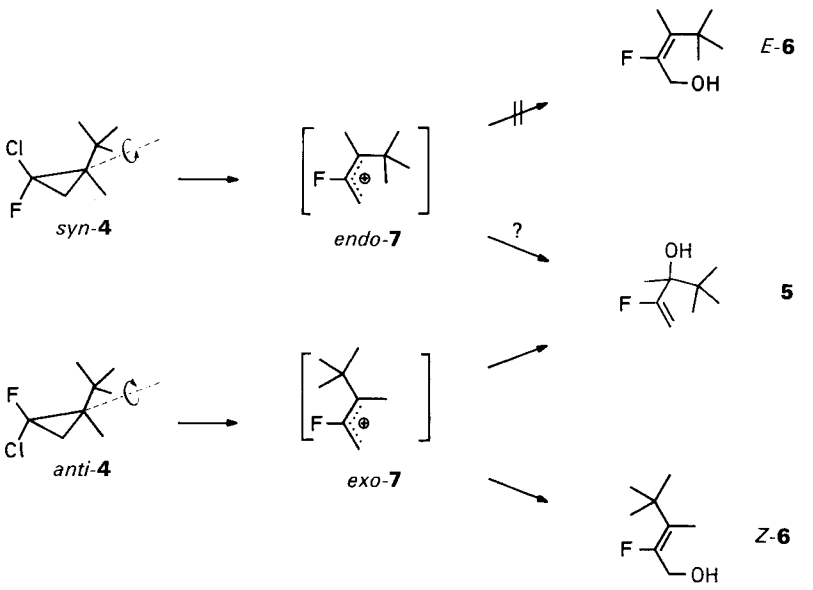
Scheme 1



In order to study the influence of steric factors on this peculiar regioselective behaviour we have prepared 2-*t*-butyl-1-chloro-1-fluoro-2-methylcyclopropane (**4**) and have treated the diastereoisomeric mixture (*syn:anti* = 1:4) with silver nitrate in water and in the presence of pyridine (see *Scheme 2*). 2-Fluoro-3,4,4-trimethyl-1-penten-3-ol (**5**) and (*Z*)-2-fluoro-3,4,4-trimethyl-2-penten-1-ol (*Z*-**6**) were obtained in yields of 56% and 19%, respectively. Thus, the product ratio tertiary/primary alcohol dropped from 90:10 (in the case of **1**) to 75:25, but the more branched product **5** is again kinetically favoured over its thermodynamically more stable isomer **6**.

[1]) Part VII of the series '*Syntheses of organofluorine compounds*'; for the preceding paper see [1].

Scheme 2



No other isomer bearing a primary hydroxyl function was detected. For stereoelectronic reasons [2] the *syn*-cyclopropane *syn*-**4** would be expected to undergo ring-opening by an inward-rotation of the *t*-butyl group, forming the allylic carbocation *endo*-**7** with the bulky ligand in the *endo*-position. The complete absence of (*E*)-2-fluoro-3,4,4-trimethyl-2-penten-1-ol (*E*-**6**) can hardly be rationalized by an isomerization of cation *endo*-**7** to *exo*-**7** since this process should require an activation energy of more than 9 kcal/mol[2]) and thus should not efficiently compete with the nearly diffusion-controlled addition of a water molecule ($\Delta G^{\neq} \leqslant 5$ kcal/mol). A more probable explanation, though still not very plausible, would be, that *syn*-**4** leads exclusively to **5**, whereas *anti*-**4** yields both regioisomers, **5** and *Z*-**6**, *via* cation *exo*-**7**[3]).

In order to disfavour the formation of the tertiary alcohol, bornane-2-*spiro*-(2′-chloro-2′-fluorocyclopropane) (**8**) was chosen as another substrate. Chlorofluorocarbene addition to 2-methylidenebornane produces almost exclusively the two *endo*-isomers of **8** (*syn*:*anti* = 1:2), while the carbene approach from the *exo* face is sterically shielded by the dimethylmethylene bridge. The respective carbocationic intermediates generated by ring opening of *syn*- and *anti*-**8** are expected to undergo

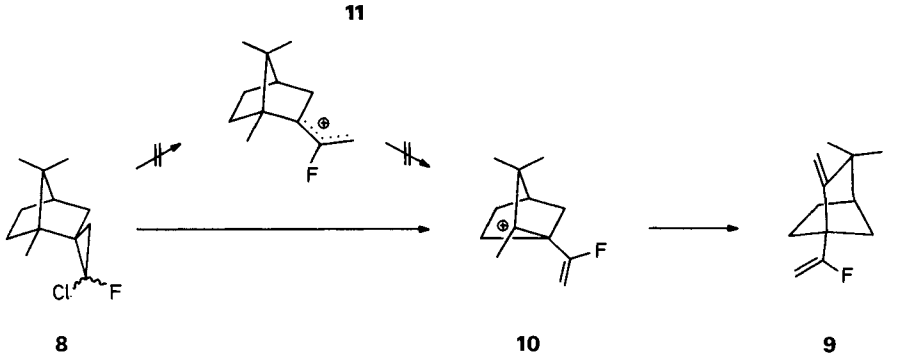
---

[2]) Estimated in the following way: take the barrier (12–13 kcal/mol [3]) for the positional exchange of the methyl groups in 1,1-dimethylallyl cation, add a correction term (4–5 kcal/mol [4]) to take into account the net inductive destabilization caused by the fluorine atom when the allyl cation is promoted from its ground state to the rotational transition state, and finally subtract 4–7 kcal/mol for steric strain which is present in the *endo*-**7** intermediate and relieved on going to *exo*-**7**.

[3]) Notice also that *syn*-**4** is the minor component of the diastereomeric mixture and that it solvolyses more slowly than does *anti*-**4** (see p. 592). Consequently only a small fraction of the products is derived from *syn*-**4**, if at all.

addition of water at the primary terminus rather than the hindered internal position. Unfortunately the solvolytic ring-opening of spirocyclopropane **8** afforded no alcohol whatsoever. The sole product isolated was identified as 1-(1-fluorovinyl)-3,3-dimethyl-2-methylidene-bicyclo[2.2.1]heptane (**9**) which results from a *Wagner/Meerwein* rearrangement of the bornane skeleton.

Scheme 3



8 **10** **9**

We must ask ourselves now whether the ionization of **8**, leading to a 2-fluoro-allylic cation, precedes the structural reorganisation or whether these two events occur simultaneously. A stepwise mechanism would imply the delocalized cation **11** to be thermodynamically less stable than the localized one (**10**). Though the fluorine at the 2-position will certainly increase the energy of the allylic species **11**, it can hardly counterbalance the effect of resonance stabilization (about 15 kcal/mol [5]). Moreover, if **10** were more stable than **11**, the analogous acyclic cation **7** should likewise rearrange to the corresponding tertiary alkyl cation, 1,2-alkyl shift generating carbocations of same or higher stability being extremely facile also in acyclic systems ($E_a < 5$ kcal/mol [6]). Thus the mechanism characterized by a fluoroallylic cation intermediate must be ruled out. On the other hand, the concept of σ-participation does not appear very convincing at first sight. Neighboring group assistance in solvolysis is generally reflected by a substantial rate enhancement, if compared to an analogous non-assisted reaction. In contrast, cyclopropanes **4** and **8** undergo ring-opening with comparable velocity, as determined by competitive kinetic measurements. More precisely, while both diastereoisomers of spiro-compound **8** react at approximately the same rate, they do so more than twice as fast as *syn*-**4**, but more slowly than *anti*-**4** by roughly a factor of 2.2 (see Fig. 1).

However, if we look for acceleration in the neighboring-group assisted solvolysis, we must not compare reactivity of **8** with that of **4**, but we have to correlate the *real* rate of solvolysis of **8** with a rate *estimate* for the hypothetical reaction passing through fluoroallylic cations. Of course, one might be tempted to attribute to the fictitious transformation **8** → **11** the same rate as that observed for the simple models **4**, which do solvolyse *via* fluoroallylic cations. However the bicyclic analogs suffer from increased non-bonded interactions, angle compression at one allylic center and steric hindrance to solvation. They would therefore be less stable than their acyclic

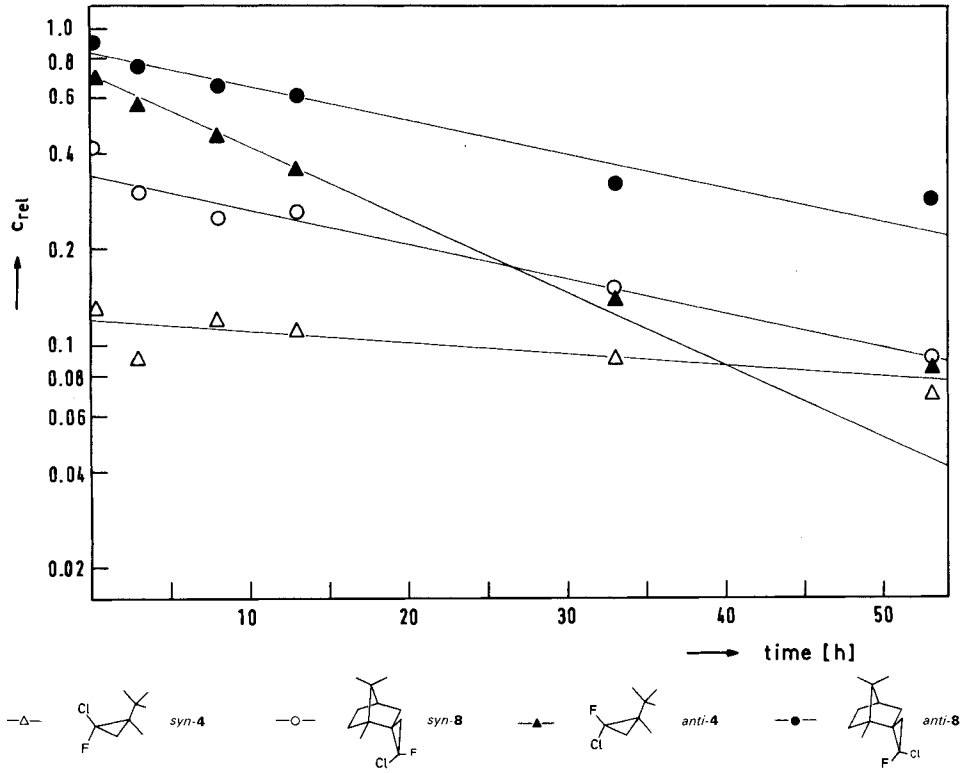


Fig. 1. *Disappearance of the* syn- *and* anti-*diastereoisomers of 2-t-butyl-1-chloro-1-fluoro-2-methyl-cyclopropane* (**4**) *and bornane-2-spiro-(2'-chloro-2'-fluoro-cyclopropane)* (**8**) *under solvolytic conditions as a function of time* (on the ordinate, relative concentration of each compound (C_{rel} = peak area *vs.* peak area of an 'internal standard' as determined by GC.); on the abscissa, reaction time in h)

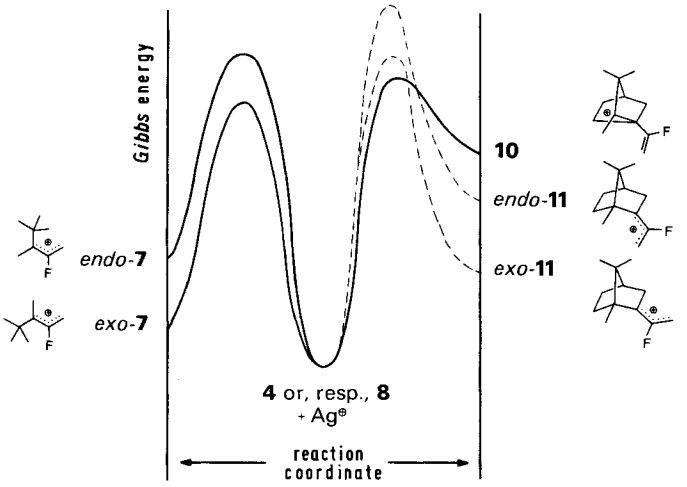


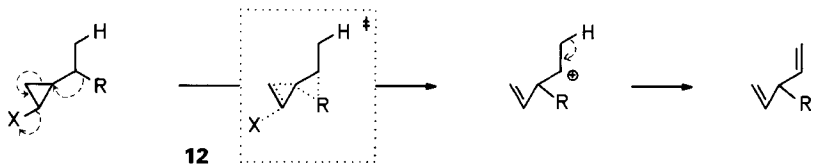
Fig. 2. *Energy profile for the solvolytic ring opening of 2-t-butyl-1-chloro-1-fluoro-2-methyl-cyclopropane* (**4**) *and bornane-2-*spiro-*(2'-chloro-2'-fluoro-cyclopropane)* (**8**) (in full lines, the real reaction pathways; in broken lines, an imaginary one)

analogs *endo*-**6** and *exo*-**6**, respectively. Consequently they would form less readily, say one or two orders of magnitude more slowly, in both stereochemical series. Under these circumstances the rearrangement to **10** offers a more attractive route because it requires a smaller investment of activation energy although it leads to a less stable cationic intermediate[4]) (see Fig. 2).

That the barrier is still relatively high is due to the excessive concertedness of the mechanism. We have to remember that the overall transformation of **8** to **9** consists of a complex sequence of elementary processes: departure of the nucleofugal leaving group (chlorine) under the influence of a silver ion, opening of the three-membered ring and double-bond formation, alkyl group migration and, finally, departure of a proton. All of these individual steps, except for the last one, have to be concerted in order to benefit from σ-participation (transition state **12**). That such a delicate venture can succeed at all is due to the essentially parallel orientation of the migrating bond to the cyclopropane bond to be cleaved.

The *'fragmentation on a round-about way'* (as represented by **12**) is characterized by 'mechanical' requirements different from those of ordinary solvolytic cyclopropane opening. The disrotatory process which usually characterizes solvolytic

Scheme 4



12

[4]) As one easily realizes (Fig. 1), this crossing-over of energy profiles can only become effective if significant activation barriers separate the reaction intermediates from the starting materials. This is in conflict with a common belief according to which a reactive intermediate and the transition state from which it emerges closely ressemble each other with respect to energetic and geometrical features. We argue now *that this approximation breaks down* in the case of solvolytic ring-opening reactions of cyclopropanes and, in general, *for all transformations where a covalent precursor on its way to a resonance-stabilized transient species must pass through transitional stages with poor orbital overlap* (for a typical example see [7]). – In their study of the ring-opening reaction of *t*-butyl-cyclopropyldiazonium ion, *W. Kirmse & H. Urbach* (Chem. Ber. *105*, 840 (1972)), have identified a product (0.7–7.8%) derived from the 2,3-dimethyl-4-penten-2-yl cation which was thought to be obtained from an intermediate *t*-butyl allyl cation, by methyl migration. (An immediate generation from the cyclopropane precursor in a concerted process, by-passing the *t*-butyl-allyl cation, has not been considered, although the postulated rearrangement was regarded as surprising). Again we would expect the allyl cation to be distinctly more stable than the localized tertiary one. If still the tertiary cation can be trapped in substantial quantities, two requirements have to be fulfilled. First, the allyl and the *t*-alkyl cation must rapidly interconvert into each other. Secondly, the solvolysis of the allyl cation (*t*-butyl allyl or **11** in the cited and present work, respectively) must be a relatively slow process, which cannot compete with the stabilization reaction of the tertiary cation (2,3-dimethyl-4-penten-2-yl or **10** respectively). The latter assumption, although not very probable, cannot be ruled out at present. – Prof. Dr. *P. v. R. Schleyer* was so kind as to read this manuscript and to suggest another mechanism which implies a concerted rearrangement of **11** (*syn* and *anti*) to afford immediately **9**. This hypothesis, however, cannot explain why *syn*- and *anti*-**8** are equally reactive whereas *syn*- and *anti*-**4** undergo ring-opening with substantially different rates.

cyclopropane cleavage is now replaced by one rotation (of the methylene group) and one inversion (at C(2) of the bornane skeleton). As a consequence, the 2-fluorovinyl group may be brought forth in any random spatial arrangement with respect to the rest of the molecule. This lack of geometrical restriction can well explain the almost identical reactivity of *syn*- and *anti*-**8**.

The authors are indebted to *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung,* Bern, for financial support (grant no. 2.467-0.75), to *Centre National de la Recherche Scientifique,* Paris, for according a leave to Dr. *Y. Bessière,* to *Hoechst* AG, Frankfurt, for a generous gift of dichlorofluoromethane, to Dr. *K.S.Y. Lau* for valuable help during the preparation of the manuscript and to Mr. *C.A. Barras* for experimental assistance.

Experimental Part

General remarks: see [1] [8].

The routine heating rate in temperature-programmed gas-phase chromatography (GC.) was 8 °C/min. The description '2 m, 20% SE-30*, 140° [4 min]→200°' means a GC. procedure using a glass (*!) column, filled with silicon rubber as a stationary phase, 20% on Chromosorb® 60/80 WAW, maintaining at 140° for 4 min, then heating up to 200° at a rate of 8°/min.

1. *2-t-Butyl-1-chloro-1-fluoro-2-methylcyclopropane* (**4**). - a) *Preparation* (see also [9]): To a heterogeneous mixture of 2,3,3-trimethyl-2-butene [10] (35 g, 0.36 mol), aqueous potassium hydroxide (105 ml, 55% in weight), and 1,4,7,10,13,16-hexaoxa-cyclooctadecane (2 g, 8 mmol), cooled to −20°, was added dichlorofluoromethane (Freon-21®, 60ml, about 0.80 mol) in three equal portions at 20 min intervals. During the addition and a further 18 h the mixture was vigorously stirred, while a dry-ice condenser prevented the low-boiling halomethane from escaping. Then the organic layer was separated. Distillation afforded unreacted trimethylbutene (b.p. 78–80°; 14.3 g, 41%) and the expected cyclopropane **4** (b.p. 60–62°/40 Torr; 14.0 g, 24%). GC. analysis of **4** (2 m, 20% C-20-M*, 100°; 2 m, 20% Ap-L*, 100°) revealed the presence of two isomers in the ratio of 4:1. On the basis of NMR. the *syn*-configuration [11] is assigned to the minor component, the *anti*-configuration to the major product. Preparative GC. (6 m, 20% C-20-M*, 85°) permitted separation of the two isomers. - MS. (260° ion source, 70° eV; *m/e*)[5]): 149 (0.1%; $M^+[^{35}Cl]-CH_3$); 84 (77%); 69 (100%).

syn-**4**: ^{1}H-NMR. ($CDCl_3$): 1.7–0.8 (*m*, complex, methylene); 1.22 (*d*, $J = 2.5$, methyl); 1.04 (*s*, *t*-butyl). - ^{19}F-NMR.: −48 ($d \times d \times q$; $J = 17$, 7 and 3).

anti-**4**: ^{1}H-NMR. ($CDCl_3$): 1.8–0.6 (*m*, complex, methylene); 1.23 (*d*, $J = 1.5$, methyl); 1.00 (*d*, $J = 1$, *t*-butyl). - ^{19}F-NMR.: −60 ($d \times d \times m$[6]), $J = 18$ and 6).

b) *Ring-opening reaction.* To a solution of silver nitrate (19 g, 0.11 mol) in water (50 ml) and pyridine (10 ml, 0.12 mol) was added cyclopropane **4** (8.2 g, 50 mmol). The mixture was then heated to gentle reflux for a period of 26 h. After cooling, it was diluted with water (50 ml) and the precipitate of silver chloride filtered off. The solid was washed with pentane (30 ml) and the liquid phase thoroughly extracted with the same solvent (5 × 30 ml). Subsequent drying and removal of solvent gave a mixture of 2-fluoro-3,4,4-trimethyl-1-penten-3-ol (**5**) and (*Z*)-2-fluoro-3,4,4-trimethyl-2-penten-1-ol (*Z*-**6**) in the ratio of 3:1 (by GC.: 2 m, 20% Ap-L*, 70° [4 min]→200°; 2 m, 20% C-20-M*, 70° [4 min]→200°; **5** precedes *Z*-**6** on both columns); yield 5.5 g (75%).

With column chromatography on silica (Kieselgel 0.04–0.06 mm; 200 g) a complete separation was achieved: pentane eluted *syn*-**4** (0.1 g), pentane/diethyl ether 4:1 **5** (3.5 g; b.p. 141–143°) and pentane/diethyl ether 1:1 *Z*-**6** (1.0 g; b.p. 180–184°).

---

[5]) Identical spectra for both isomers.

[6]) Obviously coupling with the single methyl group ($J \sim 1.5$ Hz) as well as long-range coupling [12] with the *t*-butyl hydrogen atoms ($J \sim 1$ Hz).

5: IR.: 3470*m* (O–H); 1655*s* (C=C); 1120*m* (C–O); 920+855*s* (–CF=CH_2, out-of-plane?). – ^{1}H-NMR.: 4.71 (*d*×*d*,*J* = 19 and 3, olefin. H *cis* to F); 4.66 (*d*×*d*,*J* = 51 and 3, olefin. H *trans* to F); 1.54 (*s*, hydroxyl); 1.35 (*d*,*J* = 2.5, methyl); 0.96 (*d*,*J* = 1.5, *t*-butyl [12]). – ^{13}C-NMR.: 170 (*d*,*J* = 266[7]), fluorine-bearing C); 90 (*d*,*J* = 19, terminal olefin. C); 77 (*d*,*J* = 27, hydroxylated C); 37 (*d*,*J* = 3, quart. C of *t*-butyl); 25 (*s*, 3 methyl of *t*-butyl); 22 (*s*, single methyl). – ^{19}F-NMR.: –20 (*d*×*d*[8]), *J* = 51 and 19).

$C_8H_{15}FO$ (146.2) Calc. C 65.72 H 10.34% Found C 65.95 H 10.53%

Z-**6**: IR.: 3370*s* (O–H); 1685*m* (C=C); 1015*s*, br. (C–O); 895+810*m* (C–F?). – ^{1}H-NMR.: 4.17 (*d*,*J* = 24, methylene); 2.56 (*s*, hydroxyl); 1.66 (*d*,*J* = 3, methyl in allyl position); 1.16 (*d*,*J* = 1.5, *t*-butyl [12]). – ^{13}C-NMR.: 153 (*d*,*J* = 249, fluorine-bearing C); 122 (*d*,*J* = 10, other olefin. C); 59 (*d*,*J* = 34, hydroxylated C); 35 (*s*, quart. C of *t*-butyl); 30 (*d*,*J* ≤ 3, 3 methyl groups of *t*-butyl); 14 (*d*,*J* = 6.5, allylic methyl). – ^{19}F-NMR.: –33 (*t*,*J* = 24; measured on expanded scale: broad individual peaks without splitting pattern, line width at half-height 9 Hz).

$C_8H_{15}FO$ (146.2) Calc. C 65.72 H 10.34% Found C 65.93 H 10.38%

2. Bornane-2-spiro-(2'-chloro-2'-fluorocyclopropane) (**8**). – a) *Preparation* (see also [9]): 2-Methylidenebornane was obtained by treatment of (±)-camphor (25 g, 0.16 mol) with triphenylphosphoniomethylid (from methyltriphenylphosphonium iodide, 80 g, 0.20 mol, in 200 ml tetrahydrofuran and butyllithium, 0.20 mol, 1.34M in 150 ml hexane) at reflux temperature over a period of 5 days, distillation in a 'sabre apparatus' (b.p. 55–60°/12 Torr) and purification from trace amounts of camphor by filtration of a pentane solution of the product through magnesia silica gel (Florisil®, 20-fold by weight); yield 22 g (89%); m.p. 66–68°. To a mixture of 2-methylidenebornane (15.0 g, 100 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (0.5 g, 2 mmol) were added aqueous potassium hydroxide (30 ml, 55% in weight) and dichlorofluoromethane (2×20 ml with an interval of 20 min; about 0.53 mol). The heterogeneous mixture was stirred for 24 h. The organic layer was then separated and the aqueous phase extracted once with pentane (20 ml). Distillation afforded unreacted 2-methylidenebornane (b.p. 55–60°/12 Torr; 10.4 g, 69%) and the expected spiro-compound **8** (b.p. 92–95°/7 Torr; 5.15 g, 24%). GC. analysis of **8** (2 m, 20% Ap-L*, 145°; 2 m, 20% C-20-M*, 145°) showed the presence of two components in the ratio 7:3. A sample was purified by preparative GC. (3 m, 20% SE-30*, 180°). – ^{1}H-NMR.: 1.8 (*m*, 3 methylene groups); 1.7–0.5 (*m*, 1 methine of the bornane ring and 1 methylene group of the three-membered ring); 0.96, 0.90 and 0.78 (3×*s*, 3 methyl groups). – ^{19}F-NMR.: 4 signals (each *d*×*d*×*m*) with approximate relative intensities 1:5:30:64 at –46, –48, –60 and –62, respectively.

$C_{12}H_{18}ClF$ (216.7) Calc. C 66.50 H 8.37% Found C 66.49 H 8.43%

b) *Ring-opening reaction:* A mixture of water (10 ml), pyridine (1.8 ml, 22 mmol), silver nitrate (3.8 g, 22 mmol) and the spiro-compound **8** (2.2 g, 10 mmol) was heated under reflux for 72 h. The progress of the reaction was monitored by GC. (2 m, 20% SE-30, 100° [4 min]→200°). While the starting material was gradually being consumed, only a single new product appeared. The reaction mixture was diluted with water (20 ml) and diethyl ether (10 ml), to precipitate the silver chloride which was filtered off and washed with diethyl ether (25 ml). Extraction of the filtrate with diethyl ether (5×20 ml), removal of solvent from the combined and dried organic fractions and distillation of the residue afforded 1-(1-fluorovinyl)-3,3-dimethyl-2-methylidene-bicyclo[2.2.1]heptane (**9**; b.p. 65–70°/10 Torr); yield 1.0 g (55%). – ^{1}H-NMR.: 4.90+4.70 (2×*s*, br., exocyclic methylidene); 4.71 (*d*×*d*,*J* = 49 and 3, olefin. H *cis* to F); 2.2–1.3 (*m*, 1 methine and 3 methylene groups). – ^{13}C-NMR.: 170 (*d*,*J* = 200, fluorine-bearing C); 159 (*s*, C(2)); 100 (*s*, exocyclic methylidene): 90 (*d*,*J* = 22, methylene of fluorovinyl); 57 (*d*,*J* = 27, C(1)); 48 (*s*, C(4)); 43 (*s*, C(3)); 41, 32 and 25 (3 *s*, C(5), C(6) and C(7)); 30 and 26 (2 *s*, methyl). – ^{19}F-NMR.: –18 (*d*×*d*,*J* = 50 and 18).

$C_{12}H_{17}F$ (180.3) Calc. C 79.96 H 9.51% Found C 80.14 H 9.47%

3. *Kinetics under competitive conditions.* Cyclopropane **4** (0.082 g, 5.0 mmol; *syn:anti* = 1:5.3) and **8** (0.108 g, 5.0 mmol; *syn:anti* = 1:2.0), tetradecane (0.048 g) and silver nitrate (3.8 g, 22 mmol) were dis-

---

[7]) *Correction:* The fluorine coupling constant of the halogen-bearing carbon atom in 3-fluoro-3-methyl-2-buten-1-ol is 262 Hz and not 171 Hz as erroneously stated in [1], p. 974.

[8]) No attempt was made to measure couplings smaller than 5 Hz.

solved in a mixture of pyridine (2.0 ml, 22 mmol), water (10 ml, 0.56 mol) and dioxane (30 ml). The mixture was brought to reflux and 5 ml aliquots were withdrawn at regular intervals, treated with aqueous HCl (2 ml 5N) and extracted with diethyl ether (4× 1.5 ml). The combined etheral extracts were dried and analysed by GC. (2 m, 20%, C-20-M*, 85→200°, heating rate 2°/min, for the areas of *syn*- and *anti*-**8** relative to the area of the 'internal standard' tetradecane; 2 m 20% Ap-L*, same temperature program, for area ratios of all other products with respect to tetradecane). Typically the material balance (*i.e.*, the sum of unreacted starting materials and products) was 80–90%. The disappearance of *syn*-**4**, *anti*-**4**, *syn*-**8** and *anti*-**8** as a function of time has been illustrated in Fig. 1. Relative rates approximate 1:6.7:3.0:3.0. In an independent run (similar conditions, samples withdrawn at seven different points on the time scale) the following rate ratios were found: 1:5:2.4:2.4.

REFERENCES

[1] *Y. Bessière & M. Schlosser,* Helv. *59*, 969 (1976).
[2] *R. B. Woodward & R. Hoffmann,* Angew. Chem. *81*, 797 (1969); Angew. chem. internat. Edit. *8*, 781 (1969); *C. DePuy, L. Schnack, J. Hausser & W. Wiedemann,* J. Amer. chem. Soc. *87*, 4006 (1965).
[3] *N. L. Allinger & J. H. Siefert,* J. Amer. chem. Soc. *97*. 752 (1975); and references given therein.
[4] *L. Radom, J. A. Pople & P. v. R. Schleyer,* J. Amer. chem. Soc. *95*, 8193 (1973).
[5] *J. L. Franklin & F. H. Field,* J. Amer. chem. Soc. *75*, 2819 (1953); *F. P. Lossing*, in: Mass Spectrometry (Ed.: *C. A. McDowell*), McGraw Hill, New York 1963.
[6] *M. Saunders, P. Vogel, E. L. Hagen & J. Rosenfeld,* Accounts Chem. Res. *6*, 53 (1973).
[7] *W. Tochtermann & H. O. Horstmann,* Chem. Ber. *104,* 365 (1971).
[8] *M. Schlosser, Le Van Chau & B. Saphič,* Helv. *58*, 2575 (1975).
[9] See also: *M. Schlosser, B. Spahič, C. Tarchini & Le Van Chau,* Angew. Chem. *87*, 346 (1975); Angew. Chem. internat. Edit. *14*, 365 (1975); *M. Schlosser & Le Van Chau,* Helv. *58*, 2595 (1975).
[10] *G. Edgar, G. Calingaert & R. E. Marker,* J. Amer. chem. Soc. *51*, 1483 (1929).
[11] *Syn/anti*, see: *M. Schlosser, G. Heinz & Le Van Chau,* Chem. Ber. *104,* 1921 (1971).
[13] *A. D. Cross & P. W. Landis,* J. Amer. chem. Soc. *84*, 1736 (1962); *86*, 4005 (1964); *A. D. Cross,* J. Amer. chem. Soc. *86*, 4011 (1964); *J. B. Rowbothan, M. Smith & T. Schaefer,* Canad. J. Chemistry *53*, 986 (1975); *T. Schaefer, K. Chum, K. Marat & R. E. Wasylishen,* Canad. J. Chemistry *54*, 800 (1976).