Tetrahedron Vol. 46, No. 15, pp. 5230-5236, 1990
Printed in Great Britain

0040-4020/90 $3.00+.00

RING OPENING OF *gem*-DIHALOCYCLOPROPANES : NOVEL TYPES OF 1,4-ELIMINATION REACTIONS

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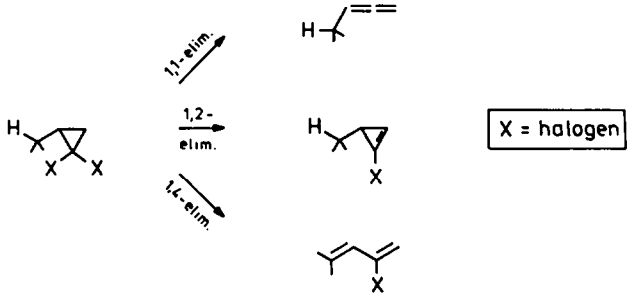
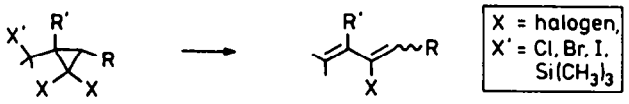
Summary : Upon treatment with tetrabutylammonium fluoride, *tert*-butyl 2,2-dichloro- and 2-chloro-2-fluoro-3,3-dimethyl-1-cyclopropanecarboxylate (1 and 3, respectively) undergo a chlorine/fluorine exchange *via* cyclopropene intermediates. As a by-product, *tert*-butyl 4-methyl-4-penten-2-ynoate (6) is formed. The same ring opened compound and, in addition, *tert*-butyl 4-chloro-4-methyl-2-pentynoate (9) are obtained besides the *gem*-dichlorocyclopropane derivative 1 when *tert*-butyl 3-methyl 2-butenoate is allowed to react with chloroform in strongly alkaline medium. - 2,2-Difluoro-3,3-dimethyl-1-cyclopropanecarbaldehyde (11) can be generated by oxidation of the corresponding alcohol. In the presence of any base, however, instantaneous ring opening and dehydrofluorination (to give 13) occur. - The solvolysis of 2,2-difluoro-3,3-dimethylcyclopropylmethyl *p*-toluenesulfonate (14) in boiling aqueous dioxane affords two ring opened products, 3,3-difluoro-2-methyl-1,4-pentadiene (17) and 3,3-difluoro-2-methyl-4-penten-2-ol (16), besides 2,2-difluoro-3,3-dimethyl-1-cyclopropylmethanol (10).

Cyclopropanes having a pair of geminal halogen substituents exhibit a whole spectrum of specific chemical reactivity [1, 2]. They may generate cyclopropylidenes, *i.e.* divalent carbon species which then isomerize by ring opening to give allenes [3] unless they are intercepted by intramolecular insertion or [1+2]-cycloaddition [4]. Alternatively, they may lose hydrogen halide by 1,2-elimination and thus produce cyclopropenes a few of which are stable enough to permit isolation [5], although in general they immediately undergo nucleophilic addition [6], tautomeric double bond shift [7] or again ring opening [8]. Finally, 1,4-dehydrohalogenation may also occur if hydrogen atoms are available in an appropriate exocyclic position [9].

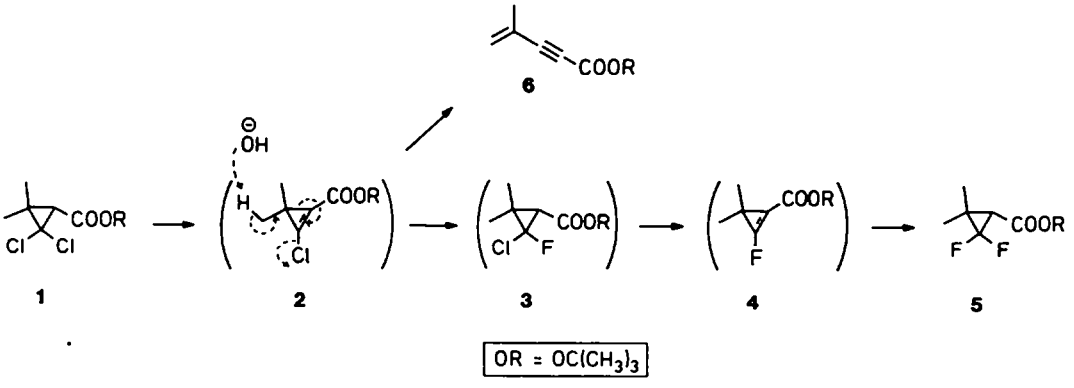


Rarely, however, the latter fragmentation mode gives a clean reaction. The ring-opening 1,4-elimination becomes a smooth and selective process only when hydrogen is replaced by halogen [10] or trimethylsilyl [11] as the electrofugal leaving group. Such modifications have allowed us to develop versatile methods for the construction of substituted, notably fluorinated dienes [10 - 12].



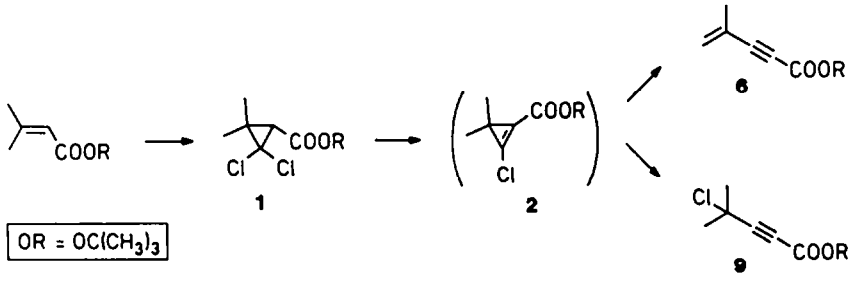
We now wish to report on three novel cases of 1,4-elimination which involve ring opening of halocyclopropanes. Several of the products isolated were unknown till now.

In an attempt to open a particularly simple access to functionalized *gem*-difluorocyclopropanes we have treated *tert*-butyl 2,2-dichloro-3,3-dimethyl-1-cyclopropylcarboxylate (1) with tetrabutylammonium fluoride. We did obtain the desired difluoro compound 5 although only with poor yield (10%). It was accompanied by the ring opened by-product *tert*-butyl 4-methyl-4-penten-2-ynoate (6, up to 12%).

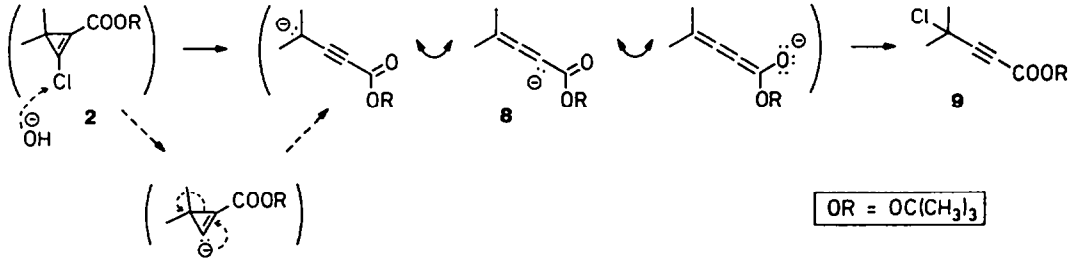


It is safe to assume a mechanism which is composed of two consecutive 1,2-elimination/nucleophilic addition sequences and which involves the cyclopropenes 2 and 4 and the chlorofluorocyclopropane 3 as transient species. Neither of them were detected as intermediates; hence they must be consumed faster than they are formed. In support of this idea, chlorofluorocyclopropane 3 was found to react with tetrabutylammonium fluoride more rapidly than the dichloro analog 1 and to afford the *gem*-difluorocyclopropane 5 as the main product (60%).

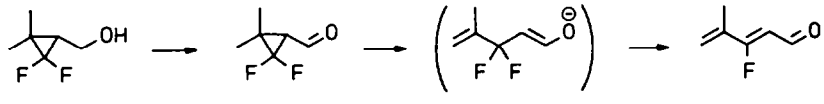
Again *tert*-butyl 4-methyl-4-penten-2-ynoate (**6**) was obtained as a by-product. Moreover, the same material (in 40% yield) emerged from the reaction between *tert*-butyl 3-methyl-2-butenoate and *in situ* generated dichlorocarbene. This time, the *gem*-dichlorocyclopropane **1** (26%) and *tert*-butyl 4-chloro-4-methyl-2-pentynoate (**9**, 25%) were isolated in addition.



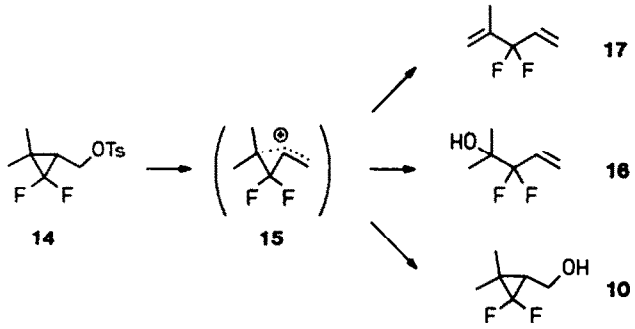
For the moment the genesis of the chloroalkyne **9** remains obscure. We can only suggest a tentative explanation. The chlorocyclopropene **2** resulting from a base promoted 1,2-dehydrohalogenation may have lost "positive" chlorine and been converted either via a cyclopropene anion **7** [13] or by direct ring opening to a resonance stabilized unsaturated ester enolate **8**. A hypochlorite intermediate, if not chlorocyclopropene **2** itself, may have transferred the formerly abstracted "positive" chlorine and thus given rise to the chloro ester **9**.



A different type of ring-opening fragmentation was encountered when we attempted to oxidize 2,2-difluoro-3,3-dimethyl-1-cyclopropylmethanol (**10**) [14] to the aldehyde **11** under Swern conditions [15]. Although it was possible to isolate and characterize the aldehyde, it proved to be extremely labile. Bases as weak as sodium hydrogen carbonate already suffice to transform it instantenously and completely to (*E*)-3-fluoro-4-methyl-2,4-pentadienal (**13**). The ease with which this 1,4-dehydrofluorination takes place is astonishing, since it does not, like cyclopropene **2**, benefit from relief of double bond strain as a special driving force. Actually, the corresponding alcohol **10** is perfectly stable against even strong bases. Thus, a concerted 1,4-elimination of hydrogen fluoride must be ruled out. We favor a step-wise process in which an enolate moiety acts as the nucleofugal leaving group. Intermediate **12** gets subsequently stabilized by fluoride expulsion.



Finally, we have converted the alcohol **10** to the tosylate **14** and studied the solvolysis of the latter. In aqueous dioxane at reflux temperatures, three products were formed : the primary alcohol **10** (10%) with retained cyclic structure and two ring-opened compounds, the tertiary alcohol **16** (31%) and the homoconjugated diene **17** (57%). Presumably these three products originate from the same precursor, the non-classical [16, 17] cation **15**.



While the ring opening of ordinary cyclopropylcarbinols under ionizing conditions is well documented [18], little is known about the behavior of difluoro analogs. A literature search has revealed a single analogy to our results : 1-(2,2-difluoro-3,3-dimethyl-1-cyclopropyl)-3-phenyl-1-propanol affords (*E*)-2-bromo-3,3-difluoro-2-methyl-7-phenyl-4-heptene (20%) when heated 10 h with 48% hydrobromic acid [19].

EXPERIMENTAL PART

For generalities : see the first article of this series [20]. ^{1}H-NMR spectra marked with an asterisk were recorded at 80 MHz rather than, as usual, at 360 MHz.

1. Preparation and Reactions of *tert*-Butyl *gem*-Dihalocyclopropanecarboxylates

***tert*-Butyl 2,2-dichloro-3,3-dimethyl-1-cyclopropanecarboxylate (1)** : Chloroform (80 mL, 0.12 kg, 1.0 mol) was added dropwise, over a period of 5 h, to a vigorously stirred mixture of *tert*-butyl 3-methyl-2-butenoate [21] (15.6 g, 100 mmol), alkylphenylpolyethylene glycol ("Triton N-101", 1.5 g), tricaprylmethylammonium chloride ("Aliquat 336", 1.0 g) and 55% aqueous potassium hydroxide (100 mL), while the temperature was maintained around 40°C. The organic layer was washed with water (3 x 50 mL) and brine (2 x 50 mL), then dried and evaporated. Distillation afforded 6.2 g (26%) of **1**; bp 41 - 43°C/0.2 mmHg. - ^{1}H-NMR (C_6D_6) : 1.94 (1 H, s), 1.40 (3 H, s), 1.34 (9 H, s), 1.02 (3 H, s). - ^{13}C-NMR (C_6D_6) : 165.2 (1 C, s), 81.4 (1 C, s, fine struct.), 69.1 (1 C, s), 41.2 (1 C, d, *J* 162, fine struct.), 32.9 (1 C, s, fine struct.), 28.1 (3 C, qhept, *J* 127.4), 24.5 (1 C, q, *J* 132, fine struct.), 17.4 (1 C, q, *J* 129, fine struct.). - MS : 182 (1%, $M^+[^{35}Cl_2]$ - C_4H_8), 165 (10%), 147 (9%), 129 (14%), 58 (100%). - Analysis : calc. for $C_{10}H_{16}Cl_2O_2$ (239.14) C 50.23, H 6.74; found C 49.99, H 7.02%.

In an analogous reaction, the phase transfer reagents "Triton N-101" and "Aliquat 336" were replaced by 1,4,7,10,13,16-hexaoxacyclooctane ("18-crown-6", 1.0 g, 3.6 mmol). This time, besides **1** (12%) two new products were formed. They were separated by preparative gas chromatography (3 m, 10% C-20M, 120 °C) and identified as *tert*-**butyl 4-methyl-4-penten-2-ynoate** (**6**, 40%) and *tert*-**butyl 4-chloro-4-methyl-2-pentynoate** (**9**, 25%). - **6** : ^{1}H-NMR ($CDCl_3$) : 5.56 (1 H, s, broad), 5.5 (1 H, m), 1.93 (3 H, s), 1.51 (9 H, s). - IR : 2950 (s), 2220 (s), 1710 (s), 1375 (m), 1305 (s), 1245 (s), 1165 (s), 1022 (m), 915 (m), 848 (m), 750 (m). - MS : 166 (6%, M^+), 151 (8%), 149 (7%), 111 (18%), 93 (100%). - Analysis : calc. for $C_{10}H_{14}O_2$ (166.22) C 72.26, H 8.49; found C 72.09, H 8.08%. - **9** : ^{1}H-NMR (C_6D_6) : 1.43 (6 H, s), 1.26 (9 H, s). - ^{13}C-NMR (C_6D_6) : 152.2 (1 C, s), 86.0 (1 C, s, fine struct.), 83.3 (1 C, s, fine struct.), 77.1 (1 C, s), 55.9 (1 C, s, fine struct.), 33.5 (2 C, qq, J_{HC} 129, ~ 4), 27.8 (3 C, qhept, J_{CH} 127, 4). - IR : 2995 (m), 2950 (w), 2230 (m), 1710 (s), 1445 (m), 1270 (s), 1160 (s), 1120 (m), 1110 (m), 900 (w), 842 (m), 750 (m). - MS (c.i., CH_4) : 205 (12%, M^+[^{37}Cl] + 1), 203 (34%, M^+[^{35}Cl] + 1), 178 (10%), 176 (27%), 168 (86%), 149 (24%), 147 (70%), 131 (8%), 129 (30%), 111 (100%). - Analysis : calc. for $C_{10}H_{15}ClO_2$ (202.68) C 59.26, H 7.46; found C 59.44, H 7.40%.

Ester **6** was independently prepared with a 26% yield by consecutive treatment of 2-methyl-1-buten-3-yne [22] with butyllithium and di-*tert*-butyl carbonate [23].

tert-**Butyl 2-chloro-2-fluoro-3,3-dimethyl-1-cyclopropanecarboxylate** (**3**) : A two-phase mixture of 1-chloro-1-fluoro-3-hydroxymethyl-2,2-dimethylcyclopropane [24] (25 g, 0.16 mol), potassium permanganate (40 g, 0.25 mol), 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6", 2.3 g, 8.6 mmol) and glacial acetic acid (5 mL) in dichloromethane (0.50 L) and water (0.70 L) was vigorously stirred 15 h at 25°C. Sodium disulfite (75 g, 0.40 mol) and, later, conc. hydrochloric acid (50 mL) were added in order to dissolve the precipitated manganese dioxide. The aqueous phase was separated and further extracted with dichloromethane (2 x 50 mL). The combined organic layers were extracted with a saturated aqueous solution of sodium hydrogen carbonate (5 × 100 ml), the combined aqueous layers were acidified with conc. hydrochloric acid to pH 2 and then reextracted with dichloromethane (5 x 250 mL). After drying and evaporation of the solvent, **2-chloro-2-fluoro-3,3-dimethyl-1-cyclopropanecarboxylic acid** was left behind as a colorless solid; 21.5 g (81%); mp 64 - 66°C (after sublimation). To this material was added a solution of *p*-toluenesulfonic acid (2 g) in dichloromethane (0.25 L) and isobutene (0.15 L, 90 g, 1.6 mol). The mixture was kept in a tightly closed flask 18 h at 25°C. The ester **3** was isolated by distillation under reduced pressure; 22.8 g (79%); bp 50 - 53 °C/1 mmHg. - ^{1}H-NMR (C_6D_6) : 1.93 (0.75 × 1 H, d, *J* 18.5), 1.77 (0.25 × 1 H, d, *J* 4.0), 1.35 (0.75 × 9 H, s), 1.33 (0.25 × 3 H, d, *J* 2.0), 1.34 (0.25 × 9 H, s), 1.31 (0.75 × 3 H, d, *J* 1.5), 0.98 (3 H, d, *J* 1.5). - MS (c.i., CH_4) : 226 (33%, M^+[^{37}Cl] + 2), 224 (100%, M^+[^{35}Cl] + 2), 188 (15%), 168 (43%). - Analysis : calc. for $C_{10}H_{16}ClFO_2$ (222.69) C 53.94, H 7.24; found C 54.10, H 7.17%.

tert-**Butyl 2,2-difluoro-3,3-dimethyl-1-cyclopropanecarboxylate** (**5**) : A solution of *tert*-butyl 2-chloro-2-fluoro-3,3-dimethyl-1-cyclopropanecarboxylate (3.3 g, 15 mmol) and tetrabutylammonium fluoride trihydrate (6.3 g, 20 mmol) in acetonitrile (100 mL) was kept 15 h at 5°C. After distillation under reduced pressure, **5** was collected as a colorless liquid; 1.85 g (60%); bp 79 - 82°C/11 mmHg. The product was further purified by preparative gas chromatography (3 m, 10% SE-30, 135°C). - ^{1}H-NMR (C_6D_6) : 1.84 (1 H, dd, *J* 13.5, 1.6), 1.33 (9 H, s), 1.26 (3 H, dd, *J* 2.3, 1.2), 0.89 (3 H, dd, *J* 2.0, 1.5). - MS : 207 (5%, M^+ + 1), 191 (4%), 179 (13%), 151 (15%), 131 (100%). - Analysis : calc. for $C_{10}H_{16}F_2O_2$ (206.23) C 58.24, H 7.82; found C 58.35, H 8.10%.

A similar reaction between the *gem*-dichlorocyclopropanecarboxylate **1** and tetrabutylammonium fluoride trihydride gave 10% of the difluoro compound **5** besides 12% of the acyclic, halogen-free ester **6**. These products were identified by gas chromatographic comparison with authentic samples (3 m 5% C-20M, 110 → 185°C at a rate of 10°C/min).

2. Oxidation and Ring Opening Dehydrofluorination of (*gem*-Difluoro-*gem*-dimethylcyclopropyl)methanol

2,2-Difluoro-3,3-dimethyl-1-cyclopropanecarbaldehyde (**11**) : Dimethyl sulfoxide (1.7 mL, 1.9 g, 24 mmol), 1,1-difluoro-3-hydroxymethyl-2,2-dimethylcyclopropane (**10**, 1.4 g, 10 mmol) and *N,N*-diisopropylethylamine (8.6 mL, 6.5 g, 50 mmol) were consecutively, with 15 min intervals, and dropwise added to a solution of oxalyl chloride (1.0 mL, 1.4 g, 11 mmol) in dichloromethane (40 mL) at -60 °C. After 5 min at 25 °C, the mixture was washed

with water (3 × 10 mL) and brine (2 × 10 mL) and evaporated under cooling (0 °C). - ^{1}H-NMR ($CDCl_3$) : 9.35 (1 H, dd, *J* 6.0, 1.5), 2.14 (1 H, ddd, *J* 12.1, 6.0, 1.5), 1.48 (3 H, dd, *J* 2.2, 1.3), 1.33 (3 H, dd, *J* 2.2, 1.3). - ^{19}F-NMR ($CDCl_3$) : -78.9 (dd, *J* 160, 2), -68.4 (ddm, *J* 160, 12). - **2,2-Difluoro-3,3-dimethyl-1-cyclopropanecarbaldehyde oxime** : mp 65 - 66 °C (after sublimation). - ^{1}H-NMR ($CDCl_3$) : 8.87 (1 H, s), 6.58 (1 H, d, *J* 7.5), 2.63 (1 H, ddd, *J* 12.6, 7.5, 2.0), 1.36 (3 H, dd, *J* 2.2, 1.5), 1.24 (3 H, dd, *J* 2.4, 1.5). - ^{19}F-NMR ($CDCl_3$) : -81.2 (d, *J* 154), -72.3 (ddm, *J* 154, 13). - MS : 149 (3%, M^+), 134 (100%), 114 (29%). - Analysis : calc. for $C_6H_9F_2NO$ (149.14) C 48.32, H 6.08; found C 48.23, H 6.11%. - **2,2-Difluoro-3,3-dimethyl-1-cyclopropanecarbaldehyde semicarbazone** : mp 141 - 142 °C. - ^{1}H-NMR ($CDCl_3$) : 10.14 (0.9 H, s), 9.55 (0.1 H, s), 6.81 (0.9 H, d, *J* 7.4), 6.26 (0.1 H, d, *J* 7.4), 5.8 (2 H, s, very broad), 2.34 (0.1 H, dd, *J* 12.2, 7.5), 2.01 (0.9 H, dd, *J* 12.4, 7.5), 1.32 (3 × 0.1 H, s, broad), 1.25 (3 × 0.9 H, s, broad), 1.18 (3 × 0.9 H, s, broad), 1.16 (3 × 0.1 H, s, broad). - ^{19}F-NMR ($CDCl_3$) : -82.4 (0.1 F, d, *J* 155), -81.1 (0.9 F, d, *J* 155), -72.3 (1 F, ddm, *J* 155, 13). - MS : 191 (4%, M^+), 127 (100%), 113 (88%). - Analysis : calc. for $C_7H_{11}F_2N_3O$ (191.18) C 43.98, H 5.80; found C 44.26, H 5.70%. - **2,2-Difluoro-3,3-dimethyl-1-cyclopropanecarbaldehyde 2,4-dinitrophenylhydrazone** : mp 155 - 156 °C (after crystallization from ethanol). - ^{1}H-NMR ($CDCl_3$) : 11.21 (1 H, s, broad), 9.13 (1 H, d, *J* 2.5), 8.37 (1 H, dd, *J* 9.4, 2.4), 7.98 (1 H, d, *J* 9.5), 7.26 (1 H, d, *J* 8.0), 2.33 (1 H, dd, *J* 12.0, 8.0), 1.42 (3 H, s, broad), 1.36 (3 H, s, broad). - ^{19}F-NMR ($CDCl_3$) : -79.7 (d, *J* 156), -71.3 (ddm, *J* 156, 12). - MS : 314 (18%, M^+), 297 (17%), 279 (28%), 149 (96%), 112 (57%), 57 (100%). - Analysis : calc. for $C_{12}H_{12}F_2N_4O_4$ (314.25) C 45.87, H 3.85; found C 45.94, H 3.82%.

3-Fluoro-4-methyl-2,4-pentadienal (13) : If a solution of 2,2-difluoro-3,3-dimethyl-1-cyclopropylcarbaldehyde (**11**) in chloroform (nmr sample !) is kept 1 week at 25 °C or its solution in tetrahydrofuran is shaken 10 min with a concentrated aqueous solution of sodium carbonate, it is quantitatively converted to 3-fluoro-3-methyl-2,4-pentadienal (**13**). The same product can be obtained by heating tosylate **14** [14] in dimethyl sulfoxide 3 min to 150 °C. It was impossible to isolate aldehyde **13** in neat form due to its high propensity for polymerization. - ^{1}H-NMR ($CDCl_3$) : 10.10 (1 H, d, *J* 7.5), 5.91 (1 H, broad), 5.60 (1 H, dd, *J* 33.4, 7.5), 5.50 (1 H, symm. m), 1.93 (3 H, d, *J* ~ 1). - ^{19}F-NMR ($CDCl_3$) : -44.7 (ddm, *J* 33.4).

3. Solvolysis of (*gem*-Difluoro-*gem*-dimethylcyclopropylmethyl)*p*-toluenesulfonate

A solution of 2,2-difluor-3,3-dimethyl-1-cyclopropylmethyl *p*-toluenesulfonate **14** [14] (1.45 g, 5.00 mmol) in dioxane (10 mL) and water (5 mL) was heated 2 h under reflux. The products were identified by gas chromatographic comparison (3 m, C-20M, 130°C; 3 m, Ap-L, 120°; 1-octanol as an internal standard) with authentic samples : **3,3-difluoro-2-methyl-1,4-pentadiene** (**8**, 57%), **3,3-difluoro-2-methyl-4-penten-2-ol** (**9**, 31%) and **2,2-difluoro-3,3-dimethyl-1-cyclopropylmethanol** [14] (**5**, 10%). The products were separated by preparative gas chromatography (3 m, 8% C-20M, 100°C). - **8** : bp 71 - 72°C/702 mmHg; n_D^{20} 1.3752. - ^{1}H-NMR ($CDCl_3$) : 5.96 (1 H, dq, *J* 17.5, 10.5), 5.68 (1 H, dt, *J* 17.1, ~ 2), 5.49 (1 H, d, *J* 10.7), 5.35 (1 H, s, broad), 5.16 (1 H, s, broad), 1.84 (3 H, s). - ^{1}H-NMR (C_6D_6) : 5.68 (1 H, dq, *J* 17.5, 10.6), 5.45 (1 H, dtd, *J* 17.6, 2.4, 0.9), 5.25 (1 H, dt, *J* ~ 2.5, ~ 2), 4.98 (1 H, d, *J* 10.7), 4.81 (1 H, d-like m, *J* ~ 1.5), 1.60 (3 H, t, *J* 2.5). - ^{19}F-NMR ($CDCl_3$) : -38.1 (d, *J* 10.5). - MS : 118 (59%, M^+), 103 (100%), 77 (65%). - Analysis : calc. for $C_6H_8F_2$ (118.13) C 61.01, H 6.83; found C 60.85, H 6.90%. - **9** : bp 122 - 123°C/705 mmHg; n_D^{20} 1.3966. - ^{1}H-NMR ($CDCl_3$) : 6.06 (1 H, dtd, *J* 17.5, 12.0, 11.2), 5.72 (1 H, dtd, *J* 17.3, 2.3, 1.0), 5.55 (1 H, dd, *J* 11.2, ~ 1), 1.95 (1 H, s), 1.29 (6 H, t, *J* 1.2). - ^{1}H-NMR (C_6D_6) : 5.91 (1 H, dtd, *J* 17.5, 12.0, 11.2), 5.55 (1 H, dtd, *J* 17.5, 2.5, 1.3), 5.09 (1 H, d, *J* 11.2), 1.66 (1 H, s, broad), 1.07 (6 H, t, *J* 1.2). - ^{19}F-NMR ($CDCl_3$) : -51.9 (d, *J* 12.0). - MS : 118 (0.2%, M^+ - 18), 121 (2%), 77 (14%), 59 (100%). - Analysis : calc. for $C_6H_{10}F_2O$ (136.14) C 52.93, H 7.40; found C 52.96, H 7.17%.

Acknowledgment : The Schweizerische Forschungsgemeinschaft zur Förderung der wissenschaftlichen Forschung (project 2000-5.099), Bern, and the Fondation Herbette Lausanne have provided generous support of the work reported in this and the two preceding articles. The authors express their gratitude also to the Deutsche Forschungsgemeinschaft for a post-doctoral fellowship granted to U.M.

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