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# *gem*-DIFLUOROCYCLOPROPANES : AN IMPROVED METHOD FOR THEIR PREPARATION

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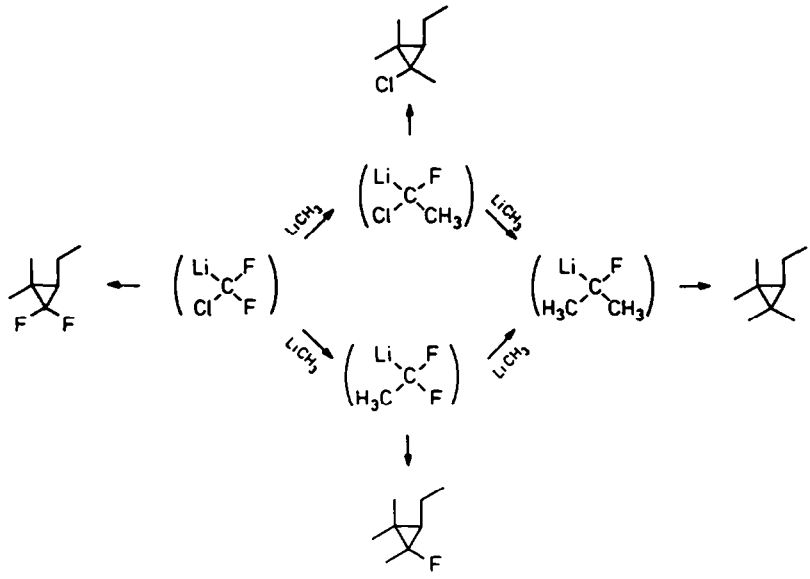
Summary : By treatment with dibromodifluoromethane and triphenylphosphine, four unfunctionalized olefins, four enethers and one bis-enether were converted to the *gem*-difluorocyclopropanes **1** - **9**. The yields were considerably increased and isomerizations at the double bonds were avoided if the reactions were carried out in the presence of a macrocyclic polyether such as "18-crown-6" and if, in addition, the reagents were employed in moderate excess.

Cyclopropanes having a pair of geminal fluoro substituents deserve attention in their own right, as a class of compounds offering potential therapeutic and notably pesticidal activity. In addition, they can be considered as precursors to specifically fluorinated ring-opened derivatives. Expedient methods for their preparation are hence quite welcome.


Several years ago we have discovered a very simple route leading to *gem*-difluorocyclopropanes. Such compounds were found to be formed when dichlorodifluoromethane ("Freon 12") was added to the mixture of an alkene and solid or ethereal methyllithium. Unfortunately, the yields were poor or moderate at best since the intermediate difluorocarbene or a corresponding carbenoid (*e.g.*, chlorodifluoromethyllithium) is prone to enter a halide/methyl substitution cascade and thus to generate new reactive species which can equally combine with

olefins by cycloaddition. With 2-methyl-2-pentene, for example, only small amounts (up to 12%) of the desired 3-ethyl-1,1-difluoro-2,2-dimethyl-cyclopropane were obtained besides several by-products, notably 3-ethyl-1-fluoro-1,2,2-trimethylcyclopropane (up to 38%), 3-ethyl-1-chloro-1,2,2-trimethylcyclopropane (up to 12%) and 3-ethyl-1,1,2,2-tetramethylcyclopropane (up to 5%). [1]



We expected enethers to be better carbene and carbenoid traps than ordinary olefins and thus to be more efficient in competing with the organolithium reagent. Nevertheless the results were disappointing as long as the enether was employed in stoichiometric amounts rather than as a cosolvent. With butyl (*Z*)-1-propenyl ether the corresponding *gem*-difluorocyclopropane 1 was formed with a maximum yield of 7% under such conditions (see table 1).

**1**

Therefore, we extended our investigation to other difluorocarbene producing reactions. A number of prominent difluorocarbene sources were deliberately excluded from this systematic comparison : difluorodiazirine [2] because of the hazards inherent in large-scale preparations; phenyl(trifluoromethyl)mercury [3] and (trifluoromethyl)trimethyltin [4] because of limits in their availability; chlorodifluoromethane in the presence of oxirane and soluble halides [5] because of the required rough reaction conditions which we believed to be incompatible with heat and base sensitive substrates. Out of the remaining sources dibromodifluoromethane (in the presence of lead [6]) and methyl chlorodifluoroacetate (in the presence of metal halides [7]) gave only low yields of

cycloadduct 1 and were abandoned in further studies. On the other hand, the thermal decarboxylation of chlorodifluoroacetate [8] and, in particular, the fluoride promoted decomposition of *in situ* generated (bromodifluoromethyl)triphenylphosphonium bromide, as described by Burton et al. [9], showed quite promising results (see Table 1).

Table 1. Yields of 2-butoxy-1,1-difluoro-3-methylcyclopropane (1) obtained upon reaction between butyl (*Z*)-propenyl ether and a variety of difluorocarbene precursors.

| carbene source | reagent | additive [a] (equivalents) | solvent [b] | time and temperature | | yield [c] |
|---|---|---|---|---|---|---|
| $Cl_2CF_2$ | $LiCH_3$ | - | HEX | 0.2 h | -75°C | 1% |
| $Cl_2CF_2$ | $LiC_4H_9$ | - | HEX | 0.2 h | -75°C | 1% |
| $Cl_2CF_2$ | $LiC(CH_3)_3$ | - | HEX | 0.2 h | -75°C | 7% |
| $Br_2CF_2$ | Pb | - | $CH_2Cl_2$ | 7 h | 40°C | 14% |
| $ClCF_2COOCH_3$ | KF | 18-crown-6 (1.0) | MEGME | 24 h | 95°C | 30% |
| $ClCF_2COOCH_3$ | LiCl | HMPT (4.0) | MEGME | 24 h | 95°C | 34% |
| $ClCF_2COONa$ [d] | - | - | TEGME | 0.5 h | 165°C | 42% |
| $BrCF_2\overset{\oplus}{P}(C_6H_5)_3$ | KF | - | MEGME | 48 h | 25°C | 60% |

a) 18-Crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane; HMPT = hexamethylphosphoric triamide.
b) HEX = hexane, MEGME = (mono)ethylene glycol dimethyl ether ("glyme"), TEGME = triethyleneglycol dimethyl ether ("triglyme").
c) Determined by gas chromatography (10 m SE-54, 70°C, dodecane as an "internal standard").
d) When 4.0 rather than 2.0 equivalents of sodium chlorodifluoroacetate were used, the yield rised to 53%.

Several attempts were made to improve the outcome of the chlorodifluoroacetate decarboxylation, however, without much success. Moreover, at the optimum reaction temperature of 165°C substantial amounts of cyclopropane 1 were lost by thermal decomposition (see Table 2). In contrast, it was possible to accelerate considerably the difluorocarbene generation from (bromodifluoromethyl)triphenylphosphonium bromide by adding catalytic amounts (typically 0.1 equivalents) of the macrocyclic polyether 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6") to the reaction mixture. Using this complexand, we were able to shorten the reaction times, to replace the expensive caesium by the cheap potassium fluoride and to use mono- rather than triethylene glycol dimethyl ether as the solvent. If, in addition, the reagents were employed in moderate excess (typically 2.0 equivalents) an almost quantitative yield was obtained (see Table 2).

Table 2. Yields of 2-butoxy-1,1-difluoro-3-methylcyclopropane (1) obtained upon reaction between butyl (*Z*)-propenyl ether and sodium or potassium chlorodifluoroacetate (2.0 equivalents) or (bromodifluoromethyl)triphenylphosphonium bromide (1.0 equivalent).

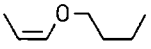
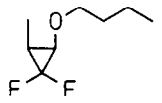
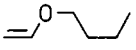
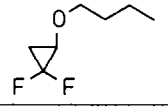
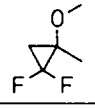
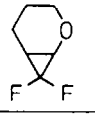
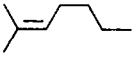
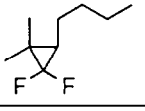
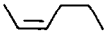
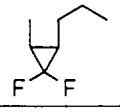
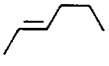
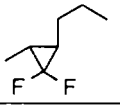
| carbene source | reagent | additive [a] (equivalents) | solvent [b] | time and temperature | yield [c] |
|---|---|---|---|---|---|
| $ClCF_2COONa$ | - | - | TEGME | 0.5 h 175°C | 42% |
| $ClCF_2COOK$ | - | 18-crown-6 (0.1) | TEGME | 0.2 h 165°C | 57% |
| $ClCF_2COOK$ [d] | - | - | TEGME | 0.2 h 165°C | 54% |
| $ClCF_2COOK$ | - | - | TEGME | 0.5 h 165°C | 46% |
| $ClCF_2COOK$ | - | - | TEGME | 1.0 h 165°C | 35% |
| $ClCF_2COOK$ | - | - | TEGME | 0.5 h 130°C | 30% |
| $ClCF_2COOK$ | - | - | TEGME | 1.5 h 130°C | 30% |
| $BrCF_2\overset{\oplus}{P}(C_6H_5)_3$ | CsF [e] | - | MEGME | 24 h 25°C | 60% |
| $BrCF_2\overset{\oplus}{P}(C_6H_5)_3$ | KF | 18-crown-6 (0.05) | MEGME | 24 h 25°C | 76% |
| $BrCF_2\overset{\oplus}{P}(C_6H_5)_3$ | KF | 18-crown-6 (0.1) | MEGME | 8 h 25°C | 82% |
| $BrCF_2\overset{\oplus}{P}(C_6H_5)_3$ [f] | KF | 18-crown-6 (0.1) | MEGME | 8 h 25°C | 99% |

a) 18-crown-6 = 1,4,7,10,16-hexaoxacyclooctadecane.
b) HEX = hexane, MEGME = (mono)ethylene glycol dimethyl ether ("glyme"), TEGME = triethyleneglycol dimethyl ether ("triglyme").
c) Determined by gas chromatography (10 m SE-54, 70°C, dodecane as an "internal standard").
d) When 4 equivalents of potassium chlorodifluoroacetate were used the yield rised to 62%.
e) Potassium fluoride gave a similar yield if the reaction time was extended to 48 h.
f) With 2.0 equivalents of the carbene source.

When this procedure was applied to a wide choice of substrates of the alkene or enether type, satisfactory to excellent yields were obtained in all cases (Table 3). In contrast, the original Burton protocol [9] gave very little product whenever an unbranched olefin rather than a more reactive [10] trialkyl substituted ethylene was employed. For example, *cis*-butene was reportedly converted to 1,1-difluoro-2,3-dimethylcyclopropane under such conditions to the extent of only 6%.

Worse, under the original conditions extensive base catalyzed isomerization [11] at the double bonds occurred with butyl (*Z*)-1-propenyl ether (20%) and, to a small extent (~ 1%), also with *cis*- or *trans*-2-hexene. On the other hand, when the reactions were conducted in the presence of "18-crown-6" polyether, the exclusively detectable products were cyclopropanes having entirely conserved the regio- and notably stereochemical integrity as predetermined by the configuration of their unsaturated precursors.

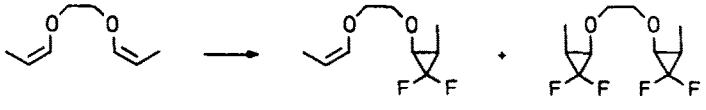
Table 3. Transfer of difluorocarbene from (bromodifluoromethyl)triphenylphosphoniumbromide to unsaturated substrats : yields of isolated and purified *gem*-difluorocyclopropanes. [a]

| substrate | cycloadduct | yield |
|---|---|---|
|  | **1**  | 82% |
|  | **2**  | 73% |
|  | **3**  | 88% |
|  | **4**  | 85% |
|  | **5**  | 89% |
|  | ***cis*-6**  | 43% [b] |
|  | ***trans*-6**  | 42% [b] |
|  | **7**  | 37% [b] |

a) For standard reaction conditions, see Table 2 and Experimental Part.

b) With 4.0 rather than 2.0 equivalents of reagent approximately 70% yield (see Experimental Part).

We are not aware of any more conclusive test on the performance of a synthetic method than to carry out a "double reaction". This means, a bifunctional substrate is allowed to undergo the chemical transformation, which one wants to evaluate, twice. In order to have a fair chance to isolate the double reaction product in reasonable quantity and with reasonable purity, each of the two reaction sites must be converted with a 70% probability at least. As a substrate carrying the required functionality twice we have selected ethylene glycol (*Z,Z*)-bis(1-propenyl) ether [(*Z,Z*-1,2-di(1-propenyloxy)ethane]. The result was quite gratifying, 79% of bis-cycloadduct **9** being isolated as a 1 : 1 mixture of *meso*- and *dl*-diastereoisomers besides some 15% of monoadduct **8**.



**8** **9**

## EXPERIMENTAL PART

### 1. General Remarks

*Starting materials* have been purchased from Fluka AG, Buchs, Aldrich-Chemie, Steinheim, or Merck-Schuchardt, Darmstadt, unless literature sources or details for the preparation are given. All commercial reagents were used without further purification.

Anhydrous *hexane* was obtained by careful azeotropic distillation, *tetrahydrofuran* by distillation from sodium wire after the caracteristic blue color of *in situ* generated sodium diphenylketyl [12] was found to persist. In case of poor quality of the crude material, the latter solvent was pretreated with cuprous chloride [13] and potassium hydroxide pellets. A suspension of finely powdered calcium hydride in *mono*- or *triethylene glycol dimethyl ether* or *dimethyl sulfoxide* was vigorously stirred 3 h at 75°C before the solvents were distilled, the two last mentioned under reduced pressure, and stored in Schlenk burettes. *Dichloromethane* was distilled from phosphorus pentoxide after having been stirred 4 h together with the drying agent.

*Ethereal extracts were dried* with sodium sulfate. Before distillation of compounds prone to radical polymerisation or sensitive to acids a spatula tip of *hydroquinone* or, respectively, *potassium carbonate* was added.

The temperature of dry ice-methanol baths is consistently indicated as -75°C, "room temperature" (22 - 26°C) as 25°C. If no reduced pressure is specified, *boiling ranges* were determined under ordinary atmospheric conditions (720 ± 25 mmHg). *Melting ranges* (mp) are reproducible after resolidification, unless otherwise stated ("dec."), and are corrected using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attempts to crystallize the liquid product have failed even at temperatures as low as -75°C.

Whenever reaction products were not isolated, their yields were determined by *gas chromatography* comparing their peak areas with that of an internal standard and correcting the ratios by response factors. The purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 - 100 and, respectively, 60 - 80 mesh particle size were chosen as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner

diameter, respectively). All packed columns were made of glass, while quartz was chosen as the material for coated, GROB-type capillary columns (≥ 10 m long). The type of the stationary phase used is abbreviated as SE-30, SE-54, OV-17 or DB-1 (silicone rubber), Ap-L (Apiezon L hydrocarbon) and C-20M or DB-WAX (polyethylene glycol).

*Infrared spectra* were recorded of films if the sample was liquid at room temperature, while solid substances were embedded in potassium bromide pellets. The intensities of absorption bands are abbreviated as s (strong), m (moderate) and w (weak).

*Nuclear magnetic resonance spectra* of hydrogen nuclei were recorded at 360 MHz, of carbon-13 nuclei at 90.6 MHz (either under broad band or gated decoupling) and of fluorine-19 nuclei at 188 MHz. Unless otherwise stated, deuterochloroform was used as the solvent. Chemical shifts refer to the signal of tetramethylsilane ($\delta$ = 0 ppm), which served as an internal standard in the case of $^1$H spectra, and of $\alpha,\alpha,\alpha$-trifluorotoluene for $^{19}$F spectra. Coupling constants ($J$) are measured in Hz. Coupling patterns are described by abbreviations : s (singulet), d (doublet), t (triplet), q (quadruplet), pent (pentuplet), hex (hexuplet), td (triplet of a doublet) and m (multiplet).

In general, *mass spectra* were obtained at a 70 eV ionization potential. The intensities of fragments relative to the base peak are given in parentheses after their molecular weight ($m/e$). When no molecular peak was observed under standard conditions, occasionally chemical ionization ("c.i.") in an ammonia or methane atmosphere was applied.

## 2. Starting Materials

Olefins, enethers, reagents and solvents have been purchased from Fluka (Buchs), Aldrich-Chemie (Steinheim), Merck-Schuchardt (Darmstadt) or Hüls (Troisdorf) unless literature sources or details for the preparation are given below. All commercial products were used without further purification.

**(*Z*)-1-Butoxypropene** [14] was obtained by base catalyzed isomerization [15] of allyl butyl ether.

**1,2-Di(allyloxy)ethane** [16] was prepared by heating a mixture of ethylene glycol (31 g, 0.50 mol), allyl bromide (0.10 L, 0.15 kg, 1.2 mol) 50% aqueous sodium hydroxide (130 mL, 0.20 kg, 2.5 mol) and tetrabutylammonium hydrogen sulfate (68 g, 0.20 mmol) 24 h to 75°C. After addition of water (200 mL) the product was isolated by extraction with pentane (4 × 25 mL) and distillation; 43.0 g (60%); bp 59 - 60°C/11 mmHg; $n_D^{20}$ 1.4338. - $^1$H-NMR ($CDCl_3$) : 5.90 (2 H, ddt, *J* 17.5, 11.5, 5.8), 5.28 (2 H, dq, *J* 17.0, 1.5), 5.17 (2 H, dq, *J* 11.0, 1.5), 4.01 (4 H, dt, *J* 6.0, 1.5), 3.61 (4 H, s).

This material (21.3 g, 150 mmol) was added to a solution of potassium *tert*-butoxide (4.5 g, 40 mmol) in anhydrous dimethylsulfoxide (40 mL) which then was kept 20 h at 50°C. After addition of water (100 mL), **1,1'-(ethylenedioxy)bis-1-propene [1,2-di(1-propenyloxy)ethane]** was extracted with pentane (3 x 50 mL) and distilled; 15.2 g (72%); bp 59 - 60°C/12 mmHg; $n_D^{20}$ 1.4451. According to gas chromatography (10 m, SE-54, 90°C; 3 m, C-20M, 130°C) the colorless liquid was composed of (*Z,Z*)- and (*Z,E*)-stereoisomers in the ratio of 96 : 4. - $^1$H-NMR ($CDCl_3$) : 5.99 (2 H, dq, *J* 6.2, 1.6), 4.43 (2 H, pent, *J* 6.5), 3.91 (4 H, s), 1.60 (6 H, dd, *J* 6.5, 1.5). - Analysis : calc. for $C_8H_{14}O_2$ (142.20) C 67.57, H 9.92; found C 67.50, H 9.81%.

## 3. *gem*-Difluorocyclopropanes

General working procedure : Upon adding dibromodifluoromethane (9.3 mL, 21.0 g, 100 mmol) to a solution of triphenylphosphine (26.2 g, 100 mmol) in ethylene glycol dimethyl ether (50 mL) a white precipitate formed instantaneously. About half of this suspension was poured into a vigorously stirred mixture of the olefin or enether (50 mmol), potassium fluoride (11.6 g, 200 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6", 1.3 g, 4.9 mmol) in ethylene glycol dimethyl ether (50 mL) and, after 5 h, the other half. After additional 5 h of stirring, always at 25 °C, the reaction mixture was diluted with pentane (250 mL) and centrifuged. The supernatant clear liquid was either distilled immediately or, more frequently, after being thoroughly washed with a 2% aqueous solution of sodium hydroxide (4 × 0.25 L).

***cis*-2-Butoxy-1,1-difluoro-3-methylcyclopropane (1)** : 6.7 g (82%); bp 50 - 51°C/25 mmHg; $n_D^{20}$ 1.3872. - $^1$H-NMR ($CDCl_3$) : 3.57 (2 H, t, *J* 6.5), 3.49 (1 H, ddd, *J* 11.0, 9.0, 2.0), 1.60 (2 H, pent-like m, *J* ~ 7), 1.6 (1 H, m), 1.40 (2 H, hex, *J* 7.5), 1.15 (3 H, ddd, *J* 6.5, 3.0, 1.5), 0.94 (3 H, t, *J* 7.5). - $^1$H-NMR ($C_6D_6$) : 3.25 (2 H, symm. m), 3.12 (1 H, ddd, *J* 10.2, 8.6, 1.8), 1.39 (2 H, m-like pent, *J* ~ 7), 1.27 (2 H, m-like hex, *J* ~ 7), 1.11 (1 H, symm. m), 0.95 (3 H, ddd, *J* 6.5, 3.0, 1.5), 0.77 (3 H, t, *J* 7.5). - $^{19}$F-NMR ($CDCl_3$) : -96.6 (d, broad, *J* 168); -65.8 (dddq, *J* 166, 17, 11, 3). - MS : 164 (0.6%, $M^+$), 57 (100%), 56 (15%), 51 (10%). - Analysis : calc. for $C_8H_{14}F_2O$ (164.20) C 58.52, H 8.59; found C 58.46, H 8.76%.

**2-Butoxy-1,1-difluorocyclopropane (2)** : 5.5 g (73%); bp 70 - 71°C/100 mmHg; $n_D^{20}$ 1.3785. - $^1$H-NMR ($CDCl_3$): 3.6 (3 H, m), 1.5 (6 H, m), 0.92 (3 H, t, *J* 7.4). - $^1$H-NMR ($C_6H_6$) : 3.2 (3 H, m), 1.36 (2 H, pent-like m, *J* ~ 7), 1.22 (2 H, hex-like m, *J* ~ 7), 1.04 (1 H, symm. m), 0.89 (1 H, symm. m), 0.77 (3 H, t, *J* 7.3). - $^{19}$F-NMR ($CDCl_3$) : - 86.1 (dddd, *J* 168, 16, 7, 3), -67.4 (dddd, *J* 166, 14, 10, 6). - MS : 150 (0.2%, $M^+$), 77 (9%), 57 (100%), 56 (15%), 51 (7%). - Analysis : calc. for $C_7H_{12}F_2O$ (150.17) C 55.99, H 8.05; found C 55.89, H 7.96%.

**1,1-Difluoro-1-methoxy-1-methylcyclopropane** [17] **(3)** : Because of the high volatility of compound 3, diethylene glycol dimethyl ether was used as the solvent . - 5.4 g (88%); bp 65 - 68°C; $n_D^{20}$ 1.3591. - $^1$H-NMR ($C_6D_6$) : 2.96 (3 H, s), 1.12 (1 H, ddd, *J* 16.5, 8.6, 4.6), 1.06 (3 H, dd, *J* 2.8, 1.9), 0.62 (1 H, ddd, *J* 14.6, 8.5, 5.7). - $^{19}$F-NMR ($C_6D_6$) : -83.6 (dddq, *J* 161, 17, 6, 3), -73.9 (dddq, *J* 161, 17, 4, 2). - MS : 102 (2%, $M^+$ - 20), 89 (14%), 60 (100%). - Analysis : calc. for $C_5H_8F_2O$ (122.11) C 49.18, H 6.60; found C 49.17, H 6.86%.

**7,7-Difluoro-2-oxabicyclo[4.1.0]heptane (4)** : 5.7 g (85%); bp 125 - 128 °C; $n_D^{20}$ 1.4097. - $^1$H-NMR ($C_6D_6$) : 3.44 (1 H, ddt, *J* 11.4, 9.0, 2.5), 3.37 (1 H, dt, *J* 10.8, 3.5), 2.7 (1 H, m), 1.4 (1 H, m), 1.3 (1 H, m), 1.0 (2 H, m), 0.8 (1 H, m). - $^{19}$F-NMR ($C_6D_6$) : -93.8 (dt, *J* 169, 2), -68.4 (dqt, *J* 169, 8, 2). - MS : 134 (7%, $M^+$), 133 (21%), 93 (70%), 84 (49%), 77 (100%). - Analysis : calc. for $C_6H_8F_2O$ (134.13) C 53.73, H 6.01, found C 53.74, H 5.90%.

**3-Butyl-1,1-difluoro-2,2-dimethylcyclopropane (5)** : 7.2 g (89%); bp 58 - 59°C/40 mmHg; $n_D^{20}$ 1.3919. - $^1$H-NMR ($CDCl_3$) : 1.4 (6 H, m), 1.20 (3 H, dd, *J* 2.8, 1.6), 1.08 (3 H, dd, *J* 2.8, 1.4), 1.02 (1 H, dtd, *J* 15.5, 7.0, 1.8), 0.92 (3 H, m-like t, *J* ~ 7.5). - $^{19}$F-NMR ($CDCl_3$) : -85.9 (d, *J* 151), -73.9 (dd, *J* 151, 15). - MS : 162 (0.1%, $M^+$), 86 (13%), 69 (14%), 57 (100%). - Analysis : calc. for $C_9H_{16}F_2$ (162.23) C 66.64, H 9.94; found C 66.76, H 10.29%.

***cis*-1,1-Difluoro-2-methyl-3-propylcyclopropane (*cis*-6)** : 2.9 g (43%) or 3.9 (58%) with 2.0 or, respectively, 4.0 equivalents of reagent; bp 104 - 105 °C; $n_D^{20}$ 1.3778. - $^1$H-NMR ($CDCl_3$) : 1.5 (6 H, m), 1.03 (3 H, ddd, *J* 6.5, 3.0, 1.2), 0.94 (3 H, t, fine structure, *J* 6.9). - $^{19}$F-NMR ($CDCl_3$) : -92.5 (d, broad, *J* 154), -63.9 (dm, *J* 154). - MS : 134 (0.3%, $M^+$), 91 (100%), 77 (61%). - Analysis : calc. for $C_7H_{12}F_2$ (134.17) C 62.67, H 9.02; found C 62.86, H 8.91%.

***trans*-1,1-Difluoro-2-methyl-3-propylcyclopropane (*trans*-6)** : 2.8 g (42%) or 4.0 g (60%) with 2.0 or, respectively, 4.0 equivalents of reagent; bp 98 - 99 °C; $n_D^{20}$ 1.3717. - $^1$H-NMR ($CDCl_3$) : 1.5 (4 H, m), 1.2 (3 H, m), 1.1 (2 H, m), 0.96 (3 H, t, fine structure, *J* 6.9). - $^{19}$F-NMR ($CDCl_3$) : -77.7 (m). - MS : 134 (0.2%, $M^+$), 91 (100%), 77 (55%). - Analysis : calc. for $C_7H_{12}F_2$ (134.17) C 62.67, H 9.02; found C 62.78, H 9.05%.

**7,7-Difluorobicyclo[4.1.0]heptane** [18] **(7,7-difluoronorcarane, 7)** : 2.5 g (37%), 3.4 g (51%) or 4.4 g (67%) with 2.0, 3.0 or 4.0 equivalents of reagent; bp 63 - 64°C/100 mmHg; $n_D^{20}$ 1.4148. - $^1$H-NMR ($CDCl_3$) : 1.8 (2 H, m), 1.7 (2 H, m), 1.54 (2 H, ddd, *J* 15.0, 5.0, 1.8), 1.3 (4 H, m). - $^1$H-NMR ($C_6D_6$) : 1.4 (2 H, m), 1.3 (2 H, m), 1.12 (2 H, ddd, *J* 15.0, 5.0, 2.0), 1.1 (2 H, m), 0.9 (2 H, m). - $^{19}$F-NMR ($CDCl_3$) : -87.4 (d, broad, *J* 156), -62.3 (dt, broad, *J* 155, 15). - MS : 132 (2.5%, $M^+$), 90 (76%), 81 (32%), 68 (100%), 56 (55%).

**1,1-Difluoro-2-methyl-3-(2'-[1"-propenyloxy]ethyloxy)cyclopropane (8)** : Two portions 100 mmol each of the triphenylphosphine-dibromodifluoromethane adduct were added in a 3 h interval to the bisenether (50 mmol) and the stirring was continued for 3 additional hours after the second addition. Distillation afforded a fraction (bp 70 - 100°C/100 mmHg) which contained the monocyclopropane 8 (approximately 10 mmol or 20%) besides the biscyclopropane 9 (approximately 20 mmol or 40%). The former was separated by preparative gas chromatography (3 m, 5% OV-17, 130°C), bp 183 - 186°C; $n_D^{20}$ 1.4180. - $^1$H-NMR ($C_6D_6$) : 5.77 (1 H, dq, *J* 6.2,

1.6), 4.37 (1 H, pent, *J* 6.2), 3.43 (2 H, symm. m), 3.28 (2 H, symm. m), 3.20 (1 H, ddd, *J* 10.8, 9.0, 2.0), 1.68 (3 H, dd, *J* 7.0, 1.8), 1.05 (1 H, symm. m), 0.95 (3 H, ddd, *J* 6.5, 3.0, 1.5). - $^{19}$F-NMR ($CDCl_3$) : -96.4 (d, broad, *J* 167), -65.8 (dddq, *J* 167, 17, 11, 3). - MS : 192 (0.4%, $M^+$), 91 (16%), 73 (19%), 47 (100%), 46 (27%). - Analysis : calc. for $C_9H_{14}F_2O_2$ (192.21) C 56.24, H 7.34; found C 56.43, H 7.01%.

**2,2'-(Ethylenedioxy)bis-(1,1-difluoro-3-methylcyclopropane) (9)** : The same quantities were applied as described in the preceding chapter, but the stirring was extended over 2 × 8 h periods. The product was isolated by distillation and collected as a colorless liquid; 9.6 g (79%); bp 93 - 95°C/11 mmHg; $n_D^{20}$ 1.3978. As gas chromatography (10 m, SE-54, 100°C; 3 m, C-20M, 130°C) revealed, two diastereoisomers were present in a 1 : 1 ratio. - $^1$H-NMR ($CDCl_3$) : 3.77 (0.5 × 4 H, s), 3.76 (0.5 × 4 H, s), 3.60 (0.5 × 4 H, ddt, *J* 11.0, 9.0, 2.0), 1.61 (2 H, symm. m), 1.15 (6 H, dm, *J* 6.9). - $^{19}$F-NMR ($CDCl_3$) : -97.0 (0.5 × 1 F, d, broad, *J* 171), -96.9 (0.5 x 1 F, d, broad, *J* 171), -65.9 (1 F, dddq, 166, 17, 11, 3). - MS : 227 (0.5%, $M^+$ - 15), 91 (100%), 71 (30%), 51 (34%). - Analysis : calc. for $C_{10}H_{14}F_4O_2$ (242.21) C 49.59, H 5.83; found C 49.74, H 6.03%.

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