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Routes from 1,1-cycloalkanedicarboxylic acids to geminal bis(polyfluoromethyl) substituted carbocycles

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Abstract

1-Fluoroformyl-1-(trifluoromethyl)cycloalkanes (**1**), prepared by treatment of 1,1-cycloalkane-dicarboxylic acids with SF_4, were efficiently reduced to 1-hydroxymethyl-1-(trifluoromethyl)-cycloalkanes (**2**). Routes for the conversion of alcohols **2** to 1-methyl-1-(trifluoromethyl)cycloalkanes (**4**), 1-fluoromethyl-1-(trifluoromethyl)cycloalkanes (**6**) and 1-difluoromethyl-1-(trifluoromethyl)cycloalkanes (**8**), via iodides **3**, triflates **5** and aldehydes **7**, respectively, were investigated.

Keywords: 1-Fluoroformyl-1-(trifluoromethyl)cycloalkanes; Bis(polytrifluoromethyl)cycloalkanes; 1-Hydroxymethyl-1-(trifluoromethyl)cycloalkanes; 1-Formyl-1-(trifluoromethyl)cycloalkanes

1. Introduction

1,1-Dimethylcycloalkanes are common fragments of terpenes and their derivatives such as retenoids, Vitamin D and pyrethroids. The search for convenient methods leading to carbocycles bearing CF_3, CHF_2 and CH_2F groups instead of one or two CH_3 groups on a quarternary carbon atom is of considerable interest for the preparation of fluorinated analogues of natural compounds. Our approach to the problem has been based on fluorination of geminal carboxylic groups with sulphur tetrafluoride. In the preceding paper [1] we described highly selective transformations of six-, five-, four- and three-membered 1,1-cycloalkanedicarboxylic acids to either bis(trifluoromethyl)cycloalkanes or to 1-fluoroformyl-1-(trifluoromethyl)cycloalkanes. The present paper deals with transformations of the COF groups in the latter compounds into CHF_2, CH_2F and CH_3 groups to give a variety of bis(polyfluoromethyl)substituted carbocycles.

2. Results and discussion

The reaction pathways are shown in Scheme 1.

In the first step, 1-fluoroformyl-1-(trifluoromethyl)cycloalkanes (**1**) were transformed into 1-hydroxymethyl-1-(trifluoromethyl)cycloalkanes (**2**) by reduction of the COF groups with $LiAlH_4$. The reductions proceeded readily in Et_2O solutions at 5–8°C affording alcohols **2** in high yields and of 97–99% purity.

Conversion of the CH_2OH group in **2** into the CH_3 group to form compounds **4a–c** created, however, some problems. Usually, hydroxymethyl groups are readily converted into methyl groups via iodides, mesylates or tosylates. In our case, however, treatment of mesylate, prepared from alcohol **2a**, with $LiAlH_4$ resulted in cleavage of the oxygen–sulphur bond which lead to almost quantitative recovery of **2a**; this was probably due to the electron withdrawing effect of the CF_3 group and thus reduced leaving groups abilities. The attempted iodination of alcohols **2** by conventional methods (48% hydroiodic acid, NaI in phosphoric acid) also failed. The above mentioned adversities are understood by considering steric hindrances to a nucleophilic attack on the carbon atom of the CH_2OH group and to the formation of pyramidal intermediate carbanions. The steric environment of the attacked carbon atom in alcohols **2** resembles that in neopentyl derivatives which are known to be extremely inert; for example, it has been found that the reaction of neopentyl alcohol with iodine and phosphorus gives only a 4–9% yield of neopentyl iodide [2]. Moreover, compounds **2a–d** are undoubtedly even more crowded than neopentyl alcohol due to the presence of a bulky CF_3 group. Alcohols **2a–c** were successfully converted into the respective iodides **3a–c** in a 50–70% yields by using methyl(triphenoxy)phosphonium iodide, formed in situ from triphenyl phosphite

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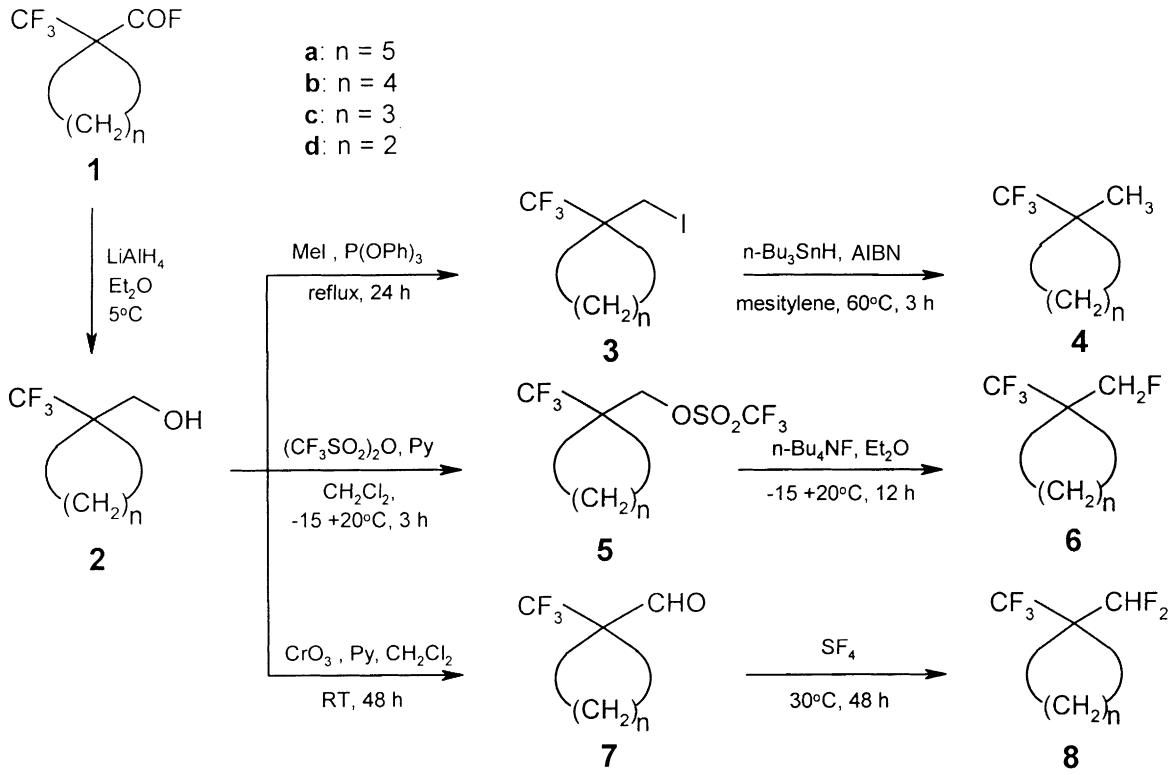


Scheme 1.

and methyl iodide, as a iodinating agent — the best procedure for iodination of sterically hindered alcohols [3,4]. Iodides **3a–c** were readily reduced to 1-methyl-1-(trifluoromethyl)cycloalkanes **4a–c** (50–80% yield) by treatment with tri-*n*-butyltin hydride in the presence of catalytic amount of AIBN, according to the literature procedure [5].

The attempted direct conversion of CH_2OH groups in alcohols **2** into CH_2F groups by treatment with SF_4 [6] or Et_2NCF_3 [7] failed. In both cases only trace amounts of 1-fluoromethyl-1-(trifluoromethyl)cycloalkanes **6** were detected by GLC–MS analyses; in the latter case the respective 1-(trifluoromethyl)-1-cycloalkyl formamides were main products. The most widely used method for the conversion of hydroxy compounds to fluoroderivatives is cleavage of esters of methanesulphonic, *p*-toluenesulphonic and especially trifluoromethanesulphonic acids with tetraalkylammonium fluorides [8]. Mesylates and tosylates of alcohols **2** were, however, not sufficiently reactive, but good results were obtained when triflates **5a–c** were treated with tetra-*n*-butylammonium fluoride; the reactions proceeded in diethyl ether at ambient temperature to give 1-fluoromethyl-1-(trifluoromethyl)cycloalkanes **6a–c**.

In the aim to convert CH_2OH groups into CHF_2 groups, alcohols **2a–c** were first oxidised to aldehydes **7a–c** using a CrO_3–pyridine reagent [9,10]. Treatment of these aldehydes **7a** and **8b** with sulphur tetrafluoride under mild conditions (general method for the preparation of difluoromethyl derivatives [6]) afforded 1-difluoromethyl-1-(trifluoromethyl)-cycloalkanes **8a** and **8b**.

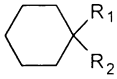
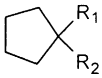
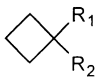
Interesting relationships between the number of fluorine atoms in the methyl groups and boiling points of *gem*-dimethylcycloalkanes has been observed (Table 1). Substitution of one of the CH_3 groups with a CF_3 group increases the boiling points of the respective cyclohexane and cyclopentane by only a few degrees while boiling points of smaller ring cycloalkanes rise by ca.12–18°C. Further fluorination (of the second CH_3 group) practically does not affect boiling points of cyclopentanes but in other cases the highest boiling points are observed for CF_3–CH_2F and CF_3–CHF_2 substituted cycloalkanes while bis(trifluoromethyl)cycloalkanes boil at the same temperature as their CF_3–CH_3 analogues. Some errors in determination of boiling points (by distillation) could not be excluded.

In conclusion, preceding [1] and the present results have shown that geminal cycloalkanedicarboxylic acids can be converted into corresponding *gem*-dimethylcycloalkanes with variable number of fluorine atoms in the methyl groups by selective fluorination of the former with SF_4 in the first step and by using known procedures in the next reaction steps. These results pave the way for the preparation of a variety of fluoromethyl analogues of naturally occurring compounds possessing geminal methyl groups.

3. Experimental

Melting points were determined in capillaries and boiling points were measured during distillation; both are

Table 1
Boiling points (°C) of 1,1-dimethylcycloalkanes and 1,1-bis(polyfluoromethyl)cycloalkanes

Compound (R_1–R_2)	CH_3–CH_3	CF_3–CH_3	CF_3–CH_2F	CF_3–CHF_2	CF_3–CF_3
	119.6[a]	124–126	147–148	136–138	124–126[d]
	87.5[a]	90–91	91–92	91–92	90–92[d]
	53.2[b]	65–66	76–78		66–68[d]
	20.6[a]	37–38[c]			44–46[d]

[a] Ref. [11].
[b] Ref. [12].
[c] Ref. [13].
[d] Ref. [1].

uncorrected. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded with a Varian Gemini 200 spectrometer at 200, 50 and 188 MHz, respectively. Chemical shifts are quoted in ppm from internal TMS for ^{1}H and ^{13}C (positive downfield) and from internal $CFCl_3$ (positive upfield). Crude mixtures of products were analysed with a Shimadzu GC-14A Chromatograph using a 3.5 m × 2 mm column packed with 5% silicone oil SE-52 on Chromosorb G. GC–MS analyses were performed with a Hewlett-Packard 5890 apparatus using a 30 m capillary column coated with a HP-5 oil. Mass spectra of pure compounds were obtained with an AMD-604 spectrometer and IR spectra with a Perkin-Elmer Spectrum 2000 instrument.

*3.1. 1-Hydroxymethyl-1-(trifluoromethyl)cycloalkanes (**2a–d**)*

A solution of acid fluorides **1a–d** [1] (40 mmol) in dry ether (50 ml) was added dropwise, while stirring, to a suspension of $LiAlH_4$ (1.7 g, 45 mmol) in ether (150 ml) precooled to 5°C in such a rate to keep the temperature at 5–8°C. After addition, the reaction mixture was stirred at 5°C for 2 h then quenched by a slow addition of 2% hydrochloric acid (200 ml) and the stirring was continued until the inorganic salt dissolved completely. The organic layer was separated dried over $MgSO_4$, ether was removed on a rotary evaporator and the residue was distilled under atmospheric pressure.

*3.1.1. 1-Hydroxymethyl-1-(trifluoromethyl) cyclohexane (**2a**)*

Yield: 86% (based on **1a**). Bp: 184–186°C. GLC purity: >98%. Analysis: found: C, 52.5; H, 7.4; F, 31.4%. Calculated for $C_8H_{13}F_3O$ (182.19): C, 52.7; H, 7.2; F, 31.3%. ^{1}H NMR (in $CDCl_3$) δ: 1.15–1.80 ppm (m, 11H); 3.79 ppm (m, CH_2). ^{13}C NMR (in $CDCl_3$): 129.4 ppm (q, $^1J_{CF}$ = 284.0 Hz, CF_3); 61.3 ppm (q, $^3J_{CF}$ = 1.9 Hz, CH_2); 44.2 ppm (q, $^2J_{CF}$ = 21.4 Hz, C-1); 25.1 ppm (m, C-2 and C-3); 20.7 ppm (s, C-4). ^{19}F NMR (in $CDCl_3$) δ: 76.4 ppm (s, CF_3). MS (EI, 70 eV) *m/z* (relative intensity, ion): 164 [24, $(M - H_2O)^+$]; 149 [15, $(M - CH_2OH - 2H)^+$]; 132 [100, $(M - CH_2OH - F)^+$]; 95 [25, $(M - CO - 2HF - F)^+$]; 81 (13, $C_6H_9^+$); 68 (13, $C_5H_8^+$).

*3.1.2. 1-Hydroxymethyl-1-(trifluoromethyl)cyclopentane (**2b**)*

Yield: 81%. Bp: 158–160°C. GLC purity: >99%. Analysis: found: C, 50.0; H, 6.8; F, 34.0%. Calculated for $C_7H_{11}F_3O$ (168.16): C, 50.0; H, 6.6; F, 3.9%. ^{1}H NMR (in $CDCl_3$) δ: 1.60–1.92 ppm (m, 9H); 3.62 ppm (d, J = 0.7 Hz, CH_2). ^{13}C NMR (in $CDCl_3$): 129.6 ppm (q, $^1J_{CF}$ = 279.7 Hz, CF_3); 64 ppm (q, $^3J_{CF}$ = 2.6 Hz, CH_2); 52.7 ppm (q, $^2J_{CF}$ = 22.6 Hz, C-1); 29.7 ppm (q, $^3J_{CF}$ = 1.8 Hz, C-2); 26.0 (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 73.6 ppm (s, CF_3). MS: 167 [0.4, $[M - H)^+$]; 150 [2, $(M - H_2O)^+$]; 149 [3, $(M - F)^+$]; 135 (19); 122 [10, $(M - C_2H_4 - H_2O)^+$]; 118 [100, $(M - CH_2OH - F)^+$]; 81 [17, $(M - H_2O - CF_3)^+$]; 77 [22, $(C_3H_3F_2)^+$]; 69 (3, CF_3^+); 67 (41, $C_5H_7^+$); 54 (13, $C_4H_6^+$); 41 (15, $C_3H_5^+$).

*3.1.3. 1-Hydroxymethyl-1-(trifluoromethyl)cyclobutane (**2c**)*

Yield: 75%. Bp: 140–141°C. GLC purity: >96%. Analysis: found: C, 45.5; H, 6.1; F, 37.0%. Calculated for $C_6H_9F_3O$ (154.13): C, 46.8; H, 5.9; F, 37.0%. ^{1}H NMR (in $CDCl_3$) δ: 1.66 ppm (s, OH); 1.90–2.10 ppm (m, 4H); 2.16–2.35 ppm (m, 2H); 3.82 (s, CH_2). ^{13}C NMR (in $CDCl_3$): 128.2 ppm (q, $^1J_{CF}$ = 279.6 Hz, CF_3); 63.6 ppm (q, $^3J_{CF}$ = 2.5 Hz, CH_2); 46.2 ppm (q, $^2J_{CF}$ = 25.6 Hz, C-1); 22.9 ppm (q, $^3J_{CF}$ = 2.9 Hz, C-2); 14.75 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 76.7 ppm (s, CF_3). MS: 136 [18, $(M - H_2O)^+$]; 134 [2, $[M - HF)^+$]; 125 [26, $(M - C_2H_5)^+$]; 106 [14, $(M - CO - HF)^+$]; 105 [44, $(M - CHOH - F)^+$]; 104 [99, $(M - CH_2OH - F)^+$]; 103 (16); 85 [14,

($M - CF_3$)$^+$]; 78 [18, ($C_3H_4F_2$)$^+$]; 77 [47, ($C_3H_3F_2$)$^+$]; 69 (5, CF_3^+); 67 (100, $C_5H_7^+$); 57 (66, $C_3H_5O^+$); 55 (9, $C_4H_7^+$); 53 (11, $C_4H_5^+$); 51 (9, $C_4H_3^+$); 42 (11, $C_3H_6^+$); 41 (23, $C_3H_5^+$).

3.1.4. 1-Hydroxymethyl-1-(trifluoromethyl)cyclopropane (**2d**)

Yield: 73%. Bp: 126–128°C. GLC purity: >97%. Analysis: found: C, 42.7; H, 5.1; F, 40.4%. Calculated for $C_5H_7F_3O$ (140.11): C, 42.9; H, 5.0; F, 40.7%. ^{1}H NMR (in $CDCl_3$) δ: 0.73–0.83 ppm (m, 2H); 1.00–1.07 ppm (m, 2H); 1.89 (s, OH); 3.73 ppm (s, CH_2); ^{13}C NMR (in $CDCl_3$): 127.0 ppm (q, $^1J_{CF} = 273.7$ Hz, CF_3); 63.4 ppm (s, CH_2); 24.9 ppm (q, $^2J_{CF} = 31.5$ Hz, C-1); 7.1 ppm (q, $^3J_{CF} = 2.7$ Hz, C-2). ^{19}F NMR (in $CDCl_3$) δ: 69.7 ppm (s, CF_3). MS: 140 (1, $M^{+\bullet}$); 139 [1, ($M - H$)$^+$]; 138 [1, ($M - 2H$)$^+$]; 125 [7, ($M - CH_3$)$^+$]; 123 [4, ($M - OH$)$^+$]; 122 [7, ($M - H_2O$)$^+$]; 119 [5, ($M - H_2F$)$^+$]; 112 [87, ($M - C_2H_4$)$^+$]; 110 [5, ($M - CH_2O$)$^+$]; 109 [4, ($M - CH_2OH$)$^+$]; 105 [20, ($M - CH_3 - HF$)$^+$]; 103 (13); 92 [81, ($M - CO - HF$)$^+$ or ($M - C_2H_4 - HF$)$^+$]; 91 [100, ($M - CO - H_2F$)$^+$]; 90 [97, ($M - CH_2OH - F$)$^+$]; 77 [47, ($C_3H_3F_2$)$^+$]; 71 [18, ($M - CF_3$)$^+$]; 69 (17, CF_3^+); 59 (10, $C_3H_4F^+$); 57 (28, $C_3H_2F^+$); 56 (17, $C_4H_8^+$); 53 (31, $C_4H_5^+$); 41 (16, $C_3H_5^+$).

3.2. 1-Iodomethyl-1-(trifluoromethyl)cycloalkanes (**3a–c**)

A mixture of alcohols **2a–c** (22 mmol), methyl iodide (4.7 g, 33 mmol) and triphenyl phosphite (7.4 g, 23.7 mmol) were gently refluxed (efficient reflux condenser was required to avoid a loss of MeI) for 24 h after which the resultant dark-red slurry was subjected to distillation under reduced pressure (50 Torr). The distillate, containing iodide **3** and phenol was dissolved in ether (100 ml) and the solution was extracted with 0.25 N aqueous NaOH (precooled to 0–5°C; 2 × 100 ml) followed by 10% aqueous Na_2SO_3 (50 ml) and finally with water (50 ml). The organic layer was separated, dried over anhydrous $MgSO_4$ and the solvent was removed on a rotary evaporator. The residue was vacuum distilled to give iodides **3a–c** as colourless liquids.

3.2.1. 1-Iodomethyl-1-(trifluoromethyl)cyclohexane (**3a**)

Yield: 67% (4.3 g, 14.7 mmol). Bp: 104–106°C/8 Torr. GLC purity: >99%. Analysis: found: C, 32.7; H, 4.1; F, 19.5; I, 43.4%. Calculated for $C_8H_{12}F_3I$ (292.08): C, 32.9; H, 4.1; F, 19.5; I, 43.5%. ^{1}H NMR (in $CDCl_3$): δ: 1.46–1.20 ppm (m, 2H); 1.90–1.56 ppm (m, 8H); 3.42 ppm (s, 2H, CH_2I). ^{13}C NMR (in $CDCl_3$): δ: 127.6 ppm (q, $^1J_{CF} = 284.2$ Hz, CF_3); 41.9 ppm (q, $^2J_{CF} = 23.4$ Hz, C-1); 28.9 ppm (s, C-2); 24.7 ppm (s, C-3); 20.5 ppm (s, C-4); 4.9 ppm (s, CH_2). ^{19}F NMR (in $CDCl_3$): δ: 76.9 ppm (s, CF_3). MS: 292 (17, $M^{+\bullet}$); 166 [8, ($M - I + H$)$^+$]; 165 [100, ($M - I$)$^+$]; 146 [5, ($M - I - F$)$^+$]; 145 [59, ($M - I - HF$)$^+$]; 125 [35, ($M - I - 2HF$)$^+$]; 123 (18); 117 [7, ($M - I - C_2H_4 - HF$)$^+$]; 55 (55, $C_4H_7^+$); 43 (21, $C_3H_7^+$); 41 (41, $C_3H_5^+$).

3.2.2. 1-Iodomethyl-1-(trifluoromethyl)cyclopentane (**3b**)

Yield: 51%. (2.5 g, 9.1 mmol). Bp: 58–59°C/11–12 Torr; 82°C/25 Torr. GLC purity: >99%. Analysis: found: C, 30.5; H, 3.5; F, 20.7; I, 45.6%. Calculated for $C_7H_{10}F_3I$ (278.08): C, 30.4; H, 3.6; F, 20.5; I, 45.6%. ^{1}H NMR (in $CDCl_3$): δ: 1.85–1.63 ppm (m, 4H); 2.10–1.90 ppm (m, 4H); 3.37 ppm (s, 2H). ^{13}C NMR (in $CDCl_3$): δ: 127.3 ppm (q, $^1J_{CF} = 282.5$ Hz, CF_3); 51.1 ppm (q, $^2J_{CF} = 23.9$ Hz, C-1); 34.1 ppm (s, C-2); 26.4 ppm (s, C-3); 10.6 ppm (s, CH_2I). ^{19}F NMR (in $CDCl_3$): δ: 74.6 ppm (s, CF_3). MS: 278 (6, $M^{+\bullet}$); 152 [7, ($M - I + H$)$^+$]; 151 [100, ($M - I$)$^+$]; 132 [5, ($M - I - F$)$^+$]; 131 [58, ($M - I - HF$)$^+$]; 123 [7, ($M - I - C_2H_4$)$^+$]; 111 [46, ($M - I - 2HF$)$^+$]; 103 [8, ($M - I - C_2H_4 - HF$)$^+$]; 77 [47, ($C_3H_3F_2$)$^+$]; 69 (4, CF_3^+); 53 (7, $C_4H_5^+$); 41 (45, $C_3H_5^+$).

3.2.3. 1-Iodomethyl-1-(trifluoromethyl)cyclobutane (**3c**)

Yield: 57% (2.9 g, 11.0 mmol). Bp: 36–38°C/12 Torr. GLC purity: >99%. Analysis: found: C, 27.2; H, 3.1; F, 21.6; I, 48.0%. Calculated for $C_6H_8F_3I$ (164.02): C, 27.3; H, 3.1; F, 21.6; I, 48.1%. ^{1}H NMR (in $CDCl_3$): δ: 2.18–1.85 ppm (m, 2H); 2.46–2.29 ppm (m, 4H); 3.44 ppm (s, 2H). ^{13}C NMR (in $CDCl_3$): δ: 125.6 ppm (q, $^1J_{CF} = 280.4$ Hz, CF_3); 44.9 ppm (q, $^2J_{CF} = 27.0$ Hz, C-1); 27.1 ppm (s, C-2); 13.2 ppm (s, C-3); 8.2 ppm (s, CH_2I). ^{19}F NMR (in $CDCl_3$): δ: 77.4 ppm (s, CF_3). MS: 264 (10, $M^{+\bullet}$); 137 [13, ($M - I$)$^+$]; 118 [6, ($M - I - F$)$^+$]; 117 [100, ($M - I - HF$)$^+$]; 109 [21, ($M - I - C_2H_4$)$^+$]; 97 [69, ($M - I - 2HF$)$^+$]; 89 [25, ($M - I - C_2H_4 - HF$)$^+$]; 77 [47, ($C_3H_3F_2$)$^+$]; 69 (5, CF_3^+); 53 (6, $C_4H_5^+$); 77 [47, ($C_3H_3F_2$)$^+$]; 41 (15, $C_3H_5^+$).

3.3. 1-Methyl-1-(trifluoromethyl)cycloalkanes (**4a–c**)

1-Iodo-1-(trifluoromethyl)cycloalkanes **3a–c** (12.4 mmol), dry benzene (5 ml, distilled from sodium metal) and azoisobutyronitrile (AIBN, 15 mg) were placed in a 25 ml three-necked bulb equipped with a thermometer, magnetic stirring bar and a rubber septum. The bulb was purged with dry argon then *n*-Bu_3SnH (5.4 g, 18.6 mmol) was injected via the septum. The reaction mixture was stirred at 60°C for 3 h after which products were distilled off under atmospheric pressure through a 5 cm long Vigreux-type column to afford compounds **4a–c** as volatile liquids. Due to high volatility, no C and H analyses were determined for compounds **4a–c**.

3.3.1. 1-Methyl-1-(trifluoromethyl)cyclohexane (**4a**)

Yield: 80% (1.65 g; 9.9 mmol). Bp: 124–126°C. GLC purity: >97%. Analysis: found: F, 34.3%. Calculated for $C_8H_{13}F_3$ (166.19): F, 34.3%. ^{1}H NMR (in $CDCl_3$) δ: 1.13 ppm (s, CH_3); 1.72–1.46 ppm (m, 8H). ^{13}C NMR (in $CDCl_3$) δ: 129.6 ppm (q, $^1J_{CF} = 282.1$ Hz, CF_3); 40.1 ppm (q, $^2J_{CF} = 24.7$ Hz, C-1); 29.7 ppm (s, C-2); 25.6 ppm (s, C-3); 20.8 ppm (s, C-4); 16.64 ppm (q, $^3J_{CF} = 2.3$ Hz, CH_3). ^{19}F NMR (in $CDCl_3$) δ: 81.3 ppm (s, CF_3). MS: 166 (1, $M^{+\bullet}$);·151 [0.5, ($M - CH_3$)$^+$]; 131 [2, ($M - CH_3 - HF$)$^+$]; 123 [1, ($M - CH_3 - C_2H_4$)$^+$]; 127 [2, ($M - HF_2$)$^+$]; 111 [2,

$(M - CH_3 - 2HF)^+$]; 97 [100, $(M - CF_3)^+$]; 69 (5, CF_3^+); 51 (7, $C_3H_4F^+$); 41 (22, $C_3H_5^+$).

3.3.2. 1-Methyl-1-(trifluoromethyl)cyclopentane (**4b**)

Yield: 65% (0.71 g; 4.6 mmol). Bp: 90–91°C. GLC purity: >97%. Analysis: found: F, 37.2%. Calculated for $C_7H_{11}F_3$ (152.16): F, 37.0%. ^{1}H NMR (in $CDCl_3$) δ: 1.17 ppm (s, 3H, CH_3); 1.50–1.35 ppm (m, 3H); 1.72–1.63 ppm (m, 3H); 2.01–1.85 ppm (m, 2H). ^{13}C NMR (in $CDCl_3$) δ: 130.5 ppm (q, $^1J_{CF} = 280.1$ Hz, CF_3); 47.4 ppm (q, $^2J_{CF} = 24.7$ Hz, C-1); 34.3 ppm (s, C-2); 25.6 ppm (s, C-3); 22.2 ppm (q, $^3J_{CF} = 2.8$ Hz, CH_3). ^{19}F NMR (in $CDCl_3$) δ: 77.5 ppm (s, CF_3). MS: 124 [1, $(M - C_2H_4)^+$]; 117 [2, $(M - CH_3 - HF)^+$]; 113 [8, $(M - HF_2)^+$]; 109 [2, $(M - CH_3 - C_2H_4)^+$]; 105 [13, $(M - C_2H_4 - F)^+$); 97 [5, $(M - CH_3 - 2HF)^+$]; 91 [7, $(M - 2HF - F)^+$); 83 [100, $(M - CF_3)^+$]; 77 [10, $(C_3H_3F_2)^+$]; 69 (5, CF_3^+); 55 (39, $C_4H_7^+$); 53 (55, $C_4H_5^+$); 42 (64, $C_3H_6^+$); 41 (32, $C_3H_5^+$).

3.3.3. 1-Methyl-1-(trifluoromethyl)cyclobutane (**4c**)

Yield: 52% (0.8 g; 5.8 mmol). Bp: 65–66°C. GLC purity: >98%. Analysis: found: F, 38.1% (an error caused by the volatility of **4c**). Calculated for $C_6H_9F_3$ (138.04): F, 41.3%. ^{1}H NMR (in $CDCl_3$) δ: 1.33 ppm (s, CH_3); 2.05–1.67 ppm (m, 2H); 2.45–2.27 ppm (m, 4H). ^{13}C NMR (in $CDCl_3$): 128.8 ppm (q, $^1J_{CF} = 278.3$ Hz, CF_3); 41.5 ppm (q, $^2J_{CF} = 28.1$ Hz, C-1); 27.5 ppm (s, C-2); 20.4 ppm (s, CH_3); 14.3 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 80.1 ppm (s, CF_3). MS: 138 (1.5, $M^{+\bullet}$); 123 [2, $(M - CH_3)^+$]; 110 [48, $(M - C_2H_4)^+$]; 103 [6, $(M - CH_3 - HF)^+$]; 99 [3, $(M - HF_2)^+$]; 95 [45, $(M - CH_3 - C_2H_4)^+$]; 91 [3, $(M - C_2H_4 - F)^+$]; 90 [18, $(M - C_2H_4 - HF)^+$]; 78 (16, $C_3H_4F_2^+$); 77 (16, $C_3H_3F_2^+$); 69 [100, CF_3^+ or $(M - CF_3)^+$]; 42 (33, $C_3H_6^+$); 41 (57, $C_3H_5^+$).

3.4. 1-(Trifluoromethyl)-1-cycloalkylmethyl triflates (**5a–c**)

Alcohols **2a–c** (11 mmol), dry CH_2Cl_2 (20 ml) and pyridine (1.5 g, 19 mmol) were placed in a 50 ml three-necked bulb equipped with a thermometer, magnetic stirring bar and a rubber septum. The bulb was purged with dry argon and cooled to −15°C then triflic anhydride (4.0 g, 14.3 mmol) was injected via the septum. The reaction mixture was allowed to warm to ambient temperature and stirred for 3 h. After dilution with CH_2Cl_2 (100 ml), the solution was washed with 1% hydrochloric acid (100 ml) precooled to 0°C followed by iced water. The organic layer was separated, dried over anhydrous $MgSO_4$ and the solvent was removed on a rotary evaporator at ambient temperature. The residue was distilled under reduced pressure to give triflates **5a–c** as colourless oils.

3.4.1. 1-(Trifluoromethyl)-1-cyclohexylmethyl trifluoromethylsulphonate (**5a**)

Yield: 85% (2.9 g; 9.3 mmol). Bp: 58–60°C/1.5 Torr. GLC purity: >99%. Analysis: found: C, 34.0; H, 3.9; F, 36.3; S, 10.3%. Calculated for $C_9H_{12}F_6SO_3$ (314.22): C, 34.40; H, 3.85; F, 36.27; S, 10.20%. ^{1}H NMR (in $CDCl_3$) δ: 1.89–1.23 ppm (m, 10H); 4.61 ppm (s, CH_2O). ^{13}C NMR (in $CDCl_3$) δ: 127.5 ppm (q, $^1J_{CF} = 283$ Hz, CF_3); 118.6 ppm (q, $^1J_{CF} = 319$ Hz, SO_2CF_3); 73.2 ppm (s, CH_2O); 43.9 ppm (q, $^2J_{CF} = 24.1$ Hz, C-1); 25.0 ppm (s, C-2); 24.6 ppm (s, C-3); 20.3 ppm (s, C-4). ^{19}F NMR (in $CDCl_3$) δ: 77.2 ppm (s, CF_3); 75.0 ppm (s, SO_2CF_3). MS: 165 [6, $(M - OSO_2CF_3)^+$]; 164 [16, $(M - HOSO_2CF_3)^+$]; 149 (32, $CF_3SO_2O^+$); 145 [18, $(M - OSO_2CF_3 - HF)^+$]; 136 [10, $(M - HOSO_2CF_3 - C_2H_4)^+$]; 135 [13, $(M - HOSO_2CF_3 - C_2H_5)^+$]; 131 [20, $(M - CH_2OSO_2CF_3 - HF)^+$]; 123 [9, $(M - HOSO_2CF_3 - 2HF)^+$]; 122 [13, $(M - HOSO_2CF_3 - 2HF - H)^+$]; 111 [17, $(M - CH_2OSO_2CF_3 - 2HF)^+$]; 95 (100, $C_1H_3O_3S^+$); 69 (47, CF_3^+); 55 (20, $C_4H_5^+$).

3.4.2. 1-(Trifluoromethyl)-1-cyclopentylmethyl trifluoromethylsulphonate (**5b**)

Yield: 84% (2.4 g; 8.1 mmol). Bp: 49–50°C/2 Torr. GLC purity: >99%. Analysis: found: C, 31.9; H, 3.4; F, 38.0; S, 10.4%. Calculated for $C_8H_{10}F_6SO_3$ (300.22): C, 32.0; H, 3.4; F, 38.0; S, 10.7%. ^{1}H NMR (in $CDCl_3$) δ: 1.85–1.55 ppm (m, 6H); 2.06–1.90 (m, 2H); 4.44 ppm (s, CH_2O). ^{13}C NMR (in $CDCl_3$) δ: 127.8 ppm (q, $^1J_{CF} = 281.1$ Hz, CF_3); 118.6 ppm (q, $^1J_{CF} = 319.4$ Hz, SO_2CF_3); 75.7 ppm (s, CH_2O); 50.7 ppm (q, $^2J_{CF} = 25.3$ Hz, C-1); 30.1 ppm (s, C-2); 25 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 75.0 ppm (s, CF_3); 74.5 (s, SO_2CF_3). MS: 163 [1, $(CH_2OSO_2CF_3)^+$]; 151 [6, $(M - OSO_2CF_3)^+$]; 150 [4, $(M - HOSO_2CF_3)^+$]; 149 [3, $(OSO_2CF_3)^+$]; 135 [15, $(M - HOSO_2CF_3 - CH_3)^+$]; 131 [26, $(M - OSO_2CF_3 - HF)^+$]; 130 [18, $(M - HOSO_2CF_3 - HF)^+$]; 122 [8, $(M - HOSO_2CF_3 - C_2H_4)^+$]; 117 [15, $(M - CH_2OSO_2CF_3 - HF)^+$]; 115 (12); 111 [17, $(M - OSO_2CF_3 - 2HF)^+$]; 109 [11, $(M - HOSO_2CF_3 - 2HF)^+$]; 97 [22, $(M - CH_2OSO_2CF_3 - 2HF)^+$]; 81 (100, HSO_3^+); 69 (52, CF_3^+); 42 (25, $C_3H_6^+$); 41 (40, $C_3H_5^+$).

3.4.3. 1-(Trifluoromethyl)-1-cyclobutylmethyl trifluoromethylsulphonate (**5c**)

Yield: 64% (2.4 g; 8.3 mmol). Bp: 78–80°C/3 Torr. GLC purity: >99%. Analysis: found: C, 29.7; H, 2.9; F, 40.0; S, 9.6%. Calculated for $C_7H_8F_6SO_3$ (286.22): C, 29.4; H, 2.8: F, 39.8; S, 11.2%. ^{1}H NMR (in $CDCl_3$) δ: 2.17–1.98 ppm (m, 2H); 2.49–2.32 ppm (m, 2H); 4.64 ppm (s, CH_2O). ^{13}C NMR (in $CDCl_3$) δ: 126.6 ppm (q, $^1J_{CF} = 279.2$ Hz, CF_3); 118.7 ppm (q, $^1J_{CF} = 319.3$ Hz, SO_2CF_3); 75.1 ppm (s, CH_2O); 44.8 ppm (q, $^2J_{CF} = 28.4$ Hz, C-1); 23.0 ppm (s, C-2); 14.5 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 77.5 ppm (s, CF_3); 75.0 (s, SO_2CF_3). MS: 137 [2, $(M - OSO_2CF_3)^+$]; 136 [29, $(M - HOSO_2CF_3)^+$]; 117 [46, $(M - OSO_2CF_3 - HF)^+$]; 109 [23, $(M - OSO_2CF_3 - C_2H_4)^+$]; 103 [9, $(M - CH_2OSO_2CF_3 - HF)^+$]; 97 [32, $(M - OSO_2CF_3 - 2HF)^+$]; 77 [18, $(M - OSO_2CF_3 - 3HF)^+$]; 69 (53, CF_3^+); 68 (5, $[M - OSO_2CF_3 - CF_3]^+$); 67 [100, $(M - HOSO_2CF_3 - CF_3)^+$]; 41 (13, $C_3H_5^+$).

3.5. 1-Fluoromethyl-1-(trifluoromethyl)cycloalkanes (**6a–c**)

Solutions of triflates **5a–c** (6.7 mmol) in dry ether (5 ml) were added dropwise to a suspension of commercial tetra-*n*-butylammonium fluoride (2.3 g, 8.7 mmol) in dry ether (20 ml) precooled to −15°C and kept under an atmosphere of argon. The reaction mixture was allowed to warm to ambient temperature and stirred for 12 h, after which products were distilled off under atmospheric pressure and redistilled through a 5 cm long Vigreux-type column to afford compounds **6a–c** as volatile liquids. Due to a high volatility, no C and H analyses were determined for compounds **6a–c**.

3.5.1. 1-Fluoromethyl-1-(trifluoromethyl)cyclohexane (**6a**)

Yield: 77% (0.95 g; 5.2 mmol). Bp: 147–148°C. GLC purity: >99%. Analysis: found: F, 41.2%. Calculated for $C_8H_{12}F_4$ (184.15): F, 41.3%. ^{1}H NMR (in $CDCl_3$) δ: 1.80–1.20 ppm (m, 10H); 4.54 ppm (d, $^1J_{HF} = 47.5$ Hz, CH2F). ^{13}C NMR (in $CDCl_3$) δ: 128.4 ppm (q, $^1J_{CF} = 283.4$ Hz, CF_3); 80.9 ppm (d, $^1J_{CF} = 176.7$ Hz, CH_2F); 44.25 ppm (dq, $^2J_{CF} = 16.2$ Hz, $^2J_{CF} = 23.2$ Hz, C-1); 24.6 ppm (s, C-2); 24.9 ppm (s, C-3); 20.6 ppm (s, C-4). ^{19}F NMR (in $CDCl_3$) δ: 77.2 ppm (d, $^4J_{HF} = 9.5$ Hz, CF_3); 232.2 ppm (t, oct, $^2J_{HF} = 47.5$ Hz, $^4J_{HF} = 4.8$ Hz, CH_2F). MS: 184 (4, $M^{+\bullet}$); 151 [17, $(M - CH_2F)^+$]; 145 [7, $(M - HF_2)^+$]; 132 [6, $(M - CH_2F - F)^+$]; 131 [66, $(M - CH_2F - HF)^+$]; 125 [6, $(M - 2HF - F)^+$]; 115 [100, $(M - CF_3)^+$]; 111 [37, $(M - CH_2F - 2HF)^+$]; 109 [12, $(M - CH_2F - C_2H_4 - HF)^+$]; 95 [96, $(M - CF_3 - HF)^+$]; 69 (6, CF_3^+); 56 (31, $C_4H_8^+$); 55 (28, $C_4H_7^+$); 42 (13, $C_3H_6^+$); 41 (74, $C_3H_5^+$); 39 (37, $C_3H_3^+$); 33 (7, CH_2F^+).

3.5.2. 1-Fluoromethyl-1-(trifluoromethyl)cyclopentane (**6b**)

Yield: 66% (0.42 g; 2.29 mmol). Bp: 91–92°C. GLC purity: >96%. Analysis: found: F, 44.5%. Calculated for $C_7H_{10}F_4$ (170.15): F, 44.7%. ^{1}H NMR (in $CDCl_3$) δ: 1.95–1.54 ppm (m, 8H); 4.35 ppm (d, $^2J_{HF} = 47.5$ Hz, CH_2F). ^{13}C NMR (in $CDCl_3$) δ: 128.5 ppm (q, $^1J_{CF} = 280.8$ Hz, CF_3); 83.4 ppm (d, $^1J_{CF} = 177.8$ Hz, CH_2F); 52.3 ppm (dq, $^2J_{CF} = 16.9$ Hz, $^2J_{CF} = 24.2$ Hz, C-1); 29.3 ppm (s, C-2); 25.9 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 74.5 ppm (d, $^4J_{HF} = 7.6$ Hz, CF_3); 223.2 ppm (tq, $^2J_{HF} = 47.5$ Hz, $^4J_{HF} = 10.7$ Hz, CH_2F). MS: 169 [1, $(M - H)^+$]; 155 [2, $(M - CH_3)^+$]; 151 [4, $(M - F)^+$]; 150 [1, $(M - HF)^+$]; 142 [4, $(M - C_2H_4)^+$]; 137 [3, $(M - CH_2F)^+$]; 135 [3, $(M - CH_3 - HF)^+$]; 131 [6, $(M - HF - F)^+$]; 130 [5, $(M - 2HF)^+$]; 122 [3, $(M - C_2H_4 - HF)^+$]; 117 [27, $(M - CH_2F - HF)^+$]; 111 [9, $(M - 2HF - F)^+$]; 109 [7, $(M - CH_2F - C_2H_4)^+$]; 103 (2); 101 [16, $(M - CF_3)^+$]; 97 [21, $(M - CH_2F - 2HF)^+$]; 95 (5); 91 [4, $(M - CF_3 - HF)^+$]; 73 [10, $(M - CF_3 - C_2H_4)^+$]; 69 (8, CF_3^+); 67 (11); 57 (6, $C_4H_9^+$); 55 (6, $C_4H_7^+$); 45 (14, $C_3H_9^+$); 43 (5, $C_3H_7^+$); 42 (100, $C_3H_6^+$); 41 (37, $C_3H_5^+$); 40 (8, $C_3H_4^+$); 39 (38, $C_3H_3^+$); 33 (8, CH_2F^+).

3.5.3. 1-Fluoromethyl-1-(trifluoromethyl)cyclobutane (**6c**)

Yield: 54% (0.25 g; 1.6 mmol). Bp: 76–78°C. GLC purity: >98%. Analysis: found: F, 41.1% (an error caused by the volatility of **8a**). Calculated for $C_6H_8F_4$ (142.08): F, 48.7%. ^{1}H NMR (in $CDCl_3$) δ: 2.15–1.90 ppm (m, 2H); 2.43–2.18 ppm (m, 4H); 4.53 ppm (d, $^2J_{HF} = 47.4$ Hz, CH_2F). ^{13}C NMR (in $CDCl_3$) δ: 127.9 ppm (q, $^1J_{CF} = 279.2$ Hz, CF_3); 82.5 ppm (d, $^1J_{CF} = 175.6$ Hz, CH_2F); 45.4 ppm (dq, $^2J_{CF} = 18.8$ Hz, $^2J_{CF} = 27.7$ Hz, C-1); 22.3 ppm (s, C-2); 14.6 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 77.4 (d, $^4J_{HF} = 6.4$ Hz, CF_3); 228.8 ppm (td, $^2J_{HF} = 47.2$ Hz, $^4J_{HF} = 2.9$ Hz, CH_2F). MS: 156 (2, $M^{+\bullet}$); 141 [1, $(M - CH_3)^+$]; 136 [7, $(M - HF)^+$]; 128 [6, $(M - C_2H_4)^+$]; 123 [27, $(M - CH_2F)^+$]; 121 [5, $(M - CH_3 - HF)^+$]; 117 [11, $(M - HF_2)^+$]; 115 [6, $(M - 2HF - H)^+$]; 109 [20, $(M - C_2H_4 - F)^+$]; 108 [8, $(M - C_2H_4 - HF)^+$]; 103 [32, $(M - CH_2F - HF)^+$]; 97 [30, $(M - 2HF - F)^+$]; 90 (97); 89 (22); 87 [33, $(M - CF_3)^+$]; 83 [21, $(M - CH_2F - 2HF)^+$]; 77 [79, $(M - CF_3 - HF)^+$]; 69 (28, CF_3^+); 67 [29, $(M - CF_3 - HF)^+$]; 59 (88, $[M - CF_3 - C_2H_4]^+$); 57 (23, $C_4H_9^+$); 55 (6, $C_4H_7^+$); 47 (100); 45 (13, $C_3H_9^+$); 43 (7, $C_3H_7^+$); 42 (32, $C_3H_6^+$); 41 (45, $C_3H_5^+$); 40 (9, $C_3H_4^+$); 39 (71, $C_3H_3^+$); 33 (22, CH_2F^+).

3.6. 1-Formyl-1-(trifluoromethyl)cycloalkanes (**7a–c**)

Methylene chloride (100 ml), pyridine (37.2 g, 0.47 mol) and CrO_3 (23.6 g, 0.24 mol) were stirred together for 1 h until a deep-orange coloured slurry was formed. 1-Hydroxymethyl-1-(trifluoromethyl)cycloalkane **2a–c** (34 mol) was added and the reaction mixture was stirred at ambient temperature for 48 h, then filtered through a silica-gel (10 cm) layer and the filtrate was washed with 10% hydrochloric acid (2 × 100 ml) followed by water (100 ml). The organic layer was dried over anhydrous $MgSO_4$ and distilled under vacuum or under atmospheric pressure of nitrogen. Due to a high volatility, no C and H were determined for compounds **7a–c**.

3.6.1. 1-Formyl-1-(trifluoromethyl)cyclohexane (**7a**)

Yield: 72% (4.4 g; 24.5 mmol). Bp: 98°C/33 mm Hg. GLC purity: >98%. IR (neat): δ: 1739.0 cm^{-1} (νs, CHO). Analysis: found: F, 31.6%. Calculated for $C_8H_{11}F_3O$ (180.08): F, 31.3%. ^{1}H NMR (in $CDCl_3$) δ: 1.40–1.18 ppm (m, 4H); 1.94–1.50 ppm (m, 6H); 9.62 ppm (s, 1H, CHO). ^{13}C NMR (in $CDCl_3$) δ: 198.3 ppm (q, $^3J_{CF} = 2.7$ Hz, CHO); 126.0 ppm (q, $^1J_{CF} = 283.6$ Hz, CF_3); 54.8 ppm (q, $^2J_{CF} = 22.6$ Hz, C-1); 24.8 ppm (s, C-2); 24.6 ppm (s, C-3); 21.3 ppm (s, C-4). ^{19}F NMR (in $CDCl_3$) δ: 73.6 ppm (s, CF_3). MS: 181 [1, $(M^+H)^+$]; 180 (0.5, $M^{+\bullet}$); 179 [2, $(M - H)^+$]; 178 [6, $(M - 2H)^+$]; 160 [4, $(M - HF)^+$]; 151 [3, $(M - CHO)^+$]; 141 [26, $(M - HF_2)^+$]; 132 [21, $(M - CO - HF)^+$]; 131 [23, $(M - COH - HF)^+$]; 121 [26, $(M - 2HF - F)^+$]; 111 [16, $(M - CO - 2HF)^+$]; 101 (40); 99 (18); 92 [24, $(M - C_2H_4)^+$]; 91 (43); 81 (36);

69 (6, CF_3^+); 55 (20, $C_4H_7^+$); 41 (48, $C_3H_5^+$); 39 (25, $C_3H_3^+$).

*3.6.2. 1-Formyl-1-(trifluoromethyl)cyclopentane (**7b**)*

Yield: 66% (1.1 g; 6.8 mmol). Bp: 127–128°C. GLC purity: >98%. IR (neat): $\nu = 1738.4\ cm^{-1}$ (νs, CHO). Analysis: found: F, 34.5%. Calculated for $C_7H_9F_3O$ (166.14): F, 34.3%. ^1H NMR (in $CDCl_3$) δ: 2.40–1.55 ppm (m, 8H); 9.70 ppm (s, 1H, CHO); ^{13}C NMR (in $CDCl_3$) δ: 195.8 ppm (q, $^3J_{CF} = 2.7$ Hz, CHO); 127.1 ppm (q, $^1J_{CF} = 280.8$ Hz, CF_3); 62.5 ppm (q, $^2J_{CF} = 23.8$ Hz, C-1); 28.5 ppm (s, C-2); 25.9 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 71.4 ppm (s, CF_3). MS: 167 [2, $(M^+H)^+$]; 166 (51, $M^{+\bullet}$); 165 [4, $(M-H)^+$]; 148 [8, $(M^+H_2O)^+$]; 146 [9, $(M-HF)^+$]; 127 [4, $(M-HF_2)^+$]; 126 [12, $(M-2HF)^+$]; 125 [100, $(M-H-2HF)^+$]; 118 [21, $(M-CO-HF)^+$]; 117 [33, $M-CHO-HF^+$]; 115 (10); 105 (45); 98 [20, $(M-CO-2HF)^+$]; 85 (57); 79 (13); 77 (43); 69 (12, CF_3^+); 67 (79); 43 (18, $C_3H_7^+$); 42 (86, $C_3H_6^+$); 41 (63, $C_3H_5^+$); 40 (11, $C_3H_4^+$); 39 (51, $C_3H_3^+$).

*3.6.3. 1-Formyl-1-(trifluoromethyl)cyclobutane (**7c**)*

Yield: 43% (1.4 g; 9.2 mmol). Bp: 96–98°C. GLC purity: >98%. IR (neat): $\nu = 1733.1\ cm^{-1}$ (νs, CHO). Analysis: found: F, 37.1%. Calculated for $C_6H_7F_3O$ (152.14): F, 37.5%. ^1H NMR (in $CDCl_3$) δ: 2.19–1.88 ppm (m, 4H); 2.53–2.28 ppm (m, 2H); 9.77 ppm (s, 1H, CHO). ^{13}C NMR (in $CDCl_3$) δ: 194.7 ppm (q, $^3J_{CF} = 3.1$ Hz, CHO); 126.1 ppm (q, $^1J_{CF} = 279.1$ Hz, CF_3); 54.8 ppm (q, $^2J_{CF} = 26.6$ Hz, C-1); 22.2 ppm (s, C-2); 14.7 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 74.6 ppm (s, CF_3). MS: 153 (1, $[M^+H]^+$); 152 (5, $M^{+\bullet}$); 151 [4, $(M-H)^+$]; 137 (4); 132 [11, $(M-HF)^+$]; 124 [6, $(M-CO)^+$]; 123 [58, $(M-CHO)^+$]; 112 [28, $(M-2HF)^+$]; 105 [17, $(M-CO-F)^+$]; 104 [53, $(M-CO-HF)^+$]; 103 [84, $(M-CHO-HF)^+$]; 95 (22); 86 (10); 85 [21, $(M-CO-HF_2)^+$]; 84 [98, $(M-CO-2HF)^+$]; 83 [100, $(M-CHO-2HF)^+$]; 77 (61); 76 (41); 75 (28); 69 (28, CF_3^+); 59 (32); 55 (35); 53 (30); 51 (23); 49 (44); 43 (23, $C_3H_7^+$); 41 (40, $C_3H_5^+$); 40 (31, $C_3H_4^+$); 39 (45, $C_3H_3^+$).

*3.7. 1-Difluoromethyl-1-(trifluoromethyl)cycloalkanes (**8a–b**)*

1-Formyl-1-(trifluoromethyl)cycloalkane **7a** or 7**b** (9 mmol) was placed in a 30 ml capacity stainless steel autoclave fitted with a needle valve, the autoclave was cooled in an acetone-dry ice bath, evacuated, then sulphur tetrafluoride (4.3 g, 40 mmol) was condensed into it. The autoclave was mechanically agitated and heated at 30°C for 48 h. After completion of the reaction, gaseous products were let off (excess SF_4, SOF_2, HF), and the residue was distilled under atmospheric pressure (some amount of NaF was added to bind free HF). Redistillation afforded compounds **8a** and **b** as volatile liquids. Due to high volatility, no C and H analyses were determined.

*3.7.1. 1-Difluoromethyl-1-(trifluoromethyl)cyclohexane (**8a**)*

Yield: 61% (1.1 g, 5.4 mmol). Bp: 136–138°C. GLC purity: >99%. Analysis: found: F, 46.1%. Calculated for $C_8H_{11}F_5$ (188.14): F, 47.0%. ^1H NMR (in $CDCl_3$) δ: 1.92–1.40 ppm (m, 10H); 5.86 ppm (t, $^2J_{HF} = 54.9$ Hz, 1H). ^{13}C NMR (in $CDCl_3$) δ: 127.7 ppm (qt, $^1J_{CF} = 283.8$ Hz, $^4J_{CF} = 3.6$ Hz, CF_3); 116.0 ppm (tq, $^1J_{CF} = 248.5$ Hz, $^4J_{CF} = 2.6$ Hz, CHF_2); 46.9 ppm (qt, $^2J_{CF} = 18.3$ Hz, $^2J_{CF} = 22.7$ Hz, C-1); 24.6 ppm (s, C-2); 24.0 ppm (s, C-3); 20.8 ppm (s, C-4). ^{19}F NMR (in $CDCl_3$) δ: 71.8 ppm (t, $^4J_{FF} = 9.6$ Hz, CF_3); 127.8 ppm (dq, $^2J_{HF} = 54.7$ Hz, $^4J_{FF} = 9.5$ Hz, CHF_2). MS: 202 (6, $M^{+\bullet}\cdot$); 182 [14, $(M-HF)^+$]; 163 [16, $(M-HF_2)^+$]; 162 [11, $(M-2HF)^+$]; 151 [65, $(M-CHF_2)^+$]; 150 [7, $(M-CHF_2-H)^+$]; 149 (17); 131 [100, $(M-CHF_2-HF)^+$]; 113 (20, $M-CF_3-HF^+$); 111 [55, $(M-CHF_2-2HF)^+$]; 93 [18, $(M-CF_3-2HF)^+$]; 91 (21); 77 (33); 69 (11, CF_3^+); 67 (22); 65 (11); 59 (18); 56 (43); 55 (32); 51 (21, CHF_2^+); 47 (11, $C_3H_7^+$); 42 (17, $C_3H_6^+$); 41 (89, $C_3H_5^+$); 40 (7, $C_3H_4^+$); 39 (47, $C_3H_3^+$).

*3.7.2. 1-Difluoromethyl-1-(trifluoromethyl)cyclopentane (**8b**)*

Yield: 52% (0.58 g, 3.1 mmol). Bp: 91–92°C. GLC purity: >99%. Analysis: found: F, 50.1%. Calculated for C7H9F5 (188.14): F, 50.5%. ^1H NMR (in $CDCl_3$) δ: 2.05–1.60 ppm (m, 8H); 5.89 ppm (t, $^2J_{HF} = 55.8$ Hz, 1H). ^{13}C NMR (in $CDCl_3$) δ: 127.4 ppm (qt, $^1J_{CF} = 280.8$ Hz, $^4J_{CF} = 5.8$ Hz, CF_3); 115.2 ppm (tq, $^1J_{CF} = 245.4$ Hz, $^4J_{CF} = 3.2$ Hz, CHF_2); 55.4 ppm (qt, $^2J_{CF} = 20.4$ Hz, $^2J_{CF} = 24.1$ Hz, C-1); 28.0 ppm (s, C-2); 26.5 ppm (s, C-3). ^{19}F NMR (in $CDCl_3$) δ: 73.2 ppm (t, $^4J_{FF} = 7.7$ Hz, CF_3); 126.9 ppm (dq, $^2J_{FF} = 55.8$ Hz, $^4J_{FF} = 7.7$ Hz, CHF_2). MS: 169 [1, $(M-F)^+$]; 168 [3, $(M-HF)^+$]; 167 [3, $(M-H_2F)^+$]; 149 [15, $(M-HF_2)^+$]; 148 [3, $(M-2HF)^+$); 140 [4, $(M-HF-C_2H_4)^+$]; 137 [6, $(M-CHF_2)^+$]; 135 (9); 129 [6, $(M-2HF-F)^+$]; 127 [11, $(M-3HF-H)^+$]; 117 [52, $(M-CHF_2-2HF)^+$]; 99 [29, $(M-CF_3-HF)^+$]; 97 [36, $(M-CHF_2-2HF)^+$]; 79 [19, $(M-CF_3-2HF)^+$]; 77 (26); 69 (12, CF_3^+); 51 (25, CHF_2^+); 42 (100, $C_3H_6^+$); 41 (43, $C_3H_5^+$); 40 (10, $C_3H_4^+$); 39 (47, $C_3H_3^+$).

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