Transformation of Carbonyl Compounds into *gem*-Difluoro Compounds with Dibromodifluoromethane/Zinc Reagent

Chang-Ming Hu,* Feng-Ling Qing and Cun-Xi Shen
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

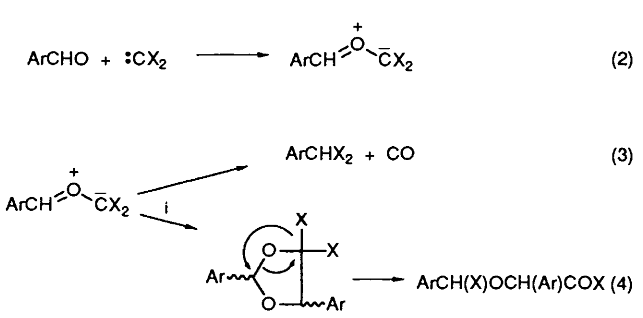
Reaction of carbonyl compounds with dibromodifluoromethane/zinc gives the *gem*-difluoro compounds (12 examples). It seems to be that the reaction involves the generation of difluorocarbene by reaction of dibromodifluoromethane with zinc, followed by production of the difluorocarbonyl ylide. Such an ylide then breaks down the corresponding CF_2 moiety.

The preparation of compounds containing *gem*-difluoro groups has been of interest to both physical chemists and biochemists, since the *gem*-difluoro group has a steric profile similar to that of the methylene group but has a very different polarity and a drastically altered reactivity.[1] Thus CF_2 could be regarded as an isopolar and isosteric replacement of oxygen.[2] This has led to the development of a few general, but somewhat limited, methods for its construction. The most widely used method is the general transformation of a carbonyl group into the CF_2 moiety by using certain metal fluorides (*e.g.*, MoF_6,[3] SF_4[4]), and in particular SF_4[5] and its most important derivative (diethylamino)sulfur trifluoride (DAST).[6] These methods, although quite popular, necessitate quite severe reaction conditions and are very expensive. It has spurred the development of methods employing a range of carbonyl-group derivatives, the reaction of hydrazones (with halogen monofluorides[7] or fluorine[8]), diazo compounds (with fluorine[9]), 1,3-dithiolanes (with bromine fluoride generated *in situ*,[10] or *p*-iodotoluene difluoride[11]), and *gem*-dihalogeno compounds (with silver tetrafluoroborate[12]) are representative of this latter class.

The reaction of dibromodifluoromethane and zinc has been well studied. For example, Dolbier has demonstrated that dibromodifluoromethane/zinc is a useful system for the synthesis of most difluorocyclopropane compounds.[13] In 1985, a remarkably simple preparation of (trifluoromethyl)zinc reagent *via* reaction of dibromodifluoromethane with zinc powder in dry dimethylformamide (DMF) was reported by Burton.[14] To the best of our knowledge, however, the reaction of carbonyl compounds with dibromodifluoromethane and zinc has not been studied. In this paper we describe the reaction of aldehydes or ketones with dibromodifluoromethane and zinc to form the corresponding *gem*-difluoro compounds.

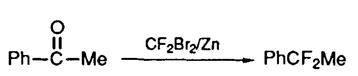
Results and Discussion

Landgrebe's work[15] has provided a body of evidence that the thermal decomposition of phenyl(trihalogenomethyl)mercury species ($PhHgCX_3$, X = Cl, Br) involves initial generation of dihalogenocarbene [equation (1)], followed by the production of dihalogenocarbonyl ylide [equation (2)]; the latter intermediate undergoes either a unimolecular decomposition to dihalide and carbon monoxide [equation (3)] or a bimolecular reaction with starting aldehyde, which culminates in the formation of acid halide [equation (4)] (Scheme 1).



Scheme 1 *Reagent:* i, ArCHO

In the light of this work, we reasoned that difluorocarbene could be used to achieve the conversion of carbonyl compounds into *gem*-difluoro compounds *via* a sequence similar to Scheme 1, involving formation of difluorocarbonyl ylide, followed by unimolecular decomposition to *gem*-difluoro compounds. The results from our initial studies, focussing on the reaction of acetophenone with dibromodifluoromethane/zinc in different solvents are set out in Table 1 and reveal that dibromodifluoromethane/zinc is an effective system for transformation of acetophenone into 1,1-difluoro-1-phenylethane **1** [equation (5)].



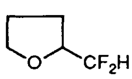
$$\mathrm{Ph{-}\overset{\overset{\large O}{\|}}{C}{-}Me} \xrightarrow{CF_2Br_2/Zn} \mathrm{PhCF_2Me} \qquad (5)$$

1

Table 1 shows that diethyl ether was the best solvent, and that 1,1-difluoro-1-phenylethane **1** was formed in higher yield when acetophenone was used as both reactant and solvent. When the reaction was carried out in dry diethyl ether, tetrahydrofuran (THF), or 1,4-dioxane, compound **2**, **3**, or **4** was always isolated as a by-product, respectively. Compounds **3** and **4** were unstable at room temperature and were slowly converted into a tarry substance. Lewis acids (*e.g.*, $AlCl_3$) could accelerate the decomposition of compounds **3** and **4**. However, with Lewis bases (*e.g.*, Et_3N) compounds **3** and **4** were stable even for two months at room temperature. It should be noted that dibromodifluoromethane was mostly converted into tetrafluoroethene when the reaction was carried out in dry diglyme.

$Et_2OCH(CF_2H)Me$

2



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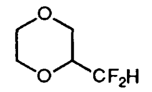


4

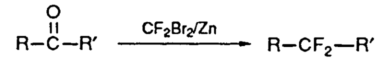
The results of treating a variety of aldehydes and ketones with dibromodifluoromethane/zinc are summarized in Table 2. The yield of the *gem*-difluoro compounds for aliphatic ketones is higher than for aromatic aldehydes (Table 2). Reaction of aliphatic aldehydes with dibromodifluoromethane/zinc gave a brown tar, which did not contain fluorine as detected by ^{19}F

Table 1 Reaction of acetophenone with dibromodifluoromethane/zinc in different solvents[a]

Entry	Solvent	Distribution of fluoro-containing products (%)[b]			
1	Diglyme			CF_2=CF_2 (80)	CF_2BrH (20)
2	Diethyl ether	**1** (40)	**2** (30)	CF_2=CF_2 (20)	CF_2BrH (10)
3	Tetrahydrofuran	**1** (20)	**3** (60)	CF_2=CF_2 (15)	CF_2BrH (5)
4	1,4-Dioxane	**1** (15)	**4** (45)	CF_2=CF_2 (20)	CF_2BrH (20)
5		**1** (60)		CF_2=CF_2 (25)	CF_2BrH (15)

[a] The mole proportions of PhCOMe:CF_2Br_2:Zn are 1:2:2 in entries 1–4. [b] Determinated by ^{19}F NMR spectroscopy.

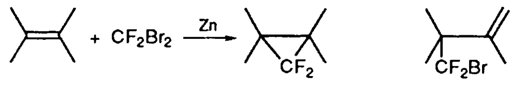
Table 2 Transformation of carbonyl compounds into *gem*-difluoro compounds with dibromodifluoromethane/zinc[a]



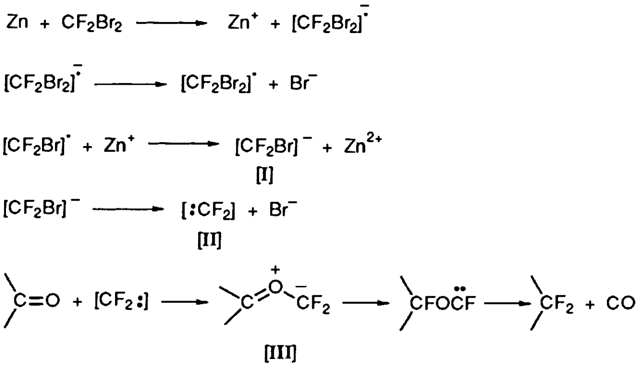
$$R-\overset{O}{\overset{\|}{C}}-R' \xrightarrow{CF_2Br_2/Zn} R-CF_2-R'$$

Entry	R	R′	Solvent	Isolated yield (%)
1	Ph	H	Et_2O	15[b]
2	*p*-MeC_6H_4	H	Et_2O	27[b]
3	*p*-$MeOC_6H_4$	H	Et_2O	34[b]
4	Me	Me		42
5	Me	Et		58
6	Me	Pr^i		56
7	Me	$[CH_2]_4Me$		60
8	Me	Bu^t		48
9	Pr^i	Pr^i		50
10	Et	Et		45

[a] Yield based on initial CF_2Br_2 except for entries 1–3, which are based on initial RCOR′. [b] By-product $EtOCH(CF_2H)Me$ was obtained.



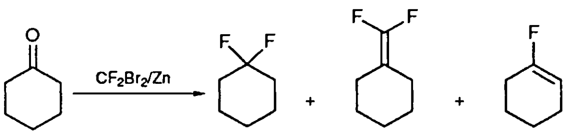
8 **9** (7)



Scheme 2

NMR spectroscopy. The reaction can be conveniently carried out in glassware. Furthermore, dibromodifluoromethane is cheap, readily available, and the method does not require drastic reaction conditions.

In the reaction of cyclohexanone with dibromodifluoromethane/zinc three compounds, **5**, **6** and **7**, were formed in the approximate molar proportions 7:1:2 [equation (6)].



5 **6** **7** (6)

In view of this successful transformation with dibromodifluoromethane, it was decided to explore the scope of the reaction with respect to the use of other difluorodihalogenomethanes. The results of these experiments are presented in Table 3, and it can be seen that bromochlorodifluoromethane reacted in the same way as did dibromodifluoromethane.

The following mechanism (Scheme 2), analogous to that proposed by Burton for a similar reaction with DMF, is suggested for such a carbonyl-into-*gem*-difluoro transformation. Electron transfer between zinc and dibromodifluoromethane produces a radical anion. A second electron transfer produces Zn and difluorobromomethide ion [I], which subsequently eliminates bromide ion to give difluorocarbene [II]. Evidence consistent with such formation was as follows: when CF_2Br_2, Zn and *p*-nitrobenzaldehyde in dry diethyl ether were mixed, neither *p*-$NO_2C_6H_4CF_2H$ nor $EtOCH(CF_2H)Me$ was detected and dibromodifluoromethane was recovered. When the reaction of CF_2Br_2, Zn and 2,3-dimethylbut-2-ene was carried out, a 25% yield of 1,1-difluoro-2,2,3,3-tetramethylcyclopropane **8** was isolated [equation (7)]. Subsequent capture of difluorocarbene by a carbonyl forms difluorocarbonyl ylide [II], which can break down to the corresponding CF_2 moiety and CO. The IR spectrum of the exit gas from the reaction mixture was identical with that of carbon monoxide. $EtOCH(CF_2H)Me$ was considered as result from difluorocarbene insertion into EtOEt.

In conclusion, we present a direct route for the transformation of carbonyl compounds into *gem*-difluoro compounds with dibromodifluoromethane/zinc. It appears that the reaction involves generation of difluorocarbene, followed by production of difluorocarbonyl ylide, which can break down the corresponding CF_2 moiety.

Experimental

B.p.s are uncorrected. IR spectra were recorded with a Perkin-Elmer 983 spectrometer. ^1H NMR spectra (60 MHz) were recorded with a Varian EM-360A instrument. $SiMe_4$ served as

Table 3 Reaction of ketones with difluorodihalogenomethanes/zinc

Entry	Ketone	Difluorodihalogenomethanes	Yield of *gem*-difluoro compound
1	acetophenone	CF_2Br_2	35
2	acetophenone	CF_2BrCl	28
3	cyclohexanone	CF_2Br_2	25
4	cyclohexanone	CF_2BrCl	32

an internal standard. ^{19}F NMR spectra (56.4 MHz) were recorded with a Varian FM-360L instrument. $CFCl_3$ served as an external standard; chemical shifts (in ppm) are negative in sign for upfield shifts. *J*-values are in Hz. Mass spectra were recorded with a Finnigan GC-MS-4021 spectrometer. Product mixtures were separated by Shanghai Analytical Factory Model 102 Gas-Liquid Chromotography with a column packed with 15% oxaper fluoroalkylene–triazine polymer.

All glassware and syringe needles were flame-dried under vacuum and cooled under dry nitrogen. Diethyl ether, 1,4-dioxane and THF were distilled from sodium benzophenone ketyl under an inert atmosphere. Diglyme was dried over potassium hydroxide at reflux overnight, distilled, and stored over 4 Å molecular sieves. All liquid aldehydes and ketones were dried over $CaSO_4$ and distilled (under N_2) before use. Zinc dust was activated by treatment with 2 mol dm^{-3} HCl, followed by washing with water and was then dried *in vacuo*. Light petroleum refers to the fraction boiling in the range 60–90 °C.

Conversion of Acetophenone into 1,1-*Difluoro*-1-*phenylethane* **1** *in Different Solvents.*—(a) *In diethyl ether. General procedure A*: A three-necked, 100 cm^3 round-bottom flask equipped with dropping funnel, magnetic stirring bar, and solid-CO_2 condenser under N_2 was charged with dry diethyl ether (30 cm^3), activated zinc dust (1.7 g, 25 mmol), and acetophenone (1.8 g, 15 mmol). CF_2Br_2 (5.4 g, 25 mmol) was added dropwise to the mixture at such a rate that the reaction temperature did not exceed 20 °C. The solution gradually turned brown; the reaction mixture was stirred for a further 2 h at reflux, and then water (30 cm^3) was added. The separated ethereal layer was washed with brine and dried (Na_2SO_4). After evaporation of solvent, the residue was chromatographed on silica gel [light petroleum–AcOEt (50:1)] to give $PhCF_2Me$ (0.7 g, 30%). The above collected solvent was fractionally distilled to give a liquid boiling at 38–41 °C; $EtOCH(CF_2H)Me$ **2** was obtained by semi-preparative GLC.

1,1-*Difluoro*-1-*phenylethane*.[6] B.p. 54–57 °C/30 mmHg; δ_F ($CDCl_3$) −86.8 (q, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 2.25 (3 H t, CF_2Me), 7.25–7.40 (3 H, m) and 7.75 (2 H, m); *m*/*z* (rel. intensity) 51 (32.7%), 77 (31.9), 127 (100) and 142 (40.1).

$EtOCH(CF_2H)Me$ **2**. δ_F($CDCl_3$) −84.4 (d, J_{HF} 75.2, CF_2); δ_H($CDCl_3$) 0.85 (6 H, m, 2 × Me), 3.55 (2 H, m, CH_2), 3.78 (1 H, m, CH) and 6.35 (1 H, t, J_{HF} 75.2, CF_2H); *m*/*z* (rel. intensity) 45 (82.0%), 51 (20.0), 59 (100) and 125 (31.0) (Found: C, 48.3; H, 8.0; F, 31.05. $C_5H_{10}F_2O$ requires C, 48.39; H, 8.06; F, 30.65%).

(b) *In THF*. Procedure A was followed except that water (60 cm^3) was added to the reaction mixture. The lower layer was separated, washed with water repeatedly, and dried over anhydrous sodium sulfate. Distillation at ambient pressure with controlled oil-bath temperature below 120 °C gave compound **3**, which was cooled immediately with solid CO_2; analysis by GLC indicated a purity of 96%. The residue was chromatographed on silica gel to give $PhCF_2Me$ **1**.

2-*Difluoromethyltetrahydrofuran* **3**. B.p. 97–99 °C; δ_F($CDCl_3$) −83.8 (d, J_{HF} 75.2, CF_2H); δ_H($CDCl_3$) 2.00 (4 H, m, 2 × CH_2), 3.60 (2 H, m, CH_2), 4.15 (1 H, m, CH) and 6.36 (1 H, t, J_{HF} 75.0, CF_2H); *m*/*z* (rel. intensity) 41 (35.9%), 51 (57.0), 55 (100) and 123 (20.7) (Found: C, 49.1; H, 6.5; F, 31.05. $C_5H_8F_2O$ requires C, 49.18; H, 6.56; F, 31.15%).

(c) *In* 1,4-*dioxane*. By following the procedure as in method (b) but in 1,4-dioxane, by-product **4** was obtained.

2-*Difluoromethyl*-1,4-*dioxane* **4**. B.p. 65–67 °C/20 mmHg; δ_F($CDCl_3$) −83.8 (d, J_{HF} 75.2, CF_2H); δ_H($CDCl_3$) 3.63–3.96 (7 H, m) and 6.40 (1 H, t, J_{HF} 75.0, CF_2H); *m*/*z* (rel. intensity) 51 (100%), 87 (12.1) and 139 (30.3) (Found: C, 43.45; H, 5.7; F, 27.6. $C_5H_8F_2O_2$ requires C, 43.48; H, 5.79; F, 27.54%).

(*Difluoromethyl*)*benzene*.[6] By following procedure A, benzaldehyde (2.2 g, 20 mmol) gave a clear liquid product (0.38 g), b.p. 131–134 °C; δ_F($CDCl_3$) −109.5 (d, J_{HF} 56.4, CF_2H); δ_H($CDCl_3$) 6.55 (1 H, t, J_{HF} 56.4, CF_2H) and 7.22–7.85 (5 H, m); *m*/*z* (rel. intensity) 51 (56.4%), 77 (21.2), 127 (100) and 128 (26.7).

1-(*Difluoromethyl*)-4-*methylbenzene*.[16] By following procedure A, *p*-tolualdehyde (2.4 g, 20 mmol) gave a product (0.76 g), b.p. 52–55 °C/30 mmHg; δ_F($CDCl_3$) −110.3 (d, J_{HF} 56.4, CF_2H); δ_H($CDCl_3$) 2.35 (3 H, s, Me), 6.75 (1 H, t, J_{HF} 56.4, CF_2H), 6.85 (2 H, m) and 7.55 (2 H, m); *m*/*z* (rel. intensity) 51 (11.0%), 91 (100), 127 (20.3), 141 (10.9) and 142 (36.0).

1-(*Difluoromethyl*)-4-*methoxybenzene*. By following procedure A, *p*-anisaldehyde (2.8 g, 20 mmol) gave a product (1.1 g), which was unstable and converted gradually into a black tar at room temperature, b.p. 82–85 °C/20 mmHg; δ_F($CDCl_3$) −107.8 (d, J_{HF} 56.4, CF_2H); δ_H($CDCl_3$) 3.85 (3 H, s, OMe), 6.65 (1 H, t, J_{HF} 56.4, CF_2H), 6.92 (2 H, m) and 7.65 (2 H, m); *m*/*z* (rel. intensity) 51 (81.3%), 127 (15.2), 157 (100), 158 (47.2) and 159 (37.8) (Found: C, 60.5; H, 5.1; F, 24.15. $C_8H_8F_2O$ requires C, 60.76; H, 5.06; F, 24.05%).

Conversion of Aliphatic Ketones into the Corresponding gem-*Difluoro Compounds. General procedure B*. A three-necked, 100 cm^3 round-bottom flask equipped with a dropping funnel, magnetic stirring bar, and solid-CO_2 condenser under N_2 was charged with dry aliphatic ketone (30 cm^3) activated zinc (3.6 g, 30 mmol), and CF_2Br_2 (5.4 g, 25 mmol) was added dropwise to the mixture, at such a rate that the reaction mixture's temperature did not exceed 30 °C; the solution gradually turned brown. The reaction mixture was stirred for a further 3 h at 35 °C, then the crude mixture was distilled at room temperature at ~10–70 mmHg and the distillate was trapped at −78 °C. Subsequent purification was by fractional distillation or GLC.

2,2-*Difluoropropane*.[17] By following procedure B, $MeCF_2Me$ was obtained from acetone; δ_F($CDCl_3$) −86.5 (hept, J_{HF} 18.8, CF_2); δ_H($CDCL_3$) 1.58 (t, J_{HF} 18.8); *m*/*z* (rel. intensity) 48 (18.5%), 52 (30.5) and 65 (100).

2,2-*Difluorobutane*.[18] By following procedure B, $MeCF_2Et$ was obtained from butan-2-one, b.p. 29–33 °C; δ_F($CDCl_3$) −94.1 (hex, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 0.93 (3 H, t, CH_2*Me*) and 1.53–1.85 (5 H, m $MeCF_2CH_2$); *m*/*z* (rel. intensity) 66 (100%), 74 (49.2) and 79 (13.2).

2,2-*Difluoro*-3-*methylbutane*.[19] By following procedure B, $MeCF_2$ was obtained from 3-methylbutan-2-one, b.p. 61–65 °C; δ_F($CDCl_3$) −98.5 (q, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 1.05 (6 H, d CH*Me*$_2$) and 1.85–2.05 (4 H, m $MeCF_2CH$); *m*/*z* (rel. intensity) 43 (100%), 58 (33.9) and 88 (22.8).

2,2-*Difluoroheptane*.[20] By following procedure B, $MeCF_2$-$[CH_2]_4Me$ was obtained from heptan-2-one, b.p. 109–113 °C; δ_F($CDCl_3$) −91.8 (hex, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 0.85 (3 H, t, $MeCH_2$), 1.28 (6 H, m, 3 × CH_2) and 1.68–2.03 (5 H, m, $MeCF_2CH_2$); *m*/*z* (rel. intensity) 43 (86.9%), 73 (100) and 116 (17.9).

2,2-*Difluoro*-3,3-*dimethylbutane*.[21] By following procedure B, $MeCF_2Bu^t$ was obtained from 3,3-dimethylbutan-2-one; δ_F($CDCl_3$) −102.1 (q, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 1.02 (9 H, s, Bu^t) and 1.65 (3 H, t, $MeCF_2$); *m*/*z* (rel. intensity) 87 (100%), 102 (54.5) and 122 (6.8).

3,3-*Difluoro*-2,4-*dimethylpentane*. By following procedure B, $Pr^iCF_2Pr^i$ was obtained from 2,4-dimethylpentan-3-one, b.p. 75–77 °C; δ_F($CDCl_3$) −120.1 (t, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 1.05 (12 H, d, 4 × Me) and 2.25 (2 H, m, 2 × CF_2CH); *m*/*z* (rel. intensity) 43 (62.4%), 73 (58.1), 101 (100), 116 (41.9) and 136 (4.9) (Found: C, 61.6; H, 10.2; F, 30.0. $C_7H_{14}F_2$ requires C, 61.76; H, 10.29; F, 27.94 %).

3,3-*Difluoropentane*.[22] By following procedure B, $EtCF_2Et$ was obtained from pentan-3-one, b.p. 61–63 °C; δ_F($CDCl_3$) −103.8 (quin, J_{HF} 18.8, CF_2); δ_H($CDCl_3$) 0.98 (6 H, t, 2 × Me) and 2.05 (4 H, m, 2 × CH_2); *m*/*z* (rel. intensity) 73 (100%), 88 (70.4) and 108 (2.4).

Reaction of Cyclohexanone with Dibromodifluoromethane/Zinc.—By following procedure B, GLC gave products **5**–**7**.

1,1-*Difluorocyclohexane* **5**.[23] δ_F($CDCl_3$) −95.8 (quin, J_{HF} 11.3, CF_2); δ_H($CDCl_3$) 1.92–2.28 (m), *m/z* (rel. intensity) 41 (100%), 57 (97.7), 80 (10.8), 100 (63.0) and 120 (8.8).

(*Difluoromethylene*)*cyclohexane* **6**.[24] δ_F($CDCl_3$) −99.8 (s, =CF_2); δ_H($CDCl_3$) 1.95–2.37 (m); *m/z* (rel. intensity) 41 (55.0%), 57 (100), 82 (21.4) and 132 (2.7).

1-*Fluorocyclohexene* **7**.[25] δ_F($CDCl_3$) −100.8 (d, J_{HF} 18.4); δ_H($CDCl_3$) 2.00–2.39 (8 H, m) and 5.40 (1 H, d, J_{HF} 18.4) *m/z* (rel. intensity) 57 (100%), 80 (10.8) and 100 (48.5).

Reaction of 2,3-*Dimethylbut*-2-*ene with Dibromodifluoromethane/Zinc.*—Procedure A was followed except that, after removal of diethyl ether, the residue was fractionally distilled to give products **8** and **9**.

1,1-*Difluoro*-2,2,3,3-*tetramethylcyclopropane* **8**.[26] B.p. 90–92 °C; δ_F($CDCl_3$) −148.5 (s, CF_2); δ_H($CDCl_3$) 0.95 (s, Me); *m/z* (rel. intensity) 41 (85.2%), 119 (100) and 134 (13.0).

4-*Bromo*-4,4-*difluoro*-2,3,3-*trimethylbut*-1-*ene* **9**. B.p. 65–68 °C/10 mmHg; δ_F($CDCl_3$) −46.8 (s, CF_2Br); δ_H($CDCl_3$) 0.956 (6 H, s, 2 × Me), 1.05 (3 H, s, Me) and 5.78 (2 H, =CH_2); *m/z* (rel. intensity) 41 (78.9%), 55 (84.5), 83 (100), 91 (92.5), 133 (74.6), 212 (10.9) and 214 (10.9) (Found: C, 39.45; H, 5.2; F, 17.6. $C_7H_{11}BrF_2$ requires C, 39.62; H, 5.19; F, 17.56%).

Acknowledgements

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