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2*H*-Heptafluorobut-2-ene as a synthon for hexafluorobut-2-yne

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Abstract

Reactions of heptafluorobut-2-ene with nucleophiles are described, in some cases giving products analogous to those previously obtained from hexafluorobut-2-yne. Depending on the conditions, hydrolysis can lead to 1,1,1,4,4,4-hexafluorobutan-2-one, or 1,1,1-trifluoroacetone. Reactions with diols, bis-phenols, ammonia and amines are also described.

Keywords: Heptafluorobut-2-ene; Hexafluorobut-2-yne

1. Introduction

There is considerable interest in synthesis of compounds containing trifluoromethyl groups, especially in the plant protection industry [1], and functional group interconversions to trifluoromethyl or direct introduction of trifluoromethyl are well established. An alternative, is the 'building-block' approach, starting with trifluoromethyl-containing molecules and much work has been described in this area. Hexafluorobut-2-yne **1** is an excellent 'building-block' for incorporating *two* trifluoromethyl groups [2], but laboratory synthesis would normally involve anhydrous hydrogen fluoride [3], and **1** is not currently produced on a commercial scale sufficient to sustain a reasonable price. Conversely, 2*H*-heptafluorobut-2-ene **2** is easy to synthesise on a laboratory scale [4], and we have demonstrated both the conversion of **2** to **1** [5] but, more importantly, the direct use of **2** in cycloaddition reactions to give products retaining the trifluoromethyl groups has also been established [5]. Here, we describe further examples of reactions of **2** with nucleophiles, which give products analogous to those which have been obtained, or might be anticipated, from **1**.

2. Results and discussion

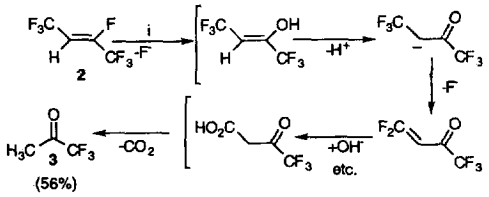
We have earlier described some chemistry involving nucleophilic attack on hexafluorobutyne **1** and heptafluorobutene **2**, and the former is much more reactive. However, this can be a problem, if a high concentration of **1** is present because competing nucleophile-induced polymerisation of **1** can occur with a variety of nucleophiles.

Hydrolysis of **2** occurs only with difficulty, but at 80 °C in the presence of base, smooth conversion to 1,1,1-trifluoroacetone **3** is obtained, via initial displacement of vinylic fluorine by hydroxide (Scheme 1).

Both trifluoromethyl groups are retained, however, in the reaction of **2** with sodium methoxide or phenoxide; product **4** was then simply hydrolysed by acid, to give the ketone **5**. Similarly, displacement of vinylic fluorine occurred in base-induced reactions of **2** with ethylene glycol or catechol, but in these cases, further reaction occurred to give the corresponding dioxole **8** and benzodioxole **9** by further intramolecular nucleophilic attack. These products have not been previously described, and in principle, derivatives **8** and **9** should be useful precursors to ketone **5**, but, unlike **4**, derivatives **8** and **9** were not hydrolysed by triflic or sulphuric acids, even under forcing conditions (Scheme 2).

Hydroquinone gave the bis-substitution product **10**, and by contrast, this compound is surprisingly unstable, giving high molecular weight material, even on standing for short periods at room temperature, and more rapidly on heating. It seems most likely that a process outlined in Scheme 3 occurs.

Ammonia and primary amines reacted with **2** to give substitution products **11** and **12**, and surprisingly, the spectro-



Scheme 1. i, Reagents and conditions, H_2O, Na_2CO_3, acentonitrile, 80 °C.

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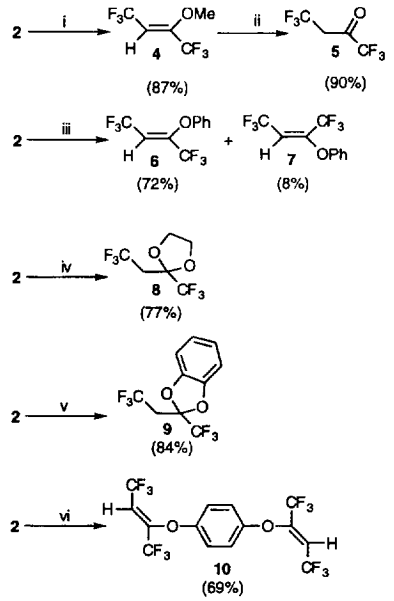
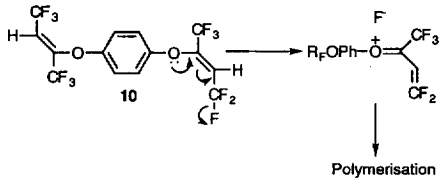
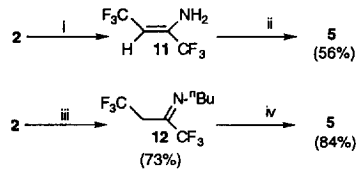


Scheme 2. Reagents and conditions (i) NaOMe, tetraglyme, room temperature; (ii) aq. triflic acid, acetonitrile; (iii) PhOH,CsF, acetonitrile; (iv) ethylene glycol, Na_2CO_3, tetraglyme, room temperature; (v) catechol, Cs_2CO_3, acetonitrile, room temperature; (vi) hydroquinone, Cs_2CO_3, acetonitrile, room temperature.



Scheme 3. Decomposition process.



Scheme 4. Reagents and conditions (i) aq. NH_3, room temperature; (ii) H_2O; (iii) *n*-butylamine, room temperature; (iv) H_3O^+, room temperature.

scopic data suggests a vinylamine structure for **11**. Indeed, **11** has been obtained previously from **1**, and the earlier workers formed the same conclusion. In contrast, the imine structure of **12** has now been established by ^{13}C NMR. Nevertheless, the vinylamine structure of **11** is most likely to be in equilibrium with the imine tautomer because, on standing, **11** was hydrolysed to ketone **5**. Imine **12** was also hydrolysed to **5**, but, in this case, acid was required to catalyse the process (Scheme 4). Surprisingly, **2** was unreactive towards diethylamine, even on heating, and this difference can only be attributed to steric factors, but the magnitude of the difference in reactivity of **2** with *n*-butylamine and diethylamine is quite unexpected.

The reactions described above indicate that **2** can be used as a synthon for hexafluorobutyne **1** in reactions with nucleophiles, and, in some cases, with considerable advantage over **1**.

3. Experimental

^1H NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250.13 MHz, a Varian Gemini VXR200 spectrometer operating at 199.98 MHz, or a Varian VXR400S spectrometer operating at 399.96 MHz. ^{19}F NMR spectra were recorded on the Bruker AC250 spectrometer operating at 235.34 MHz or on the Varian VXR400S spectrometer operating at 376.29 MHz. ^{13}C spectra were recorded on the Varian VXR400S spectrometer operating at 100.58 MHz, or the Varian Gemini VXR200 spectrometer operating at 50.29 MHz. All spectra were recorded with TMS and fluorotrichloromethane as internal references. *J* values are given in Hz. GLC–MS mass spectra were recorded on a Fisons Trio 1000 spectrometer linked to a Hewlett Packard 5890 series II gas chromatograph fitted with a 20 m cross-linked methyl silicone capillary column. All GLC–MS mass spectra were generated by electron impact. Mass spectra were recorded using a VG7070E spectrometer. FTIR spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer. Solid samples were run as KBr discs, liquid samples were run as thin films between KBr plates, and volatile samples were run in a gas cell fitted with KBr plates.

3.1. Formation of 1,1,1-trifluoroacetone 3

Fluoroalkene **2** (1.1 g, 6.0 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with water (5.7 g, 316 mmol), sodium carbonate (1.1 g, 10.4 mmol) and acetonitrile (7 ml). The tube was then evacuated, sealed and rotated in an oil bath maintained at 80 °C for 24 h. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and shown by NMR and GLC–MS to contain 1,1,1-trifluoroacetone **3** as the major component, δ_H(250 MHz; $CDCl_3$) 2.46 (s, CH_3); δ_F(235 MHz; $CDCl_3$) −85.54 (s, CF_3); δ_C(100 MHz; $CDCl_3$) 23.5 (s, CH_3), 120.1 (q, *J* 291.0, CF_3), 188.7 (q, *J* 36.2, C=O); *m/z* 43 (M^+-CF_3, 91%), 69 (M^+-CH_3C=O, 47). Volatile material was transferred into a round-bottom flask charged with 2,4-dinitrophenylhydrazine (2.1 g, 11.1 mmol), ethanol (15 ml), and sufficient conc. hydrochloric acid to dissolve the 2,4-dinitrophenylhydrazine. The flask was warmed for 10 min and then placed in a freezer. The precipitate was filtered, recrystallised from EtOH and identified as the 2,4-dinitrophenylhydrazone of 1,1,1-trifluoroacetone (0.8 g, 56%); mp 136–137 °C, (lit., [6] 139 °C); (Found: C, 37.1; H, 2.3; N, 19.0. Calc. for $C_9H_7F_3N_4O_4$: C, 37.0; H, 2.4; N, 19.2%); ν_{max}/cm^{-1} 3350, 3100, 1650–1500, 1350–1150, 800–600; *m/z* 292 (M^+, 44%), 69 (80).

3.2. Formation of (Z)-2-methoxy 1,1,1,4,4,4-hexafluorobut-2-ene 4

Fluoroalkene **2** (3.6 g, 19.8 mmol) was transferred, under reduced pressure, into a Carius tube which had previously

been charged with sodium methoxide (1.55 g, 28.7 mmol) and tetraglyme (10 ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and distilled at −78 °C/0.1 mbar and then 0 °C/0.1 mbar to leave a clear volatile liquid identified as (*Z*)-2-methoxy 1,1,1,4,4,4-hexafluorobut-2-ene **4** (3.3 g, 87%), ν_{max}/cm^{-1} 2950, 1750, 1400, 1300, 1200–1100, 600; δ_H(250 MHz; $CDCl_3$) 3.50 (3 H, s, CH_3), 5.25 (1H, q, *J* 7.5, *CH*); δ_F(235 MHz; $CDCl_3$) −58.83 (3F, s, $CHCF_3$), −71.64 (3F, s, $CFCF_3$); *m/z* 194 (M^+, 55%), 91 (100), 69 (65), by comparison with literature data [7,8].

3.3. Formation of 2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (6+7)

Fluoroalkene **2** (0.94 g, 5.1 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with freshly sublimed phenol (0.47 g, 5.0 mmol), dry caesium fluoride (0.88 g, 5.8 mmol) and acetonitrile (9 ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure. The residual white suspension was poured into a separating funnel containing water (125 ml). Ether (3×50 ml) was used to extract the organic layer. The ether layer was dried ($MgSO_4$) and evaporated. The residual clear oil was identified as a 9:1 mixture of (*Z*) and (*E*) isomers of 2-phenoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**6**+**7**) (1.0 g, 80%); (Found: C, 47.0; H, 2.3. Calc. for $C_{10}H_6F_6O$, C, 46.9; H, 2.3%). ν_{max}/cm^{-1} 3100–2850, 1700, 1650, 1575, 1200–1100, 700, 625.

The isomers were separated by preparative scale GLC (SE30/50 °C). (*Z*) isomer **6**: δ_H(250 MHz; $CDCl_3$) 6.50 (1H, q, *J* 7.8, CF_3CH), 6.98–7.28 (5H, m, OC_6H_5); δ_F(235 MHz; $CDCl_3$) −60.17 (3F, s, $CHCF_3$), −69.94 (3F, s, $CO(Ph)CF_3$); *m/z* 256 (M^+, 4%), 77 (100). (*E*) isomer **7**: δ_H(250 MHz; $CDCl_3$) 5.70 (1H, q, *J* 7.5, CF_3CH), 6.98–7.26 (5H, m, OC_6H_5); δ_F(235 MHz; $CDCl_3$) −58.83 (3F, s, CF_3), −71.64 (3F, s, $CO(Ph)CF_3$); *m/z* 256 (M^+, 29%), 77 (100).

3.4. Formation of 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-dioxole 8

Fluoroalkene **2** (4.2 g, 23.1 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with ethylene glycol (1.5 g, 24.2 mmol), sodium carbonate (6.2 g, 58.5 mmol) and tetraglyme (15 ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and shown to contain a major product, which was isolated by preparative scale GLC (SE30/40 °C), giving 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-dioxole **8** (n.c.) (4.0 g, 77%). (Found: C, 32.4; H, 3.0. $C_6H_6F_6O_2$ requires C, 32.1; H, 2.7%), ν_{max}/cm^{-1} 3000, 2950, 1350–1275, 12255–1150, 1050; δ_H(250 MHz; $CDCl_3$) 2.73 (2H, q, *J* 9.9, CF_3CH_2), 4.28 (4 H, s, OCH_2); δ_F(235 MHz; $CDCl_3$) −62.23 (3F, s, CH_2CF_3), −85.40 (3F, s, $C(OCH_2CH_2O)CF_3$); δ_C(100 MHz; $CDCl_3$) 36.04 (q, *J* 29.0, CF_3CH_2), 67.52 (s, CH_2CH_2), 103.35 (q, *J* 28.7, $C(OCH_2CH_2O)$), 122.93 (q, *J* 290.2, CF_3), 124.70 (q, *J* 272.2, CF_3); *m/z* 223 ($M^+ - 1$, 1%), 194 (13), 155 (51), 111 (100), 69 (15).

3.5. Formation of 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-benzodioxole 9

Fluoroalkene **2** (1.82 g, 10.0 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with catechol (1.08 g, 9.8 mmol), caesium carbonate (6.4 g, 19.7 mmol), and acetonitrile (10 ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 2 weeks at room temperature. It was then cooled to liquid air temperatures and opened. Volatile material was removed under reduced pressure, and the residual white suspension was poured into a separating funnel containing water (125 ml). Ether (3×50 ml) was used to extract the organic layer, which was dried ($MgSO_4$) and distilled to remove solvent. The residual clear oil was identified as 2-trifluoromethyl-2-(1,1,1-trifluoroethyl)-1,3-benzodioxole **9** (n.c.) (2.3 g, 84%). (Found: C, 44.1; H, 2.4. $C_{10}H_6F_6O_2$ requires C, 44.1; H, 2.2%); ν_{max}/cm^{-1} 3100–3025, 1775–1650, 1500, 1359–900, 725; δ_H(250 MHz; $CDCl_3$) 3.10 (2H, q, *J* 9.6, CH_2), 6.88–7.41 (4H, m, $O_2C_6H_4$); δ_F(235 MHz; $CDCl_3$) −61.15 (3F, s, CH_2CF_3), −86.86 (3F, s, $C(O_2C_6H_4)CF_3$); *m/z* 272 (M+, 24%), 203 (100), 139 (53), 69 (15).

3.6. Formation of p-phenylenedioxy-2-2'-bis-(Z-1,1,1,4,4,4-hexafluorobut-2-ene) 10

Fluoroalkene **2** (2.70 g, 14.9 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with hydroquinone (0.56 g, 5.1 mmol), caesium carbonate (3.68 g, 11.3 mmol) and acetonitrile (10 ml) against a counter current of dry nitrogen. The tube was then evacuated, sealed and rotated end over end for 5 days at room temperature. It was then cooled to liquid air temperatures, opened, and volatile material was removed under reduced pressure and the residual white suspension was poured into a separating funnel containing water (125 ml). Ether (3×50 ml) was used to extract the organic layer, which was dried ($MgSO_4$) and distilled to remove solvent. The residual solid was recrystallised from DCM/hexane, to give a white solid identified as *p*-phenylenedioxy-2-2'-bis-(*Z*-1,1,1,4,4,4-hexafluorobut-2-ene) **10** (n.c.) (2.3 g, 84%). (Found: C,

38.9; H, 1.6. $C_{14}H_6F_{12}O_2$ requires C, 38.7; H, 1.4%); ν_{max}/cm^{-1} 3000–2950, 2800, 1750–1600, 1500, 1400, 1300, 1200–1000, 800; δ_H(250 MHz; $CDCl_3$) 6.18 (2H, q, *J* 6.8, CF_3CH), 7.08 (4H, s, OCC*H*); δ_F(235 MHz; $CDCl_3$) −59.89 (3F, s, $CHCF_3$), −69.74 (3F, s, $C(OAr)CF_3$); *m/z* 433 ($M^+ - 1$, 20%), 305 (60), 111 (62), 69 (100).

3.7. Formation of 2-amino-1,1,1,4,4,4-hexafluorobut-2-ene 11, and 1,1,1,4,4,4-hexafluorobutan-2-one 5

Fluoroalkene **2** (1.90 g, 10.2 mmol) was transferred under reduced pressure into a round bottomed glass vessel (sealable via an integral Young's tap), which had previously been charged with 33% w/w aqueous ammonia solution (1.56 g, 30.6 mmol of NH_3). The flask was evacuated, sealed and stirred for 1 week at room temperature. It was then cooled to liquid air temperatures and volatile material was removed under reduced pressure, and shown to contain two major components in a 7:3 ratio. The first was identified as 2-amino-1,1,1,4,4,4-hexafluorobut-2-ene **11** δ_H(250 MHz; $CDCl_3$) 4.33 (2H, br, NH_2), 4.89 (1H, q, *J* 8.4, $CHCF_3$); δ_F(235 MHz; $CDCl_3$) −58.08 (3F, s, $CHCF_3$), −71.98 (3F, s, $C(NH_2)CF_3$); *m/z* 179 (M^+, 61%), 160 (30), 110 (32), 90 (100), 69 (11) by comparison with literature data [9]. The second was identified as 1,1,1,4,4,4-hexafluorobutan-2-one **5** δ_H(250 MHz; $CDCl_3$) 3.25 (q, *J* 8.4, $CHCF_3$); δ_F(235 MHz; $CDCl_3$) −60.97 (3F, s, CH_2CF_3), −86.92 (3F, s, $C(O)CF_3$); *m/z* 111 (M^+–CF_3, 70%), 69 (100) by comparison with literature data [8]. Volatile material was recondensed into the flask still containing the original mixture, which was then evacuated, resealed and stirred for two weeks. Volatile material was again removed under reduced pressure and were shown to contain 1,1,1,4,4,4-hexafluorobutan-2-one **5** as the major component. The volatile material was transferred into a round bottomed flask containing a solution of semicarbazide hydrogen chloride (1.5 g, 19.1 mmol) and sodium acetate (6.75 g, 82.3 mmol) in water (15 ml). The flask was stirred for 1 hour at room temperature and then placed into a fridge and left overnight. The resulting pale yellow crystals were filtered and recrystallised from hot EtOH, yielding 1,1,1,4,4,4-hexafluorobutan-2-one semicarbazone (1.4 g, 56%); mp 122–123 °C, (lit., [6] 122 °C (EtOH). (Found: C, 25.2; H, 2.1; N, 17.9. Calc. for $C_5H_5N_3O$: C, 25.3; H, 2.1; N, 17.7%); ν_{max}/cm^{-1} 3000, 2100, 1750, 1475, 1200–900, 700; *m/z* 236 ($M^+ - 1$, 6%), 57 (69), 69 (47), 43 (100).

3.8. Formation of 2-n-butylimino-1,1,1,4,4,4-hexafluorobutane 12

Fluoroalkene **2** (3.4 g, 18.7 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with *n*-butylamine (4.5 g, 60.8 mmol) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated end over end for 2 days at room temperature. It was then cooled to liquid air temperatures and the volatile material was removed under reduced pressure, and ether (3 × 15 ml) was added to the residual orange mixture, and stirred for 30 min. This slurry was then filtered, and the solid filtered was washed with more ether (2 × 10 ml). These washings were added to the original filtrate, and the ether and unreacted *n*-butylamine removed by distillation, leaving an oil which contained one major component, which was isolated by preparative scale GLC (SE30/70 °C) and identified as 2-*n*-butylimino-1,1,1,4,4,4-hexafluorobutane **12** (n.c.) (3.4 g, 73%). (Found: C, 35.9; H, 4.4; N, 5.9. $C_7H_{11}NF_6$ requires C, 35.7; H, 4.7; N, 6.0%); ν_{max}/cm^{-1} 2950, 1765, 1375, 1325, 1200–1100; δ_H(250 MHz; $CDCl_3$) 0.93 (3H, t, *J* 7.5, CH_3), 1.44 (2H, q, *J* 7.5, CH_3CH_2), 1.72 (2H, t, *J* 6.5, $CH_3CH_2CH_2$), 3.38 (2H, q, *J* 10.1, CF_3CH_2); δ_F(235 MHz; $CDCl_3$) −62.42 (3F, s, $C(NBu)CF_3$), −73.57 (3F, s, CH_2CF_3); δ_C(100 MHz; $CDCl_3$) 14.18 (s, CH_3), 20.94 (s, CH_2CH_3), 32.47 (s, $CH_3CH_2CH_2$), 53.36 (s, NCH_2), 31.77 (q, *J* 32.5, CH_2CF_3), 148.43 (q, *J* 35.1, C=N), 119.57 (q, *J* 220.5, CF_3), 123.89 (q, *J* 270.8, CF_3); *m/z* 235 (M+, 1%), 193 (24), 69 (11), 57 (100).

3.9. Formation of 5 from 4

(*Z*)-2-Methoxy-1,1,1,4,4,4-hexafluorobut-2-ene **4** (0.4 g, 2.1 mmol) was transferred under reduced pressure into a round-bottomed glass vessel (sealable via an integral Young's tap), which had previously been charged with water (7 ml) and triflic acid (1 ml). The flask was evacuated, sealed and stirred for 2 days at room temperature. It was then cooled to liquid air temperatures and opened. Ether (10 ml) was added and the ethereal layer was separated, washed with more water (2 × 10 ml), dried ($MgSO_4$) and was shown to contain 1,1,1,4,4,4-hexafluorobutan-2-one **5** by NMR and GLC–MS. The product was isolated as 1,1,1,4,4,4-hexfluorobutan-2-one semicarbazone (0.44 g, 90%) by standard procedures as reported above.

3.10. Formation of 5 from 12

2-*n*-Butylimino-1,1,1,4,4,4-hexafluorobutane **12** (0.5 g, 2.1 mmol) was transferred into a round-bottomed flask which had been previously charged with water (5 ml) which had been acidified to pH1 using 98% sulphuric acid. The mixture was stirred for 1 day at room temperature. Ether (10 ml) was then added and the ethereal layer was separated, washed with more water (2 × 10 ml), dried ($MgSO_4$) and was shown to contain 1,1,1,4,4,4-hexafluorobutan-2-one **5** by NMR and GLC–MS. The product was isolated as 1,1,1,4,4,4-hexfluorobutan-2-one semicarbazone (0.42 g, 84%) by standard procedures as reported above.

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