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Eliminations from 2*H*-Heptafluorobut-2-ene [1]

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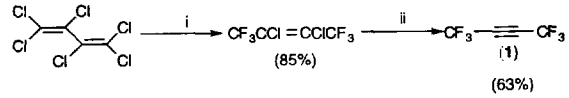
Abstract

Various approaches are described for dehydrofluorination of heptafluorobut-2-ene (**2**) to give hexafluorobut-2-yne (**1**). Molecular sieve is particularly successful. Reaction of (**2**) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) surprisingly gave the novel heterocycle (**8**) via initial nucleophilic attack. Reactions of (**2**) with other bases are also described.

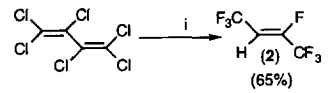
Keywords: Heptafluorobut-2-ene

1. Introduction

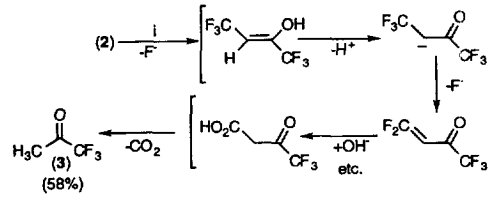
Work described in the literature demonstrates that hexafluorobut-2-yne (**1**) is a very useful synthon in cycloaddition reactions for synthesis of molecules containing two trifluoromethyl groups. The most efficient route to (**1**), developed by Henne and Finnegan [1], involves fluorination of hexachlorobuta-1,3-diene, using a mixture of antimony trifluoride dichloride and anhydrous hydrogen fluoride (Scheme 1). However, large scale reactions involving hydrogen fluoride are not easy for most academic laboratories, and (**1**) is currently expensive to purchase. In contrast, 2*H*-heptafluorobut-2-ene (**2**) is relatively easy to prepare on a reasonable scale in the laboratory by reaction of hexachlorobuta-1,3-diene with potassium fluoride, using methodology developed by Maynard [2] (Scheme 2). Therefore, we have been investigating the use of (**2**) as a synthon for hexafluorobut-2-yne (**1**) [3,4], and methodology for conversion of (**2**) into (**1**).



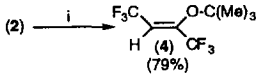
Scheme 1. (i) Reagents and conditions, SbF_3, SbF_3Cl_2, 155 °C. (ii) Zn.



Scheme 2. (i) Reagents and conditions, KF, NMP, 190 °C.



Scheme 3. (i) Reagents and conditions, KOH, Sulpholane, 0 °C.



Scheme 4. (i) Reagents and conditions, KO^{t}Bu, (^{i}Pr)$_2$O, 0 °C.

2. Results and discussion

Reactions of 2*H*-heptafluorobut-2-ene (**2**) with various bases have been explored for the elimination of hydrogen fluoride. Potassium hydroxide powder, either neat or in suspension in sulpholane, gave 1,1,1-trifluoroacetone (**3**) (58% yield), most probably via the mechanism shown in Scheme 3.

Consequently, so-called "non-nucleophilic bases" were explored, starting with potassium *t*-butoxide, but this led to simple nucleophilic displacement of vinylic fluorine, giving (**4**) Scheme 4.

DBU is a classic base for this purpose, with little evidence in the literature for nucleophilic properties, and it was extremely surprising, therefore, to observe that a colourless crystalline product was obtained by reaction of (**2**) with DBU at room temperature. Spectroscopic data pointed to the structure (**8**), and a single crystal X-ray structural analysis confirmed these deductions [5].

Formation of (**8**) probably begins with nucleophilic attack by DBU on (**2**), (Scheme 5) leading to vinylic displacement

[1] Dedicated to: our friend, Professor Alois Haas, on the occasion of his 65th birthday.

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Table 1
Formation of hexafluorobut-2-yne (**1**) from (**2**)

Temperature/°C	N_2 flow/ml min^{-1}	Length of CsF plug/cm	Yield of (**1**)/%	Recovered (**2**)/%
300	100	1	23	37
350	150	1	36	50
300	150	2	8	77

of fluoride ion followed by proton-loss to give (**5**). The further loss of fluoride ion obviously must occur from a trifluoromethyl group and it is reasonable to suggest step (**5**) to (**6**). Indeed, we have demonstrated other examples of loss of fluorine from systems closely related to (**5**). Then the cyclisation step arises from generation of the anion (**7a**), no doubt facilitated by the adjacent positively charged nitrogen, followed by cyclisation via nucleophilic attack of the ketimine on the difluoroallene (**7b**). Proton transfer to the anion provides the $-CF_2H$ group in (**8**), together with the pyrrole structure, which would be extremely difficult to account for, other than by the process shown.

Since we carried out this work, we have found three other reports in the literature where it is described that DBU clearly acts a nucleophile [6–8]. Indeed, we have established that DBU reacts as a nucleophile with a range of other unsaturated fluorocarbon systems, including (**9**)–(**11**) Scheme 6, but in each case, an intractable mixture of tarry products was obtained, that we were unable to characterise.

Hexafluorobut-2-yne (**1**) also reacted with DBU to give (**8**) (64% yield). This raises the possibility, which is difficult to firmly exclude, that formation of (**8**) from (**2**) occurs via initial formation of (**1**), followed by nucleophilic attack by DBU. However, we did not observe any hexafluorobut-2-yne (**1**) in the recovered (**2**), and, also reaction of DBU proceeds more efficiently with heptafluorobut-2-ene (**2**) than (**1**). Furthermore, the general reactivity of DBU with a variety of perfluorinated-alkenes and -cycloalkenes demonstrates that nucleophilic displacement of vinylic or allylic fluorine occurs readily.

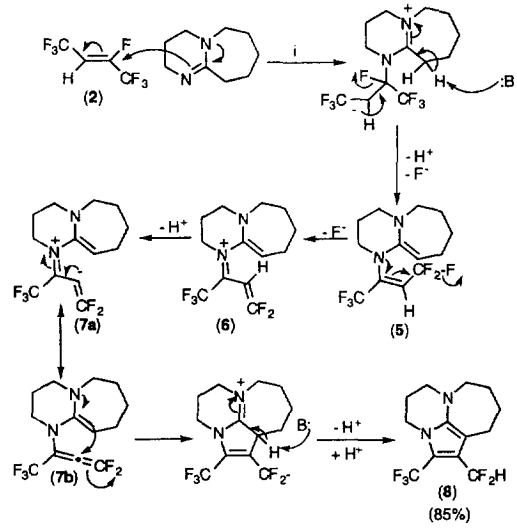
We have also explored reaction of heptafluorobut-2-ene (**2**) with DBN; reaction occurred readily, but no products could be characterised from the resulting tar.

High temperature (up to 400 °C) cracking reactions were attempted, for removal of hydrogen fluoride from (**2**), but in the absence of caesium fluoride, no reaction occurred. However, elimination of hydrogen fluoride occurred quite effectively at 350 °C, through a tube packed with caesium fluoride and quartz wool (Scheme 7 and Table 1). It is surprising that the most efficient process that we have observed so far, for the elimination of hydrogen fluoride from (**2**) involves simply the storage of (**2**) over molecular sieve (Aldrich 4A) at room temperature!

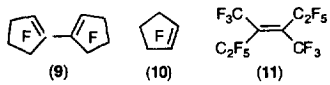
Standing for 4 weeks under these conditions, led to quantitative conversion of (**2**) to (**1**) (Scheme 6). There are previous reports in the literature, describing the use of molecular sieves for elimination of hydrogen fluoride, but not under such mild conditions, and not for this system. Use of *t*-butyl lithium for elimination, was also moderately successful, in that (**1**) was obtained in 41% yield (Scheme 7).

Elimination of hydrogen -chloride and -bromide from systems related to (**2**), occur readily and these reactions are known [9] (Scheme 8).

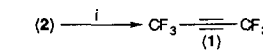
However, various attempts to effect nucleophilic displacement of vinylic fluorine in (**2**) by bromide or iodide giving (**12b** and **12c**), have been unsuccessful, although displacement by chloride ion was possible from (**2**), giving (**12a**), in 73% yield.



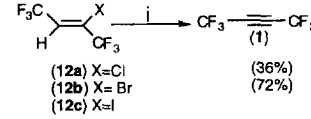
Scheme 5. (i) Reagents and conditions, DBU:(2) = 4:1, hexane, sealed tube, room temp., 2 days.



Scheme 6. Reactants with DBU.



Scheme 7. (i) Reagents and conditions: CsF, flow system, 350 °C (100% yield, 36% conv.) Molecular sieve, room temp., 4 weeks (100%) ^tBuLi, pentane, 0 °C (41%).



Scheme 8. (i) Reagents and conditions, KOH, 0 °C.

3. Experimental

^{1}H 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. FAB mass spectra were recorded using a VG7070E spectrometer, and glycerol as a solvent. 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 (3)

Fluoroalkene (**2**) (0.9 g, 5.0 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with potassium hydroxide (0.8 g, 15.0 mmol), and sulpholane (10 ml). The tube was evacuated, sealed and rotated end over end for 48 hours at room temperature. It was then cooled to liquid air temperatures and opened. The volatiles were removed under reduced pressure, and were shown 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). The volatiles were 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 hot EtOH and identified as the *2,4-dinitrophenylhydrazone of 1,1,1-trifluoroacetone* (0.9 g, 58%); mp 136–137 °C, (lit., [10] 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 (4)

Fluoroalkene (**2**) (4.2 g, 23.1 mmol) was transferred, under reduced pressure, into a round bottomed flask which had previously been charged with potassium *t*-butoxide (5.28 g, 47.0 mmol) and di-isopropyl ether (20 ml) against a counter current of dry nitrogen. The flask was allowed to warm from liquid air temperatures to 0 °C, and the volatile products were collected in a liquid air temperature trap. None were recovered. The residual ether layer was filtered, and shown to contain (*Z*)-2-*t*-butoxy-1,1,1,4,4,4-hexafluorobut-2-ene (**4**) (18.2 mmol, 79%). The product was not isolated but identified by comparison with literature data [11]. δ_H(250 MHz; $CDCl_3$) 1.44 (9 H, s, CH_3), 6.05 (1 H, q, *J* 6.5, C*H*); δ_F(235 MHz; $CDCl_3$) −57.13 (3 F, s, CF_3), −67.75 (3 F, s, CF_3); *m/z* 221 ($M^+ - 15$, 11%), 69 (30), 57 (100). (Yield by ^{19}F NMR integrated against an internal standard of 1,1,1-trifluorotoluene.)

3.3. Formation of (8)

Fluoroalkene (**2**) (0.82 g, 4.5 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (3.04 g, 20.0 mmol) and hexane (10 ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated end over end for 3 days at room temperature. It was then cooled to liquid air temperatures and the volatiles were removed under reduced pressure, and acetonitrile (3 ml) was added to the residual brown solution. This produced two layers, and the upper golden hexane layer was removed, and the lower layer was extracted by more hexane (2×10 ml). The hexane solutions were combined, and the hexane was removed by rotary evaporation to yield a pale yellow solid, which was recrystallised from warm hexane to yield colourless crystals identified as 1,9-diazabicyclo-[5.4.0]undecano-a,b-2-difluoromethyl-3-trifluoromethyl-pyrrole (**8**) (n.c.) (1.12 g, 85%), mp 63 °C. (Found C, 53.0; H, 5.2; N, 9.4. $C_{13}H_{15}N_2F_5$ requires C, 53.1; H, 5.1; N, 9.5%); n_{max}/cm^{-1} 3950, 2850, 1575, 1400, 1300–950, 800, 600; δ_H(250 MHz; $CDCl_3$) 1.51 (2 H, m, CH_2), 1.75 (2 H, m, CH_2), 2.07 (2 H, m, CH_2), 2.66 (2 H, m, CH_2), 2.98 (2 H, m, CH_2), 3.08 (2 H, m, CH_2), 3.87 (2 H, m, CH_2), 6.75 (1 H, t, *J* 54.5, CF_2H); δ_F(376 MHz; $CDCl_3$) −58.87 (3 F, t, *J* 4.9, CF_3), −106.47 (2 F, dq, *J* 54.6 and 4.9, CF_2H); δ_C(100 MHz; $CDCl_3$) 21.9 (s, CH_2), 25.0 (s, CH_2), 26.7 (s, CH_2), 31.1 (s, CH_2), 42.4 (s, CH_2), 50.1 (s, CH_2), 56.6 (s, CH_2), 104.5 (s, $CH_2C{=}$), 109.8 (qt, *J* 37.6 and 8.8, $CF_3C{=}$), 115.5 (tq, *J* 229.5 and 5.0, CF_2H), 117.5 (t, *J* 25.6, $CF_2HC{=}$), 122.0 (q, *J* 266.4, CF_3), 141.6 (s, N(N)$C{=}$); *m/z* 294 (M^+, 100%).

3.4. Formation of (8) from (1)

Hexafluorobut-2-yne (**1**) (0.6 g, 3.7 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with 1,8-diazabicyclo[5.4.0]undec-7-ene (2.9 g, 19.1 mmol) and hexane (10 ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated end over end for 3 days at room temperature. It was then cooled to liquid air temperatures and the volatiles were

removed under reduced pressure, and acetonitrile (3 ml) was added to the residual brown solution. This produced two layers, and the upper golden hexane layer was removed, and the lower layer was extracted by more hexane (2 × 10 ml). The hexane solutions were combined, and the hexane was removed by rotary evaporation to yield a pale yellow solid, which was recrystallised from warm hexane to yield colourless crystals identified as (**8**) (0.7 g, 65%), which were identical to those described above.

3.5. Formation of (*1*)

3.5.1. CsF and (2) (typical run)

Fluoroalkene (**2**) (1.77 g, 9.73 mmol) was passed through a glass pyrolysis tube (15 mm o.d.) packed with a 1 cm length plug of caesium fluoride at 300 °C, by bubbling a slow current (~100 ml/min) of nitrogen through (**2**) cooled to 0 °C. The products were collected in a trap maintained at liquid air temperatures, and were shown by GLC–MS and NMR to contain unreacted (**2**) (37%) and hexafluorobut-2-yne (**1**) (23%). The products could be separated by repeated distillation at 0 °C. For (**1**): ν_{max}/cm^{-1} 1275, 1200, 650; δ_F(235 MHz; $CDCl_3$) −55.21 (s, CF_3); δ_C(100 MHz; $CDCl_3$) 30.02 (q, J 19.4, CCF_3), 113.86 (q, J 259.8, CF_3); m/z 162 (M^+, 25%), 69 (100).

3.5.2. Molecular sieve and (2) (performed by P. Odello)

Fluoroalkene (**2**) (20.3 g, 111.5 mmol) was transferred, under reduced pressure, into a 100 ml Rotaflow which had been charged with Aldrich 4A molecular sieves (~15 cm^3) that had been previously heated to 400 °C in vacuo. After 4 weeks at room temperature, the volatiles were removed under reduced pressure, and were shown to contain hexafluorobutyne (**1**) (18.1 g, Quant.).

3.5.3. t-Butyl lithium and (2)

Fluoroalkene (**2**) (1.6 g, 8.8 mmol) was transferred, under reduced pressure, into a round bottomed flask which had previously been charged with 1.7 M pentane solution of *t*-butyl lithium (5 ml) under a counter current of dry nitrogen. The flask was stirred and allowed to warm from liquid air temperatures to 0 °C. Volatile products were collected in a trap maintained at liquid air temperatures, and identified as hexafluorobut-2-yne (**1**) (0.58 g, 41%).

3.5.4. Formation of (*12a*)

Fluoroalkene (**2**) (3.0 g, 16.5 mmol) was transferred, under reduced pressure, into a Carius tube which had previously been charged with lithium chloride (2.2 g, 51.8 mmol) and dimethylformamide (8 ml) under a counter current of dry nitrogen. The tube was evacuated, sealed and rotated in an oil bath maintained at 140 °C for 1 week. It was then cooled to liquid air temperatures and the volatiles were removed under reduced pressure, and then distilled at 0 °C/0.1 mbar. The distillate was distilled further (−78 °C/0.1 mbar) to leave a clear volatile liquid containing one component by GLC–MS identified as (*Z*)-2-chloro-1,1,1,4,4,4-hexafluorobut-2-ene (**12a**) (2.4 g, 73%) identified by comparison with literature data. [ref] ν_{max}/cm^{-1} 2950, 1750, 1400, 1350–1100, 850, 650; δ_H(250 MHz; $CDCl_3$) 6.32 (q, J 6.3, CH); δ_F(235 MHz; $CDCl_3$) −64.15 (3 F, s, CF_3), −74.03 (3 F, s, CF_3); m/z 198 (M^+, 60%), 69 (100). (Product (**12a**) was too volatile for a satisfactory elemental analysis).

Acknowledgements

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