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Cycloadditions and Nucleophilic Attack on *Z*-2*H*-Heptafluorobut-2-ene

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Abstract: Chemistry of Z-2*H*-Heptafluorobut-2-ene **1** is surveyed; cycloaddition reactions occur with a variety of benzenoid compounds, in some cases leading directly to aromatics. Addition to cyclopentadiene, followed by eliminations of hydrogen fluoride and ethyne, lead to isomeric bistrifluoromethylcyclopentadienes. Nucleophilic reactions occur readily with oxygen, nitrogen and sulphur nucleophiles and aniline provides a quinoline synthesis.

Introduction

Compounds containing trifluoromethyl groups gain increasing importance in the plant-protection[1] and the pharmaceutical industries and methodology frequently depends on functional group interconversions to trifluoromethyl or direct introduction of trifluoromethyl via. radicals, nucleophiles, or electrophiles.[2,3] Hexafluorobut-2-yne is an excellent 'building-block' for construction of systems containing *two* trifluoromethyl groups[4-8] but it is relatively expensive and a laboratory synthesis would involve anhydrous hydrogen fluoride.[9] In contrast, *Z*-2*H*-heptafluorobut-2-ene **1** is relatively easy to synthesise on a laboratory scale[10] from hexachlorobutadiene and potassium fluoride and recent developments minimise the consumption of solvent.[11] Here, we develop further the use of **1** as a synthon for hexafluorobut-2-yne in cycloaddition reactions and in reactions with nucleophiles.

Results and Discussion

We have previously demonstrated that cycloaddition reactions of *Z*-2*H*-heptafluorobut-2-ene, **1**, with furan and derivatives provide an excellent process for the synthesis of corresponding 3,4-bis(trifluoromethyl) furan derivatives.[12] In contrast, however, attempts to synthesise bis(trifluoromethyl)cyclopentadienes using analogous additions to cyclopentadiene only produced trace quantities.

Because **1** is a very electrophilic alkene derivative, then reaction with π-electron rich systems is facilitated. Reaction of **1** with anthracene occurs readily at 300 °C, to give the addition product, **2**, formed by concomitant elimination of hydrogen fluoride, Scheme 1.

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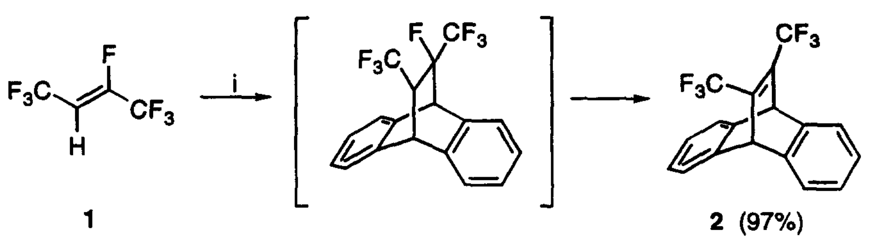
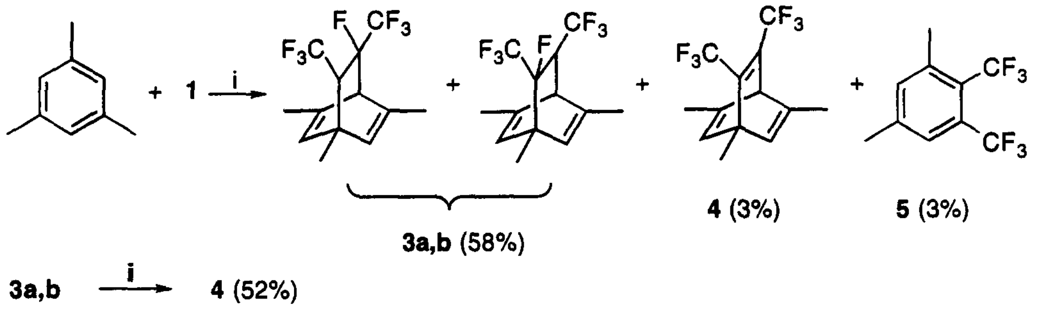
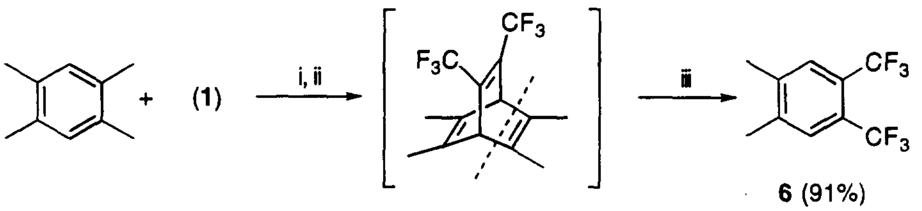


Scheme 1. *Reagents and Conditions:* i, 300 °C, anthracene, quartz tube.

However, reaction of **1** with mesitylene revealed a more complex range of products and indicates the various processes that take place in these and related systems. The isomers **3a, 3b** are the principal components of the mixture, resulting from non-regiospecific addition of **1** to mesitylene, together with the product of dehydrofluorination, **4**, and 1,2-bis(trifluoromethyl)-3,5-dimethylbenzene **5**, formed by elimination of propyne from **4**, Scheme 2. Indeed, the analogous elimination of but-2-yne from the corresponding intermediate, obtained by addition of **1** to durene is the principal process and provides a relatively efficient 'one-pot' synthesis of 1,2-bis(trifluoromethyl)-4,5-dimethylbenzene, **6**, Scheme 3.

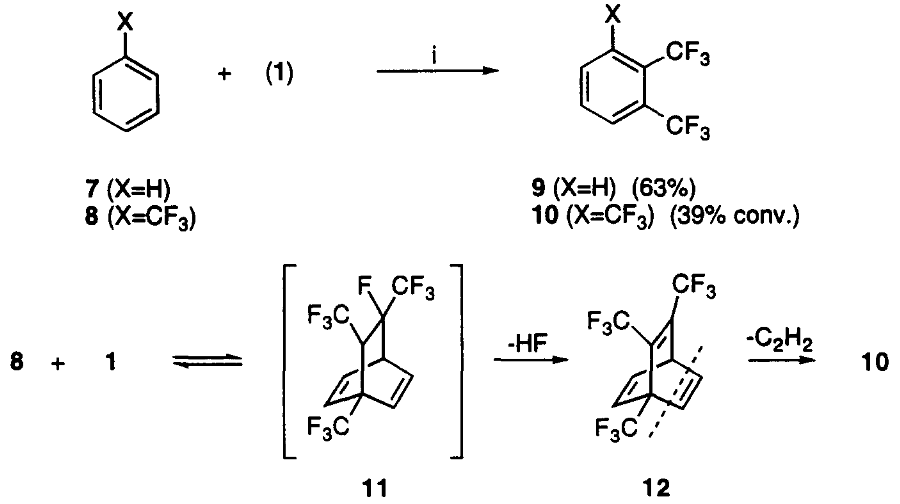


Scheme 2. *Reagents and Conditions:* i, 340 °C, steel metal tube; ii, KOH, hexane, reflux.



Scheme 3. *Reagents and Conditions:* i, 300 °C, quartz tube; ii, -HF; iii, -$CH_3C{\equiv}CCH_3$.

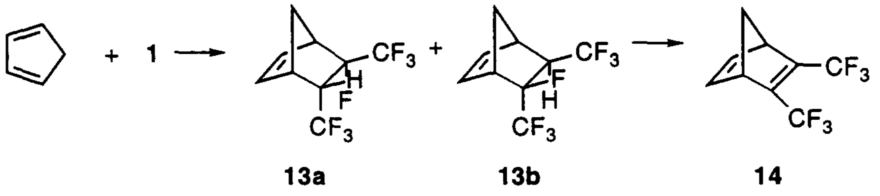
In an analogous process 1,2-bis(trifluoromethyl)benzene **9** was obtained directly from benzene **7** and, more surprisingly, 1,2,3-tris(trifluoromethyl)benzene **10** was obtained directly from trifluoromethylbenzene **8**.



Scheme 4. *Reagents and Conditions:* i, 340 °C, steel tube.

Formation of the most crowded isomer **10** is remarkable and a convincing rationalisation of this observation is based on an assumption that the addition step eg. formation of **11**, Scheme 4 is reversible. Therefore, the formation of **10** will be controlled by the non-reversible elimination of hydrogen fluoride and we envisage that this could occur much faster from **11** than from the other possible isomers because of a significant acidifying effect of the bridgehead trifluoromethyl group, on the relevant carbon-hydrogen bond.

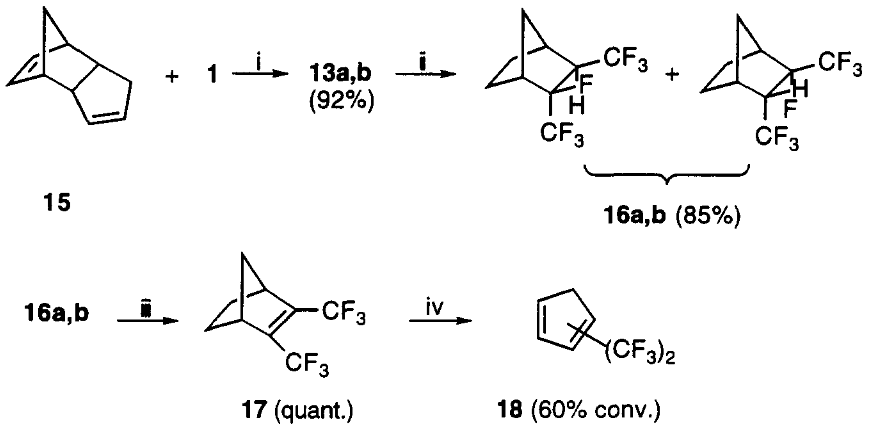
We have also re-investigated additions of **1** to cyclopentadiene as a route to bis(trifluoromethyl)cyclopentadienes, Scheme 5.



Scheme 5.

The addition step proceeds readily to give adducts **13a** and **13b**[12] from which **14** is obtained with base. However, thermal elimination of ethyne from **14** could not be achieved with any reasonable efficiency. Therefore, we have explored the reduction of **13a,b** prior to elimination of hydrogen fluoride, followed by pyrolytic elimination of ethene and the overall process is shown in Scheme 6. Adducts **13a,b** were obtained efficiently by thermal reaction of **1** with the dimer of cyclopentadiene **15**, albeit for a prolonged reaction time.

Then reduction was achieved simply by hydrogen over platinum giving **16a,b** and then this mixture was dehydrofluorinated to give **17**.



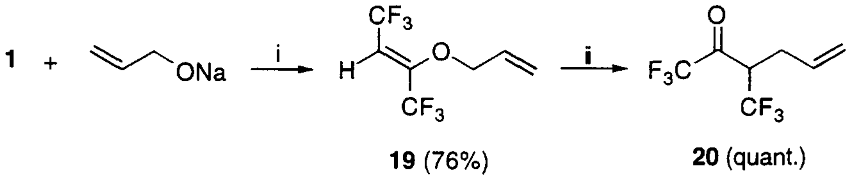
Scheme 6. *Reagents and Conditions:* i, 180°C, 6 d, steel tube; ii, H_2, Pt/C, hexane, R.T.; iii, KOH, hexane, R.T.; iv, 450°C, flow/N_2/quartz.

Pyrolysis of **17** required a high temperature, in a flow system through a quartz tube, and a 60% conversion to a mixture of bis(trifluoromethyl)cyclopentadienes **18** was obtained, together with starting material. Clearly, 1,5-shifts[13] of hydrogen and probably trifluoromethyl occur in the cyclopentadiene derivatives, at the high temperature, to give this complex mixture. However, glc-ms established the presence of the cyclopentadiene derivatives and F-19 and H-1 nmr spectra confirmed the composition of this mixture.

Thus, cycloaddition reactions of **1** now provide a variety of approaches to 5- and 6- membered ring systems containing two trifluoromethyl groups.

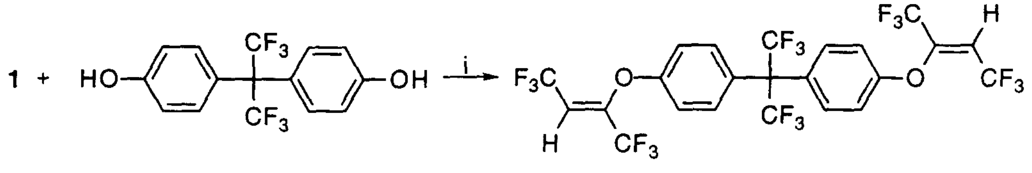
The fluorinated alkene **1** is also very susceptible to nucleophilic attack and some examples have been discussed previously,[14] while here, we describe some reactions of oxygen, nitrogen, and sulphur nucleophiles.

Allyl alcohol reacted smoothly with **1**, to give the product **19**, by vinylic displacement of fluorine, Scheme 7.



Scheme 7. *Reagents and Conditions:* i, R.T.; ii, 80 °C.

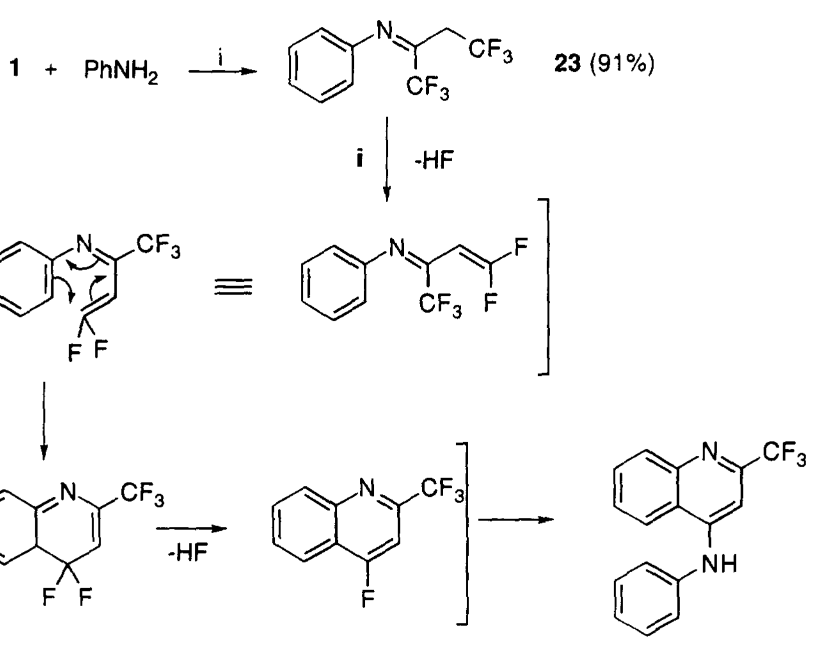
Then, Claisen rearrangement of **19** to **20** occurred very smoothly, at 80 °C; the latter compound has been obtained previously in one step from hexafluorobut-2-yne, in a base induced reaction with allyl alcohol at 50°C, but no intermediate was reported[15] in that case. Vinylic displacement of fluorine from **1** also occurs with bisphenol AF, **21**, giving the novel monomer **22**, Scheme 8.



21 **22** (88%)

Scheme 8. *Reagents and Conditions:* i, K_2CO_3, CH_3CN, R.T.

We have also demonstrated that **1** could be a source of quinoline derivatives because reaction with aniline gave first the imine **23**, and then further reaction with base gave the quinoline derivative **24**, Scheme 9.

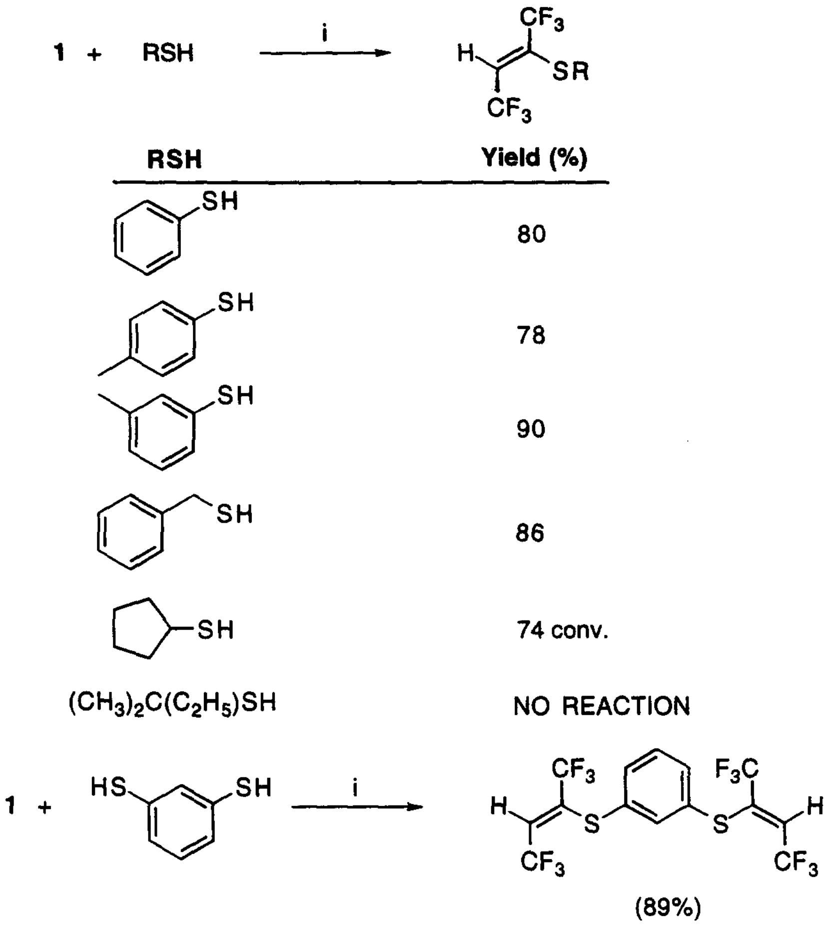


23 (91%)

24 (53%)

Scheme 9. *Reagents and Conditions:* i, K_2CO_3, CH_3CN, R.T.; ii, KOH, hexane, R.T.

We are unaware of any reports of reactions of **1** with sulphur nucleophiles but the examples illustrated in Scheme 10 demonstrate that these nucleophiles react very efficiently.



Scheme 10. *Reagents and Conditions:* i, K_2CO_3, CH_3CN, R.T.

This survey of reactivity of the fluorinated alkene **1** demonstrates that the latter is a very versatile 'building-block' for the construction of a variety of molecules containing one, two or more trifluoromethyl groups.

Experimental

All starting materials that were obtained commercially were used as received. ^{19}F and ^{1}H NMR spectra were recorded using either a Bruker AC 250, a Varian VXR 400S, or a Bruker AMX 500 NMR spectrometer. ^{13}C NMR spectra were recorded using either a Varian VXR 400S or a Bruker AMX 500 spectrometer. (Unless stated all samples run in $CDCl_3$, ^{19}F referenced to $CFCl_3$ and all J values are given in Hz). Infrared spectra were recorded on a Perkin-Elmer 1600 FT/IR spectrometer using KBr discs (solid samples) or thin films between two

KBr plates (liquid samples), or a sealed gas cell fitted with KBr plates (gas samples). GLC mass spectra were obtained using a VG Trio 1000 spectrometer linked to a Hewlett-Packard 5890 Series II gas chromatograph fitted with a 25 m cross linked silicone capillary column. Carbon, hydrogen and nitrogen elemental analyses were obtained using a Carlo Erba 440 Elemental Analyser.

Diels-Alder Reactions

Benzenoid Systems

General Procedure for Quartz Tubes. A quartz tube (1 cm^3), charged with *Z*-2*H*-heptafluorobut-2-ene (**1**) and a benzene derivative, was evacuated, sealed and heated in a furnace maintained at 300 °C for 24 h. After the reaction was completed the tube was opened and the contents removed. Vacuum sublimation was carried out to afford a single product.

11,12-Bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene **2**. - Anthracene (0.12 g, 0.7 mmol) and *Z*-2*H*-heptafluorobut-2-ene **1** (0.18 g, 1.0 mmol) gave *11,12-bis(trifluoromethyl)-9,10-dihydro-9,10-ethenoanthracene* **2** (0.23 g, 97%) identified by comparison of spectra with literature data[16]; mp 105-107°C (lit.,[16] 110°C); δ_F (235MHz) -61.7 (s); δ_C (100MHz) 51.1 (s, 9-C), 121.9 (q, $^1J_{C\text{-}F}$ 271.6, CF_3), 123.9 (s, 1 or 2-C), 125.9 (s, 1 or 2-C), 142.8 (s, 4a-C), 143.8 (q, $^2J_{C\text{-}F}$ 39.5, 11-C); δ_H (250MHz) 5.46 (s, 9-H), 7.07 (AA'XX', 1 or 2-H), 7.40 (AA'XX', 1 or 2-H); *m/z* (EI^+) 340 (M^+, 59.6%).

1,2-Bis(trifluoromethyl)-4,5-dimethylbenzene **6**. - 1,2,4,5-Dimethylbenzene (0.13 g, 1.0 mmol) and *Z*-2*H*-heptafluorobut-2-ene **1** (0.18 g, 1.0 mmol) gave *1,2-bis(trifluoromethyl)-4,5-dimethylbenzene* **6** (0.22 g, 91%) identified by comparison with literature data[17]; δ_F (235MHz) -61.9 (s); δ_C (100MHz) 19.6, (s, CH_3), 123.1 (q, $^1J_{C\text{-}F}$ 274.3, CF_3), 129.0 (s, 3-C), 131.5 (q, $^2J_{C\text{-}F}$ 83.6, 1-C), 141.2 (s, 4-C); δ_H (250MHz) 2.37 (3H, s, CH_3), 7.58 (1H, s, 3-H); *m/z* (EI^+) 242 (M^+, 45.5%).

General Procedure for Sealable Metal Tubes. A sealable stainless steel metal tube (40 or 90 cm^3), charged with *Z*-2*H*-heptafluorobut-2-ene **1** and benzene or a derivative, was evacuated, sealed and heated in a rocking furnace maintained at 340 °C (~130 atm.) for 60 h. After the reaction was completed the tube was opened and the contents removed. Distillation under reduced pressure was carried out to afford a single product.

1,2-Bis(trifluoromethyl)benzene **9**. - Benzene (25.0 g, 321 mmol) and *Z*-2*H*-heptafluorobut-2-ene **1** (9.1 g, 50 mmol) gave *1,2-bis(trifluoromethyl)benzene* **9** (6.7 g, 63%), identified by comparison with literature data[18]; bp 139-141°C (lit.,[19] 143°C); (Found: C, 45.0; H, 2.0. $C_8H_4F_6$ requires C, 44.9; H, 1.9%); υ_{max}/cm^{-1} 3090-3035 (arom. CH) and 1033-1312 (CF); δ_F (376MHz) -59.4 (s); δ_H (250MHz) 7.69 (2H, AA'MM'XX', 3 or 4-H), 7.86 (2H, AA'MM'XX', 3 or 4-H); *m/z* (EI$^+$) 214 (M$^+$, 81.4%).

1,2,3-Tris(trifluoromethyl)benzene **10**. - Trifluoromethylbenzene (29.5 g, 202 mmol) and *Z*-2*H*-heptafluorobut-2-ene **1** (9.1 g, 50 mmol) gave *1,2,3-tris(trifluoromethyl)benzene* **10** (33% coversion of trifluoromethylbenzene by GLCMS), identified by comparison with literature data[18]; δ_F (235MHz) -60.1 (2F, s, 1 and 3-CF_3), -63.9 (1F, s, 2-CF_3); δ_H (250MHz) 8.01 (2H, m, 4-H), 8.12 (1H, s, 5-H); *m/z* (EI$^+$) 282 (M$^+$, 35.1%).

1,3,5-Trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene **4**. - 1,3,5-Trimethylbenzene (6.4 g, 53.3 mmol) and *Z*-2*H*-heptafluorobut-2-ene **1** (5.0 g, 27.5 mmol) gave a mixture of *1,3,5-trimethyl-8-fluoro-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,-diene* **3a**, *1,3,5-trimethyl-7-fluoro-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,-diene* **3b** (58% by GLCMS, **3a,b** combined); *m/z* (EI$^+$) 302 (M$^+$, 31.3%), *1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene* **4** (3%); *m/z* (EI$^+$) 282 (M$^+$, 55.8%), *1,2-bis(trifluoromethyl)-3,5-dimethylbenzene* **5** (3%); *m/z* (EI$^+$) 242 (M$^+$, 34.6%) and recovered 1,3,5-trimethylbenzene. The mixture was added to a slurry of powdered potassium hydroxide (9.5 g, 170 mmol) in hexane (50 cm^3) and heated under reflux for 15 h. After this time the reaction mixture was added to water and extracted with hexane (3 x 70 cm3), removal of the solvent and redistillation gave *1,3,5-trimethyl-7,8-bis(trifluoromethyl)bicyclo[2.2.2]octa-2,5,7-triene* **4** (4.0 g, 52%); bp 49-52°C / 4 mmHg; (Found: C, 55.6; H, 4.4. $C_{13}H_{12}F_6$ requires C, 55.3; H, 4.3%); υ_{max}/cm^{-1} 2865-3016 (CH), 1607, 1686 and 1729 (C=C) and 1042-1375 (CF); δ_F (376MHz) -59.0 (1F, s, 7 or 8-CF_3), -67.8 (1F, s, 7 or 8-CF_3); δ_H (250MHz) 2.29 (6H, s, 3-CH_3), 2.30 (3H, s, 1-CH_3), 3.76 (1H, s, 4-H), 6.82 (2H, s, 2-H); *m/z* (EI$^+$) 282 (M$^+$, 55.8%).

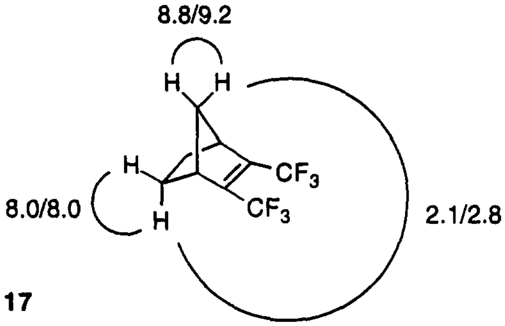
Cyclopentadiene Systems

Endo- and *exo- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* **13a** and **13b**. - *Z*-2*H*-Heptafluorobut-2-ene **1** (20.0 g, 0.11 mol) was transferred, under reduced pressure, to a sealable stainless steel tube (40 cm^3) that had previously been charged with dicyclopentadiene (7.9 g, 0.6 mol) under a counter current of dry nitrogen. The tube was evacuated, sealed and heated in a rocking furnace maintained at 180 °C for 6 d, under autogeneous pressure. Once reaction was complete the tube was cooled to liquid air temperatures, opened and recovered fluoroalkene **1** removed by distillation at atmospheric pressure. The residue was filtered, redistilled and shown to contain 2 components in approximately 4:3 ratio (**13a**:**13b**), identified as isomers of *5-*

fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene **13a** and **13b** (25.0 g, 92%) by comparison with literature data[12]; bp 24-26 °C / 7 mmHg (lit.,[12] 85.6 °C); (Found: C, 43.2; H, 2.7. $C_9H_7F_7$ requires C, 43.5; H, 2.8%); υ_{max}/cm^{-1} 2900, 2974, 3004 and 3086 (CH) and 1068-1386 (CF); *endo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* **13a**; δ_F (376MHz) -63.4 (3F, d, $^3J_{F-F}$ 7.9, 5-CF_3), -78.1 (3F, d, $^3J_{F-H}$ 4.1, 6-CF_3) assigned on the basis of F-H coupling, -180.3 (1F, q, $^3J_{F-F}$ 8.6, 5-F); δ_H (250MHz) 1.70 (2H, bs, 7-H), 3.00 (1H, dqd, $^3J_{H-F}$ 12.0, $^3J_{H-F}$ 8.8, $^4J_{H-H}$ 3.2, 6-H), 3.19 (1H, bs, 1 or 4-H), 3.39 (1H, bs, 1 or 4-H), 6.23 (1H, dd, $^3J_{H-H}$ 5.2, $^4J_{H-H}$ 3.6, 2 or 3-H), 6.53 (1H, m, 2 or 3-H); *m/z* (EI$^+$) 248 (M$^+$, 3.4%); *exo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* **13b**; δ_F (376MHz) -64.7 (3F, d, $^3J_{F-F}$ 9.4, 5-CF_3), -76.7 (3F, s, 6-CF_3), -176.9 (1F, m, 5-F); δ_H (250MHz) 1.86 (1H, d, $^3J_{H-H}$ 9.6, 7-H), 2.32 (1H, d, $^2J_{H-H}$ 8.0, 7-H), 2.52 (1H, dqd, $^3J_{H-F}$ 15.2, $^3J_{H-F}$ 8.8, $^4J_{H-H}$ 2.0, 6-H), 3.19 (1H, bs, 1 or 4-H), 3.24 (1H, bs, 1 or 4-H), 6.15 (1H, m, 2 or 3-H), 6.44 (1H, m, 2 or 3-H); *m/z* (EI$^+$) 248 (M$^+$, 2.8%).

Endo- and *exo- 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane* **16a** and **16b**. - A mixture of endo- and exo- 5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene **13a** and **13b** (17.2 g, 69.4 mmol) was dissolved in hexane (20 cm^3) and hydrogenated in Parr apparatus for 15 h in the presence of a platinum catalyst on activated carbon (2 g). Catalyst was removed by filtration through celite and distillation gave a mixture of *endo-* and *exo- 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane* **16a** and **16b** (14.8 g, 85%); bp 38-40 °C / 10 mmHg; (Found: C, 43.4; H, 3.6. $C_9H_9F_7$ requires C, 43.2; H, 3.6%); υ_{max}/cm^{-1} 2900 and 2987 (CH) and 1045-1389 (CF); a mixture of isomers (ratio*ca.* 4:3, **16a**:**16b**) enabling spectra to be assigned to *endo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]heptane* **16a**; δ_F (376MHz) -61.5 (3F, m, 2-CF_3), -80.4 (3F, m, 3-CF_3), -188.6 (1F, m, 2-F); *m/z* (EI$^+$) 250 (M$^+$, 2.6%); and *exo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]heptane* **16b**; δ_F (376MHz) -64.4 (3F, m, 2-CF_3), -75.4 (3F, s, 3-CF_3), -171.8 (1F, m, 2-F); *m/z* (EI$^+$) 250 (M$^+$, 0.9%).

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene **17**. - A mixture of *endo-* and *exo-* 2-fluoro-2,3-bis(trifluoromethyl)bicyclo[2.2.1]heptane **16a** and **16b** (14.0 g, 56.0 mmol) was added dropwise to a slurry of powdered potassium hydroxide (10.0 g, 178.6 mmol) in hexane (20 cm^3), stirred and refluxed for 48 h. Reaction could be monitored by ^{19}F NMR, and once reaction was complete the reaction mixture was added to water (100 cm^3) and extracted with dichloromethane (3 x 100 cm^3). Removal of the solvent, followed by redistillation gave a colourless oil identified as *2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene* **17** (12.9 g, 100%); bp 57-59 °C / 44 mmHg; (Found: C, 47.2; H, 3.6. $C_9H_{10}F_6$ requires C, 47.0; H, 3.5%); υ_{max}/cm^{-1} 2886 and 2964 (CH), 1669 (C=C) and 1037-1364 (CF); δ_F (376MHz) -60.6 (s); δ_C (100MHz) 24.2 (s, 5-C), 44.2 (s, 1-C), 48.1 (s, 7-C), 121.0 (q, $^1J_{C\text{-}F}$ 271.2, 2-CF_3), 139.4 (q, $^2J_{C\text{-}F}$ 40.0, 2-C); δ_H (250MHz) 1.28 (1H, dm, $^2J_{H\text{-}H}$ 9.2, 7-H), 1.32 (2H, dd, $^2J_{H\text{-}H}$ 8.0, $^4J_{H\text{-}H}$ 2.8, 5-endo-H), 1.68 (1H, dt, $^2J_{H\text{-}H}$ 8.8, $^4J_{H\text{-}H}$ 2.1, 7-H), 1.89 (2H, d, $^2J_{H\text{-}H}$ 8.0, 5-exo-H), 3.30 (2H, s, 1-H); *m/z* (EI$^+$) 202 (M^+-28, 100%).



17

***Bis(trifluoromethyl)cyclopentadiene* 18**. - 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene **17** (5.0 g, 21.7 mmol) was passed dropwise through a glass tube in a furnace maintained at 450 °C. Volatile material (4.6 g) was collected in a series of traps cooled to liquid air temperatures and was shown to contain an isomeric mixture of *bis(trifluoromethyl)cyclopentadienes* **18** (60%); (Found: M^+, 202.0217. $C_7H_4F_6$ requires M^+, 202.0954); δ_F (376MHz) -61.7 (s), -61.8 (s), -61.9, (s) -63.8 (s), -66.4 (s); δ_H (250MHz) 2.67 (bs), 3.29 (bs), 4.06 (q, $^3J_{H\text{-}F}$ 9.1), 6.4-7.1 (m); *m/z* (EI$^+$) 202 (M^+, 15.1%), recovered 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene **17** (12%) and unidentified material (28%).

Nucleophilic Addition Reactions

General Procedure with Potassium Carbonate. A Carius tube (60 cm^3), charged with *Z*-2*H*-heptafluorobut-2-ene **1**, potassium carbonate, acetonitrile and nucleophilic species, was evacuated, sealed and rotated end-over-end at room temperature for 15 h. After the reaction was completed the tube was opened and any volatile material transferred to a cold trap under reduced pressure. The residual solid was then placed in a separating funnel containing water (100 cm^3) and dichloromethane (3 x 50 cm^3) was used to extract the organic layer, which was dried ($MgSO_4$) and the solvent removed by rotatory evaporation. Further distillation under reduced pressure was carried out to afford a single product.

Oxygen Nucleophiles.

***Bis(trifluoromethyl)methylenedi-p-phenylenedioxy-2,2'-bis(1,1,1,4,4,4-hexafluorobut-2-ene),* 22.** - 2,2-Di(4-hydroxyphenol)hexafluoropropane (1.6 g, 4.8 mmol), *Z*-2*H*-heptafluorobut-2-ene **1** (3.7 g, 20.3 mmol), potassium carbonate (3.5 g, 25.7 mmol) and acetonitrile (20 cm^3) gave *bis(trifluoromethyl)methylenedi-p-phenylenedioxy-2,2'-bis(1,1,1,4,4,4-hexafluorobut-2-ene),* **22** (2.8 g, 88%); (Found: C, 42.1; H, 1.5. $C_{23}H_{10}F_{18}O_2$ requires C, 41.8; H, 1.5%); υ_{max}/cm^{-1} 3115 (CH), 1608 and 1511 (arom.C=C), 1700 (C=C) and 1061-1384 (CF); δ_F (376MHz) -59.7 (1F, d, $^3J_{F\text{-}H}$ 7.1, 4-F), -64.2 (1F, s, 1-F or 4'-CCF_3), -69.7 (1F, s, 1-F or 4'-CCF_3); δ_C (100MHz) 63.9 (septet, $^2J_{C\text{-}F}$ 25.5, 4'-*C*(CF_3)$_2$), 112.2 (qq, $^2J_{C\text{-}F}$ 37.0, $^3J_{C\text{-}F}$ 3.8, 3-C), 116.3 (s, 4'-C), 119.1 (q, $^1J_{C\text{-}F}$ 278.1, CF_3), 121.1 (q, $^1J_{C\text{-}F}$ 271.3, CF_3), 124.1 (q, $^1J_{C\text{-}F}$ 287.3, CF_3), 129.5 (s, 2'-C), 132.0 (s, 3'-C), 146.9 (qq, $^2J_{C\text{-}F}$ 36.2, $^3J_{C\text{-}F}$ 4.9, 2-C), 156.2 (s, 1'-C); δ_H (250MHz) 6.23 (1H, q, $^3J_{H\text{-}F}$ 7.2, 3-H), 7.03 and 7.37 (4H, AB, J_{AB} 136.0, 2' and 3'-H); *m/z* (EI$^+$) 660 (M$^+$, 26.8%).

Nitrogen Nucleophiles.

1,1,1,4,4,4-Hexafluoro-2-phenyliminobutane **23**. - Aniline (0.73 g, 7.8 mmol), *Z*-2*H*-heptafluorobut-2-ene **1** (3.2 g, 17.6 mmol), potassium carbonate (3.3 g, 24.3 mmol) and acetonitrile (10 cm^3) gave *1,1,1,4,4,4-hexafluoro-2-phenyliminobutane* **23** (1.8 g, 91%); bp 32-34 °C (5 mmHg); (Found: C, 46.9; H, 2.7; N, 5.4. $C_{10}H_7F_6N$ requires C, 47.1; H, 2.7; N, 5.5%); υ_{max}/cm^{-1} 2961, 3037 and 3071 (CH), 1487 and 1597 (arom.C=C), 1687 (C=C) and 1053-1343 (CF); δ_F (376MHz) -60.5 (1F, tq, $^3J_{F\text{-}H}$ 9.8, $^5J_{F\text{-}F}$ 6.0, 4-F), -64.2 (1F, q, $^5J_{F\text{-}F}$ 5.6, 1-F); δ_C (100MHz) 33.2 (q, $^2J_{C\text{-}F}$ 32.8, 3-C), 117.8 (s, 2'-C), 118.8 (q, $^1J_{C\text{-}F}$ 278.5, 1 or 4-CF_3), 122.8 (q, $^1J_{C\text{-}F}$ 278.1, 1 or 4-CF_3), 125.9 (s, 4'-C), 129.5 (s, 3'-C), 146.4 (s, 1'-C), 150.1 (q, $^2J_{C\text{-}F}$ 33.9, 2-C); δ_H (250MHz) 3.33 (2H, q, $^3J_{H\text{-}F}$ 9.6, 3-H), 6.77 (2H, d, $^3J_{H\text{-}H}$ 7.6, 2'-H), 7.22 (1H, t, $^3J_{H\text{-}H}$ 7.2, 4'-H), 7.41 (2H, t, $^3J_{H\text{-}H}$ 8.0, 3'-H); *m/z* (EI$^+$) 255 (M$^+$, 38.9%).

Sulfur Nucleophiles.

Z-1,1,1,4,4,4-Hexafluoro-2-(3-methylphenylthio)but-2-ene. - *m*-Thiocresol (1.0 g, 8.1 mmol), *Z*-2*H*-heptafluorobut-2-ene **1** (3.1 g, 17.0 mmol), potassium carbonate (3.3 g, 24.3 mmol) and acetonitrile (20 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-(3-methylphenylthio)but-2-ene* (2.1 g, 90%); bp 42-44 °C (5 mmHg); (Found: C, 46.0; H, 2.7. $C_{11}H_8F_6S$ requires C, 46.2; H, 2.8%); υ_{max}/cm^{-1} 2928 and 3064 (CH), 1477 and 1594 (arom.C=C), 1637 (C=C) and 1054-1366 (CF); δ_F (376MHz) -58.5 (1F, dq, $^3J_{F\text{-}H}$ 7.1, $^5J_{F\text{-}F}$

1.5, 4-F), -64.0 (1F, s, 1-F); δ_C (100MHz) 21.1 (s, 3'-CH_3), 121.4 (q, $^1J_{C\text{-}F}$ 272.0, 1 or 4-C), 121.4 (q, $^1J_{C\text{-}F}$ 277.0, 1 or 4-C), 126.9 (qq, $^2J_{C\text{-}F}$ 36.3, $^3J_{C\text{-}F}$ 4.9, 3-C), 127.5 (s, 3'-C), 129.1 (s), 130.2 (s), 130.4 (s), 133.8 (s), 138.3 (qq, $^2J_{C\text{-}F}$ 33.2, $^3J_{C\text{-}F}$ 4.9, 2-C), 139.3 (s, 1'-C); δ_H (250MHz) 2.33 (3H, s, 3'-CH_3), 6.63 (1H, qq, $^3J_{H\text{-}F}$ 9.6, $^4J_{H\text{-}F}$ 0.8, 3-H), 7.15 (1H, m, 4' or 6'-H), 7.17 (1H, m, 4' or 6'-H), 7.22 (1H, t, $^3J_{H\text{-}H}$ 7.4, 5'-H), 7.29 (1H, s, 2'-H); *m/z* (EI^+) 286 (M^+, 64.3%).

1,3-Bis(Z-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene. - 1,3-Dithiolbenzene (1.0 g, 7.0 mmol), *Z*-2*H*-heptafluorobut-2-ene **1** (3.7 g, 20.3 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (25 cm^3) gave *1,3-bis(Z-3,3,3-trifluoro-1-trifluoromethylprop-2-enylthio)benzene* (2.9 g, 89%); bp 58-60 °C (3 mmHg); (Found: C, 35.8; H, 1.2. $C_{14}H_6F_{12}S_2$ requires C, 36.1; H, 1.3%); υ_{max}/cm^{-1} 3080 (CH), 1462 and 1573 (arom.C=C), 1639 (C=C) and 1074-1359 (CF); δ_F (376MHz) -58.6 (1F, d, $^3J_{F\text{-}H}$ 7.9, 4-F), -64.4 (1F, s, 1-F); δ_C (100MHz) 121.2 (q, $^1J_{C\text{-}F}$ 277.0, 1 or 4-C), 121.2 (q, $^1J_{C\text{-}F}$ 272.0, 1 or 4-C), 128.6 (qq, $^2J_{C\text{-}F}$ 36.6, $^3J_{C\text{-}F}$ 4.9, 3-C), 130.2 (s, 2'-C), 130.3 (s, 4'-C), 133.9 (s, 5'-C), 137.1 (s, 1'-C), 139.3 (m, 2-C); δ_H (250MHz) 6.72 (1H, q, $^3J_{H\text{-}F}$ 7.2, 3-H), 7.3-7.6 (1H, m, 2', 4' and 5'-H); *m/z* (EI^+) 466 (M^+, 17.4%).

Z-1,1,1,4,4,4-Hexafluoro-2-phenylthiobut-2-ene. - Thiophenol (1.0 g, 9.1 mmol), 2*H*-heptafluorobut-2-ene **1** (2.7 g, 15.0 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (10 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-phenylthiobut-2-ene* (2.0 g, 81%); bp 34-36 °C (4 mmHg); (Found: C, 44.0; H, 2.2. $C_{10}H_6F_6S$ requires C, 44.1; H, 2.2%); υ_{max}/cm^{-1} 3080 (CH), 1478 and 1582 (arom.C=C), 1637 (C=C) and 1069-1325 (CF); δ_F (376MHz) -58.5 (1F, dq, $^3J_{F\text{-}H}$ 7.1, $^5J_{F\text{-}F}$ 1.1, 4-F), -64.0 (1F, s, 1-F); δ_C (100MHz) 121.3 (q, $^1J_{C\text{-}F}$ 277.0, 1 or 4-C), 121.4 (q, $^1J_{C\text{-}F}$ 268.6, 1 or 4-C), 127.1 (qq, $^2J_{C\text{-}F}$ 36.6, $^3J_{C\text{-}F}$ 5.3, 3-C), 129.3 (s, 2'-C), 129.4 (s, 4'-C), 130.9 (q, $^2J_{C\text{-}F}$ 48.0, 2-C), 133.4 (s, 3'-C), 135.7 (s, 1'-C); δ_H (250MHz) 6.65 (1H, qq, $^3J_{H\text{-}F}$ 7.2, $^4J_{H\text{-}F}$ 0.8, 3-H), 7.3-7.5 (5H, m, 2', 3' and 4'-H); *m/z* (EI^+) 272 (M^+, 70.4%).

Z-1,1,1,4,4,4-Hexafluoro-2-(4-methylthio)but-2-ene. - *p*-Thiocresol (1.0 g, 8.1 mmol), 2*H*-heptafluorobut-2-ene **1** (3.3 g, 18.1 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (10 cm^3) gave *Z-1,1,1,4,4,4-hexafluoro-2-(4-methylthio)but-2-ene* (1.8 g, 78.8%); bp 51-53 °C (5 mmHg); (Found: C, 45.9; H, 2.7. $C_{11}H_8F_6S$ requires C, 46.2; H, 2.8%); υ_{max}/cm^{-1} 2871-3079 (CH), 1493 (arom.C=C), 1637 (C=C) and 1048-1325 (CF); δ_F (376MHz) -58.4 (1F, d, $^3J_{F\text{-}H}$ 7.1, 4-F), -63.8 (1F, s, 1-F); δ_C (100MHz) 21.2 (s, 4'-CH_3), 121.4 (q, $^1J_{C\text{-}F}$ 277.3, 1 or 4-C), 121.5 (q, $^1J_{C\text{-}F}$ 272.0, 1 or 4-C), 125.1 (s, 4'-C), 125.9 (qq,

$^2J_{C\text{-}F}$ 36.3, $^3J_{C\text{-}F}$ 5.4, 3-C), 130.1 (s, 2'-C), 133.9 (s, 3'-C), 138.8 (qq, $^2J_{C\text{-}F}$ 32.8 $^3J_{C\text{-}F}$ 4.6, 2-C), 139.9 (s, 1'-C); δ_H (250MHz) 2.26 (3H, s, 4'-CH_3), 6.49 (1H, q, $^3J_{H\text{-}F}$ 6.0, 3-H), 7.07 and 7.31 (4H, AB, J_{AB} 96.0, 2' and 3'-H); *m/z* (EI$^+$) 286 (M$^+$, 100%).

Z-1,1,1-4,4,4-Hexafluoro-2-(phenylmethylthio)but-2-ene. - Benzyl mercaptan (1.5 g, 12.1 mmol), 2*H*-heptafluorobut-2-ene **1** (3.3 g, 18.1 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (20 cm^3) gave *Z-1,1,1-4,4,4-hexafluoro-2-(phenylmethylthio)but-2-ene* (2.9 g, 84%); bp 52-54 °C (5 mmHg); (Found: C, 45.9; H, 3.0. $C_{11}H_8F_6S$ requires C, 46.2; H, 2.8%); υ_{max}/cm^{-1} 2950-3087 (CH), 1496 (arom.C=C), 1631 (C=C) and 1049-1327 (CF); δ_F (376MHz) -59.1 (1F, d, $^3J_{F\text{-}H}$ 7.5, 4-F), -64.7 (1F, s, 1-F); δ_C (100MHz) 38.5 (s, 1'-CH_2), 121.4 (q, $^1J_{C\text{-}F}$ 272.0, 1 or 4-C), 121.7 (q, $^1J_{C\text{-}F}$ 276.6, 1 or 4-C), 126.3 (qq, $^2J_{C\text{-}F}$ 36.2, $^3J_{C\text{-}F}$ 5.7, 3-C), 128.1 (s, 4'-C), 128.8 (s, 2'-C), 129.2 (s, 3'-C), 135.0 (s, 1'-C), 138.0 (qq, $^2J_{C\text{-}F}$ 33.6 $^3J_{C\text{-}F}$ 5.0, 2-C); δ_H (250MHz) 4.15 (2H, s, 1'-CH_2), 6.57 (1H, qq, $^3J_{H\text{-}F}$ 6.8, $^4J_{H\text{-}F}$ 1.6, 3-H), 7.32-7.37 (5H, m, 2', 3' and 4'-H); *m/z* (EI$^+$) 286 (M$^+$, 2.3%).

Z-2-Cyclopentylthio-1,1,1,4,4,4-hexafluorobut-2-ene. - Cyclopentyl mercaptan (1.0 g, 9.8 mmol), *Z*-2*H*-heptafluorobut-2-ene **1** (2.7 g, 15.0 mmol), potassium carbonate (4.3 g, 31.4 mmol) and acetonitrile (20 cm^3) gave *Z-2-cyclopentylthio-1,1,1,4,4,4-hexafluorobut-2-ene* (1.8 g, 70%); δ_F (376MHz) -59.7 (1F, s, 4-F), -65.5 (1F, s, 1-F); *m/z* (EI$^+$) 264 (M$^+$, 7.5%).

General Procedure without Potassium Carbonate. A Carius tube (60 cm^3), charged with 2*H*-heptafluorobut-2-ene **1**, solvent (if required) and nucleophilic species, was evacuated, sealed and rotated end-over-end at room temperature. After the reaction was completed the tube was opened and any volatile material transferred to a cold trap under reduced pressure. The residual solid was then placed in a separating funnel containing water (100 ml) and dichloromethane (3 x 50 cm^3) was used to extract the organic layer, which was dried ($MgSO_4$) and the solvent removed on a rotatory evaporator. Further distillation under reduced pressure was carried out to afford a single product.

Nitrogen Nucleophiles.

1,1,1,4,4,4-Hexafluoro-2-phenylaminobutane **23**. - Aniline (0.7 g, 7.0 mmol), *Z*-2*H*-heptafluorobut-2-ene **1** (2.6 g, 14.3 mmol) and acetonitrile (10 cm^3) were allowed to react for 60 h and gave ***1,1,1,4,4,4-hexafluoro-2-phenylaminobutane*** **23** (0.6 g, 34%); bp 32-34 °C (5 mmHg); (Found: C, 46.9; H, 2.7; N, 5.4. $C_{10}H_7F_6N$ requires C, 47.1; H, 2.7; N, 5.5%); υ_{max}/cm^{-1} 2961, 3037 and 3071 (CH), 1487 and 1597 (arom.C=C), 1687 (C=C) and 1053-1343 (CF); δ_F (376MHz) -60.5 (1F, tq, $^3J_{F\text{-}H}$ 9.8, $^5J_{F\text{-}F}$ 6.0, 4-F), -64.2 (1F, q, $^5J_{F\text{-}F}$ 5.6, 1-F); δ_C (100MHz) 33.2 (q, $^2J_{C\text{-}F}$ 32.8, 3-C), 117.8 (s, 2'-C), 118.8 (q, $^1J_{C\text{-}F}$ 278.5, 1 or 4-CF_3), 122.8 (q, $^1J_{C\text{-}F}$ 278.1, 1 or 4-CF_3), 125.9 (s, 4'-C), 129.5 (s, 3'-C), 146.4 (s, 1'-C), 150.1 (q, $^2J_{C\text{-}F}$ 33.9, 2-C); δ_H (250MHz) 3.33 (2H, q, $^3J_{H\text{-}F}$ 9.6, 3-H), 6.77 (2H, d, $^3J_{H\text{-}H}$ 7.6, 2'-H), 7.22 (1H, t, $^3J_{H\text{-}H}$ 7.2, 4'-H), 7.41 (2H, t, $^3J_{H\text{-}H}$ 8.0, 3'-H); *m/z* (EI$^+$) 255 (M$^+$, 38.9%).

Oxygen Nucleophiles.

[Z-1-Trifluoromethyl-3,3,3-trifluoroprop-1-enyl]prop-2-enyl ether **19**. - The sodium salt of allyl alcohol (2.4 g, 30.0 mmol) and *Z*-2*H*-heptafluorobut-2-ene **1** (4.0 g, 22.0 mmol) were allowed to react for 15 h and gave *[1-trifluoromethyl-3,3,3-trifluoroprop-1-enyl]prop-2-enyl ether* **19** as a volatile product (3.7 g, 76%); bp 40-42 °C; (Found: C, 38.3; H, 2.8. $C_7H_6F_6O$ requires C, 38.2; H, 2.7%); υ_{max}/cm^{-1} 2897 (CH), 1690 and 1743 (C=C) and 1023-1402 (CF); δ_F (376MHz) -57.8 (1F, d, $^3J_{F\text{-}H}$ 7.5, 4-F), -70.0 (1F, s, 1-F); δ_C (100MHz) 74.8 (s, 1'-C), 105.2 (qq, $^2J_{C\text{-}F}$ 37.0, $^3J_{C\text{-}F}$ 4.6, 3-C), 119.2 (q, $^1J_{C\text{-}F}$ 278.5, 1 or 4-C), 119.6 (s, 3'-C) 121.8 (q, $^1J_{C\text{-}F}$ 270.1, 1 or 4-C), 131.2 (s, 2'-C), 150.1 (qq, $^2J_{C\text{-}F}$ 33.9, $^3J_{C\text{-}F}$ 5.3, 2-C); δ_H (250MHz) 4.58 (2H, d, $^3J_{H\text{-}H}$ 5.6, 1'-H), 5.32 (1H, dd, $^2J_{H\text{-}H}$ 1.2, $^3J_{H\text{-}H}$ 10.4, 3'-trans-H), 5.40 (1H, dd, $^3J_{H\text{-}H}$ 17.2, $^2J_{H\text{-}H}$ 1.2, 3'-cis-H), 5.75 (1H, q, $^3J_{H\text{-}F}$ 7.6, 3-H), 5.95 (1H, ddt, $^3J_{H\text{-}H}$ 17.2, $^3J_{H\text{-}H}$ 10.4, $^3J_{H\text{-}H}$ 5.6, 2'-H); *m/z* (EI$^+$) 220 (M$^+$, 3.7%).

1,1,1-Trifluoro-3-trifluoromethyl-5-hexen-2-one **20**. - A Carius tube (60 cm^3) charged with [Z-1-Trifluoromethyl-3,3,3-trifluoroprop-1-enyl]prop-2-enyl ether **19** (3.7 g, 16.8 mmol) was evacuated, sealed and heated to 80 °C for 24 h. After reaction was complete the tube was opened and no volatile material was transfered when connected to a cold trap under reduced pressure. The residual oil was then distilled by heating under reduced pressure to afford a single product identified by comparison with authentic spectra as *1,1,1-trifluoro-3-trifluoromethyl-5-hexen-2-one* **20** (3.7 g, 100%); bp 88-90 °C (lit.,[15] 88.5-89 °C); (Found: C, 38.3; H, 2.7. $C_7H_6F_6O$ requires C, 38.2; H, 2.7%); υ_{max}/cm^{-1} 2359 (CH), 1773 (C=O), 1647 (C=C) and 1117-1399 (CF); δ_F (376MHz) -66.4 (1F, d, $^3J_{F\text{-}H}$ 5.3, 3-CF_3), -79.5 (s, 1-F); δ_C (100MHz) 30.8 (s, 4-C), 49.8 (q, $^2J_{C\text{-}F}$ 27.5, 3-C), 114.7 (q, $^1J_{C\text{-}F}$ 291.4, 1-C or 3-CF_3), 120.4 (s, 6-C) 123.3 (q, $^1J_{C\text{-}F}$ 281.1, 1-C or 3-CF_3), 130.6 (s, 5-C), 185.6 (qm, $^2J_{C\text{-}F}$ 38.1, 2-C); δ_H (250MHz) 2.71 (2H, m, 4-H), 3.85 (1H, dqd, $^3J_{H\text{-}H}$ 9.6, $^3J_{H\text{-}F}$ 7.2, $^3J_{H\text{-}H}$ 5.2, 3-H), 5.15 (1H, dd, $^2J_{H\text{-}H}$ 3.2, $^3J_{H\text{-}H}$ 1.2, 6-trans-H), 5.19 (1H, bs, 6-cis-H), 5.67 (1H, t, $^3J_{H\text{-}H}$ 10.0, 5-H), ; *m/z* (EI$^+$) 219 (M$^+$-1, 21.4%).

Formation of 2-Trifluoromethyl-4-(*N*-phenylamino)-quinoline 24.

2-Trifluoromethyl-4-(N-phenylamino)-quinoline **24**. - 2-Phenylimino-1,1,1,4,4,4-hexafluorobutane **1** (1.0 g, 3.9 mmol) was added dropwise to a stirred slurry of powdered potassium hydroxide (2.0 g, 35.7 mmol) in hexane (50 cm^3) and left at room temperature for 60 h. After the reaction was complete the hexane was removed on a rotatory evaporator, the resultant slurry added to water and extracted with dichloromethane (3 x 50 cm^3). Solvent was removed on a rotatory evaporator and the resultant solid purified by vacuum sublimation [oil bath temperature 100 °C (<1 mmHg)] to afford a single white crystalline product identified as *2-trifluoromethyl-4-(N-phenylamino)-quinoline* **24** (0.3 g, 53%); mp 140-142 °C; (Found: C, 66.5; H, 3.8; N, 9.9. $C_{16}H_{11}F_3N_2$ requires C, 66.7; H, 3.8; N, 9.7%); υ_{max}/cm^{-1} 3222 (NH), 2925 (CH), 1495-1586 (arom.C=C) and 1027-1401 (CF); δ_F (376MHz) -67.5 (s); δ_C (100MHz) assigned by comparison to spectra from similar compounds[20] 97.1 (bs, 3-C), 121.0 (s, 5-C), 122.7 (s, 4'-C), 123.2 (q, $^1J_{C-F}$ 274.6, 2-CF_3), 125.4 (s, 2'-C), 126.9 (s, 6-C), 127.9 (s, 8-C), 130.1 (s, 7-C), 130.9 (s, 3'-C), 132.0 (s, 4a-C), 140.7 (s, 1' or 4-C), 149.3 (s, 1' or 4-C), 149.4 (q, $^2J_{C-F}$ 33.2, 2-C), 153.0 (s, 8a-C); δ_H (250MHz) 7.06 (1H, s, 3-H), 7.29 (1H, m, 4'-H), 7.40 (2H, dd, $^3J_{H-H}$ 8.0, $^4J_{H-H}$ 0.8, 2'-H), 7.49 (2H, m, 3'-H), 7.64 (1H, m, 6-H), 7.80 (1H, m, 7-H), 8.02 (1H, d, $^3J_{H-H}$ 8.8, 8-H), 8.36 (1H, d, $^3J_{H-H}$ 8.4, 5-H); *m/z* (EI^+) 288 (M^+, 100%).

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