Fluorinated acetylenes.
Part 13 [1]. Synthesis of 1,6-diphenyl-3,3,4,4-tetrafluorohexa-1,5-diyne

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Abstract

The title compound (**6**) may be conveniently synthesised via the three-stage route:

$$\mathrm{PhC{\equiv}CLi + CF_2Br_2} \xrightarrow[(46\%)]{\mathrm{THF}} \underset{(\mathbf{7})}{\mathrm{PhC{\equiv}CCF_2Br}} \xrightarrow[(60\%)]{\mathrm{NaI/Me_2CO}} \underset{(\mathbf{8})}{\mathrm{PhC{\equiv}CCF_2I}}$$

$$\mathbf{8} \xrightarrow[(67\%)]{\mathrm{Zn/Ac_2O/CH_2Cl_2}} \underset{(\mathbf{6})}{\mathrm{PhC{\equiv}CCF_2CF_2C{\equiv}CPh}}$$

In the first stage the alkyne $PhC{\equiv}CBr$ is also produced, and this undergoes reaction with iodine generated in the second stage to give the alkene (*E*)-$PhCI{=}CBrI$ (**10**) (up to 9.5%). Other by-products formed in the second stage, depending on the conditions employed, are the 1,4-diyne $PhC{\equiv}CCF_2C{\equiv}CPh$ (**12**), isolated in 3.5% yield, and 1-iodo-2,3-naphtho-4-phenyltetrafluorocyclobutene (**11**), isolated in 11.5% yield. Mechanisms are advanced to account for all the products isolated.

Introduction

Having successfully prepared 1,4-diynyl esters of the type $(CF_3C{\equiv}C)_2CRO_2CR$ (R = Me or Ph) and studied their cycloaddition reactions with various 1,3-dienes [2, 3], routes to fluorinated 1,5-diynes were investigated [1]. However, reaction of 3,3,3-trifluoropropynyl-lithium with benzil and α-halogenoacetophenone, followed by the addition of benzoyl chloride, did not afford the desired 1,5-diynes **1** and **2**. Also, treatment of the oxirane **3** formed from α-bromoacetophenone, with lithium phenylacetylide followed by the addition of benzoyl chloride, did not yield 1,5-diyne **4** [1].

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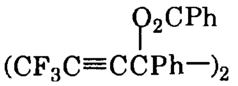
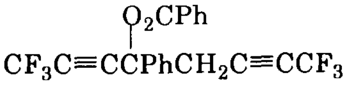


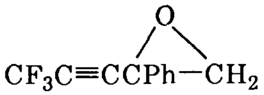
$(CF_3C\equiv C\overset{O_2CPh}{C}Ph{-})_2$

(1)



$CF_3C\equiv C\overset{O_2CPh}{C}PhCH_2C\equiv CCF_3$

(2)



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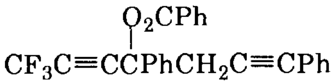


$CF_3C\equiv C\overset{O_2CPh}{C}PhCH_2C\equiv CPh$

(4)

The report [4] of the successful synthesis of 1,4-diynes of type **5** via the sequence:

$$THPOCH_2C\equiv CLi \xrightarrow[THF]{CF_2ClBr} THPOCH_2\equiv CCF_2Br \xrightarrow[Me_2CO]{NaI}$$

$$THPOCH_2C\equiv CCF_2I \xrightarrow[THF]{RC\equiv CLi} \underset{(5)}{THPOCH_2C\equiv CCF_2C\equiv CR}$$

(THP = tetrahydropyran-2-yl) has prompted an investigation of the following route to the 1,5-diyne **6**.

$$PhC\equiv CLi \xrightarrow{CF_2Br_2} \underset{(7)}{PhC\equiv CCF_2Br} \xrightarrow[Me_2CO]{NaI} \underset{(8)}{PhC\equiv CCF_2I} \xrightarrow{coupling} \underset{(6)}{(PhC\equiv CCF_2-)_2}$$

The results of that study are now reported.

Results and discussion

The (bromodifluoromethyl)alkyne **7** was prepared by the reported method [5] in three experiments using different amounts of reactants (Table 1), the best yield obtained being 46% after distillation (experiment 1). However, alkyne **7** was shown by its mass (m/z 183/181, $C_8H_5Br^+$) and ^{13}C NMR [δ 80.1 (Ph$C\equiv$) and 49.7 ($\equiv$CBr) ppm] spectra to be contaminated with the bromoalkyne PhC$\equiv$CBr (**9**) in variable amounts in the different experiments (up to *c.* 10%).

The formation of bromoalkyne **9** was not noted in the reported preparation of alkyne **7** [5], but the reaction of $THPOCH_2C\equiv CLi$ with CF_2ClBr was observed to give alkynes $THPOCH_2C\equiv CCF_2Br$ (52%) and $THPOCH_2C\equiv CBr$ (25%) [4].

The formation of alkynes **7** and **9** is considered to involve a single-electron transfer (SET) process (Scheme 1).

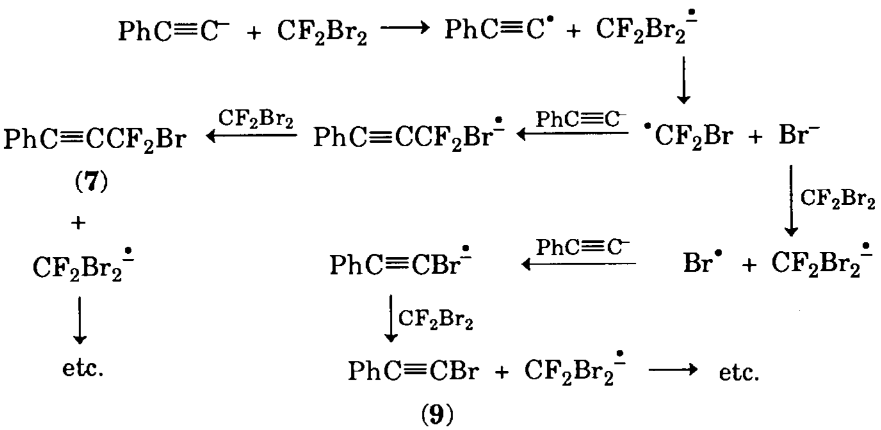
In the second stage, the mixture of alkynes **7** and **9** and sodium iodide was heated under reflux, and the results obtained are also given in Table 1. The best yield of iodoalkyne **8** (60%) was obtained using a 4:1 molar ratio of I^- to alkyne **7**, and a long reflux time (35 h).

Iodoalkyne **8** is also presumed to arise by a SET process (Scheme 2).

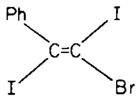
TABLE 1

Preparation of alkynes $PhC{\equiv}CCF_2Br$ (**7**) and $PhC{\equiv}CCF_2I$ (**8**)

Alkyne	Reaction conditions	Experiments		
		1	2	3
7	$PhC{\equiv}CLi$ (mol)	0.20	0.45	0.10
	CF_2Br_2 (mol)	0.25	0.48	0.10
	THF (cm^3)	200	300	100
	Temp. (°C)	−20 to 0	−20 to 0	−20 to 0
	Yield of **7** (mol)	0.09	0.13	0.035
	(%)	46	30	35
8	**7** (mol)	0.09	0.13	0.03
	NaI (mol)	0.37	0.80	0.20
	Ratio **7**/NaI	*c.* 1:4	*c.* 1:6	*c.* 1:6
	Reflux (h)	35	20	31
	Products (%) **8**	60	28	42
	10	0.5	0.5	9.5
	11	11	<1	<1
	12		3.5	<1



Scheme 1.



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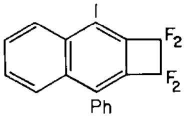
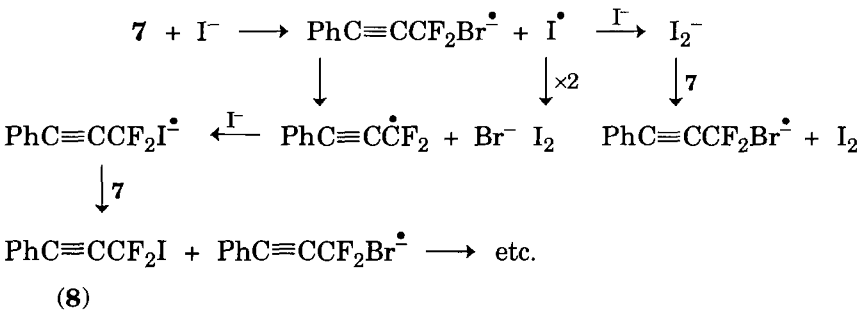


(11)

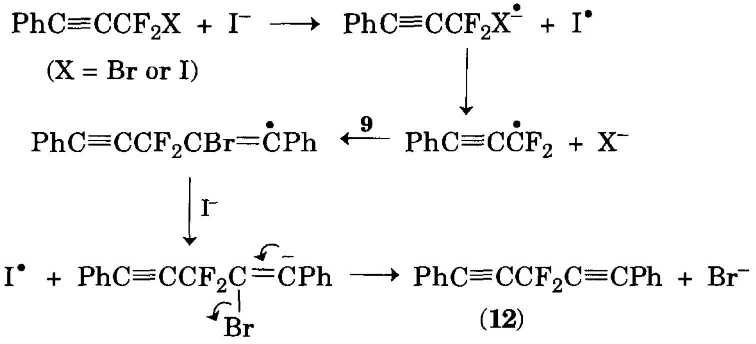
$PhC{\equiv}CCF_2C{\equiv}CPh$

(12)

The by-products **10–12** were detected in all the reactions (TLC, ^{19}F NMR spectroscopy) and they were obtained pure from the experiments in



Scheme 2.



Scheme 3.

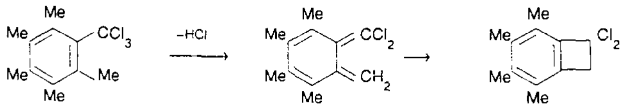
which they were produced in the highest yields. The structure of the naphthocyclobutene **11** [6] and the stereochemistry of the alkene **10** [7] were established by X-ray crystallography.

Alkene **10** was formed by electrophilic addition of iodine across the acetylenic triple bond in the bromoalkyne **9**, while the 1,4-diyne **12** could arise via reaction of the radical $PhC{\equiv}C\dot{C}F_2$ with bromoalkyne **9** (Scheme 3).

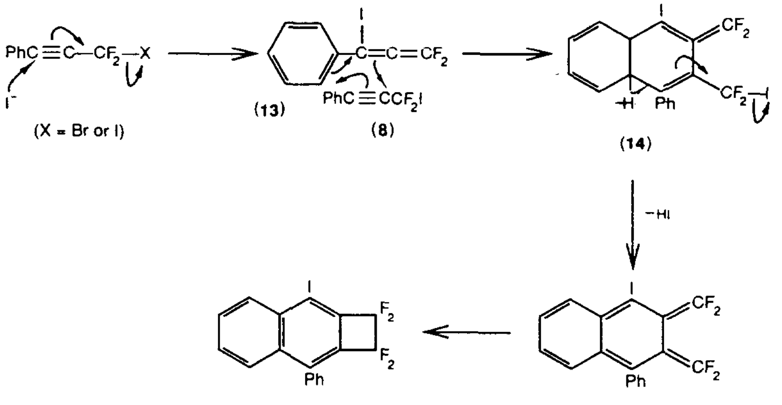
The remaining isolated product, the cyclobutene derivative **11**, could have arisen via rearrangement of either bromide **7** or iodide **8** to the allene **13**. The well-known alkyne–allene rearrangement could also have given allene **13** from alkyne **8**, but such isomerisations occur under base-catalysed conditions [8]. The Diels–Alder adduct **14** formed from allene **13** and alkyne **8** would be expected to eliminate hydrogen iodide readily and ring closure of the resulting diene **15** would afford cyclobutene **11** (Scheme 4).

In support of this mechanism, it has been proposed [9] that intermediate **16** is involved in the base-catalysed intramolecular cyclisation of the 1,6-diyne **17** to afford the naphthocyclopentene **18** (Scheme 5).

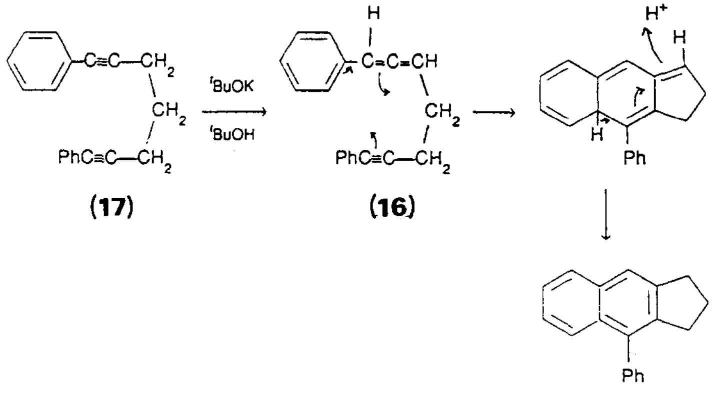
A comparable cyclisation has been observed when pentamethylbenzotrichloride was heated at 110 °C [10], i.e.



Coupling of the type $2RCF_2I \rightarrow RCF_2CF_2R$ occurs readily with various metals, more especially zinc [11, 12] and copper [13, 14]. Reaction of the iodoalkyne **8** with both these metals was investigated as a means of preparation of the 1,5-diyne **6**.

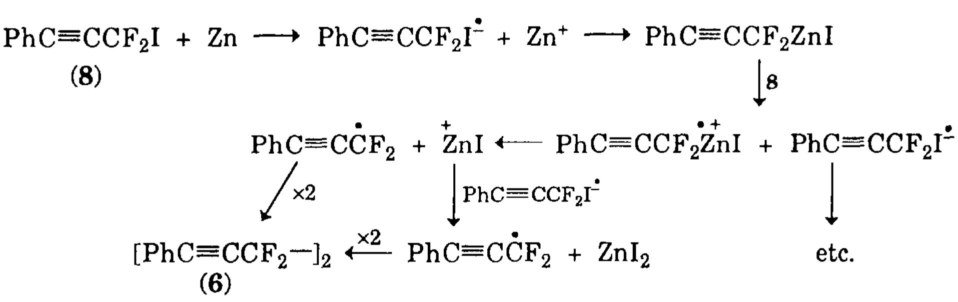


Scheme 4.



Scheme 5. (18)

A solution of alkyne **8** in dichloromethane in the presence of granulated zinc (2:3 molar ratio) and acetic anhydride was heated under reflux (16 h). After removal of the acetic anhydride and solvent, the residue was purified by DCFC to give the 1,5-diyne **6** (67%), which is presumed to be formed by a SET mechanism (Scheme 6).



Scheme 6.

In a second experiment, a solution of alkyne **8** in DMF in the presence of copper bronze (1:2 molar ratio) was heated under reflux (1 h). A complex mixture of products was formed of which 1,5-diyne **6** was a major component (^{19}F NMR spectroscopy, *c.* 60%).

The 1,5-diyne **6** has thus been synthesised successfully from phenylacetylene and dibromodifluoromethane, but an initial study of its cycloaddition reactions with furan and diazomethane has been disappointing. With furan (1:1 molar ratio) in dichloromethane, reaction die not take place at 50 °C (7 d) or 95 °C (3 d), but at 125 °C (4 d) a black tar was obtained together with unchanged **6** (60% recovered). Treatment of an ethereal solution of **6** with an excess of diazomethane at 0 °C gave only unchanged **6** (100% recovered).

Experimental

Starting materials

Phenylacetylene and dibromodifluoromethane were commercial samples and their purity was checked before use. Lithium phenylacetylide was made by the slow addition of phenylacetylene to a stirred solution of n-butyllithium (1.6 M solution in hexane) in anhydrous THF under nitrogen at −20 °C in a flask fitted with a cold finger (−78 °C), and stirring was continued for 0.5 h.

General techniques

Reaction product mixtures were separated, and certain products were purified, by dry column flash chromatography (DCFC) using silica (Merck Kieselgel 60H) and eluants as given in the text; light petroleum is the petroleum ether fraction, b.p. 40–60 °C.

IR, NMR [^{1}H (220 MHz), ^{19}F (84.6 MHz) and ^{13}C (75.0 MHz and including DEPT 135°) with samples as solutions in $CDCl_3$ and external tetramethylsilane (TMS), external trifluoroacetic acid (TFA) and internal TMS as the respective references; chemical shifts to low field of reference designated positive] and routine mass under electron impact (EI) or chemical ionisation (CI, with

NH_3 gas) conditions spectra were recorded on instruments described previously [2]. Accurate mass measurements were carried out on a Kratos Concept high resolution spectrometer.

Preparation of 3-bromo-3,3-difluoro-1-phenylpropyne (7)

(a) Experiment 1

Dibromodifluoromethane (50.0 g, 0.25 mol) was bubbled into a stirred solution of lithium phenylacetylide [prepared from n-butyl-lithium (12.90 g, 0.20 mol) and phenylacetylene (20.60 g, 0.20 mol)] in THF (200 cm^3) at −20 °C (1 h) and then the temperature was raised first to 0 °C (1 h) and then to room temperature and stirring was continued (4 h). The THF was removed (rotary evaporator), water (200 cm^3) was added and the aqueous phase was extracted with diethyl ether (3×50 cm^3). The combined organic phase was washed with hydrochloric acid (2 M, 50 cm^3) then with water (3×50 cm^3) and dried ($MgSO_4$). Fractional distillation of the material gave a fraction, b.p. 101 °C at 6 mmHg, which was shown by its ^{13}C NMR and mass spectra to be 3-bromo-3,3-difluoro-1-phenylpropyne (**7**) (21.2 g, 91.8 mmol, 46%) contaminated with a small amount (*c.* 2%) of 2-bromo-1-phenylacetylene. ^{19}F NMR δ: 47.5 (CF_2Br) ppm. ^{13}C NMR δ: 132.2, 130.8 and 128.6 (3s, arom. =CH); 118.7 (s, ipso-C_6H_5); 101.2 (t, $\mathit{CF}_2BrC{\equiv}C$, $^1J = 289$ Hz); 90.0 (t, $CF_2BrC{\equiv}\mathit{C}$, $^3J = 6$ Hz); and 80.7 (b, $CF_2Br\mathit{C}{\equiv}C$, $^2J = 39$ Hz) ppm. Mass spectrum (EI) (*m/z*): 232/230 (1.7%, M^+); 213/211 [1.2, $(M-F)^+$]; 151 [100.0, $(M-Br)^+$]; 77 (3.3, $C_6H_5{}^+$); and 75 (10.3, $C_6H_3{}^+$). [For 2-bromo-1-phenylacetylene: ^{13}C NMR δ: 132.0, 128.7 and 128.3 (3s, arom. =CH); 122.7 (s, ipso-C_6H_5); 80.1 (s, $Ph\mathit{C}{\equiv}C$); and 49.7 (s, $Br\mathit{C}{\equiv}C$) ppm. Mass spectrum (*m/z*): 182/180 (7.8%, M^+); and 101 [9.3, $(M-Br)^+$].

(b) Experiment 2

The preparation was repeated on a larger scale using n-butyl-lithium (28.80 g, 0.45 mol), phenylacetylene (45.90 g, 0.45 mmol), dibromodifluoromethane (100.0 g, 0.48 mol) and THF (300 cm^3). Work-up as in experiment 1, gave alkyne **7** (30.09 g, 0.13 mol, 30%) contaminated with a small amount (*c.* 2%) of 2-bromo-1-phenylacetylene (^{13}C NMR spectroscopy).

(c) Experiment 3

A repeat of the reaction on a small scale using n-butyl-lithium (6.50 g, 0.1 mol), phenylacetylene (10.3 g, 0.1 mol), dibromodifluoromethane (25.0 g, 0.1 mol) and THF (100 cm^3) gave alkyne **7** (8.04 g, 34.8 mmol, 35%) contaminated with a considerable amount (*c.* 10%) of 1-bromo-2-phenylacetylene (^{13}C NMR spectroscopy).

Preparation of 3,3-difluoro-3-iodo-1-phenylpropyne (8)

(a) Experiment 1

A solution of bromoalkyne **7** (prepared as in experiment 1) (20.29 g, 87.9 mmol) in acetone (100 cm^3) and a solution of sodium iodide (55.0 g, 0.37 mol) in acetone (200 cm^3) were mixed and then heated under reflux

(35 h) under a nitrogen atmosphere with monitoring (^{19}F NMR spectroscopy). After cooling, a mixture of hexane (300 cm^3) and water (300 cm^3) was added, the organic layer separated and the aqueous layer extracted with hexane (5 × 20 cm^3). The combined organic material was dried ($MgSO_4$) and the solvent removed (rotary evaporator) to give a residue (20.3 g) which was shown by TLC (light petroleum) to contain a major ($R_F = 0.57$) and two minor ($R_F = 0.42$ and 0.32) components. Separation of the mixture (*c.* 7 g batches) by DCFC (same eluant) gave the following compounds:

(i) 3,3-Difluoro-3-iodo-1′-phenylpropyne (**8**) (nc) (14.72 g, 52.9 mmol, 60%). Analysis: Found: C, 39.2; H, 2.0; F, 13.6%; mol. wt., 277.9404. $C_9H_5F_2I$ requires: C, 38.9; H, 1.8; F, 13.6%; mol. wt., 278.0403. ^{1}H NMR δ: 7.52–7.13 (complex, C_6H_5) ppm. ^{13}C NMR δ: 132.1, 130.7 and 128.6 (3s, arom. =CH); 119.0 (t, ipso-C_6H_5, $^4J = 2$ Hz); 90.8 (t, $CF_2IC{\equiv}\mathit{C}C$, $^3J = 6$ Hz); 83.8 (t, $CF_2I\mathit{C}{\equiv}C$, $^2J = 34$ Hz); and 72.0 (t, $\mathit{C}F_2IC{\equiv}C$, $^1J = 298$ Hz) ppm. IR ν_{max} (cm^{-1}): 2250 (s, C≡C str.); 1120 and 1075 (s, C–F str.); and 650 (s, C–I str.). Mass spectrum (EI) (m/z): 278 (2.0%, M^+); 259 [52.5, $(M-F)^+$]; 151 [100.0, $(M-I)^+$]; 127 (19.5, I^+); 120 (31.4, $C_8H_5F^+$); 101 (25.3, $C_8H_5{}^+$); 99 (20.6, $C_7H_5{}^+$); and 51 (18.5, $C_4H_3{}^+$).

(ii) (*E*)-1-Bromo-1,2-di-iodo-2-phenylethene (**10**) (nc) (0.15 g, 0.35 mmol, 0.5%). Analysis: Found: C, 22.1; H, 1.1%; mol. wt., 436 and 434. $C_9H_5BrI_2$ requires: C, 22.1; H, 1.1%; mol. wt., 435. M.p. 68 °C. ^{1}H NMR δ: 7.3–7.1 (mult., C_6H_5) ppm. ^{13}C NMR δ: 146.6 (s, ipso-C_6H_5); 129.5, 129.3 and 128.6 (3s, arom. =CH); 105.5 (s, $CBrI{=}\mathit{C}I$); and 57.6 (s, $\mathit{C}BrI{=}C$) ppm. IR ν_{max} (cm^{-1}): 1485 and 1440 (s, C=C str.); 695 (s, C–Br str.); and 656 (s, C–I str.). Mass spectrum (EI) (m/z): 436/434 (23.9%, M^+); 309/307 [60.8, $(M-I)^+$]; 182/180 [100.0, $(M-I_2)^+$]; 101 (23.0, $C_8H_5{}^+$); 75 (23.3, $C_6H_3{}^+$); and 51 (23.8, $C_4H_3{}^+$). The stereochemistry was confirmed by an X-ray crystallographic study [7].

(iii) 1-Iodo-2,3-naphtho-4-phenyltetrafluorocyclobutene (**11**) (nc) (2.13 g, 5.0 mmol, 11%). Analysis: Found: C, 50.5; H, 2.3; F, 17.5%; mol. wt., 428. $C_{18}H_9F_4I$ requires: C, 50.5; H, 2.1; F, 17.8%; mol. wt., 428. M.p. 148 °C. ^{1}H NMR δ: 8.13 (d, 1H, $J = 7.5$ Hz); 7.90 (d, 1H); 7.55 (t, 1H); and 7.21 (mult., 5H, C_6H_5) ppm. ^{19}F NMR δ: −31.0 and −25.1 (2s, $2CF_2$) ppm. ^{13}C NMR δ: 142.6 and 136.6 (2tt, $2CF_2{-}\mathit{C}{=}$, $^2J = 25$ Hz, $^3J = 12$ Hz); 138.2 (s, ipso-C_6H_5); 135.1 and 133.6 (2s, arom. =C); 132.3, 129.9, 129.7, 129.2, 129.0, 128.9 and 128.0 (7s, arom. =CH); 120.4 and 119.4 (2tt, $CF_2{-}CF_2$, $^1J = 291$ Hz, $^2J = 27$ Hz); and 89.5 (t, =CI, $^3J = 4$ Hz) ppm. IR ν_{max} (cm^{-1}): 1110 (s, C–F str.); and 550 (m, C–I str.). Mass spectrum (EI) (*m/z*): 428 (100%, M^+); 301 [45.1, $(M-I)^+$]; 300 [47.2, $(M-HI)^+$; 281 (12.0, $C_{18}H_8F_3{}^+$); 280 (27.3, $C_{18}H_7F_3{}^+$); and 231 (9.1, $C_{17}H_8F^+$). The structure was determined by X-ray crystallography [6].

(*b*) *Experiment 2*

A solution of bromoalkyne **7** (from experiment 2) (30.0 g, 0.13 mol) and sodium iodide (120.0 g, 0.80 mol) in acetone (750 cm^3), heated under reflux (20 h) under a nitrogen atmosphere and worked-up as in the previous experiment gave a crude product (15.1 g) which was shown by TLC (light petroleum) to contain one major ($R_F = 0.57$) and three minor ($R_F = 0.42$, 0.35 and 0.31) components. Separation by DCFC (same eluant) gave (i) alkyne **8** (10.1 g, 36.4 mmol, 28%), (ii) alkene **10** (0.19 g, 0.40 mmol, 0.5%) and (iii) 3,3-difluoro-1,5-diphenylpenta-1,4-diyne (**12**) (nc) (1.08 g, 4.3 mmol, 3.5%). Analysis: Found: C, 80.6; H, 3.9%, mol. wt., 252. $C_{17}H_{10}F_2$ requires: C, 80.9; H, 4.0%; mol. wt., 252. ^1H NMR δ: 7.73–7.52 (mult., o-C_6H_5); and 7.49–7.31 (mult., m- and p-C_6H_5) ppm. ^{19}F NMR δ: -14.8 (s, CF_2) ppm. ^{13}C NMR δ: 133.0, 131.0 and 129.2 (3s, arom. =CH); 120.4 (t, ipso-C_6H_5, $^4J = 2$ Hz); 102.6 (t, $\mathit{C}F_2C{\equiv}C$, $^1J = 224$ Hz); 87.6 (t, $CF_2C{\equiv}\mathit{C}$, $^3J = 6$ Hz); and 81.8 (t, $CF_2\mathit{C}{\equiv}C$, $^2J = 43$ Hz) ppm. IR ν_{max} (cm^{-1}): 2250 (s, C≡C str.); and 1310 and 1120 (s, C–F str.) Mass spectrum (EI) (m/z): 252 (93.1%, M^+); 251 [100.0, $(M-H^+)$]; 233 [31.9, $(M-F)^+$]; 202 (88.1, $C_{16}H_{10}{}^+$); and 200 (20.2, $C_{16}H_8{}^+$). The fourth component could not be obtained pure but was identified as the cyclobutene **11** (<1%) by ^{19}F NMR spectroscopy.

(c) Experiment 3

A solution of alkyne **7** (from experiment 3) (7.50 g, 32.5 mmol) and sodium iodide (30.0 g, 0.20 mol) in acetone (200 cm^3), heated under reflux (31 h) and then worked-up as in experiment 1, gave crude product (5.92 g). The major components were separated by DCFC (light petroleum) and identified as alkyne **8** (3.81 g, 13.8 mmol, 42%) and alkene **10** (1.33 g, 3.1 mmol, 9.5%). Small amounts of cyclobutene **11** and of the 1,4-diyne **12** were also present (^{19}F NMR spectroscopy).

Coupling of 3,3-difluoro-3-iodo-1-phenylpropyne (8)

(a) Using zinc

A solution of acetic anhydride (3.99 g, 39.1 mmol) in dichloromethane (5 cm^3) was added dropwise to a stirred mixture of granulated zinc (1.82 g, 27.8 mmol) and alkyne **8** (5.00 g, 18.0 mmol) in dichloromethane (5 cm^3). The resulting mixture was heated under reflux (16 h) with the reaction monitored by ^{19}F NMR spectroscopy and then cooled to room temperature and filtered. The filtrate was cooled to 0 °C, water (20 cm^3) was added and stirring was continued (1 h). The organic layer was separated, the aqueous layer was extracted with dichloromethane (3×10 cm^3) and the combined organic material dried ($MgSO_4$) and the solvent removed (rotary evaporator) to afford a semi-solid product (5.50 g). This material was shown by TLC [light petroleum/dichloromethane (6:1 v/v)] to contain one major ($R_F = 0.35$) and several minor components. The major component was separated by DCFC (same eluant) and was identified as 3,3,4,4-tetrafluoro-1,6-diphenylhexa-1,5-diyne (**6**) (nc) (1.81 g, 6.0 mmol, 66%). Analysis: Found: C, 71.8; H, 3.1; F, 25.4%; mol. wt., 302. $C_{18}H_{10}F_4$ requires: C, 71.5; H, 3.3; F, 25.2%; mol. wt., 302. M.p., 43 °C. ^1H NMR δ: 7.60–7.30 (mult., C_6H_5) ppm. ^{19}F NMR δ: -20.2 (s, CF_2) ppm. ^{13}C NMR δ: 133.1, 131.1 and 129.3 (3s, arom. =CH); 119.9 (s, ipso-C_6H_5); 109.1 (tt, CF_2, $^1J = 245$ Hz, $^2J = 37$ Hz); 91.4 (br., $CF_2C{\equiv}\mathit{C}$); and 77.0 (t, $CF_2\mathit{C}{\equiv}C$, $^2J = 37$ Hz) ppm. IR ν_{max} (cm^{-1}):

2250 (s, C≡C str.); and 1260 and 1135 (s, C−F str.). Mass spectrum (CI) (*m/z*): 320 [0.6%, $(M+NH_4)^+$]; 303 [13.5, $(M+H)^+$]; 302 (38.6, M^+); 283 [41.1, $(M-F)^+$]; 282 [17.1, $(M-HF)^+$]; 151 (100.0, $PhC_3F_2{}^+$); 148 (18.1, $C_9H_3F_2{}^+$); and 102 (50.2, $C_8H_6{}^+$).

(b) Using copper

A solution of alkyne **8** (1.00 g, 3.6 mmol) in DMF (20 cm^3) was added to copper bronze (0.46 g, 7.2 mmol) and the mixture heated under reflux (1 h) under an atmosphere of nitrogen with the reaction being monitored by ^{19}F NMR spectroscopy. The resulting material was filtered, water (10 cm^3) added to the stirred filtrate and stirring continued (15 min). Separation of the organic layer, extraction of the aqueous layer with diethyl ether (3×4 cm^3) and the organic material combined and dried ($MgSO_4$) and the solvent removed (rotary evaporator) gave a dark-brown semi-solid (0.70 g). This product was shown by ^{19}F NMR spectroscopy to contain 1,5-diyne **6** (*c.* 60%) and a large number of other components.

*Attempted cycloaddition reactions of 3,3,4,4-tetrafluoro-1,6-diphenylhexa-1,5-diyne (**6**)*

(a) With furan

A mixture of 1,5-diyne **6** (2.00 g, 6.6 mmol) and furan (0.45 g, 6.6 mmol) in dichloromethane (5 cm^3) was heated *in vacuo* in a Rotaflo tube at 50 °C for 1 week, but reaction did not take place (^1H and ^{19}F NMR spectroscopy). A further quantity of furan (0.90 g, 13.2 mmol) was syringed into the tube which was heated first at 95 °C for 3 d (reaction had not occurred) and then at 125 °C for 4 d. The solvent was removed *in vacuo* and the black tar (1.95 g) subjected to DCFC [light petroleum/dichloromethane (6:1 v/v)] to give only unchanged diyne **6** (1.20 g, 4.0 mmol, 60%).

(b) With diazomethane

A solution of diazomethane (1.20 g, 28.6 mmol) in diethyl ether (200 cm^3) was added slowly to a stirred solution of 1,5-diyne **6** (3.00 g, 9.9 mmol) in ether (10 cm^3) at 0 °C. The resulting solution was stirred at 0 °C (2 h) and then slowly allowed to warm to room temperature before being stored overnight with the excess of diazomethane able to evaporate. After removal of the ether, the residue was identified as unchanged diyne **6** (3.00 g, 9.9 mmol, 100% recovered).

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