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OLIGOMERIC POLYPARATETRAFLUOROPHENYLENE VINYLENES: A NEW SYNTHESIS BASED ON THE NUCLEOPHILIC SUBSTITUTION OF THE PARA FLUORINE DURING THE REACTION OF (E)-2-(PENTAFLUOROPHENYL)ETHENYL LITHIUM WITH HEXAFLUOROBENZENE

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SUMMARY

(E)-2-(Pentafluorophenyl)ethenyl bromide (3) has been prepared by three routes: (i) bromination of 2,3,4,5,6-pentafluorocinnamic acid (5) gave 1,2-dibromo-2-(pentafluorophenyl)propionic acid (6) which was converted into 1,1,2-tribromo-2-(pentafluorophenyl)ethane (7) via the Hunsdiecker reaction; (3) was formed by the debromination of (7) with zinc; (ii) the reaction of (6) with red mercuric oxide and bromine gave (3) and (7); (iii) hydroboration of 2,3,4,5,6-pentafluorophenylethyne (8) with catecholborane followed by hydrolysis of the intermediate gave (E)-2-(pentafluorophenyl)ethenyl boronic acid (9) which on treatment with alkali and bromine gave (3). The boronic acid (9) was converted into (E)-2-(pentafluorophenyl)ethenyl iodide (4) with alkali and iodine. The bromo compound (3) was inactive towards magnesium and n-butyllithium brought about fluorine replacement to give (10). The iodo compound (4) formed the lithium derivative (11) with n-butyllithium which reacted in C_6F_6 to give (E)-decafluorostilbene (12) and oligomeric compounds, (13), (14) and (15); in the absence of C_6F_6, oligomer (16) was formed which had a conductivity $< 10^{-10}$ S cm^{-1}.

INTRODUCTION

Polyparaphenylenevinylenes have been prepared by a variety of routes including dehydrochlorination reactions of *αα'*-dichloro-1,4-xylene [1] and Wittig condensation reactions [2], but by far the most important route used currently employs *αα'*-dialkylsulphonium-1,4-xylene dihalides which on

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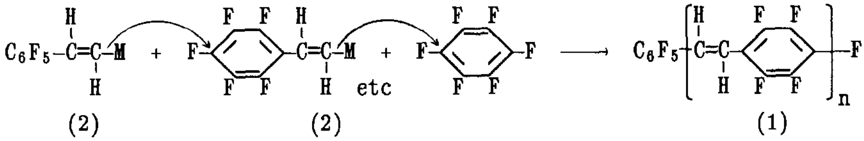
reaction with base give a water-soluble precursor polymer. When this material is heated, polyparaphenylenevinylene is formed [3]. The stereochemistry about the double bonds in these systems is considered to be (E-)(trans), any (Z-)(cis) double bonds being readily isomerised by refluxing with iodine in xylene.

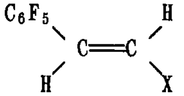
In this paper we describe a completely different approach for the synthesis of polyparatetrafluorophenylenevinylene (1) in which the stereochemistry in the double bonds is pre-determined in the monomer. The basic reaction is the self nucleophilic substitution of the para fluorine in (E)-2-(pentafluorophenyl)ethenyl organometallic compounds (2), with hexafluorobenzene providing a suitable end group (C_6F_5) in some reactions (Scheme 1).



Scheme 1.

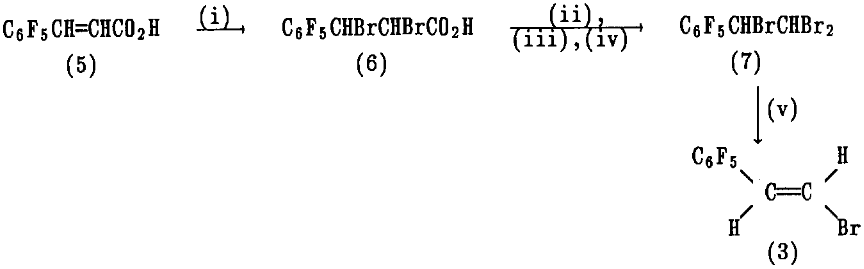
RESULTS AND DISCUSSION

Two precursors have been examined for this polymer synthesis: the (E)-bromo and -iodo compounds (3) and (4) respectively. Three methods



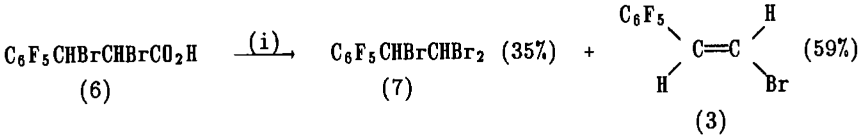
(3) X = Br
(4) X = I

have been used to synthesize (E)-2-(pentafluorophenyl)ethenyl bromide (3). The first method involved reacting 2,3,4,5,6-pentafluorocinnamic acid (5)[4] with bromine and carrying out a Hunsdiecker reaction [5] on the resulting 1,2-dibromopropionic acid (6) to form the tribromo derivative (7), followed by debromination with zinc in tetrahydrofuran (Scheme 2). The second route to compound (3), the Cristol modification of the Hunsdiecker reaction, avoided the isolation of the silver salt and is shown in Scheme (3) [6]. The third synthesis of compound (3) involved the



Reagents: (i) Br_2; (ii) NaOH; (iii) $AgNO_3$; (iv) Br_2; (v) Zn/THF.

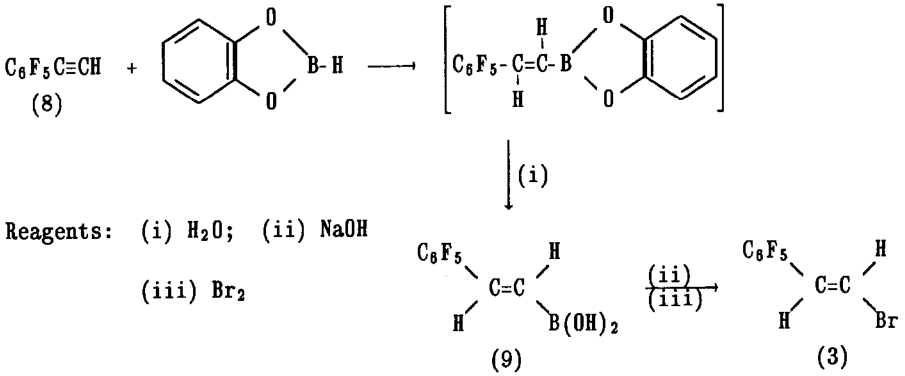
Scheme 2.



Reagents: (i) HgO/Br_2

Scheme 3.

hydroboration of 2,3,4,5,6-pentafluorophenylethyne (8) [7] with catecholborane followed by hydrolysis of the intermediate ester to give the boronic acid (9), which was then treated with alkali and bromine (Scheme 4).

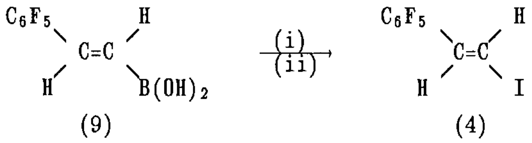


Reagents: (i) H_2O; (ii) NaOH

(iii) Br_2

Scheme 4.

The latter procedure was a modification of the one described by Brown for the synthesis of (E)-iodoethenes [8], and we have used it in an identical manner to prepare the iodo compound (4) (Scheme 5).

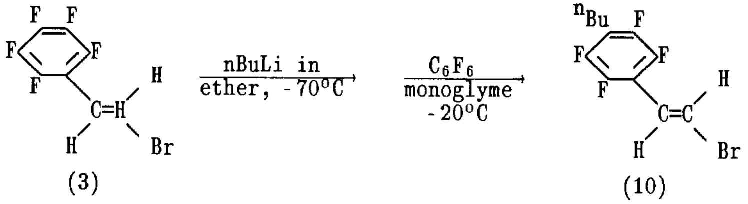


Reagents: (i) NaOH; (ii) I_2.

Scheme 5.

The stereochemistry about the double bonds in (3) and (9) was unequivocal by ^1H n.m.r., since the coupling constants $J_{1-H,2-H}$ 14.5 and 19 Hz respectively, were consistent only with the trans orientation of the vicinal hydrogen atoms. The stereochemistry in (4) could not be determined by ^1H n.m.r. since the protons appeared as one signal, having identical chemical shifts and was deduced from its subsequent reaction products following lithiation and reaction with C_6F_6 (see later).

We first attempted to convert (E)-2-(pentafluorophenyl)ethenyl bromide (3) into the Grignard reagent, but even after activating the magnesium with iodine in tetrahydrofuran, only starting material was recovered from the reaction. The attempted lithiation of compound (3) in diethyl ether followed by the addition of hexafluorobenzene and monoglyme resulted in the nucleophilic displacement of fluorine to give (10), rather than metallation (Scheme 6). The ^{19}F n.m.r. spectrum of (10) showed only two magnetically different fluorines, indicating the para orientation of the bromovinyl and n-butyl substituents. Consequently we turned our attention



Scheme 6.

to (E)-2-(pentafluorophenyl)ethenyl iodide (4) which was expected to be more susceptible than the bromo compound (3) to lithiation. Preliminary experiments in diethyl ether as before showed that while some metallation did occur, once again fluorine replacement took place. To eliminate this interfering reaction, compound (4) was reacted in hexane at -20° with n-butyllithium whereupon a white precipitate, presumed to be the lithium derivative (11), was formed. The suspension was added to hexafluorobenzene in tetrahydrofuran at -70°C and the mixture warmed to -20°C to give a dark ink blue colour. Acidification of the mixture produced a bright yellow solid which failed to dissolve completely in any common organic solvent; nevertheless, the material which did dissolve in dichloromethane was separated by a combination of sublimation and chromatography to give two products: the (E)-stilbene (12) [9] and compound (13) with three aromatic rings present* which were fully characterised, while a third component (14) with four aromatic rings (identified by an accurate mass measurement in a mass spectrometry experiment) was isolated in ca. 80% purity (Scheme 7). The para orientation of the two vinyl groups of the central ring in (13) was deduced by ^{19}F n.m.r. spectroscopy. There were only four magnetically different fluorines present in the spectrum, with intensities in the ratio 2:2:2:1, corresponding to 2-F/6-F, 3-F/5-F, 2'-F-/6'-F, and 4-F respectively. The structure of the compound containing four aromatic rings, (14), was shown by the presence of five magnetically different fluorines resonances in the ^{19}F n.m.r. spectrum, with intensities in the ratio 2:2:2:2:1 corresponding to 2-F/6-F, 3-F/5-F, 2'-F/6'-F, 3'-F/5'-F, and 4-F, respectively. The U.V. spectra of (12), (13) and (14) all showed λ_{max} going to longer wavelengths, characteristic of (E)-(trans) orientations about the CH=CH bond and confirmed the supposition that the original iodo compound did indeed have the (E)-configuration shown in (4). It was presumed that the bright yellow insoluble material, obviously having more extensive conjugation, was oligomeric material (15), but this was not examined.

The experiment shown in Scheme 7 was repeated, only with the C_6F_6 absent in stage (ii). The mixture turned blue-black and had gelatinous consistency, but on acidification, a brilliant yellow precipitate was again formed, some of which tended to stick tenaciously to the glass reaction vessel. This product was subjected to extraction in a Soxhlet apparatus with various solvents to leech out low molecular materials; elemental analysis provided the only rough probe to its identity, namely, the oligomer designated (16) with an average of ca. 12 repeating units (Scheme 8), by analogy with (13) and (14).

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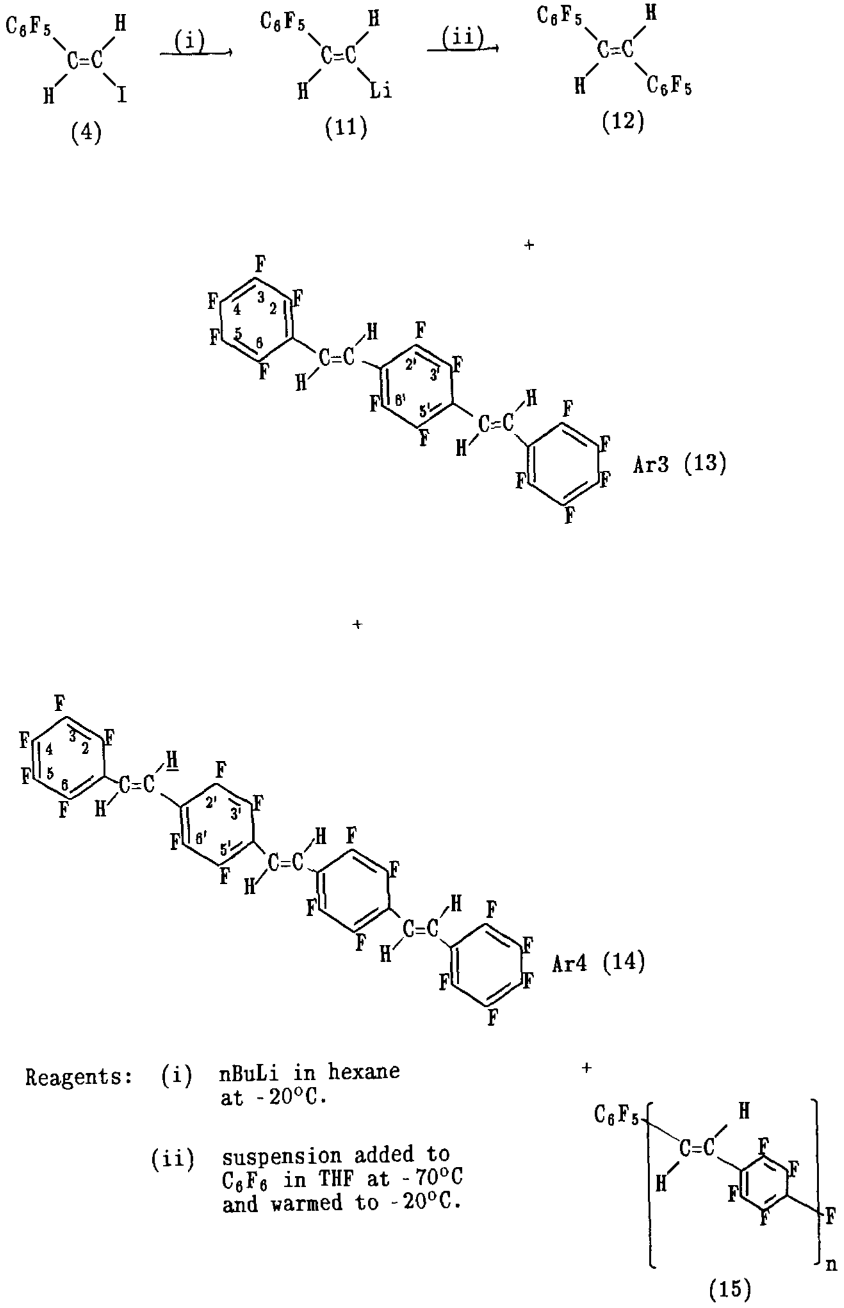
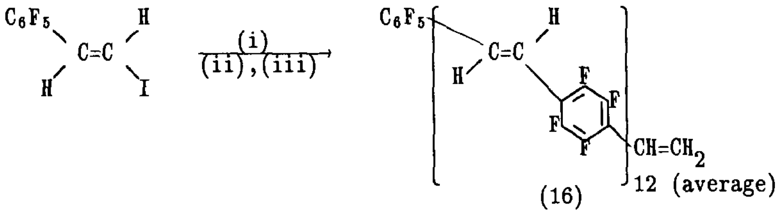
*Because of the complex names of these compounds, for simplicity compound (13) is called (E)-Ar3 and (14), (E)-Ar4 indicating compounds which contain three and four aromatic rings respectively.



Reagents: (i) nBuLi in hexane at -20°C.

(ii) suspension added to C_6F_6 in THF at -70°C and warmed to -20°C.

Scheme 7.



Reagents: (i) nBuLi in hexane at -20°C.
(ii) suspension added to THF at -70°C and warmed to -20°C.
(iii) H_3O^+

Scheme 8.

The electrical conductivity of (16) was of considerable interest. However, the instrumentation available indicated that its specific conductivity was less than 10^{-10} S cm^{-1}. Attempted doping of (16) using iodine or bromine were unsuccessful (no colour change) - which can be rationalised on the basis of the presence of the highly electronegative fluorine substituents inhibiting oxidation of the molecule. On the other hand, the deep blue-black colour of the material produced in the reaction prior to acidification was strongly suggestive of a reduced ('n-doped') state. Treatment of (16) with sodium naphthalenide in tetrahydrofuran, however, caused a vigorous reaction, but no viable product could be isolated.

EXPERIMENTAL

N.m.r. spectra were obtained with a Bruker AC250 [^1H (250 MHz) and ^{19}F (235 MHz)]. Chemical shifts are downfield from internal $SiMe_4$ (δ_H), or upfield (and therefore negative in value) from internal $CFCl_3$ (δ_F). Mass spectroscopy data were obtained with a VG7070E instrument. Molecular ions M^+ are quoted for electron ionisation.

Reaction of (E)-2,3,4,5,6-pentafluorocinnamic acid (5) with bromine

A solution of (E)-2,3,4,5,6-pentafluorocinnamic acid (5) (2.86 g, 12 mmol) in dry chloroform (200 ml) was treated with bromine (2.0 g, 12.5 mmol) and the mixture was stirred for 1 h under irradiation for a 100 W domestic lamp. Evaporation of the solvent and residual bromine in vacuo gave 1,2-dibromo-2-(pentafluorophenyl)propionic acid (nc) (6) (4.73 g, 99%) mp 158-159°C [from light petroleum (bp 100-120°C)] (Found: C, 26.99;

H, 0.65%. $C_9H_3Br_2F_5O_2$ requires C, 27.16; H, 0.76%); $\delta_H(CDCl_3)$ 5.14 (d, CH), 5.68 (d, CH) and 9.21 ppm (br, CO_2H), $J_{1-H,2-H}$ 11.9 Hz; $\delta_F(CDCl_3)$ -139.5 and -141.6 (both br, unassigned non-equivalent 2-F, 6-F), -151.0 (t, 4-F), -160.5 ppm (t, 3-F/5-F).

Preparation of 1,1,2-tribromo-2-(pentafluorophenyl)ethane (7)

(a) Via the Hunsdiecker Reaction

1,2-Dibromo-2-(pentafluorophenyl)propionic acid (6) (15.48 g; 38.8 mmol) was dissolved in aqueous sodium hydroxide (196 ml, 0.198 M; 38.8 mmol) and treated with silver nitrate solution (7.81 g, in 100 ml water; 45.9 mmol). The precipitate was filtered, washed with cold water and dried *in vacuo* at 20°C/3 x 10^{-3} mmHg for 120 h to yield silver 1,2-dibromo-2-(pentafluorophenyl)propionate (17.34 g; 89%).

The silver salt (17.34 g; 34.4 mmol) was suspended in dry carbon tetrachloride (300 ml), treated with bromine (5.70 g; 35.6 mmol) and the mixture was stirred at room temperature for 30 h. The mixture was filtered, the filtrate evaporated, and the residue distilled *in vacuo* to give *1,1,2-tribromo-2-(pentafluorophenyl)ethane (nc) (7)* (8.1 g, 54%) bp 40-50°/3 x 10^{-3} mmHg. (Found: C, 22.43; H, 0.36%; M^+, 436, 434, 432, 430; $C_8H_2Br_3F_5$ requires C, 22.17; H, 0.46%; M, 436, 434, 432, 430); $\delta_H(CDCl_3)$ 5.61 (d, CH) and 6.18 ppm (d, CH), $J_{1-H,2-H}$ 10.8 Hz; $\delta_F(CDCl_3)$ -140.6 (br, 2-F/6-F), -151.6 (t, 4-F), -160.7 ppm (td, 3-F/4-F).

(b) Via the Cristol Modification

1,2-Dibromo-2-(pentafluorophenyl)propionic acid (6) (0.421 g; 1.06 mmol) dissolved in carbon tetrachloride (50 ml) was treated with red mercuric oxide (0.196 g, 0.90 mmol) followed by bromine in carbon tetrachloride (1.95 ml, 0.542 M; 1.06 mmol) and the mixture was heated under reflux in the dark for 4.5 h. The mixture was filtered, the filtrate evaporated and the residue was separated by flash chromatography on silica (15 x 3.5 cm diameter) using light petroleum (bp 40-60°C) as eluant to give two components: *(E)-2-(pentafluorophenyl)ethenyl bromide (nc) (3)* (0.170 g, 59%) bp 30°C/3 x 10^{-3} mmHg (Found: C, 35.06; H, 0.70%; M^+, 272, 264. $C_8H_2BrF_5$ requires C, 35.20; H, 0.74%; M, 272, 274); $\delta_H(CDCl_3)$ 7.08 (d, CH) and 7.25 ppm (d, CH), $J_{1-H,2-H}$ 14.5 Hz; $\delta_F(CDCl_3)$ -142.7 (dd, 2-F/6-F), -154.8 (t, 4-F) and -162.5 ppm (td, 3-F/5-F); and 1,1,2-tribromo-2-(pentafluorophenyl)ethane (7) (0.159 g, 35%).

Debromination of 1,1,2-tribromo-2-(pentafluorophenyl)ethane (7)

The tribromo compound (7) (7.45 g, 17.2 mmol), zinc dust (1.51 g, 23.1 mmol) and dry tetrahydrofuran (60 ml) were heated together under reflux for 6 h. The mixture was filtered and the filtrate acidified (2 M sulphuric acid) and extracted with ether. The extracts were dried ($MgSO_4$), the solvents evaporated and the residue distilled in vacuo to give (E)-2-(pentafluorophenyl)ethenyl bromide (3) (3.65 g, 78%) bp 30°C/3 x 10^{-3} mmHg.

Preparation of (E)-2-(Pentafluorophenyl)ethenylboronic acid (9)

2,3,4,5,6-Pentafluorophenylethyne (5.24 g, 27 mmol) and freshly distilled catecholborane (3.23 g, 27 mmol) were heated together at 70°C under an atmosphere of nitrogen for 30 h. The mixture was cooled to room temperature and volatile components evaporated in vacuo at 5 x 10^{-3} mmHg. The solid remaining (8.34 g) was hydrolysed by stirring with water over 1.5 h and the white crystalline solid filtered to give (E)-2-(pentafluorophenyl)ethenyl boronic acid (nc) (9) (3.82 g, 60%) mp 163-164° (from water) (Found: C, 40.26; H, 1.61%, M+1 , 239 (CI). $C_8H_4BF_5O_2$ requires C, 40.38; H, 1.69%; M, 238); δ_H ($^2H_6$ acetone) 6.45 (d, CH), 7.19 (d, CH) and 7.23 ppm [s, $B(OH)_2$], $J_{1\text{-}H,2\text{-}H}$ 19 Hz; δ_F ($^2H_6$ acetone) -144.2 (m, 2-F/6-F), -157.0 (t, 4-F) and -164.3 ppm (m, 3-F/5-F).

Reactions of (E)-2-(Pentafluorophenyl)ethenylboronic acid (9)

(a) Formation of (E)-2-(pentafluorophenyl)ethenyl bromide (3)

A mixture of the boronic acid (9) (1.31 g, 5.22 mmol) dissolved in aqueous sodium hydroxide (8.5 ml, 2 M; 17 mmol) and dichloromethane (40 ml) was cooled to 0°C and treated with bromine (0.833 g, 5.52 mmol) in dichloromethane (10 ml). After 1 h, the organic phase was separated, the aqueous phase extracted with dichloromethane and the combined organic phases dried ($MgSO_4$). The solvent was evaporated and the residue distilled in vacuo to give (E)-2-(pentafluorophenyl)ethenyl bromide (3) (1.0 g, 66%) bp 30°/3 x 10^{-3} mmHg.

(b) Formation of (E)-2-(pentafluorophenyl)ethenyl iodide (4)

A mixture of the boronic acid (9) (2.31 g, 9.71 mmol) dissolved in aqueous sodium hydroxide (0.193 M, 151 ml; 29 mmol) and dichloromethane (100 ml) was cooled to 0°C and treated with iodine (4.0 g, 15.7 mmol) in dichloromethane (250 ml). After 18 h, the organic phase was separated, the aqueous phase extracted with dichloromethane and the combined organic phases dried ($MgSO_4$). The solvent was evaporated and the residue distilled in vacuo to give (E)-2-(pentafluorophenyl)ethenyl iodide (nc) (4) (2.68 g, 88%) bp 40°C/3 x 10^{-3} mmHg (Found: C, 29.75; H, 0.55%; M^+, 320. $C_8H_2F_5I$ requires C, 30.03; H, 0.63%; M, 320); δ_H($CDCl_3$) 7.41 ppm (s), the two vinylic protons having identical shifts; δ_F($CDCl_3$) -143.6 (m, 2-F/6-F), -154.6 (t, 4-F) and -162.5 ppm (m, 3-F/5-F).

Attempted lithiation of (E)-2-(pentafluorophenyl)ethenyl bromide (3) and subsequent reaction with hexafluorobenzene

The bromide (3) (0.40 g, 1.47 mmol) in dry diethyl ether (30 ml) was treated with n-butyllithium in hexane (0.93 ml, 1.58 M; 1.47 mmol) at -70°C. After 2 h, hexafluorobenzene (0.68 g, 3.66 mmol) in dry monoglyme (20 ml) was added, the temperature was raised to -20°C, and after a further 16 h, the mixture was acidified (2 M sulphuric acid) and extracted with ether. The extracts were dried ($MgSO_4$), the solvent evaporated, and the crude product purified by chromatography on silica (15 x 5 cm diameter) using light petroleum (bp 40-60°C) as eluant to give (E)-2-(4-n-butyl-2,3,5,6-tetrafluorophenyl)ethenyl bromide (nc) (10) (0.25 g, 55%) which distilled onto a cold finger at 30°/3 x 10^{-3} mmHg (Found: C, 46.52; H, 3.48%; M^+ 310, 312. $C_{12}H_{11}BrF_4$ requires C, 46.33; H, 3.56%. M, 310, 312); δ_H($CDCl_3$) 0.94 (t, CH_3), 1.39 (m, $C\underline{H}_2CH_3$), 1.57 (m, $C\underline{H}_2CH_2CH_3$), 2.71 (t, $C\underline{H}_2CH_2CH_2CH_3$), 7.11 and 7.21 ppm (both d, unassigned 1-H, 2-H) $J_{1-H,2-H}$ 14.3 Hz; δ_F($CDCl_3$) -144.5 and -145.7 ppm (both m, unassigned 2-F/6-F and 3-F/5-F) with intensities in the ratio 1:1, respectively.

Lithiation of (E)-2-(pentafluorophenyl)ethenyl iodide (4)

(a) Subsequent reaction with hexafluorobenzene

The iodide (4) (1.0 g; 3.12 mmol) in dry hexane (30 ml) was treated with n-butyllithium in hexane (2.06 ml, 1.52 M; 3.13 mmol) at -20°C. After 1 h, the resultant white suspension was added to hexafluorobenzene (4.07 g; 21.9 mmol) in dry tetrahydrofuran (100 ml) at -70°C, the mixture raised to -20°C and after a further 18 h, the blue/black mixture was acidified (2 M sulphuric acid) and extracted with dichloromethane. The combined extracts were filtered to remove a bright yellow solid suspension [presumed to be the oligomeric material (15)]; the filtrate was dried ($MgSO_4$) and the solvent evaporated. The crude product (0.87 g) was sublimed at 160°/5 x 10^{-3} mmHg and the sublimate separated by flash chromatography on silica (17 x 6 cm diameter) using light petroleum (bp 40-60°C) as eluant to give (E)-decafluorostilbene (12) (0.073 g,; 7%) mp 101-102°C [from light petroleum (bp 40-60°C)] (lit. [9], mp 96.5-97.5°C) (Found: C, 46.42; H, 0.80%; M^+, 360. $C_{14}H_2F_{10}$ requires C, 46.68; H, 0.56%; M, 360); $\delta_H(CDCl_3)$ 7.32 ppm (s); $\delta_F(CDCl_3)$ -142.3 (m, 2-F/6-F, relative intensity 2), -154.0 (t, 4-F, relative intensity 1), -162.5 (m, 3-F/5-F, relative intensity 2); and (E)-Ar(3) (nc) (13)* (0.031 g, 2%) mp 202.5-203°C [from light petroleum (bp 100-120°C)] (Found: C, 49.25; H, 0.98%; M^+, 354. $C_{22}H_4F_{14}$ requires C, 49.46; H, 0.75%; M, 534). δ_H ($^2H_8$ toluene) 7.35 ppm (br, overlapping); δ_F ($^2H_8$ toluene) -143.0 (m, 2-F/6-F, relative intensity 2), -144.0 (s, 2'-F/6'-F, relative intensity 2), -154.8 (t, 4-F, relative intensity 1) and -163.1 ppm (m, 3-F/5-F, relative intensity 2).

Slower moving fractions from the column (0.090 g) were dissolved in boiling light petroleum (bp 60-80°C) and rechromatographed on silica (10 x 7.5 cm diameter) running the lagged column at 45-55°C and using hot light petroleum (bp 60-80°C) as eluant to give further E-Ar3* (13) (0.080 g, 5%), and an impure sample of (E)-Ar4* (14) (0.005 g; 0.6%) (Found: accurate mass analysis 708.0123. $C_{30}H_6F_{18}$ requires 708.0182); δ_F ($^2H_8$ toluene) -142.9 (m, 2-F/6-F, relative intensity 2), -143.7 and -143.9 (both m, 2'-F/6'-F, relative intensity 2, and 3'-F/5'-F, relative intensity 2, unassigned), -154.8 (t, 4-F, relative intensity 1) and -163.1 ppm (bm, 3-F/5-F, relative intensity 2).

(b) Self nucleophilic substitution on tetrahydrofuran

The iodide (4) (1.0 g, 3.12 mmol) in dry hexane (10 ml) was treated with n-butyllithium in hexane (2.05 ml, 1.52 M; 3.11 mmol) at -20°C. After 1 h, the white suspension was added to dry tetrahydrofuran (40 ml) at -70°C, the mixture raised to -20°C, and after a further 18 h, the blue/black gelatinous mixture was acidified (2 M sulphuric acid). A bright yellow solid was produced which was filtered, washed with water and placed in a Soxhlet apparatus. The solid was extracted for 48 h in turn with: water, ethanol, water, ethanol and diethyl ether to give the bright yellow solid designated (16) (Found: C, 54.70; H, 1.61%; "nitrogen" registered 2.12% but this anomalous result is often observed with polymeric materials. Compound (16) having an average of twelve tetrafluorophenylene vinylene units requires C, 54.74; H, 1.20%),

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* See earlier footnote for this structure designation.

ACKNOWLEDGEMENT

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