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THE ATTEMPTED SYNTHESIS OF POLYPARATETRAFLUOROPHENYLENE VINYLENE VIA WATER-SOLUBLE AND ORGANIC SOLVENT-SOLUBLE PRECURSOR POLYMERS

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SUMMARY

2,3,5,6-Tetrafluoro-1,4-xylene-αα'-bis(dimethylsulphonium bromide) (5) and the related -αα'-bis(diethylsulphonium chloride) (6) were prepared by the reaction of αα'-dibromo-2,3,5,6-tetrafluoro-1,4-xylene (7) with dimethyl sulphide and of αα'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene (7a) with diethyl sulphide, respectively. Compound (5) with aqueous alkali was converted into the dibromo compound (7), with no evidence of polymer being formed. Compound (6) failed to give any viable product with aqueous alkali. 2,3,5,6-Tetrafluorobenzene was converted into 1,4-diallyl-2,3,5,6-tetrafluorobenzene (14) via a copper (I) intermediate, and gave 2,3,5,6-tetrafluorobenzene-1,4-diethanal (13) on treatment with ozone. Reaction of 1,4-dilithio-2,3,5,6-tetrafluorobenzene (12) with the dialdehyde (13) failed to give a viable polymer soluble in organic solvents.

INTRODUCTION

The most important route currently employed to synthesize polyparaphenylenevinylenes is via a precursor polymer prepared by the reaction of αα'-dialkylsulphonium-1,4-xylene dihalides (1) with sodium hydroxide in water. The water-soluble precursor polymer (2) formed under mild conditions is first purified and then heated to form the polyparaphenylenevinylene (3) (Scheme 1) [1]. In this paper we report the results of our attempts to apply this methodology to prepare polyparatetrafluorophenylenevinylene (4) via an analogous water-soluble precursor

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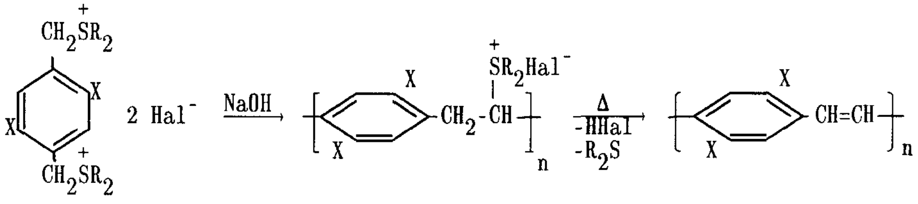


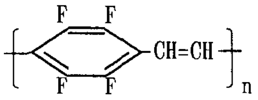
(1) (2) (3)

Scheme 1.

polymer, and also via a precursor polymer soluble in organic solvents.

RESULTS AND DISCUSSION

Two salts (5) and (6) were prepared as starting materials to investigate the water soluble precursor polymer route. αα'-Dibromo-2,3,5,6-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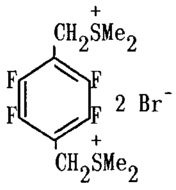
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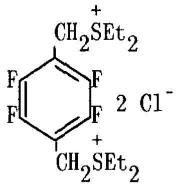
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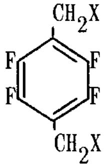
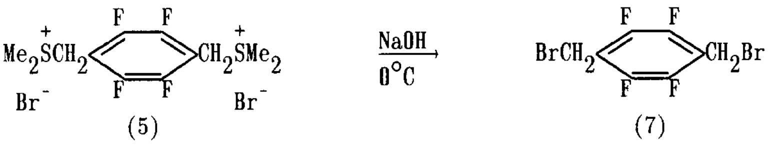

(7) X = Br
(7a) X = Cl

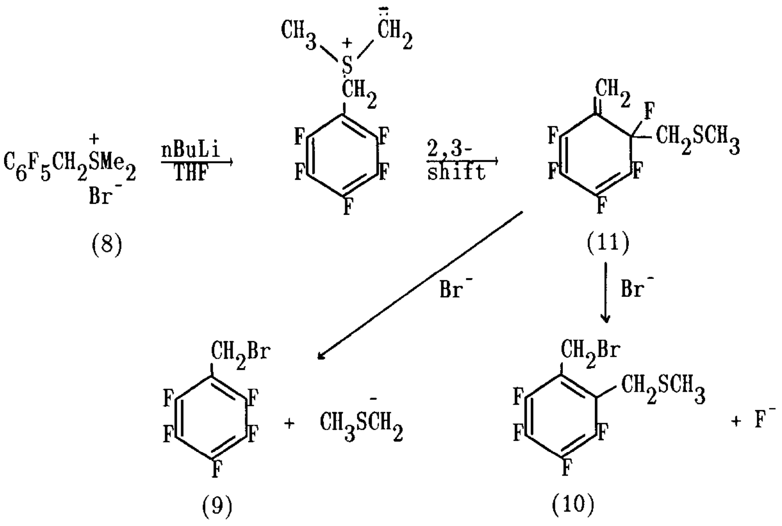
tetrafluoro-1,4-xylene (7), a known compound [2], reacted with dimethyl sulphide to give (5), and αα'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene (7a), which was unknown before this work began, readily formed (6) with diethyl sulphide; compound (7a) was prepared from 2,3,5,6-tetrafluoro-1,4-benzenedimethanol [3] and thionyl chloride.

The attempted polymerisation of the bis(dimethylsulphonium bromide) (5) with sodium hydroxide in water was carried out under the standard conditions prescribed in the literature [4]. The only product isolated from the reaction, however, was the dibromide (7) (32%) (Scheme 2); no viable material which could be described as a precursor polymer was obtained. Previously, using a different base (n-butyllithium in



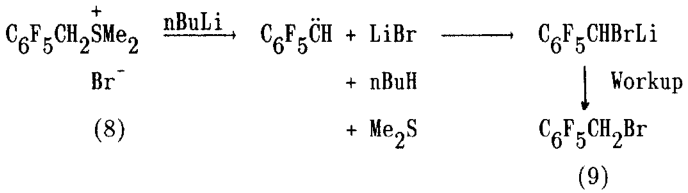
Scheme 2.

tetrahydrofuran), 2,3,4,5,6-pentafluorobenzyl(dimethyl)sulphonium bromide (8) had been converted into 2,3,4,5,6-pentafluorobenzyl bromide (9) (33%) and 3,4,5,6-tetrafluoro-2-methylthiomethylbenzyl bromide (10) (2.5%), (along with other products), and a rationalisation for their formation was proposed from a common intermediate (11) resulting from an initial 2,3-sigmatropic shift, (Scheme 3) [5]. While the loss of $CH_3S\overset{-}{C}H_2$ was regarded as an unusual leaving group, the direct conversion of the sulphonium bromide (8) to (9) in aqueous solution does not take place,



Scheme 3.

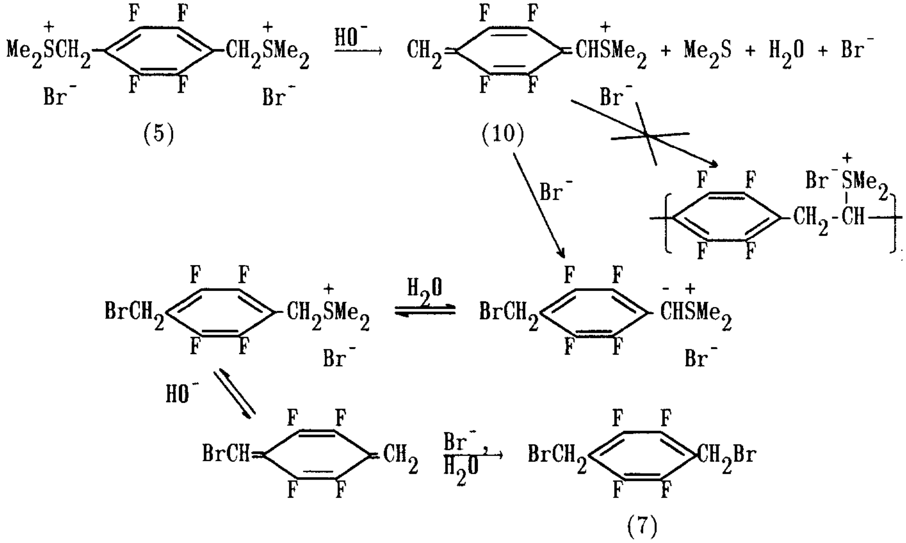
even at 100°C [6], so that the base must play a crucial role in the reaction. Another plausible route is the formation of a carbene intermediate [7] (Scheme 4) and a similar mechanism could be invoked to explain the formation of the dibromo compound (7) from (5). Yet another possible mechanism for the formation of (7) is via the one usually



$$\underset{\substack{Br^- \\ (8)}}{C_6F_5CH_2\overset{+}{S}Me_2} \xrightarrow{nBuLi} C_6F_5\ddot{C}H + LiBr + nBuH + Me_2S \longrightarrow C_6F_5CHBrLi \xrightarrow{Workup} \underset{(9)}{C_6F_5CH_2Br}$$

Scheme 4.

considered to be the route to the precursor polymer, shown in Scheme 5 [8], but it is not obvious why this alternative reaction of the xylylene (10) should take place.

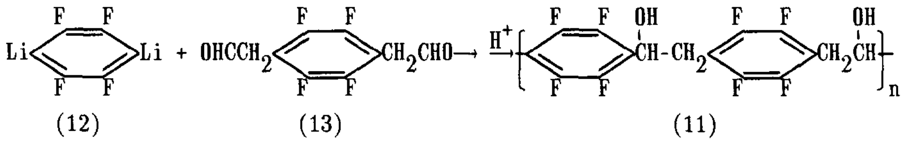


Scheme 5.

Treatment of the bis(diethylsulphonium chloride) (6) with base was anticipated to be less prone to complications than the bis(dimethylsulphonium bromide) (5), since Cl^- is less nucleophilic than Br^- and the acidity of the αCH in $\overset{+}{S}CH_2CH_3$ was expected to be less than in $\overset{+}{S}CH_3$ [required for a (2,3) rearrangement reaction]. The appearance of a green colouration in the reaction suggested the possible formation of an ylide and on work-up of the mixture and dialysis to remove small molecules from the aqueous solution, evaporation did give a coating on a silica plate.

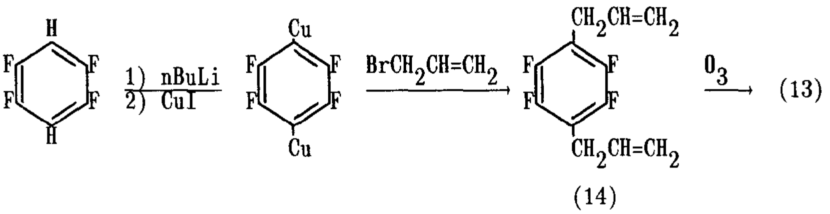
However, no profound change in colour occurred when the coating was heated at 270°C for 24 h., so it was concluded that no authentic precursor polymer had been formed.

We considered the possibility of synthesising a precursor polymer which would be soluble in organic solvents, for conversion to polyparatetrafluorophenylenevinylene (4) via a simple dehydration reaction. Polymer (11) seemed to be a realistic target since the dilithium derivative (12) is well known [9] and the dialdehyde (13) was regarded as an attainable starting material from the 1,4-diallyl



Scheme 6.

compound (14) via ozonolysis. Previously, allyl-2,3,4,5,6-pentafluorobenzene had been prepared from pentafluorophenylcopper and allyl bromide [10], and we applied this methodology to make compound (14) (74%), which was then cleaved with ozone to give (13) (66%) Scheme 7.



Scheme 7.

The polymerisation reaction shown in Scheme 6 was attempted by forming the dilithium compound (12) in tetrahydrofuran at -70°C and adding the dialdehyde (13). The crude product was soluble in ether, but the ^{19}F n.m.r. was very complex. A film was cast and heated in vacuo at 250°C for 24 hours but there was no change in colour as a result of increased conjugation. At 300° the film changed to an orange/brown colour but at such a high temperature, no simple interpretation can be given to the observation. We conclude that the precursor polymer (11) was not formed under the conditions used, presumably since the low temperature used to maintain the integrity of (12) caused premature precipitation of low molecular weight lithium salts on reaction with (13).

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 VG 7070E instrument.

Preparation of αα'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene (7a)

2,3,5,6-Tetrafluoro-1,4-benzenedimethanol (8.68 g) and freshly distilled thionyl chloride (20 ml) were heated together under reflux for 5 h and the excess reagent removed by distillation. Sublimation of the residue at 55°C/0.01 mm Hg gave αα'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene (nc) (7a) (9.90 g, 97%) m.p. 77-78°C [from light petroleum bp (40-60°)] (Found: C, 38.94; H, 1.44%; M^+, 246, 248. $C_8H_4Cl_2F_4$ requires C, 38.90; H, 1.63%; M, 246, 248); δ_H ($CDCl_3$) 4.67 ppm (s, CH_2); δ_F ($CDCl_3$) -143.2 ppm (s).

Preparation of 2,3,5,6-Tetrafluoro-1,4-xylene-αα'bis(dimethylsulphonium bromide) (5)

A mixture of αα'-dibromo-2,3,5,6-tetrafluoro-1,4-xylene (7) (1.5 g), dimethyl sulphide (2.21 g), water (12 ml) and methanol (50 ml) was heated at 50°C for 1 h, concentrated by evaporation in vacuo and poured into acetone to precipitate 2,3,5,6-tetrafluoro-1,4-xylene-αα'bis (dimethylsulphonium bromide) (nc) (5) (1.43 g, 70%) mp 176-177°C (from methanol) (Found: C, 31.04; H, 3.25%. $C_{12}H_{16}Br_2F_4S_2$ requires C, 31.32; H, 3.5%); δ_H (D_2O) 2.94 (s, CH_3) and 4.84 ppm (s, CH_2); δ_F ($CDCl_3$) -137.9 ppm (s).

Preparation of 2,3,5,6-tetrafluoro-1,4-xylene-αα'-bis(diethylsulphonium chloride) (6)

A mixture of αα'-dichloro-2,3,5,6-tetrafluoro-1,4-xylene (7a) (2.83 g), diethyl sulphide (8.3 g), water (12 ml) and methanol (50 ml) was heated at 50°C for 480 h, concentrated by evaporation in vacuo and poured into acetone to precipitate 2,3,5,6-tetrafluoro-1,4-xylene-αα'-bis-(diethylsulphonium chloride) (nc) (6) (2.90 g; 59%) (Found: C, 41.44; H, 6.24%. $C_{16}H_{24}Cl_2F_4S_2.2H_2O$ requires C, 41.47; H, 6.09%); δ_H (D_2O) 1.49 (t, 2 x $\underline{CH_3}$-CH_2) 3.45 (q, 2 x $\underline{CH_2}CH_3$), 4.80 (H_2O) 4.87 (s, CH_2S); δ_F(D_2O) -138.1 ppm.

Attempted polymerisation of the bis(sulphonium) salts

(a) Using the bis(sulphonium bromide) (5)

A solution of compound (5) (0.200 g; 0.43 mmol) in water (2 ml) at 0°C was degassed with nitrogen and treated with aqueous sodium hydroxide solution (2.25 ml; 0.193 M; 0.43 mmol) and the mixture stirred at 0°C for 2 h. A solid had precipitated from the solution and after neutralising with aqueous hydrobromic acid, the solid was separated by centrifugation and sublimed at 80°C/2 x 10^{-3} mm Hg and was identified by i.r. as αα'-dibromo-2,3,5,6-tetrafluoro-1,4-xylene (7) (0.047 g, 32%). No gel expected for a precursor polymer was ever apparent in the reaction product.

(b) Using the bis(sulphonium chloride) (6)

A suspension of compound (6) (0.50 g; 1.1 mmol) in water (5.85 ml) at 0°C was degassed with nitrogen and treated with aqueous sodium hydroxide solution (2.34 ml; 0.5 M; 1.2 mmol). After 2 h the pH of the dark green mixture was adjusted to 6.65 with dilute hydrochloric acid and dialysed using Visking seamless dialysis tubing (pore size 24 Å; diameter 14 mm) for 3 days. Evaporation of the dialysed solution in air gave a coating on a silica plate which did not change profoundly when heated at 270°C for 24 h.

Preparation of 1,4-diallyl-2,3,5,6-tetrafluorobenzene (14)

2,3,5,6-Tetrafluorobenzene (7.0 g; 40 mmol) in dry tetrahydrofuran (300 ml) at -70°C was treated with n-butyllithium (61.8 ml; 1.51 M; 93 mmol) and after 35 min. anhydrous copper (I) iodide (19.6 g) was added and the mixture stirred at -70°C for a further 4 h. After the addition of allyl bromide (17.6 g; 145 mmol) at ≤ -60°C, the mixture was stirred at room temperature for 18 h, diluted with ether and washed first with ammonia solution (2 x 15 ml; 2 M) and then with sulphuric acid (2 M). The organic phase was dried ($MgSO_4$), the solvents evaporated in vacuo, and the residual oil distilled to give 1,4-diallyl-2,3,5,6-tetrafluorobenzene (nc) (14) (7.88 g, 74%) bp 50°C/0.08 mm Hg (Found: C, 62.30; H, 4.32%; M^+, 230. $C_{12}H_{10}F_4$ requires C, 62.60; H, 4.38%; M, 230); δ_H ($CDCl_3$) 3.34 (d, $\underline{CH_2}CH=CH_2$), 4.95 and 5.00 ($CH_2CH=\underline{CH_2}$) and 5.77 ppm (m, $CH_2\underline{CH}=CH_2$); δ_F ($CDCl_3$) -146.1 ppm.

Preparation of 2,3,5,6-tetrafluorobenzene-1,4-diethanal (13)

The diallyl compound (14) (1.52 g; 6.6 mmol) in dry dichloromethane (80 ml) at -20°C was treated with 6-7% ozone in oxygen for 120 min (13.3 mmol O_3 passed using KI/I_2 calibration). The resultant blue solution was stirred with zinc dust in acetic acid (50 ml; 50% v/v) for 1.5 h, the mixture filtered and the organic phase extracted with water (3 x 100 ml) and dried ($MgSO_4$). Evaporation of the solvents in vacuo gave 2,3,5,6-tetrafluorobenzene-1,4-diethanal (nc) (13) (1.02 g, 66%) mp 161-162°C [from diethyl ether/light petroleum (bp 40-60°C)]. (Found: C, 51.28; H, 2.72%; M^+, 234. $C_{10}H_6F_4O_2$ requires C, 51.30; H, 2.58%; M, 234); δ_H ($CDCl_3$) 3.91 (CH_2) and 9.78 ppm (s, CHO); δ_F ($CDCl_3$) -143.2 ppm.

Attempted polymerisation reaction of 2,3,5,6-tetrafluorobenzene-1,4-diethanal (13) with 1,4-dilithio-2,3,5,6-tetrafluorobenzene (12)

2,3,5,6-Tetrafluorobenzene (0.2 g, 1.33 mmol) in dry tetrahydrofuran (15 ml) at -70°C was treated with n-butyllithium in hexane (1.51 M; 1.88 ml; 2.84 mmol). After 0.5 h, the diethanal (13) (0.32 g, 1.37 mmol) in dry tetrahydrofuran (5 ml), pre-cooled to -70°C, was added and the mixture stirred for 0.5 h. The reaction temperature was raised to room temperature, and after 18 h, the mixture was acidified with sulphuric acid (2 M) and extracted with ether. The organic extracts were washed with water, the solvent evaporated and the residue, dried in vacuo at 10^{-3} mm Hg, consisted of a yellow powder (0.4 g) and a yellow film (20 mgm). The film was heated in vacuo at 250°/3 x 10^{-3} mm Hg for 24 h and showed no change in colour; at 300°/3 x 10^{-3} mm Hg, the film changed colour to orange/brown.

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