Received: February 22, 1990; accepted: June 21, 1990

OLIGOMERS DERIVED FROM THE NUCLEOPHILIC SUBSTITUTION OF THE PARA FLUORINE DURING THE REACTION OF 1-PENTAFLUOROPHENYL-1-LITHIO-ETHENE WITH HEXAFLUOROBENZENE

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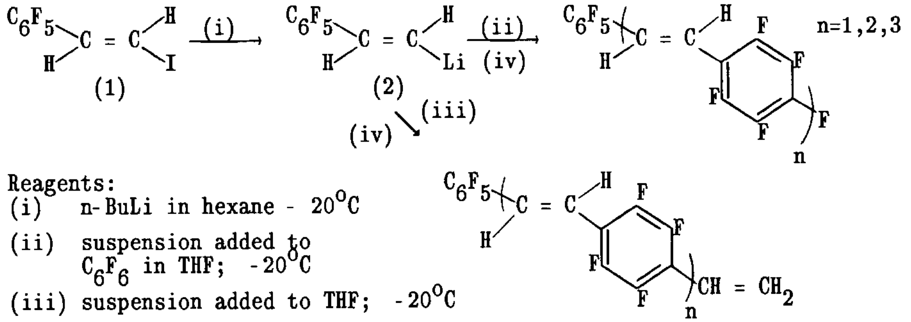
SUMMARY

The para fluorine in 1-bromo-1-(pentafluorophenyl)ethene (3) is replaced exclusively by sodium methoxide to give 1-bromo-1-(4-methoxy-2,3,5,6-tetrafluorophenyl)-ethene (4) and 2,3,5,6-tetrafluoro-4-methoxyphenylethyne (5). Lithiation of (3) with n-butyllithium and reaction with hexafluorobenzene gave 1,1-bis-(pentafluorophenyl)ethene (7), Ar 3*(8), Ar4*(9), Ar5*(10), and Ar6*(11). (*For an explanation of these notations see text). With magnesium in tetrahydrofuran, the bromo-compound (3) gave an intractable polymeric material, the structure of which, by analogy with the reactions of the lithium compound, is proposed as (6).

INTRODUCTION

In the preceding paper [1], we described the lithiation of (E)-2-(pentafluorophenyl)ethenyl iodide (1) and the subsequent oligomerisation of the

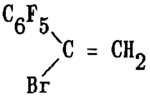


Reagents:
(i) n-BuLi in hexane - $20^{\circ}C$
(ii) suspension added to C_6F_6 in THF; $-20^{\circ}C$
(iii) suspension added to THF; $-20^{\circ}C$
(iv) H_3O^+

Scheme 1.

0022-1139/90/$3.50

lithio-derivative (2) in the presence and absence of hexafluorobenzene (Scheme 1). Prior to that work we had carried out related experiments with the supposed geometrical isomer of (2) by lithiation of what previously had been described as 'cis-1-bromo-2-pentafluorophenylethylene' the major product from the dehydrobromination of 1,2-dibromo-1-(pentafluorophenyl)ethane with KOH [2]. Recently, however, a closer examination of the original ^1H n.m.r. data ($J_{1-H,\ 2-H}$ 2 Hz) indicated that the material was actually 1-bromo-1-(pentafluorophenyl)ethene (3). The



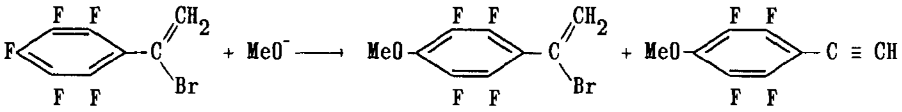
(3)

minor component from the dehydrobromination reaction, originally assigned as (3)[2] has now been identified as (E)-2-(pentafluorophenyl)ethenyl bromide, also described in the preceding paper[1].

We have confirmed this new assignment of structure (3) by ^{13}C n.m.r.spectroscopy which showed one (and one only) singlet carbon in the proton-decoupled spectrum appearing as a triplet in the spin-coupled spectrum (CH_2). In this paper we report the results of our experiments in terms of the true structure of the compound used.

RESULTS AND DISCUSSION

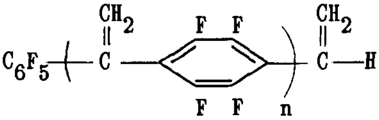
Reaction of compound (3) with sodium methoxide established that the para fluorine was exclusively substituted to give (4) accompanied by dehydrobrominated material (5) (Scheme 2). Other workers have reported the replacement of the para fluorine in 2,3,4,5,6-pentafluorophenylethene [3].



(3) (4) (5)

Scheme 2.

The bromo-compound (3) was reacted in THF under reflux with magnesium which had been activated using 1,2-dibromoethane. A pale brown polymer was formed which was totally insoluble in all common organic solvents; it was very hydrophobic and had not melted at 380°C but its organic nature was demonstrated when it gave a smokey luminous flame on combustion. A closer examination of the precipitate showed that it was contaminated by particles of magnesium which could not be removed by simple treatment with acid, and because of the intractable nature of the material, no firm conclusions could be drawn about its structure, but in view of other work reported in this paper, it could be (6).



(6)

Organolithium reagents are more reactive than related Grignard reagents so it was expected that reactions involving the lithium derivative of (3) would occur under mild conditions. Compound (3) was reacted with n-butyllithium in ether (to avoid possible nucleophilic displacement of para fluorine) at -70°C. Hexafluorobenzene (to provide a C_6F_5-end group) and then monoglyme or THF were added to the solution and the temperature raised to -20°C. Using a combination of sublimation and chromatography on silica with solvents of varying polarity, low yields of materials containing two (7), three (8), four (9), and five (10) aromatic rings were separated and totally characterised (Scheme 3)*; the oligomer with six aromatic rings (11) was obtained in ca. 75% purity. The para orientation of the two vinyl groups of the central ring in (8) 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, (9), was shown by the presence of five magnetically different fluorine resonances in the ^{19}F nmr spectrum, two of which overlapped, with intensities in the ratio of 2:2:4:1 corresponding to 2-F/6-F, 3-F/5-F, overlapping 2'-F/6'-F and 3'-F/5'-F, and 4-F respectively; in compound (10), three resonances due to 2'-F/6'-F, 3'-F/5'-F and 2"-F/6"-F all overlapped.

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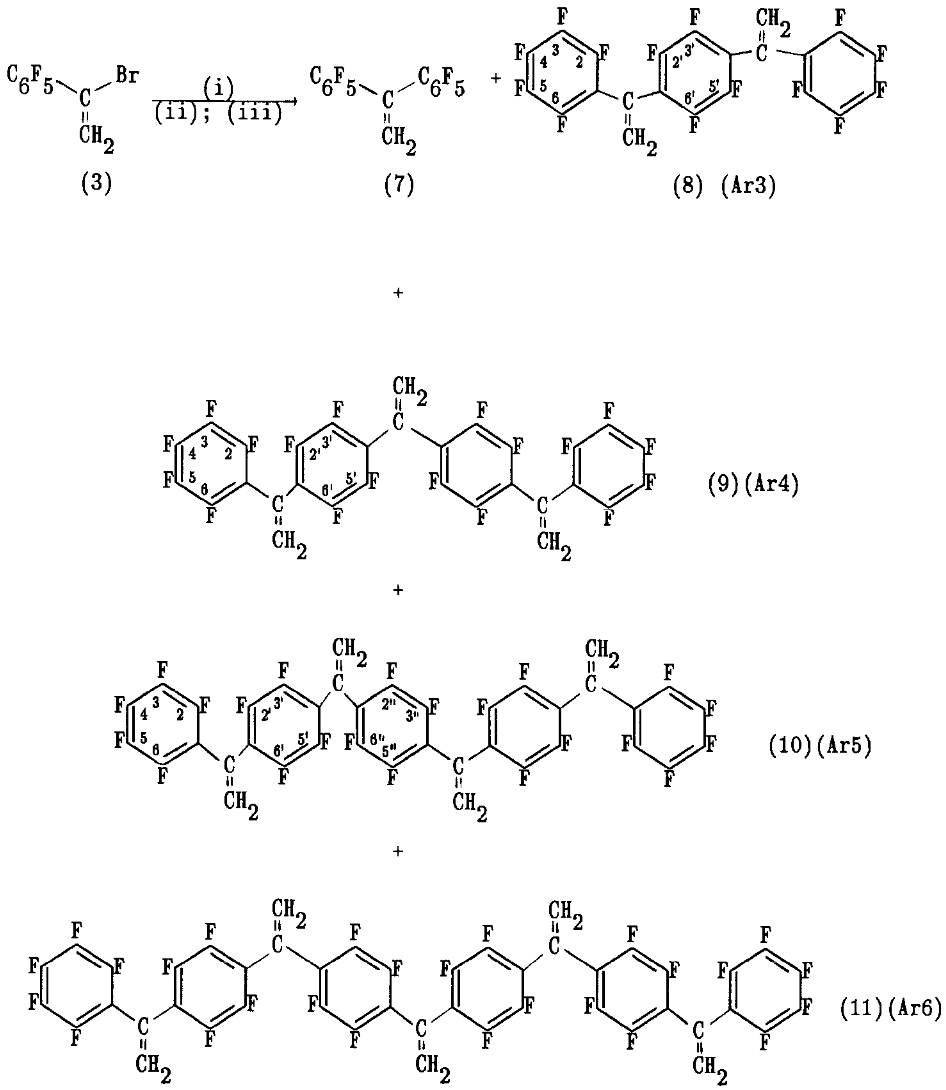
* Because of the complex names of these compounds, for simplicity, compounds (8), (9), (10), and (11) are called Ar3, Ar4, Ar5, and Ar6, indicating compounds which contain three, four, five and six aromatic rings respectively.



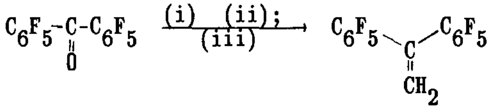
Reagents: (i) nBuLi in ether at -70°C;

(ii) C_6F_6 and monoglyme at -20°C

(iii) H_3O^+

Scheme 3.

Compound (7), 1,1-bis(pentafluorophenyl)ethene has also been synthesised (89%) by an alternative route starting from decafluorobenzophenone(12)[4] as shown in Scheme 4.

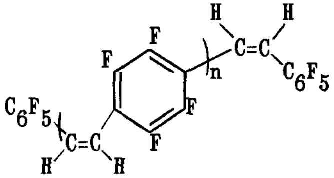


(12) (7)

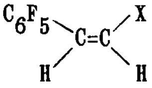
Reagents: (i) MeMgI; (ii) H_3O^+; (iii) P_2O_5

Scheme 4.

Our original objective in this work was to produce oligomers and polymers with stereochemistry exemplified by structures(13). However



(13)



(14)

(Z)-2-(pentafluorophenyl)ethenyl iodide (14, X=I) required for this work is unknown at the present time and a potential synthetic route to (Z)-2-phenylethenyl iodide was unsuccessful[5]. Brown has described a route to (Z)-2-phenylethenyl bromide from phenylethyne and catecholborane [5] and presumably the (Z)-bromo compound (14, X=Br) could be prepared in a similar manner. However, this material is expected to react in the same way as (E)-2-(pentafluorophenyl)ethenyl bromide towards n-butyllithium, undergoing nucleophilic substitution of the para fluorine rather than halogen-metal exchange[1], so that there is no obvious route for the synthesis of (13).

EXPERIMENTAL

N.m.r. spectra were obtained with a Bruker AC 250 [^1H (250 MHz), ^{19}F (235 MHz) and ^{13}C (62.9 MHz)]. Chemical shifts are downfield from internal $SiMe_4$ (δ_H), (δ_C), or upfield (and therefore negative in value) for internal

$CFCl_3$ (δ_F). Mass spectroscopy data were obtained with a VG 7070E instrument. Molecular ions M^+ are quoted for electron ionisation.

Dehydrobromination of 1,2-dibromo-1-(pentafluorophenyl)ethane

This reaction was carried out by the literature method[2] and the major product, previously described as "cis-1-bromo-2-pentafluorophenylethylene", is actually 1-bromo-1-(pentafluorophenyl)ethene (3), δ_C ($CDCl_3$) 126.5 ppm (singlet in proton-decoupled spectrum, triplet in spin-coupled spectrum, $\underline{C}H_2$).

Reaction of 1-bromo-1-(pentafluorophenyl)ethene (3) with sodium methoxide

The bromo-compound (3) (1.0 g, 3.66 mmol) in dry methanol (50 ml) was heated under reflux with sodium methoxide in methanol (10 ml, 0.435 M; 4.35 mmol) for 4 h. The mixture was acidified (2 M sulphuric acid), extracted with diethyl ether and the dried ($MgSO_4$) extracts evaporated. ^1H n.m.r. spectroscopy of residue showed the presence of two new components and unreacted starting material (3) in the ratio 73:20:7 respectively. Compound (3) was removed from the mixture by evaporation in vacuo (22°C/5 x 10^{-3} mm Hg) and the residue was separated by gas-liquid chromatography (on a 10% SE coated column at 200°C) to give the major component, an oil, 1-bromo-1(4-methoxy-2,3,5,6-tetrafluorophenyl)ethene(nc)(4) (Found: C, 37.96; H, 1.75%; M^+, 286. $C_9H_5BrF_4O$ requires C, 37.92; H, 1.77%; M, 286); δ_H ($CDCl_3$) 4.12 (t, OCH_3), 6.03 and 6.17 ppm (both d, unassigned $C\underline{H}_2$), $J_{H,H}$ 1.7 Hz; δ_F ($CDCl_3$) -141.8 and -158.3 ppm (unassigned 2-F, 6-F/3-F, 5-F); and the minor component, 2,3,5,6-tetrafluoro-4-methoxyphenylethyne(nc)(5) mp 54-55°C. (Found: C, 53.26; H, 1.98%; M^+, 204. $C_9H_4F_4O$ requires C, 52.96; H, 1.98%; M, 204); δ_H ($CDCl_3$) 3.45 (s, C≡CH) and 4.12 ppm (t, OCH_3); δ_F ($CDCl_3$) -137.9 and -158.1 (unassigned 2-F, 6-F/3-F, 5-F); ν_{max} 3320 cm^{-1} (CH of C≡C-H).

Reaction of 1-bromo-1-(pentafluorophenyl)ethene (3) with magnesium in dry tetrahydrofuran

Magnesium (0.20 g) in dry tetrahydrofuran (5 ml), activated with 1,2-dibromoethane, was treated with the bromo compound (3) (0.53 g). An exothermic reaction occurred and the mixture was heated under reflux for 17 h. After the addition of sulphuric acid (2 M), the mixture was stirred for 4 h, and the brown solid filtered, washed first with water then with ether, and finally dried in vacuo. Close inspection of the solid (0.143 g) showed that it contained small particles of magnesium, and was very hydrophobic; it had not melted at 380°C but its organic nature was demonstrated when it gave a smokey luminous flame on combustion. It could have had the structure (6). The carbon analyses on the material were variable and usually low because of the presence of the magnesium (C, 46-52%). Compound (6) with n = 10 requires C, 54.6%.

Lithiation of 1-bromo-1-pentafluorophenylethene (3) and subsequent reaction with hexafluorobenzene

The bromo compound (3) (1.81 g; 6.62 mmol) in dry diethylether (20 ml) was treated with n-butyllithium in hexane (4.42 ml, 1.56 M; 6.9 mmol) at -70°C. After 2 h, hexafluorobenzene (2.703 g, 14.5 mmol) in dry monoglyme (20 ml) was added, the temperature was raised to -20°C, and after 15 h the mixture was acidified (2 M sulphuric acid). The products were extracted with dichloromethane, the extracts dried ($MgSO_4$) and the solvents evaporated. The crude residue (2.12 g) was separated by chromatography on silica (15 x 3 cm diameter) using light petroleum (bp 40-60°C) as eluant to give three components: (i) 1,1-bis(pentafluorophenyl)ethene(nc)(7) (0.78 g, 34%) mp 56.5-57.5°C [from light petroleum (bp 40-60°C)]. (Found: C, 46.78; H, 0.71%; M^+, 360. $C_{14}H_2F_{10}$ requires C, 46.68; H, 0.56%; M, 360); δ_H ($CDCl_3$) 6.02 ppm (s = CH_2); δ_F ($CDCl_3$) -142.2 (m, 2-F, 6-F), -154.1 (t, 4-F), and -162.0 (m, 3-F, 5-F); λ_{max} ($CDCl_3$) 241 mm (ε 7400); ν_{max} 1657 cm^{-1} (C=C); (ii) Ar3(nc)(8) (0.421 g, 30%) mp 162-162.5 [from light petroleum (bp 80-100°C)]. (Found: C, 49.77; H, 0.70%; M^+, 534. $C_{22}H_4F_{14}$ requires C, 49.46; H, 0.75%; M, 534); δ_H ($CDCl_3$) 6.02 and 6.07 ppm (both s, olefinic CH in the ratio 1:1; δ_F ($CDCl_3$) -142.1 (2-F/6-F, relative intensity 2), -142.7 (2'-F/6'-F, relative intensity 2), -154.3 (t, 4-F relative intensity 1), -162.1 ppm (3-F/5-F, relative intensity 2); λ_{max} (CH_2Cl_2) 245.7nm (ε, 24,000); ν_{max} 1630 and 1660 cm^{-1}(C=C); and (iii) Ar4(nc)(9) (0.0563 g, 3%) mp

167-168°C [from light petroleum (bp 100-120°C)] (Found: C, 51.15; H, 0.87%; M^+, 708. $C_{30}H_6F_{18}$ requires C, 50.85; H, 0.85%; M, 708); δ_H ($CDCl_3$) 6.03 and 6.08 ppm (both s, olefinic CH) in the ratio 1:2 respectively; δ_F ($CDCl_3$) -142.0 (2-F/6-F, relative intensity 2), -142.6 (unassigned and overlapping 2'-F/6'-F and 3'-F/5'-F, relative intensity 4), -154.3 (t, 4-F, relative intensity 1), -162.1 ppm (3-F/5-F, relative intensity 2); λ_{max} (CH_2Cl_2) 243.8 nm (40, 200); ν_{max} 1630 and 1655 cm^{-1} (C=C).

The column was washed with methanol to recover strongly retained components from this and other identical experiments, and the material was rechromatographed on silica (15 x 3 cm) using toluene-light petroleum (bp 40-60°C) (7:93 v/v) as eluant to give more Ar4(9) and two further products: (iv) Ar5(nc)(10) mp 223-224°C [from high petroleum (bp 100-120°C) (Found: C, 51.72; H, 0.98%; M^+, 882. $C_{38}H_8F_{22}$ requires C, 51.72; H, 0.91%; M, 882); δ_H ($CDCl_3$) 6.02 and 6.07 ppm (both s, olefinic CH) in the ratio 1:3 respectively; δ_F ($CDCl_3$) -142.0 (2-F/6-F, relative intensity 2), -142.6 (unassigned overlapping 2'-F/6'-F, 3'-F/5'-F and 2"-F/6"-F, relative intensity 6) -154.3 (t, 4-F, relative intensity 1), -162.1 ppm (3-F/5-F, relatively intensity 2); λ_{max} (CH_2Cl_2) 248.0 nm (ϵ 39,800); ν_{max} 1630 and 1658 cm^{-1} (C=C); and (v) Ar6(11) (ca. 75% pure) (Found: M^+, 1056, $C_{46}H_{10}F_{26}$ requires M, 1056).

Reaction of decafluorobenzophenone with methylmagnesium iodide followed by dehydration of the product with phosphorus pentoxide

Decafluorobenzophenone [4] (0.290 g) in dry diethyl ether (5 ml) was treated with methylmagnesium iodide prepared from methyl iodide (1.40 g) in dry diethyl ether (5 ml) and excess magnesium. The mixture was heated under reflux for 3 h, acidified (2 M sulphuric acid) and extracted with ether. The extracts were dried ($MgSO_4$), the solvent evaporated and the residue purified by chromatography on silica using chloroform as eluant. The pure alcohol (not characterised) (0.277 g) was covered with a layer of P_2O_5 and heated in an oil bath at 165°C. After 20 mins, the mixture was sublimed at ca. 100°C/0.05 mm Hg to give 1,1-bis-(pentafluorophenyl)ethene(7) (0.255 g; 89%) which had an i.r. identical with the material described above.

ACKNOWLEDGEMENT

We thank the SERC for a grant (to SDM).

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