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GENERATION AND THERMAL POLYMERIZATION OF 1-FLUORO-2-PHENYLACETYLENE

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SUMMARY

Some routes to the synthesis of 1-fluoro-2-phenylacetylene were attempted. Although the halogen exchange of chloro- and bromophenylacetylenes and dehydrobromination of dibromofluorophenylacetylene were unsuccessful, defluorosilylation of 1,1-difluoro-2-phenyl-2-trimethylsilylethene (which was prepared by lithiation of bromodifluorovinylbenzene followed by silylation with chlorotrimethylsilane) with CsF gave an oligomer of fluorophenylacetylene. The reaction of the phenyldifluorovinylsilane with CsF in DMF in the presence of phenylazide afforded a 1,3-dipolar cycloadduct, fluorodiphenyl-1,2,3-triazole. Vapor phase vacuum pyrolysis of the phenyldifluorovinylsilane yielded the acetylene, which spontaneously polymerized.

INTRODUCTION

Recently, many types of organic conductors and semiconductors have been synthesized because of their versatility for use as polymer batteries and so on [1]. Polyacetylene (1) is a typical organic conductor and the conductivity is increased remarkably by doping with iodine or alkali metals [1,2]. However, the doped polyacetylenes have some drawbacks, namely lack of durability, and sensitivity towards oxidation. Yamabe *et al.* [3] suggested that the introduction of fluorine may

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enhance the conductivity of the polymer, besides overcoming some disadvantages. In the course of our study of the synthesis of novel fluorine-containing polyarylacetylenes for use as organic semiconductors [4], we chose polyfluorophenylacetylene (2) as a synthetic target. In this paper, we describe some attempts to synthesize the logical monomer 1-fluoro-2-phenylacetylene (3).

$\left(CH{=}CH \right)_n$ $\quad\quad$ $\left(C_6H_5C{=}CF \right)_n$ $\quad\quad$ $C_6H_5C{\equiv}CF$

1 $\quad\quad$ 2 $\quad\quad$ 3

Although there are some reports on the syntheses, polymerizations and applications of difluoroacetylene and fluoroacetylene [5,6], few studies of alkyl- [7] or arylfluoroacetylenes [8] have been reported heretofore. In the case of fluorophenylacetylene, Schlosser *et al.* attempted its preparation from the reaction of phenylethynyllithium and $FClO_4$, but the product was diphenyldiacetylene [8]. They have speculated that fluorophenylacetylene 3 has high electrophilicity and reactivity.

RESULTS AND DISCUSSION

(a) Attempts at halogen exchange on haloacetylenes.

Since spray-dried KF is known as a reactive nucleophilic reagent for fluorination of alkyl halides [9], the halogen exchange reactions of 1-chloro- and 1-bromo-2-phenylacetylenes (4a, b) with spray-dried KF were attempted under various

$C_6H_5{-}C{\equiv}CX$ $\quad\quad$ 4a, X=Cl, b, X=Br

conditions; heating at 120°C in DMF, irradiation of ultrasonics at room temperature, refluxing in toluene in the presence of a catalytic amount of 18-crown-6, heating at 180°C in HMPA, and finally heating without any solvent at 300°C under reduced pressure. However, none of the above reactions gave any fluorine-containing product, affording only decomposition products derived from the starting materials. Although no

MO-calculations are known, the *sp*-orbital of an acetylene bond appears to be at rather low energy level on the basis of the remarkable stability of acetylide anions. Thus, the haloacetylenes 4a,b are probably quite soft electrophiles, while fluoride anion is one of the hardest nucleophiles. This suggests that halogen exchange reactions of the haloacetylenes will be difficult.

(b) Dehydrobromination of (fluorodibromoethyl)benzene.

t-Butylfluoroacetylene has been reported in a patent [10] to be generated from dehydrobromination of *t*-butyldibromofluoroethane with KOH. However, the reactions of (1,2-dibromo-2-fluoroethyl)benzene (5) with KOH under various conditions gave only complex mixtures. For instance, the reaction of 5 and KOH in refluxing methanol yielded a complex mixture, but GC-MS analysis of the mixture revealed the presence of a component (<1%) of which the molecular weight was 152. The mass spectrum suggests that the structure of this component is 6, the methanol addition product of acetylene 3. The fluorophenylacetylene 3 itself could not be isolated by this method.

C_6H_5–CHBrCHFBr

5

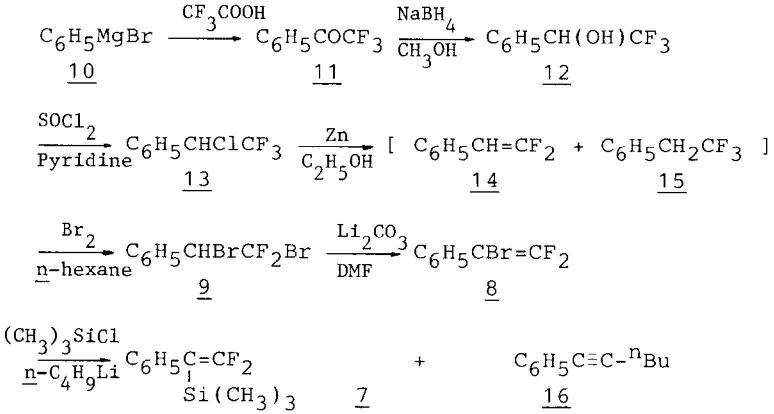
C_6H_5–CH=CF–OCH_3

6

(c) Defluorosilylation of the phenyl difluorovinylsilane.

After starting this study, Hiyama *et al.* reported the generation and the spontaneous polymerization of difluoroacetylene from the reaction of trifluorovinylsilane and CsF [6]. Thus, it was expected that the phenyl derivative 3 also might be generated from defluorosilylation of silane 7. Although the bromide 8, which was converted to silane 7 by subsequent silylation, was reported to be prepared from the dibromide 9 by treatment with Li_2CO_3 [11], we modified the reported preparation sequence to 9 because of the unsatisfactory yields.

Phenyl Grignard reagent 10 was treated with trifluoroacetic acid to yield trifluoroacetophenone 11 according to the method reported by Dishart *et al.* [12], and 11 was converted to alcohol 12 in 89 % yield by $NaBH_4$ reduction. Chlorination of alcohol 12 with thionyl chloride gave chlorotrifluoride 13 in 83 % yield. Dechlorofluorination of 13 to difluorostyrene 14 was carried out with Zn in refluxing ethanol though a small amount of by-product 15 was also produced. The dechlorinated products were taken up in n-hexane solution without any purification and the solution was treated with bromine at room temperature to afford the desired dibromide 9 (65 % from 13). The bromide 8 was obtained according to the known procedure [11].



$$\underset{10}{C_6H_5MgBr} \xrightarrow{CF_3COOH} \underset{11}{C_6H_5COCF_3} \xrightarrow[CH_3OH]{NaBH_4} \underset{12}{C_6H_5CH(OH)CF_3}$$

$$\xrightarrow[Pyridine]{SOCl_2} \underset{13}{C_6H_5CHClCF_3} \xrightarrow[C_2H_5OH]{Zn} [\ \underset{14}{C_6H_5CH{=}CF_2} + \underset{15}{C_6H_5CH_2CF_3}\ ]$$

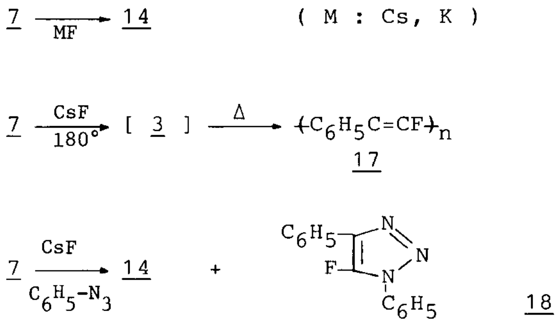
$$\xrightarrow[n\text{-hexane}]{Br_2} \underset{9}{C_6H_5CHBrCF_2Br} \xrightarrow[DMF]{Li_2CO_3} \underset{8}{C_6H_5CBr{=}CF_2}$$

$$\xrightarrow[n\text{-}C_4H_9Li]{(CH_3)_3SiCl} C_6H_5\underset{Si(CH_3)_3}{C}{=}CF_2 \quad 7 \quad + \quad \underset{16}{C_6H_5C{\equiv}C\text{-}{}^nBu}$$

Treatment of 8 with n-butyllithium in THF at -78°C followed by addition of chlorotrimethylsilane gave only n-butylphenylacetylene (16). Apparently, lithiation of 8 occurred smoothly, but the lithio derivative was unstable even at -78°C, due to the elimination of LiF to form fluorophenylacetylene 3 which was then attacked rapidly by the excess n-butyllithium. To avoid the elimination of LiF, n-butyllithium was carefully added dropwise into a mixture of bromide 8 and chlorotrimethylsilane in THF at -78°C. In this way, the desired silane 7 was successfully obtained in 49 % yield accompanied by the by-product 16 (9 %) which was readily separated by a simple distillation.

The reactions of silane 7 with CsF or KF (with 18-crown-6) gave only difluorostyrene 14, the proton-exchange product of 7. This proton-exchange reaction was probably caused by a trace amount of water incorporated with the fluoride salts.

Accordingly, the silane 7 was treated with CsF (which had been freshly dried over a flame) in a sealed tube without any solvent at 180°C for 8 days. As the reaction proceeded, the mixture became brown and viscous and finally solidified as a very viscous black mass. This amorphous material was purified by successive reprecipitations from benzene – *n*-hexane. The IR spectrum revealed an absorption due to conjugated double bonds (1668 cm^{-1}, br), and in the ^1H-NMR spectrum, no resonance appeared except in the aromatic proton region. Since the Mw was *ca.* 1200 (polystyrene standard), the structure of this material is an oligomer 17 ($n \simeq 10$; 18 % yield). However, the elemental analysis data shows considerable loss of fluorine probably due to hydrolysis and/or thermal carbonization. It was established that fluorophenylacetylene 3 was generated in the reaction of silane 7 with CsF by a trapping experiment with phenylazide in DMF to afford triazole 18 (3.3 %) at 100°C, though the main product was again difluorostyrene 14 (28 %; GLC yield). The regiochemistry was determined by comparison of the ^1H-NMR spectra of 18 and the parent triazoles [13].



It was anticipated that the defluorosilylation reaction would also occur thermally as well as by fluoride ion attack, because of the remarkable thermodynamic stability of the Si-F bond. In fact, vacuum vapor-phase pyrolysis of the silane 7 at 600°C (0.2 mmHg, contact time = ca. 10 s) in a quartz tube gave a longer chain polymer 2 (Mw ≃ 19000) than the oligomer 17 in

54 % yield, and fluorine was almost retained. Since the yellow polymer 2 appeared on the wall of a -78°C trap while the reaction had been going on, the monomer acetylene 3 appears to be unstable and reactive even at -78°C. The IR spectrum also revealed the longer chain with the red-shift absorption assignable to the conjugated double bond (1640 cm^{-1}). The mechanisms of both the oligomerization of the acetylene 3

$$\underline{7} \xrightarrow[600^{\circ}]{\Delta} [\ \underline{3}\ ] \xrightarrow[-78^{\circ}]{} \underline{2}$$

generated by the fluoride ion induced reaction, and the polymerization of the product of vacuum pyrolysis might be thermally induced radical reactions. However, the difference of the molecular weights is probably attributable to the difference of the concentrations of the monomer 3 in the respective reaction systems and the reaction temperatures.

In conclusion, various attempts to synthesise 1-fluoro-2-phenylacetylene 3 were tried. Although the isolation of 3 was unsuccessful due to its intrinsic reactivity, its polymer 2 was obtained by the vapor-phase pyrolysis of the silane 7. The electric character of the polymer is now under investigation.

EXPERIMENTAL

Melting points were taken in a sealed tube on a Mitamura Riken's micro melting point measurement apparatus and are uncorrected. IR spectra were obtained on a JASCO IR-810 infrared spectrophotometer. ^{1}H- and ^{19}F- NMR spectra were recorded on a Hitachi R-22 instrument at 90 MHz and a Hitachi R-20B instrument at 56.45 MHz, and chemical shifts are reported in parts per million (δ) relative to Me_4Si as an internal standard for ^{1}H and to CF_3COOH as an external standard for ^{19}F. Mass spectra and GC-MS analyses were performed on a Shimazu GC-MS 7000 (column; 2 m column packed with silicone OV-17). GLC analyses were carried out by using a Shimazu GC-7A gas chromatograph with 2 m silicone KF-96 column at 100-230°C under 35 ml/min current of He. The known intermediates 12, 13, 9, and

16 gave satisfactory elemental analyses. The molecular weights of polymers were estimated with a Toyo Soda HLC-8024A GPC (THF), and the calibration curve for polystyrene was used to calculate the molecular weights.

(a) Attempts at halogen exchange reactions of haloacetylenes.

Some experiments were attempted as mentioned in the text, but no fluorine-containing product was obtained. For example: A mixture of bromophenylacetylene (4b, 905 mg, 5.0 mmol), 18-crown-6 (264 mg), spray-dried KF (1.90 g, 33 mmol) and toluene (20 ml) was stirred at refluxing temperature under an atmosphere of argon for 24 h. However, no volatile product was detected by GLC analysis and TLC (SiO_2, *n*-hexane) analysis revealed that the mixture contained many decomposition products. No further separation nor purification was carried out.

(b) Dehydrobromination of (fluorodibromoethyl)benzene.

Reaction of 5 and KOH in methanol

A mixture of 5 (347 mg, 1.23 mmol) and 85 % KOH (200 mg, 3.0 mmol) in methanol (5 ml) was refluxed for 20 min. There were many peaks in the gas chromatogram of the reaction mixture, and GC-MS analysis showed that the molecular weight of one component was 152: MS m/z (%) 153 (M^++1, 6), 152 (M^+, 60), 137 (M^+-CH_3, 23), 109 (M^+-CH_3-CO, 100), 83(13), 63 (10), 51 (10).

(c) Defluorosilylation of the phenyl difluorovinylsilane.

2,2,2-Trifluoro-1-phenylethanol (12).

To an ice-cooled and stirred mixture of trifluoroacetophenone (11, 26.1 g, 150 mmol) and methanol (75 ml) was added portionwise $NaBH_4$ (2.85 g, 75 mmol) in 30 min at 0°C and the mixture was stirred overnight at room temperature. The mixture was then poured into ice-water (200 ml) and extracted with ether. The extracts were combined and dried with Na_2SO_4.

After removal of the solvent, distillation under reduced pressure gave the alcohol <u>12</u> (23.6 g, 89 %):bp. 61-4°C (5 mmHg) (lit. 53-4.5°C, 2 mmHg [14]); IR (neat film on KBr) 3400, 3030, 1265, 1170, 1125, 703 cm^{-1}; ^{19}F-NMR (CCl_4) 0.46 (d, J=7 Hz); ^{1}H-NMR (CCl_4) 7.26 (s, 5H), 4.77 (q, J=7 Hz, 1H), 3.4 (m, 1H); MS m/z 176(24, M^+), 107 (100), 79 (98).

<u>1-Chloro-2,2,2-trifluoro-1-phenylethane (13).</u>

To a stirred mixture of <u>12</u> (20.5, 131 mmol), pyridine (10.4 g, 132 mmol) and benzene (10 ml) protected by a drying tube ($CaCl_2$) was added dropwise $SOCl_2$ (31.0 g, 262 mmol) in 10 min at room temperature. Then, the mixture was refluxed for 2 h, poured into ice-water (200 ml), and extracted with ether. The combined extracts were successively washed with water and then saturated Na_2CO_3 aqueous solution, and dried with Na_2SO_4. After removal of the solvent, distillation under reduced pressure gave the pure chloride <u>13</u> (18.8 g, 83 %): bp. 56-7°C (13 mmHg) (lit. 70-1°C, 27 mmHg [14]); IR (neat film on KBr) 3030, 1260, 1168, 1100, 6950 cm^{-1}; ^{19}F-NMR (CCl_4) 11.1 (d, J=7 Hz); ^{1}H-NMR (CCl_4) 7.3 (m, 5H), 4.99 (q, J=7Hz 1H); MS m/z 196 (6, M^++2), 194 (19, M^+), 125 (100).

<u>1,2-Dibromo-2,2-difluoroethylbenzene (9).</u>

A mixture of chloride <u>13</u> (26.0 g, 134 mmol) and zinc turnings (8.76 g, 134 mmol) in anhydrous ethanol (100 ml) was stirred under refluxing for 10 h, then poured into water (300 ml), and extracted with <u>n</u>-hexane. The combined extracts were successively washed with water and dried with Na_2SO_4. From GLC analysis, the solution contained a 9:1 mixture of difluorostyrene <u>14</u> and the dechlorinated product <u>15</u>. GC-MS analysis of the mixture confirmed the structures of the products (m/z 140 (M^+) for <u>14</u> and 160 for <u>15</u> (M^+) [15]), and the GC retention time of <u>14</u> was identical with that of an authentic sample [15]. The mixture was brominated without any separation. To the stirred <u>n</u>-hexane solution was added bromine (16.3 g, 102 mmol) in one portion. The mixture was stirred for 5 h at room temperature, and then diluted with ice-water (200 ml). To the ice-cooled and stirred mixture were added portionwise $NaHSO_3$

and $NaHCO_3$ until the solution turned colorless. The organic layer was separated and the aqueous layer was extracted with n-hexane. The combined n-hexane solution was washed with water and dried with Na_2SO_4. After removal of the solvent and of the by-product 15, distillation under reduced pressure gave dibromide 9 (26.9 g, 65 %): bp. 85-7°C (4 mmHg) (lit. 75-6°C, 2 mmHg [11]); IR (neat film on KBr) 3025, 1185, 1103, 9037, 6930 cm^{-1}; The ^{19}F- and ^{1}H-NMR spectra, and the mass spectrum were identical with the reported spectral data [11].

(1-Bromo-2,2-difluorovinyl)benzene (8) was obtained by the procedure of Burton *et al.* [11].

1,1-Difluoro-2-phenyl-trimethylsilylethene (7) (nc).

To a stirred mixture of bromide 8 (6.57 g, 30 mmol) and chlorotrimethylsilane (4.91 g, 45 mmol) in anhydrous THF (50 ml) was carefully added dropwise n-butyllithium n-hexane solution (1.6 M, 28 ml, 44.8 mmol) at -78 – -70°C in 1 h under an atmosphere of argon , the mixture was stirred at -78°C for 5 h, and then warmed up to room temperature overnight. The mixture was poured into water (100 ml), and the organic layer was separated. The aqueous layer was extracted with n-hexane. The combined extracts were washed with water and dried with Na_2SO_4. After removal of the solvent, distillation under reduced pressure gave the silane 7 (3.11 g, 49 %) as colorless oil and the acetylene 16 (0.31 g, 7%): Silane 7 had bp. 79-82°C (21 mmHg); IR (neat film on KBr) 3050, 3020, 2955, 2895, 1692, 1602, 1248, 1215, 840, 762, 698 cm^{-1}; ^{19}F-NMR (CCl_4) 8.9 (d, J=13 Hz), 1.1 (d, J=13 Hz); ^{1}H-NMR (CCl_4) 7.5-6.9 (m, 5 H), 0.15 (s, 9 H); MS m/z (%) 213 (M^++1, 6), 212 (M^+, 36), 120 (30), 115 (38), 81 (27), 73(16), 49 (16): Analysis: Found: C, 62.14; H, 6.70 %: $C_{11}H_{14}F_2Si$ requires C, 62.23; H, 6.65 %: Acetylene 16 had bp. 85-7°C (3 mmHg) (lit. 94-5°C, 4 mmHg [16]); IR (neat film on KBr) 3050, 2955, 2230, 1600, 1493, 1065, 755, 692 cm^{-1}; ^{1}H-NMR (CCl_4) 7.5-1 (m, 5H), 2.5-3 (m, 2H), 1.7-3 (m, 4H), 1.1-0.8 (m, 3H); MS m/z (%)158 (M^+, 75), 143 (100).

Reaction of silane 7 with KF.

A mixture of silane 7 (159 mg, 0.75 mmol), spray-dried KF (36 mg, 0.6 mmol) and 18-crown-6 (60 mg, 0.23 mmol) in anhydrous THF (5 ml) was stirred at room temperature for 60 h under nitrogen atmosphere. GLC analysis of the mixture showed that the volatile product was only difluorostyrene 14, and any purification was not carried out.

Reaction of silane 7 with CsF in a sealed tube at 180°C.

A mixture of silane 7 (3.10 g, 15 mmol) and CsF (freshly dried over flame, 200 mg, 1.3 mmol) was stirred at 180°C in a sealed glass tube under reduced pressure (100 mmHg N_2 atmosphere at room temperature) for 8 days. The resulting black mass was washed with *n*-hexane (5 ml) and diluted with $CHCl_3$ (25 ml). Evaporation of the solvent and successive reprecipitation from benzene – *n*-hexane gave oligomer 17 (330 mg, 18 %): mp. 250-60°C; Mw = 1189; Mn = 868; IR (neat film on KBr) 3050, 2915, 1668, 1600, 1498, 1442, 748, 692 cm^{-1}; ^1H-NMR ($CDCl_3$) 8.0-6.0 (m): Analysis: Found: C, 83.10; H, 4.03; F, 7.33 %: $(C_8H_5F)_n$ requires C, 79.99; H, 4.20; F, 15.82 %.

5-Fluoro-1,4-diphenyl-1,2,3-triazole (18) (nc).

To a stirred mixture of silane 7 (400 mg, 1.88 mmol), phenylazide (226 mg, 1.92 mmol) and *n*-dodecane (51 mg, GLC standard) in anhydrous DMF (6 ml) was added CsF (10 mg, 0.07 mmol) in one portion at 100°C, and the mixture was kept stirring 4 h. GLC analysis showed that the resulting mixture contained 14 (74 mg, 28 %). After removal of the solvent and volatile products under reduced pressure (40°C, 10 mmHg), successive preparative TLC (SiO_2, CH_2Cl_2) yielded triazole 18 as pale yellow crystals(15 mg, 3.3 %): mp. 98-100°C; UV (EtOH) $\lambda_{max}(\log \varepsilon)$ 242 nm (4.44); IR (KBr) 3050, 1635, 1600, 1518, 1442, 1365, 1262, 752, 685 cm^{-1}; ^{19}F-NMR ($CDCl_3$) -71.6 (s); ^1H-NMR ($CDCl_3$) 8.0-7.1 (m); MS m/z (%) 240 (M^++1, 1), 241 (M^+, 5), 212 (25), 211 (100), 210 (60), 190 (17), 183 (25), 165 (16), 149 (11), 108 (15): Analysis: Found: C, 70.16; H, 4.31; N, 17.52 %: $C_{14}H_{10}N_3F$ requires C, 70.28, H, 4.21, N, 17.56 %.

Vapor phase vacuum pyrolysis of silane 7.

Vaporized silane 7 (2.00 g, 9.4 mmol) was led through a quartz tube (10 mm in diameter) heated to 600°C in a 30 cm-long electric furnace under vacuum (0.2 mmHg), and the end of the pyrolysis tube was connected with a flask immersed in a dry ice – ethanol bath and further with a trap in a liq. N_2 bath. It took 44 h to consume 7; contact time corresponds to ca 10 s. The polymer formed in the traps was dissolved with hot $CHCl_3$, and precipitated by addition of methanol followed by filtration (520 mg, 46 %): mp 250-260°C; Mw = 19492; Mn = 2999; IR (KBr) 3045, 3010, 1640, 1598, 1490, 1440, 1192, 758, 692 cm^{-1}; ^{1}H-NMR ($CDCl_3$) 8.0-6.5 (m): Analysis: Found: C, 77.97; H, 4.17; F, 14.05: $(C_8H_5F)_n$ requires C, 79.99; H, 4.20; F, 15.82 %.

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