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THE SYNTHESIS AND ATTEMPTED POLYMERIZATION OF AN α,β,β-TRIFLUOROSTYRENE DISUBSTITUTED BY HEXAFLUORO-2-PROPANOL GROUPS

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SUMMARY

The preparation of [(5-(trifluoroethenyl)-1,3-phenylene)bis[2,2,2-trifluoro-1-trifluoromethylethylidene]oxy]-bis[trimethylsilane] **2** in excellent isolated yield from the corresponding aryl iodide **4** is described. The synthesis features conversion of the known dialcohol **3** to the trimethylsilyl ether **4** which gave excellent protection against organometallic reagents and allowed the $Pd(PPh_3)_4$ catalyzed coupling with trifluoroethenylzinc bromide. Compound **2** exhibited good thermal stability with little propensity to form the corresponding F-cyclobutane dimer at room temperature.

INTRODUCTION

Numerous high performance polymers have been prepared from hexafluoroacetone [1]. The majority of these are derived from hexafluorobisphenol-A. While tetrakis(trifluoromethyl)benzenedimethanols **1** have been used in the preparation of either condensation polymers or acrylic esters [2], comparatively few have maintained a pendant hexafluoro-2-propanol group. The strong hydrogen bonding properties of this pendant group have been described in similar polymers [3]. Our need for a highly fluorinated polymer with this potentially valuable property prompted the synthesis and study of polymers of the novel disubstituted α,β,β-trifluorostyrene **2.**

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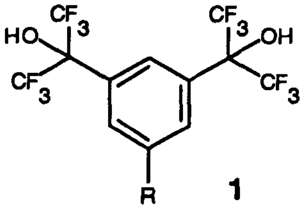
RESULTS AND DISCUSSION

Synthetic routes to α, β, β-trifluorostyrenes have been available for numerous years [4], albeit in poor to modest yield. Our adaptation of Heinze and Burton's improved procedure [5] gave **2** in excellent yield. As acidic functionalities could not be tolerated in the synthesis, the protection of the sterically crowded tertiary dialcohol **3** was necessary. The conversion to the trimethylsilyl ether proved quantitative, convenient, and provided good protection in further manipulations. The reaction of **3** with hexamethyldisilazane at reflux yielded **4**, whereas hexamethylsiloxane did not react to an appreciable extent. The dialcohol **3** is readily regenerated by dissolution in a protic solvent such as methanol or water. These mild conditions are better than the harsh and degradative treatment with aluminium trichloride/ chlorobenzene required to cleave similar methyl ethers of **1** [6].



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The palladium catalyzed coupling reaction of **4** with trifluoroethenylzinc bromide proceeded well and represents a significant improvement over similar transition metal mediated coupling reactions [7]. The reaction must be stirred vigorously as the reactants were miscible in dimethylformamide, while the product **2** was immiscible and partitioned the reagents between the two phases. The workup simply involved phase separation and distillation (Fig. 1.).

α, β, β-Trifluorostyrenes are ordinarily resistant to the usual free radical polymerization methods [8]. It has been suggested that the facile [2+2] cycloaddition reaction to form diphenyl-E-cyclobutane interferes with formation of high polymer [9]. The qualitative observation that some electron rich α, β, β-trifluorostyrenes are susceptible to dimerization [4g,10] is conversely supported by our results. Electron poor **2** gave no evidence of dimerization after two years at room temperature without inhibition. After 16 days at 105°C **2** had begun to decompose, with some higher boiling products observed by GLPC analysis. From these results we speculated that radical polymerization of **2** would favorably compete with dimerization.

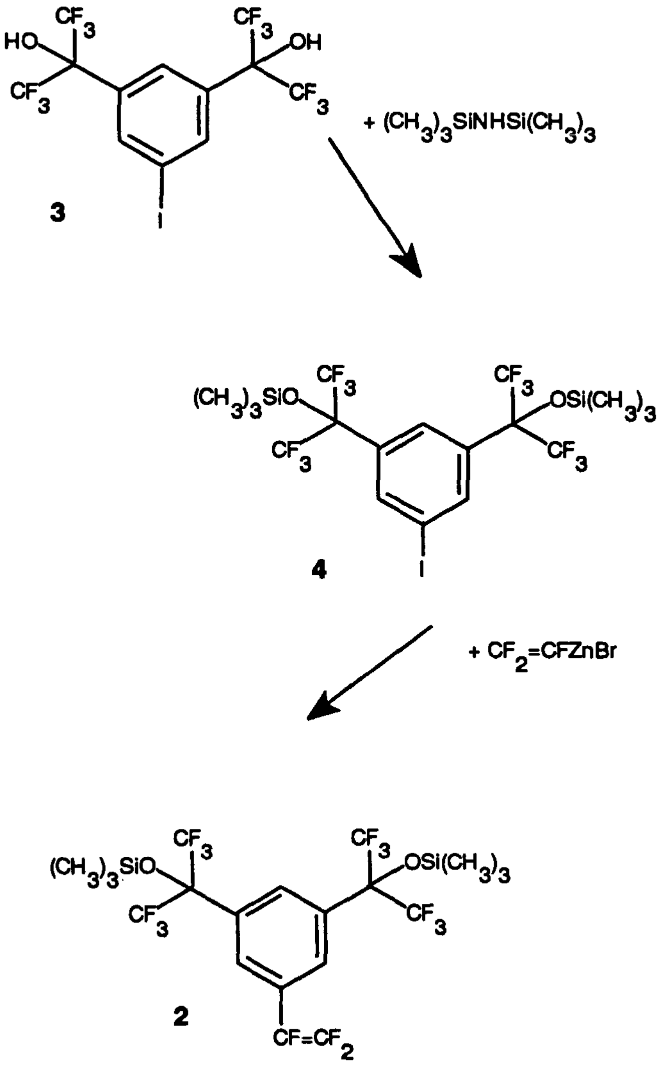

Fig. 1. Reaction scheme to substituted α,β,β-trifluorostyrene **2**.

Free radical polymerization of the monomer **2** was difficult, though it did yield 12% of a poorly characterized solid upon azobisisobutyronitrile initiated homopolymerization. The infrared spectrum of the product did not display the CF_2=CF- absorbance at 1759 cm^{-1}. There was no GLPC evidence for dimeric products in the reaction mixture which boil higher than monomer **2**. The bulk copolymerization of **2** with trifluoroethene did not yield any polymer, while the control polymerization of trifluoroethene gave 89% conversion to poly(trifluoroethene).

EXPERIMENTAL

All boiling points were determined during fractional distillation and are uncorrected. ^1H and ^{19}F NMR spectra were recorded on a Varian EM-390 spectrometer at 89.98 and 84.67 MHz respectively. ^{19}F NMR spectra are referenced against external $CFCl_3$ and ^1H NMR spectra against internal tetramethylsilane. FTIR spectra were recorded on a Perkin-Elmer Model 1800 Double Beam Instrument as neat films on NaCl blocks. Elemental analyses were performed by Schwarzkopf Microanalytic Laboratory.

[(5-Iodo-1,3-phenylene)bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]oxy]bis[trimethylsilane], (4) (nc)

Hexamethyldisilazane (24.8 g, 0.154 mole) and 5-iodo-$\alpha,\alpha,\alpha',\alpha'$-tetrakis(trifluoromethyl)-1,3-benzenedimethanol (3) [11] (50.6 g, 0.094 mole) were heated together at 94°C for 64 hrs, the excess disilazane was removed in vacuo at room temperature, and the residue distilled through a short path apparatus to yield 63.1 g (0.096 mole, 101%) of the titled compound as a clear and colorless oil: bp 99-105°C/ <0.1 mmHg (100% GLPC purity); d^{20} 1.496; n^{27} 1.4284; ^{19}F NMR ($CDCl_3$) -73.3 ppm (s); ^1H NMR($CDCl_3$) 0.22 ppm (s, 18H), 8.03 ppm (s, 1H), 8.10 ppm (s, 2H); FTIR (cm^{-1}, absorbance) 3101 (0.069), 2953 (0.156), 2906 (0.082), 1599 (0.086), 1572 (0.181), 1441 (0.128), 1433 (0.123), 1423 (0.122), 1298 (0.338), 1260 (0.422), 1218 (0.431), 1204 (0.465), 1156 (0.343), 1039 (0.193), 1028 (0.251), 998 (0.148), 973 (0.361), 956 (0.145), 880 (0.347), 848 (0.363), 819 (0.183), 762 (0.261), 727 (0.339), 707 (0.284), 701 (0.269), and 633 cm^{-1} (0.219). Analytical. Calculated for $C_{18}H_{21}F_{12}IO_2Si_2$: C, 31.77%; H, 3.11%; F, 33.51%. Found: C, 31.91%; H, 2.85%; F, 34.34%.

[(5-(Trifluoroethenyl)-1,3-phenylene)bis[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]oxy]bis[trimethylsilane]. (2) (nc)

Trifluoroethenylzinc bromide was prepared from Zn (6.6 g, 0.10 atom), bromotrifluoroethene (20.8 g, 0.13 mole), and DMF (50 mL) by the previously described procedure [12]. The excess CF_2=CFBr was removed *in vacuo*, the residue was filtered through a Schlenk funnel (coarse frit), *tetrakis*(triphenylphosphine)palladium (0.969 g, 1%) and 4 (51.7 g, 0.07 mole) added and the reaction mixture stirred at 50°C for 21 hrs. The product was separated as a clear oil to yield 40.5 g (0.065 mole, 83%) of the crude titled compound which was distilled through a 10 cm vigreux column: bp 63-65°C/ <0.1 mmHg; 100% GLPC purity; d^{20} 1.334; n^{25} 1.4014; ^{19}F NMR ($CDCl_3$) -74.1ppm (s, 12 F), -97.4 ppm (dd, 1F), -112.8 ppm (dd, 1F), -178.1 ppm (dd, 1F); ^1H NMR ($CDCl_3$) 0.26 ppm (s, 18H), 7.87 ppm (s, 2H), 7.99 ppm (s, 1H); FTIR (cm^{-1}, absorbance) 3128 (0.053), 2966 (0.178), 2907 (0.067), 1759 (0.465), 1611 (0.090), 1573 (0.063), 1462 (0.119), 1451 (0.122), 1413 (0.110), 1302 (0.637), 1260 (0.680), 1203 (0.684), 1156 (0.611), 1146 (0.549), 1077 (0.357), 1071 (0.325), 1032 (0.293), 974 (0.635), 951 (0.097), 891 (0.569), 877 (0.617), 849 (0.623), 762 (0.400), 738 (0.266), 728 (0.593), 705 (0.439), 693 (0.161), 634 (0.267), and 629 cm^{-1} (0.281). Analytical. Calculated for $C_{20}H_{21}F_{15}O_2Si_2$: C, 38.47%; H, 3.39%; F, 45.64%. Found: C, 38.00%; H, 3.01%; F 45.08%.

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