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PRELIMINARY NOTE

SYNTHESIS AND CHARACTERIZATION OF MONO- AND BIS(PENTAFLUOROSULFUR)DIACETYLENE

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SUMMARY

The synthesis of novel, high density, diacetylene monomers has been achieved by the preparation of mono- and bis(pentafluorosulfur) diacetylene. The derivatives are readily prepared by the addition of pentafluorosulfur bromide (SF_5Br) to diacetylene (C_4H_2) and subsequent dehydrobromination. Details of the synthesis and properties of these compounds are discussed.

Direct methods to prepare mono- or disubstituted derivatives of diacetylene have not been available. Previously, only the syntheses of symmetrical derivatives of diacetylene were reported by the indirect, multi-stepped route involving coupling reactions of the appropriate acetylenic fragments. Furthermore, very few fluorinated diacetylene derivatives[1,2] have been synthesized by this method. As a part of our continued interest in modifying the properties of materials by directly incorporating perfluorosulfur groups (SF_5) into olefins[3] and acetylenes[4] using pentafluorosulfur bromide (SF_5Br), we recently developed a method to prepare the unsymmetrical monosubstituted and symmetrical disubstituted derivatives of diacetylene. This report describes the syntheses and some physical properties of both mono(pentafluorosulfur)diacetylene, $SF_5C{\equiv}C\text{-}C{\equiv}CH$, and bis(pentafluorosulfur)diacetylene, $SF_5C{\equiv}C\text{-}C{\equiv}CSF_5$.

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Millimole quantities of SF_5Br and diacetylene, HC≡C-C≡CH, were reacted overnight at -78^o in a one liter round bottom flask, fitted with a Teflon/Pyrex stopcock and a condensation tip, giving a 50% yield of the 1:1 addition product $F_5SC(H)=C(Br)-C{\equiv}CH$ (I). This compound was a clear liquid with a vapor pressure of less than 5 torr at room temperature. Compound (I) was isolated by vacuum distillation through a 0^o trap into a collection trap cooled to -23^o. The gas phase infrared spectrum contained principal absorptions at 3325 cm^{-1} (m) (ν(HC≡C)), 3110 cm^{-1} (w) (ν(HC=C)), 2120 cm^{-1}(w) (ν(C≡C)), 1620 cm^{-1} (w) with a shoulder at 1590 cm^{-1} (ν(C=C)), 880 cm^{-1} (vs) (ν(S-F)), and 603 cm^{-1} (m) (δ(S-F)). Other absorptions at 1295 cm^{-1} (w), 1008 cm^{-1} (m), 920 cm^{-1} (m), 720 cm^{-1} (w) and 657 cm^{-1} (m) were unassigned. The ^{19}F NMR spectrum[5] in Freon-11 contained only one AB_4 pattern (δ_A=-61.0 and δ_B=-71.5 ppm, J_{A-B}= 141.1 Hz), which is consistent with an SF_5 group. The ^{1}H NMR spectrum contained a quintet (δ=7.45 ppm, J_{H-B}=7.8 Hz) due to a p coupling with the equatorial sulfur-fluorines and a singlet in the spectral region of acetylene hydrogens (δ=3.88 ppm) in a ratio of 1:1.07. The mass spectrum contained the appropriate Br clusters and the fragmentation pattern (reported for ^{79}Br) contained a parent-ion at m/e 256, in addition to major fragments at 147 (SC_3Br^+), 128 (C_4HBr^+), 127 (SF_5^+), 89 (SF_3^+) and 70 (SF_2^+).

Dehydrobromination of (I) by excess KOH occurred at 25^{o}C to give an approximate 50% yield of the mono(pentafluorosulfur)diacetylene, $SF_5C{\equiv}C-C{\equiv}CH$ (II). The identity of the compound was confirmed by gas phase molecular weight measurements (found, 174; theory, 176) and spectroscopic data. In the gas phase infrared spectrum, a medium absorption at 3340 cm^{-1} (ν(HC)), a medium absorption at 2260 cm^{-1} ($\nu(SF_5C{\equiv}C)$), a weak absorption at 2080 cm^{-1} (ν(HC≡C)), variable intensity absorptions at 1350, 1140, 1100 and 990 cm^{-1} were unassigned, while very strong S-F bands were at 900, 850, 650, 620 and 590 cm^{-1}. The ^{19}F NMR spectrum[5] in Freon-11 contained only one AB_4 pattern (δ_A=-70.0 and δ_B=-78.1 ppm; J_{A-B}=141.5 Hz). The ^{1}H NMR spectrum contained a singlet absorption at δ=2.45 ppm relative to TMS, which is within the range (2-3 ppm) characteristic of protons bonded to acetylenic structures. A relatively simple mass spectral fragmentation pattern contained a strong parent ion at m/e= 176, together with major fragments at 157 ($SF_4C_4H^+$), 127 (SF_5^+), 89 (SF_3^+), 68 (SC_3^+) and 49 (C_4H^+). The experimentally determined vapor pressure equation, log $P_{(mm)}$= 7.70 - (1593/T), yielded an extrapolated boiling point of 57.6^o, ΔH_{vap} of 7.28 kcal/mol, and ΔS_{vap} of 22.0 eu. The density of the liquid at 25^{o}C was found to be 1.42 g/cc.

The disubstituted adduct $F_5SC(H)=C(Br)-C(Br)=C(H)SF_5$ (III) was prepared in a 50% yield by reacting a 2:1 mole ratio of SF_5Br and HC≡C-C≡CH, respectively, at -45°. This compound was a clear liquid with a vapor pressure of much less than 1 Torr at 25° and was removed from the reaction vessel with a syringe after pumping away the volatile fractions. Attempts to further purify this material by gas chromatography and fractional distillation under vacuum were unsuccessful due to a thermally induced reaction. The ^{1}H NMR spectrum contained only one quintet pattern indicating each proton was coupled to a separate SF_5- group and equivalent. The ^{19}F NMR spectrum contained only one AB_4 pattern indicative of equivalent SF_5 groups. Based on the NMR spectra, the purity of (III) was estimated to be better than 95%. The structure assignment was supported by the liquid phase infrared spectrum which contained an olefinic C-H stretch, (3105 cm^{-1}(m)), a C=C stretch, (1668 cm^{-1}(w)), S-F stretches (930 and 840 cm^{-1} (vs)) and an S-F deformation (600 cm^{-1} (s)). Other infrared absorptions at 1590 (w), 1320 (w), 1280 (w), 1068 (w), 1017 (m), 720 (m), 645 (m) and 578 cm^{-1} (m) were unassigned. The ^{1}H NMR spectrum contained a regular quintet (δ=6.85 ppm, J_{H-B}=7.5 Hz) and the ^{19} NMR spectrum[5] contained an AB_4 pattern (δ_A=-62.2; δ_B=-70.0 ppm; J_{A-B}=135.4 Hz). The mass spectral fragmentation pattern (reported for ^{79}Br) contained clusters for 1 or 2 bromines as indicated, and a parent-ion at m/e=462, together with the following fragments; m/e=443 ($S_2 F_9 C_4 H_2 Br_2^+$), 382 ($S_2 F_{10} C_4 H Br^+$), 335 ($SF_5 C_4 H_2 Br_2^+$), 226 ($SC_3 Br_2^+$), 208 ($C_4 H_2 Br_2^+$), 186 ($SF_2 C_3 H Br^+$), 166 (SFC_3Br^+), 158 (Br_2^+), 147 ($SC_3 Br^+$), 128 ($C_4 H Br^+$), 127 (SF_5^+), 89 (SF_3^+), 70 (SF_2^+).

Dehydrobromination of (III) by excess KOH proceeded readily at 25°C resulting in a yield of approximately 50% for the bis(pentafluorosulfur)diacetylene, $SF_5C≡C-C≡CSF_5$ (IV). Identification of the clear, liquid compound was corroborated by gas phase molecular weight measurements (found, 298; theory, 302) and spectroscopic data. The gas phase infrared spectrum has a medium absorption at 2180 cm^{-1} (ν(C≡C)) and very strong S-F bands at 920, 890, 620 and 600 cm^{-1}. The ^{19}F NMR spectrum[5] in Freon-11 contained only one AB_4 pattern (δ_A=-66.4 and δ_B=-77.0 ppm; J_{A-B}=169.2 H_z) which was consistent with equivalent SF_5 groups. The mass spectral fragmentation pattern contained a strong parent ion at m/e=302, together with major fragments at m/e=283 ($S_2 F_9 C_4^+$), 175 ($SF_5 C_4^+$), 137 ($SF_3C_4^+$), 127 (SF_5^+), 118 ($SF_2 C_4^+$), 89 (SF_3^+), 86 ($F_2C_4^+$), 80 (SC_4^+), 70 (SF_2^+), 67 (FC_4^+), 44 (SC^+) and 31 (CF^+). The experimentally determined vapor pressure equation, log $P_{(mm)}$ =7.80-(1860/T), yielded an extrapolated boiling point of 105°, ΔH_{vap}

of 8.51 kcal/mol, and ΔS_{vap} of 22.5 eu. The density of the liquid was measured as 1.72 g/cc at 25^{o} compared to 0.7364 g/cc (0^{o})[6] for diacetylene which again demonstrates the ability of SF_5 group substitution to greatly enhance the density of molecules.

Both $SF_5C{\equiv}C{-}C{\equiv}CH$ and $SF_5C{\equiv}C{-}C{\equiv}CSF_5$ are relatively stable liquids at 25^{o} with vapor pressures of approximately 220 and 36 mm respectively. However, on standing at 25^{o} under fluorescent lighting both compounds gradually change from clear, colorless liquids to clear, amber colored liquids. The IR spectra of the head-gases above the amber liquids were identical to the original products and, after vacuum transferring the compounds, the colorless appearances returned leaving trace amounts of non-volatile, amber residues in the original traps. Initial experiments indicate that bis(pentafluorosulfur)diacetylene forms low molecular weight polymers when heated. We are continuing to investigate the polymerization reactions and to characterize these polymers.

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5 Chemical shift values are given for the most intense lines of the A and B portions of the AB_4 spectra and J_{AB} values are estimated from the basic doublet pattern of the B portion.

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