Strained Molecules

Crystal Structure of a Dewar Benzene Derivative Formed from Fluoro(triisopropylsilyl)acetylene**

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Halogenoacetylenes are probably one of the most intriguing classes of acetylene compounds. Although some synthetic routes to 1-haloacetylenes have been reported, there are very few reports on the syntheses of 1-fluoroacetylenes.[1] In 1959, the first synthesis of 1-fluoroacetylene itself was accomplished by Middleton and Sharkey, who used pyrolysis of fluoromaleic anhydride.[2] Five years later Viehe and et al. reported the synthesis of *tert*-butylfluoroacetylene, which trimerized spontaneously to afford the highly strained benzene valance isomers below 0 °C.[3] However, to the best of our knowledge, no fluoroacetylene derivatives aimed specifically to be synthetically useful has been examined with one exception.[4] This omission stems from the instability of fluoroacetylene compounds and their explosive nature. In connection to our ongoing research in the development of monofluorinated building blocks,[5] we have considered the corresponding fluorosilylacetylene as a promising candidate for a fluoroethynylation reagent. As the addition of silylacetylenes to carbonyl compounds catalyzed by fluoride ions has already been reported,[6] the corresponding fluorosilylacetylene should generate the fluoroethynyl anion species by means of the fluoride source. In addition, we expected that the introduction of the bulky silyl substituents should enhance the stability of fluoroacetylene. On the basis of these ideas, we chose and prepared fluoro(triisopropylsilyl)acetylene (**1**; see Scheme 1) as the first example of a silylated fluoroacetylene. Although the preparation of **1** worked well, **1** did not function as a fluoroethynyl anion towards carbonyl compounds at this stage. However, to our delight, we discovered that spontaneous trimerization of **1** generally occurred to give the corresponding 1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)bicyclo[2,2,0]hexa-2,5-dien **3** (Dewar benzene) as a stable solid.[7] Herein, we report the preparation of **1** and the crystal structure of **3**.

One possible procedure for the synthesis of **1** would be the silylation of metal fluoroacetylide. As a THF/ether solution

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[**] We greatly thank F-Tech Co. Ltd., for a gift of 1,1-difluoroethylene and Chisso Co. Ltd., for a gift of chlorotriisopropylsilane. The Dewar benzene derivative is 1,2,4-Trifluoro-3,5,6-tris(triisopropylsilyl)bicyclo[2,2,0]hexa-2,5-dien

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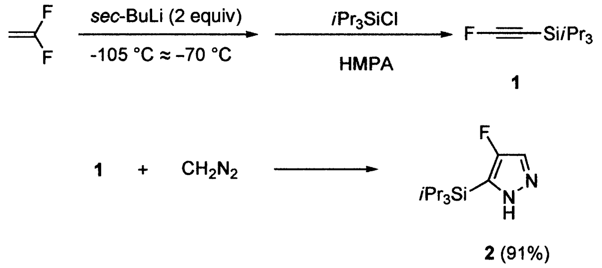
that contained fluoroacetylene was prepared from 1,1-difluoroethylene by using one equivalent of *sec*-BuLi, we anticipated that the use of two equivalents of *sec*-BuLi would cause deprotonation of fluoroacetylene generated to produce the corresponding lithium fluoroacetylide. According to a slightly modified procedure reported by Sauvêtre and Normant,[8] lithium fluoroacetylide was prepared by using two equivalents of *sec*-BuLi to 1,1-difluoroethylene at −70 °C. The successive addition of chlorotriisopropylsilane and hexamethyl phosphoramide (HMPA) to the resulting lithium fluoroacetylide solution afforded the desired product **1** in high yield (Scheme 1). The GC–MS spectrometric analysis of **1** gave a single peak that corresponded to the molecular formula of $C_{11}H_{21}FSi$. The ^{19}F NMR spectrum showed a signal from the terminal fluorine atom at −186.8 ppm. The chemical shift of a fluorine atom bonded to an sp carbon atom is roughly comparable to the signal obtained for fluorochloroacetylene (−219 ppm).[4] Although the purification of **1** was possible by silica-gel column chromatography with hexane as eluent, evaporation of the solvent afforded the pale yellow–green oil, which soon turned brown due to decomposition. This behavior suggested to us that **1** can be safely handled only as a hexane solution for a short time at room temperature in a similar way to that of *tert*-butylfluoroacetylene.[3] Consequently, we kept the solution of **1** in the refrigerator at −20 °C to avoid decomposition. Although its accurate yield was not obtained due to its unstable nature, we estimated the yield of **1** to be at least 91 % based on its transformation to the corresponding fluoropyrazole (**2**; Scheme 1).



Scheme 1. Synthesis of fluoro(triisopropylsilyl)acetylene (**1**).

On the other hand, when we checked the purity of **1** by GC–MS spectrometric analysis about four months after the initial synthesis, a new major peak appeared at *m/z* 472. We attempted to separate this compound from the mixture by using silica-gel column chromatography. The compound was successfully isolated as a white solid, which was readily soluble in hexane and melted from 84.5 °C to 85.5 °C. The ^{19}F NMR spectrum displayed three signals at $\delta = -80.62$ (s), -168.31 (d, $J = 10.9$ Hz), -174.60 ppm (d, $J = 10.9$ Hz), respectively. The ^{13}C NMR spectrum showed six downfield signals at $\delta = 100.8$–175.6 ppm. The final structural determination of the compound was achieved by X-ray crystallography. The X-ray diffraction data were collected at 93 K. An ORTEP drawing of compound **3** is shown in Figure 1. The structure of **3** was 1,2,4-trifluoro-3,5,6-tris(triisopropylsilyl)-bicyclo[2,2,0]hexa-2,5-dien (Dewar Benzene). Although the molecular structures of seven Dewar benzene derivatives have so far been determined by means of the X-ray diffraction,[9] this is the first example of a fluorinated Dewar benzene derivative to be confirmed by X-ray diffraction.[10] The following features of this fluorinated Dewar benzene derivative are noteworthy: 1) The central C3−C6 bond (1,535(4) Å) is the shortest known bond length of its type compared with the structures of other Dewar benzene derivatives. 2) The dihedral angles between the two cyclobutene rings (the folding angle) range from 123.3(2) to 123.0(2)°, thus, compound **3** has the widest dihedral angle for a Dewar benzene derivative. 3) Steric repulsive forces between neighboring triisopropylsilyl groups give rise to the lengthening of the corresponding carbon–carbon double bond (C1−C2) in the four-membered ring (1.380(4) Å) compared to the double bond on the opposite side of the molecule (C4−C5) average 1.341(4) Å). 4) Fluorine atoms occupy both bridgehead carbon atoms, which suggests that a possible precursor of **3** is 1,2-difluoro-3,4-bis(triisopropylsilyl)cyclobutadiene.[11]

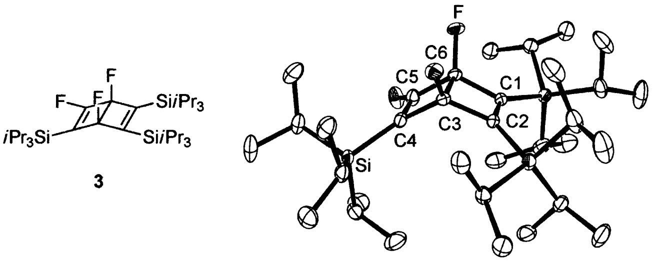


Figure 1. ORTEP drawing of the structure **3** with thermal ellipsoids shown at the 50 % probability level (hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: C1-C2 1.380(4), C2-C3 1.563(4), C3-C4 1.552(4), C4-C5 1.341(4), C5-C6 1.500(4), C1-C6 1.549(4), C3-C6 1.535(4), C1-Si2 1.902(3), C2-Si1 1.905(3), C4-Si3 1.894(3), C3-F1 1.386(3), C5 C1-F2 1.352(3), C6-F3 1.385(3), C1-C2-C3 93.0(2), C2-C1-C6 92.7(2), C3-C4-C5 88.0(2), C4-C5-C6 99.4(2), C2-C3-C4 123.0(2), C1-C6-C5 122.3(2).

In conclusion, we have demonstrated the first preparation of fluorosilylacetylene, **1**, from 1,1-difluoroethylene in one step. The spontaneous trimerization of **1** afforded not the fluorinated benzene derivative but the stable fluorinated Dewar benzene derivative **3**. Studies on the reactivity, property, and trimerization mechanism of **3** are in progress in our laboratories.

Experimental Section

General: Melting point: Yanako micro melting point apparatus MP-S3. NMR: JEOL AL-300 and Bruker DRX600. Chemical shifts were reported as δ values (ppm) relative to internal tetramethylsilane (^{1}H and ^{13}C) or benzotrifluoride (^{19}F) in $CDCl_3$ unless otherwise noted. GC–MS: JEOL JMS-AMII15 mass spectrometer. IR: Perkin Elmer SPECTRUM 2000 FT-IR. Elemental analysis: the Service Centre of the Elementary Analysis of Organic Compound affiliated with the Faculty of Science, Kyushu University. Analytical thin layer chromatography (TLC) and column chromatography were performed on silica gel 60 F_{254} (Merck) and silica gel 60 (40–63 mm), respectively. THF and ether were used after distillation from sodium benzophenone ketyl radical. HMPA was used after distillation from CaH_2.

A 100 mL two-neck flask equipped with a magnetic stir bar, a stopcock, and a three-way stopcock, was charged with 40 mL of THF under argon. *sec*-BuLi (15.0 mL, 14.4 mmol) was added dropwise by syringe at −78 °C to the stirred mixture. After this mixture had been stirred for an additional 10 min, the solution was cooled to −105 °C in a liquid N_2/ethanol bath. At this temperature, argon was replaced with 1,1-difluoroethylene (balloon). The mixture was gradually warmed to −70 °C. Chlorotriisopropylsilane (1.45 mL, 6.8 mmol) and HMPA (3 mL) were successively added to the solution by syringe. After the addition had been completed, the reaction mixture was allowed to warm to 0 °C. Hexane and aqueous sodium bicarbonate ($NaHCO_3$) was carefully added to the resulting solution. After the resultant mixture was extracted with ether, the combined ethereal solution was dried over sodium sulfate and filtered through a short silica-gel column (ether as an eluent). After the addition of 7.0 mg of phenothiazine to the solution, the solution was concentrated to half its original volume. The same concentration procedure was repeated three times after the addition of a half volume of *n*-hexane to the solution in each procedure. The solution was finally concentrated to about 3 mL, then the resulting solution was directly purified by chromatography on silica gel (hexane as an eluent) to give the desired product (**1**) as a hexane solution. Samples were routinely stored in a sample bottle at −20 °C, which showed no deterioration by GC–MS analysis over a 4 week period. After about 4 months, the solution was concentrated and the residue was purified by column chromatography on silica gel (hexane as an eluent) to give **3** as a white solid (599.5 mg, 44 %) (Not optimized for trimerization conditions).

3: $R_f = 0.82$; hexane; mp 84.5–85.5 °C; elemental analysis calcd (%) for $C_{33}H_{63}F_3Si_3$: C 65.94, H 10.56; found: C 65.82, H 10.52; $\delta_F =$ −80.62 (s), −168.31 (d; $J_{FF} = 10.9$ Hz), −174.60 ppm (d; $J_{FF} =$ 10.9 Hz); $\delta_C =$ 11.8 (s), 13.2 (s), 13.7 (s), 18.3 (s), 18.90 (s), 18.94 (s), 19.2 (s; overlapped), 19.5 (s), 100.8 (ddd; $J_{CF} = 270.7, 40.5, 21.7$ Hz), 105.2 (ddd; $J_{CF} = 263.6, 22.7, 20.5$ Hz), 129.9 (dt; $J_{CF} = 27.8, 4.0$ Hz), 168.8 (dd; $J_{CF} = 22.9, 2.8.$ Hz), 171.1 (ddd, $J_{CF} = 371.6, 24.5, 13.9$ Hz), 175.6 ppm (dd, $J_{CF} = 22.8, 12.2$ Hz); $\delta_H =$ 1.0–1.3 ppm (m); $\tilde{\nu} =$ 2951, 2869, 1598, 1470, 1324, 1200, 1153, 1065, 1017, 882, 692, 673 cm^{-1}.

Single crystals of **3** suitable for X-ray crystallographic analysis were grown by recrystallization from hexane. Crystal data for **3** ($C_{33}H_{63}F_3Si_3$) :$M_r = 601.10$, $T = 93(2)$ K, triclinic, space group $P\bar{1}$, $a =$ 8.8247(19), $b = 12.566(3)$, $c = 17.350(5)$ Å, $\alpha = 91.373(13)°$, $\beta =$ 99.892(10)°, $\gamma = 97.728(11)°$, $V = 1875.9$ Å3, $Z = 2$, $Dx =$ 1.064 $Mg\,m^{-3}$, $\mu = 0.160\ mm^{-1}$, $\lambda = 0.71075$ Å, $\theta_{max} = 27.41°$, 17897 measured reflection, 8437 independent reflections, 370 refined parameters, GOF = 1.111, $R[F^2 > 2\sigma[F^2]] = 0.0576$, $wR(F^2) = 0.2106$. The intensity data were collected on a Rigaku RAXIS-RAPID diffractometer. The structure was solved by direct methods (SIR92) and the non-hydrogen atoms were refined anisotropically by full-matrix least-squares procedures on F^2 for all reductions (SHELXL97). All hydrogen atoms were positioned geometrically and refined as riding. CCDC 230758 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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