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Preparation and Molecular Structure Determination of Dialkynyliodonium Salts: $(RC{\equiv}C)_2I^{+}\,{}^{-}OTf$

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There is considerable current interest in multicoordinate, polyvalent (hypervalent) main-group species.[1] Among the oldest, most interesting, most extensively investigated polyvalent main-group compounds are those of iodine.[2] Multicoordinated iodine compounds, with at least one organic ligand, have been known since the discovery of $PhICl_2$ by Willgerodt in 1886.[3] In the intervening 100 years, thousands of polycoordinated iodine compounds have been reported, the most common class being the diaryliodonium salts **1**. The latest members of this family, the

$$\underset{\mathbf{1}}{Ar_2I^+ \cdot X^-} \qquad \underset{\mathbf{2}}{RC{\equiv}CI^+Ph \cdot X^-} \qquad \underset{\mathbf{3}}{(RC{\equiv}C)_2I^+ \cdot X^-}$$

alkynyl(phenyl)iodonium species[4] **2**, have become valuable reagents for the ready preparation of diverse functionalized acetylenes[5] and other useful transformations.[6,7]

Conspicuously absent from the family of polycoordinated iodine compounds, with one or more organic ligands, are the dialkynyliodonium species **3**. In this communication we report the preparation and the molecular structure of the previously unknown dialkynyliodonium triflates **6**. Compounds **6** can be prepared in 46–83% yield in a single step by the reaction of the appropriate (trimethylsilyl)acetylenes **4** with iodosyl triflate (**5**)[8] in CH_2Cl_2.

$$2RC{\equiv}CSiMe_3 + O{=}IOTf \xrightarrow[-(Me_3Si)_2O]{CH_2Cl_2,\ -78^\circ\ \text{to RT}} (RC{\equiv}C)_2I^+ \cdot {}^-OTf$$

4 a R = *t*-Bu
b R = SiMe₃
c R = Si(*i*-Pr)₃

5

6 a R = *t*-Bu
b R = SiMe₃
c R = Si(*i*-Pr)₃

Table I. Selected Key Bond Distances for **6c**[a]

bond	distance, Å	bond	distance, Å
I–C2	2.02 (1)	C3–C4	1.17 (1)
I–C3	2.01 (1)	Si1–C1	1.86 (1)
C1–C2	1.16 (1)	Si2–C4	1.85 (1)

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

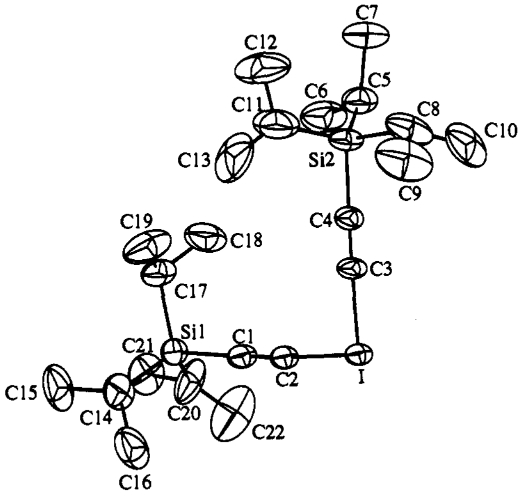

Figure 1. ORTEP representation of the cationic portion of dialkynyliodonium triflate **6c**.

Iodonium salts **6** are isolated from the reaction mixture by crystallization as white, microcrystalline solids, with their stability strongly dependent on the nature of the substituent R. Thus compound **6c**, bearing the bulky triisopropylsilyl groups at the acetylenic carbons, melts without decomposition at 138 °C, can be stored indefinitely at room temperature, and is stable toward oxygen, water, and even the action of nucleophilic reagents. Compounds **6a,b** are considerably less stable, react with water and other nucleophiles, and decompose over several days at room temperature. Moreover, dialkynyliodonium salts without bulky substituents at the β-acetylenic carbon, such as R = H, CH_3, C_2H_5, Ph, etc., are unstable even at temperatures below 0 °C, and our attempts at their preparation have so far failed.

Compounds **6a–c** are fully characterized by multinuclear NMR, IR, and high-resolution mass spectra.[9] Specifically, in the FAB mass spectrum the expected molecular peaks of the cationic parts of salts **6a–c** are observed. The ^{13}C NMR spectra for all compounds show signals typical for acetylenic carbons in iodonium salts,[4,6,7] as well as resonances of the triflate anion and the appropriate signals of the alkyl carbons. The IR spectra of compounds **6a–c** display signals characteristic for C≡C absorptions in alkynyliodonium salts between 2100 and 2200 cm^{-1}. However, in contrast to the monoalkynyliodonium salts **2**, the IR spectra of compounds **6a–c** show *two* different signals for the acetylenic absorption. This is likely a consequence of the pseudo-trigonal-bipyramidal geometry (vide infra) around the trivalent io-

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[9] For **6a**: yield 46% mp 100–102 °C dec; IR (CCl_4) 2976, 2187, 2152, 1261, 1173, 1036 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.3 (s); ^{13}C NMR ($CDCl_3$) δ 20 ($I^+C{\equiv}C$), 29 and 31 (t-C_4H_9), 117 ($I^+C{\equiv}C$), 120 (quart., J = 318 Hz, CF_3); ^{19}F NMR ($CDCl_3$) δ 78.0 (s, CF_3); mass spectrum (FAB) m/z (%) 289 (100) $[M - TfO^-]^+$; HRMS for $C_{12}H_{18}I$ $[M - TfO^-]^+$ calcd 289.045203, found 289.044664. For **6b**: yield 43%; mp 70 °C dec; IR (CCl_4) 2963, 2145, 2100, 1261, 1173, 1037 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.23 (s); ^{13}C NMR ($CDCl_3$) δ −1 ($SiMe_3$), 42 ($I^+C{\equiv}C$), 119 ($I^+C{\equiv}C$), 120 (quart., J = 319 Hz, CF_3); ^{19}F NMR ($CDCl_3$) δ 77.8 (s, CF_3); mass spectrum (FAB) m/z (%) 321 (100) $[M - TfO^-]^+$; HRMS for $C_{10}H_{18}ISi_2$ $[M - TfO^-]^+$ calcd 320.999061, found 320.998439. For **6c**: yield 83%; mp 137–139 °C; IR (CCl_4) 2945, 2867, 2140, 2097, 1463, 1259, 1173, 1024 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 1.07 (m); ^{13}C NMR (CD_2Cl_2) δ 11 (CH), 18 (CH_3), 44 ($I^+C{\equiv}C$), 117 ($I^+C{\equiv}C$), 120 (quart., J = 319 Hz, CF_3); ^{19}F NMR ($CDCl_3$) δ 77.8 (s, CF_3); mass spectrum (FAB) m/z (%) 489 (100) $[M - TfO^-]^+$; HRMS for $C_{20}H_{42}ISi_2$ $[M - TfO^-]^+$ calcd 489.186861, found 489.180480.

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Table II. Selected Key Bond Angles for **6c**[a]

bond	angle, deg	bond	angle, deg
C2–I–C3	92.6 (4)	Si1–C1–C2	177 (1)
I–C2–C1	177 (1)	Si2–C4–C3	177 (1)
I–C3–C4	177 (1)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digit.

donium atom,[2,4] with two different arrangements for the alkynyl groups in **6**: axial and equatorial. From the fact that in most alkynyl(phenyl)iodonium salts, where the acetylenic group is known[4] to be in the axial position, the IR stretching of the C≡C is generally above 2150 cm^{-1}, we assign the higher C≡C frequencies in **6** to the axial alkyne unit and the lower one to the equatorial one. Hence, on the IR time scale the axial and equatorial alkynyl groups are differentiated. However, the ^{13}C NMR as well as ^{1}H NMR spectra of iodonium salts **6a–c** in $CDCl_3$ in the temperature range from 25 to −80 °C display only single resonances for each of the different carbons and protons due to degenerate isomerization, presumably by rapid pseudorotation around the iodine atom.[10]

The structure of the disubstituted iodonium triflate **6c** was unambiguously established by a single-crystal X-ray analysis.[11] Selected bond distances and bond angles are summarized in Tables I and II, and the ORTEP representation is shown in Figure 1. The structural data reveal two normal C–C triple bonds with the usual bond lengths and angles, with C_{sp}–I distances of 2.02 Å, typical for iodonium salts,[2,4] and a C–I–C angle close to 90°, as expected for iodonium salts with a pseudo-trigonal-bipyramidal geometry and consistent with the 10-I-3 nature in the Martin–Arduengo formalism.[12] The distance between the iodine atom and the nearest oxygen of the triflate anion is 2.7 Å, which supports the ionic nature of compound **6c**; the C2–I–O and C3–I–O angles are approximately 90° and 180°, respectively. Furthermore, the ORTEP diagram (Figure 1) clearly illustrates how the bulky triisopropylsilyl groups shield the triple bond thereby making it less susceptible to attack by external reagents and thus stabilizing the molecule. This principle for the stabilization of very reactive acetylenes with bulky substituents may be applied in the future to the synthesis of such unusual, hitherto unknown compounds as acetylenic derivatives of heavy noble gases, alkynyl triflate esters, diazonium salts, and other acetylenic derivatives with highly reactive leaving groups.

In conclusion, we have reported the first synthesis of novel dialkynyliodonium triflates **6**. Only those compounds with bulky substituents on the β-position of the acetylene are stable at room temperature. A single-crystal X-ray structure confirms the pseudo-trigonal-bipyramidal, or T-shaped, geometry of these species with *two* different alkynyl ligands, one axial and one equatorial, around the central iodine in the solid state. Likewise, two different C≡C absorptions are observed in the IR spectrum due to the different axial and equatorial alkynyl groups. However, the NMR spectra (both ^{1}H and ^{13}C) indicate rapid interconversion of the axial and equatorial alkynyl ligands even at −80 °C.

Acknowledgment. This work was supported by the NCI of NIH (2ROCA16903).

Supplementary Material Available: Tables of X-ray crystal and structural data for compound **6c** (9 pages); tables of observed and calculated structure factors for **6c** (12 pages). Ordering information is given on any current masthead page.

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Clear Evidence for the Formation of α-Disulfoxides and Other Intermediates in the *m*-CPBA Oxidation of Bridged Bicyclic Thiosulfinates

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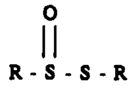
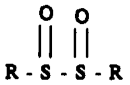
The oxidation of organic disulfides has provided an extremely rich chemistry dating as far back as 1846.[1] Thiosulfinates **1**, the initial oxidized product, are well-known.[2–4] The next step is the most controversial.[5,6] α-Disulfoxides **2** would be expected by HSAB theory;[7] however to date, only thiosulfonates **3** have been isolated.[8–11]



$R-\overset{O}{\overset{\|}{S}}-S-R$

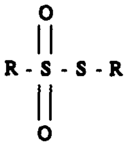
(1)



$R-\overset{O}{\overset{\|}{S}}-\overset{O}{\overset{\|}{S}}-R$

(2)

(1a) R = CH_2-CH=CH_2



$R-\underset{\underset{O}{\|}}{\overset{O}{\overset{\|}{S}}}-S-R$

(3)

$R-\overset{O}{\overset{\|}{S}}-O-S-R$

(4)

Freeman reported the first direct evidence for the existence of α-disulfoxides in a complex mix during the low-temperature (−20 °C) *m*-CPBA oxidation of symmetrical dialkyl thiosulfinates.[12] Freeman's results suggested that the α-disulfoxide **2** was formed and then rearranged to the thiosulfonate, possibly through an *O,S*-sulfenyl sulfinate intermediate **4**. Other experiments reported by Oae[13] and Kice[14] and ourselves[15] have provided further, indirect

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