Heteroatom Chemistry
Volume 22, Number 3/4, 2011

Synthesis and Structure of Aliphatic Phenylchloronium Ylide

Masahito Ochiai,[1] Norihiro Tada,[1] Kazunori Miyamoto,[1]
and Motoo Shiro[2]

[1]*Graduate School of Pharmaceutical Sciences, University of Tokushima, 1-78 Shomachi, Tokushima 770-8505, Japan*

[2]*Rigaku Corporation, 3-9-12 Matsubara, Akishima, Tokyo 196-8666, Japan*

Received 30 July 2010

ABSTRACT: *Aliphatic phenylchloronium ylide with bis(trifluoromethylsulfonyl)-methylidene group was synthesized. Thermal transylidation of 4-(trifluoromethyl)phenylbromonium bis(trifluoromethylsulfonyl)methylide in chlorobenzene as a solvent at 130°C afforded phenylchloronium bis(trifluoromethylsulfonyl)methylide in a moderate yield. Phenylbromonium and phenyliodonium ylides were also prepared by the thermal transylidation to bromo- and iodobenzenes. The reaction probably involves initial thermal generation of bissulfonylcarbene (Tf_2C:), followed by nucleophilic attack of a halobenzene toward the electron-deficient carbene center. Solid-state structures of these aliphatic phenylhalonium ylides were analyzed and compared with each other.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:325–330, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20683

INTRODUCTION

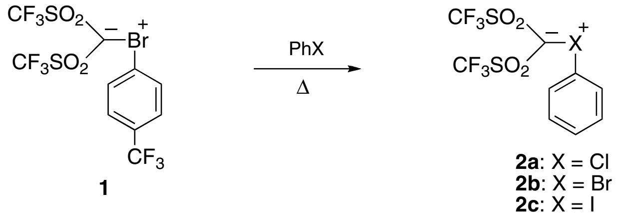
Aryliodonium ylides are readily accessible and have found many applications in modern organic synthesis [1,2]. They serve as excellent progenitors for generation of singlet carbenes [3] and metal-carbenoids [1], because of the very high, hyperleaving group ability of aryl-λ^3-iodanyl groups [4]. They are potential substitutes for explosive and toxic diazo compounds [1]. Very recently, synthesis of stable aliphatic arylbromonium ylides was reported and their structures were elucidated by X-ray crystal analysis [5]. Arylbromonium ylides function as more effective progenitors for generation of carbenes and metal-carbenoids than aryliodonium ylides, owing to the vastly enhanced hyperleaving group ability of aryl-λ^3-bromanyl groups [5b]. On the other hand, little is known concerning the chemistry of chloronium ylides.

In 1954, a transient formation of a highly labile chloronium ylide was suggested in the thermal decomposition of ethyl diazoacetate in benzal chloride [6a]. Bis(methoxycarbonyl)carbene generated from the photolysis of dimethyl diazomalonate in allyl chlorides affords allylic carbon-chlorine insertion products via a 2,3-sigmatropic rearrangement of initially formed chloronium ylides [6c]. Stable aromatic chloronium ylides, in which the ylide carbanions were stabilized through aromatization in heterocyclic rings have been prepared by the thermolysis of diazodicyanoimidazole in chlorobenzene [7]. We have synthesized aliphatic phenylchloronium ylide **2a** from 4-(trifluoromethyl)phenylbromonium bis(trifluoromethylsulfonyl)methylide (**1**) through the thermal alkylidene transfer reaction to chlorobenzene, albeit in a low yield (Scheme 1) [5b].

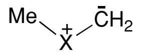
Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

Correspondence to: Masahito Ochiai; e-mail: mochiai@ph.tokushima-u.ac.jp.

Contract grant sponsor: Grant-in-Aid for Scientific Research (B) (JSPS).



SCHEME 1



	C–X–C angle in degrees
3a: X = F	122.9
3b: X = Cl	122.2
3c: X = Br	122.4
3d: X = I	122.3

SCHEME 2

Experimentally determined solid-state structures of chloronium ylides are not available. Jubert and co-workers have reported the theoretical calculations on the structures of four kinds of parent methylhalonium ylides **3** and on the nature of halogen-ylidic carbon bonds (Scheme 2) [8]. Very interestingly, their calculations showed that the values of the C—X—C bond angle of halonium ylides **3a–d** are nearly constant between 122° and 123° [8a]. This is in marked contrast with the calculated C—X—C angles in dimethylhalonium cations, which decrease in the order Me_2F^+ (122.4°) > Me_2Cl^+ (104.9°) > Me_2Br^+ (101.3°) > Me_2I^+ (98.1°). In fact, X-ray analysis revealed that the C—X—C angle (97.3°) of diphenyl-λ^3-bromane (Ph_2BrBr) is greater than that (92.7°) of Ph_2IBr [9], and the F—X—F angle (95.9°) of F_2Cl^+ SbF_6^- is larger than that (93.5°) of F_2Br^+ SbF_6^-[10].

We report, herein, synthesis and solid state structure analysis of phenylchloronium ylide **2a**. Furthermore, phenylbromonium **2b** and phenyliodonium ylides **2c** were synthesized and their X-ray structures were determined to compare each other especially on the emphasis in differences in the C—X—C bond angles of **2** [11]. Synthesis and solid state structure of phenyliodonium ylide **2c** have been reported (see [11]).

RESULTS AND DISCUSSION

Synthesis of Phenylhalonium Ylides

Heating a 0.01 M suspension of substituted bromonium ylide **1** [5a] prepared from *p*-trifluoromethylphenyl(difluoro)-λ^3-bromane [12] by the ligand exchange with bis(trifluoromethylsulfonyl) methane in chlorobenzene at 130°C for 1 h afforded phenylchloronium ylide **2a** in 24% yield, after purification by preparative TLC (Scheme 1). In a similar manner, phenylbromonium **2b** (130°C, 4 h) and phenyliodonium ylides **2c** (160°C, 1 h) were prepared in 48% and 87% yields, respectively.

The finding that the rates of decomposition of bromonium ylide **1** are independent of the concentrations of iodobenzene is not compatible with a carbenoid mechanism for the transylidation, which involves a rate-limiting nucleophilic attack of iodobenzene on the negatively charged ylidic carbon atom of **1** [5b]. Thus, the transylidation reaction probably involves initial thermal generation of free bissulfonylcarbene (Tf_2C:) from arylbromonium ylide **1** via facile reductive elimination of *p*-(trifluoromethyl)bromobenzene because of the hyperleaving group ability of aryl-λ^3-bromanyl groups [5b]. The subsequent nucleophilic attack of a halobenzene toward the electron-deficient carbene center will produce a halonium ylide **2**.

Structure of Phenylhalonium Ylides

Single crystals of phenylchloronium ylide **2a** suitable for X-ray crystallographic analysis were obtained by recrystallization from dichloromethane-hexane. Figure 1a illustrates an ylide structure of **2a**, in which two independent but closely related molecules constitute a nearly centrosymmetric dimer structure. Table 1 shows selected interatomic distances (Å), angles (°), torsion angles (°), and root mean square (rms) deviation (Å) from the least-squares planes. The four atoms C1, Cl1, S1, and S2 are coplanar with rms deviation of 0.0143(11) Å from their least-squares plane and with the sums of the C1-centered bond angles $\Sigma°C1 = 359.91°$, indicating a planar sp^2 hybridization of the ylide carbanion C1. These results hold for the ylide carbanion C10 with $\Sigma°C10 = 359.63°$. In addition, both CF_3—S bonds occupy the positions nearly perpendicular to this plane with anti relationship to each other (see torsion angles shown in Table 1). These structural features are closely related to those of the reported α-chloro- and α-bromobis(phenylsulfonyl)methide anions, in which similar anti-planar structure **4** has been calculated to be more stable by 1.8 (X = Cl) and 1.4 (X = Br) kcal mol^{-1} than anti-pyramidal structure **5** (Scheme 3) [13].

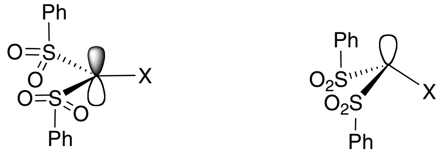
The ylidic Cl1—C1 and Cl2—C10 bond distances of 1.716 and 1.725 Å are considerably shorter than those of Cl1—C2 and Cl2—C11 bonds (1.794 and 1.785 Å) but comparable to the reported $C_{sp}2$—Cl(I) single bond length (a mean value of bond lengths determined by X-ray: 1.734 Å) [14]. These

TABLE 1 Selected Interatomic Distances (Å), Angles (°), Torsion Angles (°), and rms Deviations (Å) from Least-Squares Planes of Halonium Ylides **2**

	2a		***2b***		2*c*	
C1–X1, C10–X2	1.716(2)	1.725(2)	1.8647(18)	1.8666(18)	2.0382(19)	2.0272(17)
C2–X1, C11–X2	1.794(2)	1.785(2)	1.9453(18)	1.9487(19)	2.1013(18)	2.1283(19)
C1–S1, C10–S3	1.697(2)	1.704(2)	1.7005(19)	1.6994(18)	1.6881(19)	1.6847(19)
C1–S2, C10–S4	1.701(2)	1.694(2)	1.697(2)	1.699(2)	1.6933(19)	1.7011(19)
S1–C8, S3–C17	1.856(2)	1.834(3)	1.842(2)	1.846(2)	1.840(2)	1.840(2)
S2–C9, S4–C18	1.853(2)	1.851(2)	1.839(2)	1.837(2)	1.837(2)	1.835(2)
C1–X1–C2, C10–X2–C11	107.44(10)	107.98(10)	104.92(7)	104.29(8)	101.15(7)	100.73(7)
X1–C1–S1, X2–C10–S3	118.12(13)	117.07(13)	117.76(10)	117.96(10)	119.44(10)	117.68(9)
X1–C1–S2, X2–C10–S4	116.82(12)	117.00(12)	117.08(10)	116.82(9)	118.26(10)	117.93(9)
S1–C1–S2, S3–C10–S4	124.97(12)	125.56(13)	124.60(10)	124.89(11)	122.30(11)	124.09(10)
C8–S1–C1–X1, C17–S3–C10–X2	−99.41(14)	100.74(15)	−100.40(12)	100.21(12)	−94.21(11)	−96.06(11)
C9–S2–C1–X1, C18–S4–C10–X2	−88.13(13)	88.23(14)	−85.02(11)	84.66(11)	−87.40(12)	−80.61(12)
C8–S1–C1–S2, C17–S3–C10–S4	84.15(16)	−86.45(17)	88.45(14)	−86.59(14)	86.27(13)	90.33(13)
C9–S2–C1–S1, C18–S4–C10–S3	88.35(16)	−84.58(16)	86.19(13)	−88.61(14)	92.12(13)	92.99(13)
rms[a], rms[b]	0.0143(11)	0.0290(11)	0.0372(9)	0.0285(9)	0.0021(9)	0.0276(9)

[a] Rms deviation (Å) for C1, X1, S1, and S2 from their least-squares plane.

[b] Rms deviation (Å) for C10, X2, S3, and S4 from their least-squares plane.



4 X = Cl, Br **5**

SCHEME 3

results suggest little double-bond character for the ylidic carbon chlorine bond as well as a negligibly small electrostatic attraction between the oppositely charged Cl and ylidic C, probably because of a high electronegativity of chlorine [15]. It has been shown that the C—X bond of ylides R_nX^+-$C^-R'R''$ is longer than a single bond, when X is a highly electronegative atom (N, O) (see [15]). The Cl1—C2 and Cl2—C11 distances are comparable to those of Ph_2ClBPh_4 and Ph_2ClBF_4·18-crown-6 complex [16]. The C1—Cl1—C2 and C10—Cl2—C11 bond angles are 107.44° and 107.98°, respectively.

The lone pair orbital at the ylidic carbon atom of **2a** bisects the O—S—O angle and therefore is nearly parallel to the S—CF_3 bonds, which probably indicates that negative hyperconjugation $n_C - \sigma^*_{S-CF3}$ is important in determining the conformation of **2a**. Both short C_{ylidic}—S bond lengths with an average value of 1.699 Å, and large S-CF_3 distances (1.849 Å) are in a good agreement with these considerations. These results are reminiscent of the preferred planar, staggered conformation of α-sulfonyl carbanion derived from trifluoromethyl methyl sulfone, in which negative hyperconjugation $n_C - \sigma^*_{S-CF3}$ plays a critical role in determining the preferred conformation [17]. In addition to these interactions, Cl1—C2 and Cl2—C11 bonds well overlap with the lone pair orbital, which probably reflects the participation of another negative hyperconjugation $n_C - \sigma^*_{Cl-Ph}$. This kind of negative hyperconjugation $n_N - \sigma^*_{Br-Ar}$ was suggested in the solid-state structure of triflylimino-λ^3-bromane (p-$CF_3C_6H_4Br$ = NTf) [18]. These stabilizing interactions as well as the highly electron-withdrawing power of triflyl groups with a large Hammett substituent constant of 0.96 (σ_p) will be responsible for the thermally stable nature of phenylchloronium ylide **2a** [19].

In addition to the intramolecular short Cl1···O2, Cl1···O4, Cl2···O6, and Cl2···O8 contacts [2.9968(15), 3.0158(16), 2.9946(15), and 3.0031(16) Å] secondary bondings to one of the sulfonyl oxygen atoms of an adjacent molecule were found with Cl1···O8 and Cl2···O4 distances of 3.2132(15) and 3.2072(15) Å, which constitutes a centrosymmetric dimer structure.

Closely related stereostructures of phenylbromonium **2b** and phenyliodonium ylides **2c** were evaluated by X-ray analyses and are depicted in Figs. 1b and 1c, respectively. Structural data are shown in Table 1, which indicate a planar sp^2 hybridization of the ylide carbanion C1 in both halonium ylides. The Br1—C1 and Br2—C10 distances of phenylbromonium ylide **2b** are comparable to those of the reported vinylic Csp^2—Br(III) single bond (1.886 and 1.911 Å) of vinyl-λ^3-bromanes [20]. On the other

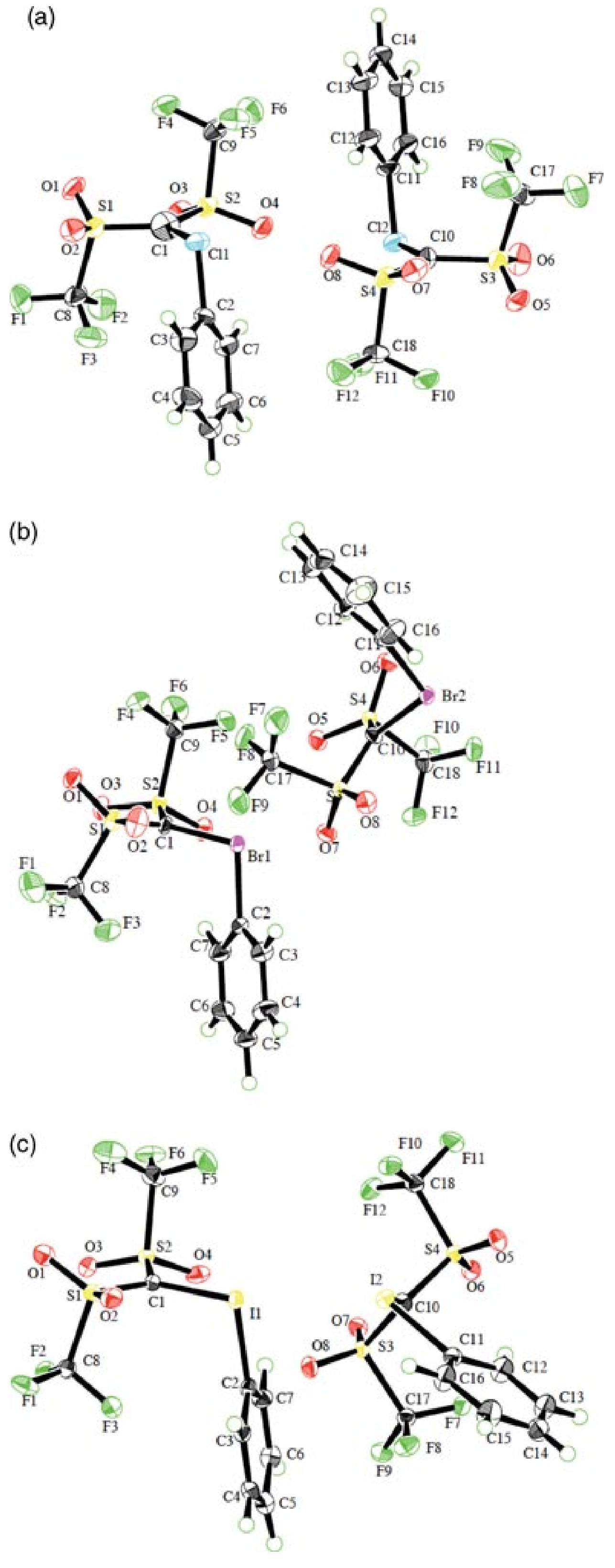


FIGURE 1 ORTEP structures of halonium ylides (thermal ellipsoids drawn at the 50% probability level): (a) chloronium ylide **2a**, (b) bromonium ylide **2b**, and (c) iodonium ylide **2c**.

hand, the I1—C1 and I2—C10 lengths of ylide **2c** are shorter than those of the vinylic Csp^2—I(III) bond (2.12 and 2.14 Å) of vinyl-λ^3-iodanes [21]. Again, the negative hyperconjugations $n_C - \sigma^*_{S-CF3}$, $n_C - \sigma^*_{Br-Ph}$, and $n_C - \sigma^*_{I-Ph}$ seem to be responsible for the preferred conformation in these halonium ylides **2b** and **2c**.

In contrast to the theoretical result that the values of the C—X—C bond angle of halonium ylides **3b–d** are independent of a halogen atom (X) and nearly constant [8a], the corresponding average values determined by X-ray analysis of halonium ylides **2** decrease monotonically in the order 107.71° for **2a** > 104.61° for **2b** > 100.94° for **2c**. This is probably due to the increasing nonbonded repulsions between the two organic substituents [bis(trifluoromethylsulfonyl)methylidene and phenyl groups] on λ^3-halogans in **2** on going from I to Br to Cl, the atomic size being decreased in this order. Similar order of decrease in the C—X—C bond angle of diphenyl(tetrafluoroborato)-λ^3-halogan·18-crown-6 complexes was observed in the solid-state structures: 99.03(5)° for λ^3-chlorane > 95.6(2)° for λ^3-bromane > 91.6(1)° for λ^3-iodane [16,22].

In conclusion, three kinds of aliphatic phenylhalonium ylides **2** were synthesized from 4-(trifluoromethyl)phenylbromonium ylide **1** by thermal transylidation to halobenzenes at 130–160°C. Solid-state structures of these phenylhalonium ylides **2** were determined and compared with each other.

EXPERIMENTAL

Materials and Methods

4-(Trifluoromethyl)phenylbromonium bis[(trifluoromethyl)sulfonyl]methylide (**1**) was synthesized by the reaction of bis(trifluoromethylsulfonyl)methane with difluoro[4-(trifluoromethyl)phenyl]-λ^3-bromane [12] in acetonitrile [5a].

IR spectra were recorded on Perkin Elmer 1720 FT-IR spectrometers. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-AL300 or JNM-AL400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on either a JEOL JMX-SX 102A Waters LCT Premier, or Shimadzu model GCMS-QP 505 spectrometer. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Melting points were determined with a Yanaco micromelting points apparatus and are uncorrected.

*Synthesis of Phenylchloronium Bis(trifluoromethylsulfonyl)methylide (**2a**)*

A suspension of 4-(trifluoromethyl)phenylbromonium methylide **1** (23 mg, 0.045 mmol) in chlorobenzene (4.5 mL) was heated rapidly (within a few minutes) to 130°C under Ar and the resulting clear colorless solution was stirred for 1 h at the temperature. After cooling, the mixture was concentrated in vacuo to remove excess chlorobenzene. Purification by preparative TLC (hexane-dichloromethane, 5:5) gave phenylchloronium bis(trifluoromethylsulfonyl)methylide **(2a)** (4.1 mg, 24%) as a colorless solid: colorless leaflets (recrystallized from dichloromethane-hexane): mp 73.5–74.5°C; IR (ν, cm^{-1}): 2962, 1593, 1387, 1261, 1205, 1093, 1020, 864, 800, 602, 505; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, $J = 7.7$ Hz, 2H), 7.79 (t, $J = 6.6$ Hz, 1H), 7.71 (dd, $J = 7.7, 6.6$ Hz, 2H); ^{1}H NMR (400 MHz, acetone-d_6): δ 8.13 (d, $J = 7.8$ Hz, 2H), 7.96–7.83 (m, 3H);^{13}C NMR (75 MHz, acetone-d_6): δ 144.5, 135.2, 133.6, 127.9, 120.7 (q, $^1J_{CF} = 324.3$ Hz), 77.7 (sept, $^3J_{CF} = 4.7$ Hz); HRMS (ESI, positive): Calcd for $C_9H_5ClF_6NaO_4S_2$ $[(M + Na)^+]$ 412.9120; found: 412.9115; Anal Calcd for $C_9H_5ClF_6O_4S_2$: C, 27.67; H, 1.29; found: C, 27.51; H, 1.48.

*Synthesis of Phenylbromonium Bis(trifluoromethylsulfonyl)methylide (**2b**)*

A suspension of 4-(trifluoromethyl)phenylbromonium methylide **1** (24 mg, 0.048 mmol) in bromobenzene (0.48 mL) was heated rapidly (within a few minutes) to 130°C in the air and the resulting clear colorless solution was stirred for 4 h at the temperature. After cooling, the mixture was concentrated *in vacuo* to remove excess bromobenzene. Purification by preparative TLC (hexane-ethyl acetate, 6:4) gave phenylbromonium bis(trifluoromethylsulfonyl)methylide **(2b)** (10 mg, 48%) as a colorless solid: colorless prisms (recrystallized from acetone-ethyl acetate-hexane): mp 117–118°C; IR (ν, cm^{-1}): 3097, 1560, 1469, 1452, 1379, 1201, 1126, 989, 901, 741, 671, 640, 598, 567, 505; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, $J = 8.4$ Hz, 2H), 7.78 (t, $J = 7.4$ Hz, 1H), 7.66 (dd, $J = 8.4, 7.4$ Hz, 2H); ^{13}C NMR (75 MHz, acetone-d_6): δ 139.0, 134.4, 133.2, 130.2, 120.8 (q, $^1J_{CF} = 324.7$ Hz), 72.2 (sept, $^3J_{CF} = 4.2$ Hz); HRMS (ESI, positive): Calcd for $C_9H_5BrF_6NaO_4S_2$ $[(M + Na)^+]$ 456.8615; found 456.8574; Anal. Calcd for $C_9H_5BrF_6O_4S_2$: C, 24.84; H, 1.16; found: C, 24.74; H, 1.37.

*Synthesis of Phenyliodonium Bis(trifluoromethylsulfonyl)methylide (**2c**)*

A suspension of 4-(trifluoromethyl)phenylbromonium methylide **1** (27 mg, 0.054 mmol) in iodobenzene (0.54 mL) was heated rapidly (within a few minutes) to 160°C under argon, and the resulting clear colorless solution was stirred for 1 h at the temperature. After cooling, the reaction mixture was purified by silica gel column chromatography using hexane and ethyl acetate to give phenyliodonium bis(trifluoromethylsulfonyl)methylide (**2c**) [11]. (22.3 mg, 87%) as a colorless solid: colorless prisms (recrystallized from dichloromethane-hexane): mp 151.5–152.5°C; IR (ν, cm^{-1}): 3076, 1583, 1562, 1469, 1444, 1367, 1200, 1120, 985, 741, 640, 598; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, $J =$ 7.9 Hz, 2H), 7.78 (t, $J = 7.5$ Hz, 1H), 7.58 (dd, $J = 7.9, 7.5$ Hz, 2H); HRMS (ESI, positive): Calcd for $C_9H_5F_6INaO_4S_2$ $[(M + Na)^+]$ 504.8476; found 504.8477.

Crystal Structure Determination

Single crystal X-ray data for **2** were collected at −173°C (**2a**), −180°C (**2b**), and −160°C (**2c**) on a Rigaku Raxis Rapid imaging plate area detector with graphite monochromated Cu Kα or Mo Kα radiation. The structure was solved by direct methods using SHELX97 [23] or SIR97 [24] and expanded using Fourier techniques [25]. Refinement on $F2$ was carried out by a full-matrix least-squares technique. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model.

Supplementary Material

The CCDC-779233, CCDC-779234, and CCDC-779235 for **2a**, **2b**, and **2c** contain the supplementary crystallographic data for this paper. The data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk.

ACKNOWLEDGMENT

We thank Central Glass Co. Ltd., Japan for a generous gift of BrF_3.

REFERENCES

[1] Reviews: (a) Muller, P. Acc Chem Res 2004, 37, 243–251; (b) Zhdankin, V. V.; Stang, P. J. Chem Rev 2002, 102, 2523–2584; (c) Varvoglis, A. The Organic Chemistry of Polycoordinated Iodine; VCH: New York, 1992; (d) Koser, G. F. In The Chemistry of Functional Groups, Supplement D; Patai S.; Rappoport. Z.; (Eds.); Wiley: New York, 1983; Ch. 18.

[2] (a) Moreau, B.; Charette, A. B. J Am Chem Soc 2005, 127, 18014–18015; (b) Ochiai, M.; Kitagawa, Y.; Yamamoto, S. J Am Chem Soc 1997, 119, 11598–11604; (c) Moriarty, R. M.; Prakash, O.; Vaid, R. K.; Zhao, L. J Am Chem Soc 1989, 111, 6443–6444; (d) Hadjiarapoglou, L.; Spyroudis, S.; Varvoglis, A. J Am Chem Soc 1985, 107, 7178–7179; (e) Moriarty, R. M.; Bailey, B. R.; Prakash, O.; Prakash, I. J Am Chem Soc 1985, 107, 1375–1378; (f) Gudrinietse, E.; Neiland, O.; Vanag, G. J Gen Chem USSR 1957, 27, 2777–2780.

[3] Camacho, M. B.; Clark, A. E.; Liebrecht, T. A.; DeLuca, J. P. J Am Chem Soc 2000, 122, 5210–5211.

[4] (a) Ochiai, M. In Topics in Current Chemistry; Wirth, T. (Eds.); Springer: Berlin, 2003; Vol. 224, pp. 5–68; (b) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. J Am Chem Soc 1995, 117, 3360–3367.

[5] (a) Ochiai, M.; Tada, N.; Murai, K.; Goto, S.; Shiro, M. J Am Chem Soc 2006, 128, 9608–9609; (b) Ochiai, M.; Tada, N.; Okada, T.; Sota, A.; Miyamoto, K. J Am Chem Soc 2008, 130, 2118–2119.

[6] (a) Gutsche, C. D.; Hillman, M. J Am Chem Soc 1954, 76, 2236–2240; (b) Pirrung, M. C.; Zhang, J.; Lackey, K.; Sternbach, D. D.; Brown, F. J Org Chem 1995, 60, 2112–2124; (c) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Nakaido, S.; Migita, T. J Am Chem Soc 1972, 94, 3870–3876; (d) Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. J Org Chem 1981, 46, 5094–5102; (e) Dias, H. V. R.; Browning, R. G.; Polach, S. A.; Diyabalanage, H. V. K.; Lovely, C. J. J Am Chem Soc 2003, 125, 9270–9271.

[7] (a) Sheppard, W. A.; Webster, O. W. J Am Chem Soc 1973, 95, 2695–2697; (b) Janulis, E. P.; Arduengo, A. J. J Am Chem Soc 1983, 105, 3563–3567.

[8] (a) Jubert, A.; Okulik, N.; Michelini, M. C.; Mota, C. J. A. J Phys Chem A 2008, 112, 11468–11480; (b) Noronha, L. A.; Judson, T. J. L.; Dias, J. F.; Santos, L. S.; Eberlin, M. N.; Mota, C. J. A. J Org Chem 2006, 71, 2625–2629; (c) Olah, G. A.; Rasul, G.; Hachoumy, M.; Burrichter, A.; Prakash, G. K. S. J Am Chem Soc 2000, 122, 2737–2741.

[9] Khotsyanova, T. G.; Babushkina, T. A.; Saatsazov, V. V. Izv Akad Nauk SSSR Ser Fiz 1975, 39, 68–71.

[10] (a) Edwards, A. J.; Jones, G. R. J Chem Soc A 1969, 1467–1470; (b) Edwards, A. J.; Sills, R. J. C. J Chem Soc A 1970, 2697–2699.

[11] Zhu, S.-Z. Heteroatom Chem 1994, 5, 9–18.

[12] (a) Frohn, H. J.; Giesen, M. J Fluorine Chem 1998, 89, 59–63; (b) Ochiai, M.; Nishi, Y.; Goto, S.; Shiro, M.; Frohn, H.-J. J Am Chem Soc 2003, 125, 15304–15305.

[13] Prakash, G. K. S.; Wang, F.; Mathew, T.; Rasul, G.; Haiges, R.; Stewart, T.; Olah, G. A. Angew Chem, Int Ed 2009, 48, 5358–5362.

[14] Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. J Chem Soc, Perkin Trans 2 1987, S1–S19.

[15] Kirmse, W. Eur J Org Chem 2005, 237–260.

[16] Ochiai, M.; Suefuji T. Unpublished results, 2005.

[17] Raabe, G.; Gais, H.-J.; Fleischhauer, J. J Am Chem Soc 1996, 118, 4622–4630.

[18] Ochiai, M.; Kaneaki, T.; Tada, N.; Miyamoto, K.; Chuman, H.; Shiro, M.; Hayashi, S.; Nakanishi, W. J Am Chem Soc 2007, 129, 12938–12939.

[19] Hansch, C.; Leo, A.; Taft, R. W. Chem Rev 1991, 91, 165–195.

[20] (a) Ochiai, M.; Nishi, Y.; Mori, T.; Tada, N.; Suefuji, T.; Frohn, H. J. J Am Chem Soc 2005, 127, 10460–10461; (b) Miyamoto, K.; Shiro, M.; Ochiai, M. Angew Chem, Int Ed 2009, 48, 8931–8934.

[21] (a) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. Tetrahedron 1988, 44, 4095–4112; (b) Ochiai, M.; Kunishima, M.; Fuji, K.; Shiro, M.; Nagao, Y. J Chem Soc, Chem Commun 1988, 1076–1077.

[22] Ochiai, M.; Suefuji, T.; Miyamoto, K.; Tada, N.; Goto, S.; Shiro, M.; Sakamoto, S.; Yamaguchi, K. J Am Chem Soc 2003, 125, 769–773.

[23] Sheldrick, G. M. SHELX97, 1997.

[24] Altomare, A.; Burla, M.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A.; Polidori, G.; Spagna, R. J Appl Cryst 1999, 32, 115–119.

[25] Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system; Technical Report of the Crystallography Laboratory, University of Nijmegen, Nijmegen, The Netherlands, 1999.