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Synthesis and Characterization of Bromonium Ylides and Their Unusual Ligand Transfer Reactions with N-Heterocycles

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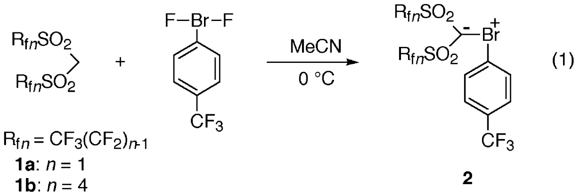
Iodonium ylides, in which the ylide carbanions are stabilized by two electron-withdrawing substituents, such as carbonyl or sulfonyl groups, are readily accessible and have found many applications in modern organic synthesis.[1,2] In contrast to sulfonium and phosphonium ylides, they serve as excellent progenitors for generation of singlet carbenes (or carbenoids)[3] because of the very high leaving group ability of aryl-λ^3-iodanyl groups[4] and are potential substitutes for explosive and toxic diazo compounds in metal−carbenoid reactions.[5] On the other hand, little is known concerning the chemistry of the related group 17 bromonium ylides because a method for their syntheses is not available.

In 1968, a transient formation of a highly labile bromonium ylide was suggested by Koser in the reaction of a singlet carbene, generated from 3,5-di-*tert*-butylbenzene 1,4-diazooxide by photolysis, with 2,6-diisopropyl-4-bromophenol.[6] Stable aromatic pseudo bromonium ylides, in which the ylide carbanions were stabilized through delocalization to aromatic rings, have been prepared by the thermolysis of diazodicyanoimidazole in bromobenzenes;[7] however, no stable and well-established aliphatic bromonium ylides are known. We report herein, for the first time, the synthesis, isolation, and characterization of stable aliphatic bromonium ylides **2** whose structures were firmly established by X-ray crystal analyses. Interestingly, the bromonium ylides **2** selectively undergo transfer of the aryl group to nitrogen heterocycles, such as pyridines, yielding *N*-arylpyridinium salts.



Exposure of bis(trifluoromethylsulfonyl)methane (**1a**)[8] to *p*-trifluoromethylphenyl(difluoro)-λ^3-bromane[9] (1.1 equiv) in acetonitrile at 0 °C for 3 h under argon resulted in the formation of perfluoroalkylsulfonyl-substituted bromonium ylide **2a** in 94% yield (eq 1). Solid phase reaction (25 °C/5 min) without using a solvent afforded a 67% yield of **2a**. Reaction with bis(nonafluorosulfone) **1b** (acetonitrile/0 °C/3 h) yielded the bromonium ylide **2b** in 89% yield. The ylide **2a** is soluble in acetone, methanol, and ethyl acetate, but not in the less polar solvents hexane and dichloromethane. These ylides **2** are quite stable and can be stored indefinitely at room temperature. Even in solution (acetone-d_6), no decomposition of **2a** was detected to a discernible extent when it was left standing in the air at 23 °C for three months. The ylide **2a** can be heated to melting without any decomposition, but the continuous heating at 180 °C for 5 min resulted in the complete disappearance with formation of *p*-(trifluoromethyl)bromobenzene.

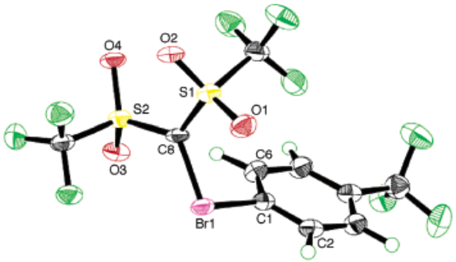


Figure 1. ORTEP drawing of **2a**. Selected bond lengths (Å) and angles (deg): Br(1)−C(1) 1.951(3), Br(1)−C(8) 1.868(3), S(1)−C(8) 1.704(4), S(2)−C(8) 1.700(3), C(1)−Br(1)−C(8) 103.9(2), Br(1)−C(8)−S(1) 117.4(1), Br(1)−C(8)−S(2) 116.7(2), S(1)−C(8)−S(2) 125.4(2).

Key to the success of the synthesis of **2** seems to be the presence of two highly electron-withdrawing perfluoroalkylsulfonyl groups ($\sigma_p = 0.96$ for CF_3SO_2),[10] which stabilize the ylide carbanions through delocalization of the negative charge; thus, in contrast to the highly acidic bissulfones **1** (pK_a = ca. −1 for **1a**),[8] less acidic methylene compounds, such as $PhSO_2(CF_3SO_2)CH_2$ (pK_a = 5.1), $(CF_3CO)_2CH_2$ (pK_a = 5.3), $(n\text{-}C_3F_7CO)_2CH_2$, and dimedone (p$K_a$ = 5.2), showed no evidences for formation of the stable bromonium ylides under our conditions.

Solid state structure of **2a**, obtained by recrystallization from hexanes−ethyl acetate at −30 °C, illustrates a ylide structure (Figure 1): the four atoms Br1, C8, S1, and S2 are coplanar with the root mean square deviation of 0.0359(2) Å from their least-squares planes and with the sums of the C8-centered bond angles $\sum$°C8 = 359.5°, indicating an sp^2 hybridization of the ylide carbanion C8. The Br1−C8 distance of 1.868 Å is considerably shorter than that of Br1−C1 bond (1.951 Å), but comparable to the reported vinylic Csp^2−Br(III) single bond (1.886 Å) of a vinyl-λ^3-bromane.[11] These results suggest little double-bond character for the ylidic bond as well as a negligibly small electrostatic attraction between the oppositely charged Br1 and C8, probably because of a high electronegativity of Br.[12] The C1−Br1−C8 bond angle of 103.9° is considerably greater than that (98.2°) for the bissulfonyl iodonium ylide $(CF_3SO_2)_2C^-{-}I^+Ph$.[13,14] This is probably due to the increased nonbonded repulsions between the two organic substituents on Br(III) with a decreased atomic size. In addition to the intramolecular short Br1⋯O1 contact, a nearly linear C8−Br1⋯O2* ($x - 1/2$, $-y - 1/2$, z) secondary bonding to one of the sulfonyl oxygen atoms of an adjacent molecule was found with a Br⋯O distance of 2.987(2) Å, which links individual molecules of **2a** into infinite zigzag chains (Figure S1).[15]

Iodonium ylides undergo transylidations with various N, P, As, S, and Se nucleophiles under thermal, catalytic, or photochemical conditions;[1] for instance, reaction of the iodonium bis(carboethoxy)methylide $(EtO_2C)_2C^-{-}I^+Ph$ with pyridine under heating produced the pyridinium ylide $(EtO_2C)_2C^-{-}N^+C_5H_5$ with reductive elimination of PhI.[16] In a marked contrast, instead of transylidations, the bromonium ylide **2** undergoes an arylation of N-heterocycles

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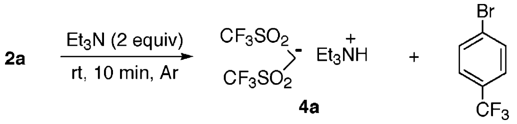
Table 1. Arylation of N-Heterocycles with Bromonium Ylide **2**[a]

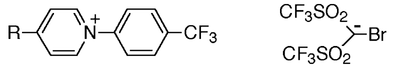
entry	2	N-heterocycle	time	3	yield (%)[b]
1	**2a**	pyridine	3 days	**3a**	77
2	**2a**	4-*tert*-butylpyridine	24 h	**3b**	81
3	**2a**	4-(dimethylamino)pyridine	2 h[c]	**3c**	54
4	**2a**	4,4′-bipyridine	18 h	**3d**	(97)
5	**2a**	*N*-methylimidazole	3 days	**3e**	(94)
6	**2b**	pyridine	24 h	**3f**	84

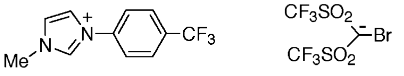
[a] Conditions: 1:2 **2**:N-heterocycle, dichloromethane, 45 °C, Ar. [b] Isolated yields. Numbers in parentheses are ^{1}H NMR yields. [c] Reaction was carried out at room temperature.

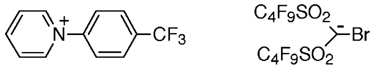
Scheme 1



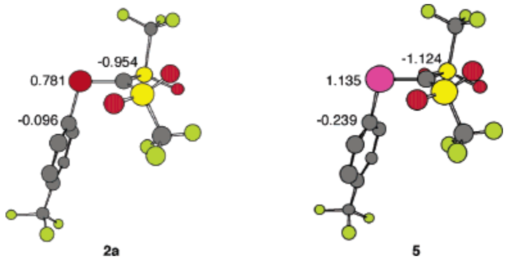
selectively with concomitant reductive elimination of bissulfonylbromomethanide anion (Table 1); thus, exposure of ylide **2a** to pyridine (2 equiv) in dichloromethane at 45 °C for 3 days under argon afforded *N*-(*p*-trifluoromethylphenyl)pyridinium bissulfonylbromomethanide **3a** in 77% yield, with no evidences for transylidations (entry 1).[17,18] 4,4′-Bipyridine and *N*-methylimidazole produced the pyridinium **3d** and imidazolium salts **3e**, respectively, in high yields. Interestingly, this N-arylation of pyridine seems to be specific for the bromonium ylides **2**, and no formation of pyridinium salt **3a** was observed in the reaction with bissulfonyl iodonium ylide $(CF_3SO_2)_2C^-{-}I^+C_6H_4$-*p*-$CF_3$ **5**, which was recovered unchanged under our conditions. Formation of these ammonium salts **3** probably involves a rate-limiting nucleophilic attack of N-heterocycles to the aromatic *ipso* carbons of **2**, generating Meisenheimer-type complexes, which in turn expel the bissulfonylbromomethanide anion as a leaving group. A greater electron-withdrawing nature of λ^3-bromanyl groups compared to that of λ^3-iodanyl groups seems to be responsible for these differences in reactivity between the bromonium and iodonium ylides.[19]


R : **3a** (H), **3b** (*t*-Bu), **3c** (Me_2N), **3d** (4-pyridyl)


3e


3f

Interestingly, use of trialkylamines dramatically changed the reaction course and, instead of the N-arylation, bromoarene was liberated selectively; thus, reaction of **2a** with triethylamine (2 equiv) at room temperature for 10 min afforded triethylammonium bissulfonylmethanide **4a** (76%)[20] and *p*-(trifluoromethyl)bromobenzene (97%) (Scheme 1). Similarly, use of *N*-benzylpiperidine produced the corresponding piperidinium methanide **4b** quantitatively.



2a **5**

Figure 2. Optimized structures of **2a** and **5** with natural charges at C_{ylide}, C_{ipso}, Br, and I calculated with the B3LYP/LanL2DZ method (Gaussian 03W).

To shed light on the reactivity differences between bromonium and iodonium ylides, density functional theory (DFT) calculations on the ylides **2a** and **5** were carried out (Figure 2). The calculated structure of **2a** is in a good agreement with the solid state structure shown in Figure 1. Natural charges via the natural population analysis (NPA) show that the Br(III) atom in **2a** is apparently less positive than the I(III) atom in **5**, probably reflecting the greater electronegativity of bromine relative to iodine.[21] The remaining positive charge in **2a** is mostly delocalized on the aryl group (Figure S3), which makes possible the facile S_NAr reaction with N-heterocycles.

Supporting Information Available: Experimental details, Scheme S1, Figures S1−S3, and X-ray crystallographic data in CIF format for **2a** and **3f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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