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COMMUNICATIONS

Published on Web 10/04/2007

A New Type of Imido Group Donor: Synthesis and Characterization of Sulfonylimino-λ^3-bromane that Acts as a Nitrenoid in the Aziridination of Olefins at Room Temperature under Metal-Free Conditions

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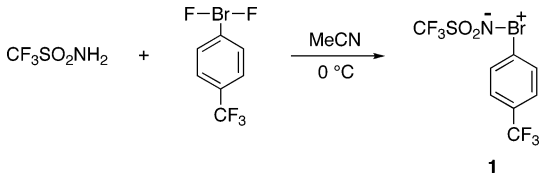
Phenyl(sulfonylimino)-λ^3-iodanes PhI=NSO_2Ar are readily accessible from sulfonamides by the reaction with phenyl-λ^3-iodanes[1] and have found many applications in modern organic synthesis.[2] Because of the hyper-leaving-group ability of aryl-λ^3-iodanyl groups,[3] they serve as excellent nitrene (nitrenoid) progenitors either in the aziridination of alkenes or in the amidation of alkanes via C−H insertion using copper or rhodium catalysts.[4] In the past decade, the research activity in this area has surged.[5]

On the other hand, little is known about the chemistry of the related group 17 sulfonylimino-λ^3-bromanes because a method for their syntheses is not available. We report herein, for the first time, the synthesis, isolation, and characterization of a stable sulfonylimino-λ^3-bromane **1** whose structure was firmly established by X-ray crystal analysis. The imino-λ^3-bromane **1** serves as an efficient imido group donor and directly undergoes aziridination of olefins stereospecifically with retention of original stereochemistry. It should be noted that the aziridination proceeds at room temperature using limiting amounts of alkenes under transition-metal-free conditions.

Exposure of trifluoromethanesulfonamide ($TfNH_2$) to *p*-trifluoromethylphenyl(difluoro)-λ^3-bromane[6] (1 equiv) in acetonitrile at 0 °C for 10 min in a Teflon PFA vessel under argon afforded trifluoromethylsulfonylimino-λ^3-bromane **1** in 98% yield as a white solid, after repeated decantation with hexane (Scheme 1). This is the first example for the synthesis of imino-λ^3-bromanes. Because of a highly aggregated polymeric nature,[7] the iminoiodane PhINTs is insoluble in organic media such as dichloromethane and acetonitrile, being employed for transition-metal-catalyzed aziridination and C−H insertion. The insoluble nature makes it difficult to improve catalytic efficiencies and complicates mechanistic studies.[8] In marked contrast, the imino-λ^3-bromane **1** is readily soluble in these solvents. The imino-λ^3-bromane **1** is fairly stable in the solid state and can be stored for more than 2 months without any decomposition in a refrigerator (at 4 °C) under argon. In solution (0.02 M in $CDCl_3$), however, it decomposes at 23 °C with a half-life time ($t_{1/2}$) of 1 h and produces a mixture of triflylamide and *p*-(trifluoromethyl)bromobenzene quantitatively. It is more stable in a coordinating solvent such as acetonitrile ($t_{1/2}$ = 42 h at 23 °C). Brief heating to melting (at 85 °C) resulted in the complete disappearance of **1** with formation of the amide (80%) and the bromoarene (82%). The ^{1}H NMR spectrum in $CDCl_3$ showed a set of signals assigned to the disubstituted phenyl group [δ 8.12 (*o*) and 7.92 (*m*) ppm]. The ^{13}C resonance of the *ipso* carbon atom appeared at δ 138.9 ppm.

Key to the success of the synthesis of imino-λ^3-bromane **1** seems to be the presence of a highly electron-withdrawing triflyl group

Scheme 1



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with σ_p of 0.96,[9] which stabilizes the negative charge at the nitrogen atom. Less acidic *p*-toluenesulfonamide, however, showed no evidence for formation of the corresponding iminobromane under our conditions.

The solid-state structure of imino-λ^3-bromane **1** (Figure 1), obtained by recrystallization from dichloromethane/hexane at 5 °C, illustrates a centrosymmetric dimer with a Br_2O_2 rhomboid structure (Br1···O1 3.0361(18) and Br1···O1* 3.0603(19) Å),[10] which stands in marked contrast to the polymeric zigzag chain structure of PhINTs with an I−N···I−N··· backbone.[7] The Br1−N1 distance of 1.846 Å is in a good agreement with the sum of the covalent radii for Br (1.14 Å) and N (0.70 Å)[11] and comparable to the reported bond lengths for *N*-bromobenzamide (1.843 Å), *N*-bromosuccinimide (1.817 Å), and bromamine-T (TsNBrNa, 1.870 Å).[12] The result suggests little double-bond character for the "ylidic" Br−N bond of **1** as well as a negligibly small electrostatic attraction between the oppositely charged Br1 and N1.[13] The C1−Br1−N1 bond angle of 100.94° is considerably greater than that (95.8°) reported for PhINTs,[7a] probably because of the increased nonbonded repulsions between the two substituents on Br(III) with a decreased atomic size.

A fully optimized structure of phenyl(triflylimino)-λ^3-bromane PhBr=NSO_2CF_3 at the MP2/6-311+G(d) level in the Gaussian 03 program[14] was found to be essentially superimposable on the X-ray dimeric structure of **1** shown in Figure 1, except for the CF_3 group (Figure S1). The calculated dimeric structure is by 18.6 kcal mol^{-1} more stable than that of the monomer. Natural charges via the natural population analysis (Br, +0.825 and N, −1.004) indicate a highly polarized Br−N single bond (Table S1).[15] NBO calculations predict that negative hyperconjugation of the nitrogen lone pair orbital with the σ^* Br1−C1 and S1−C8 bond orbitals probably plays an important role in stabilizing the imino-λ^3-bromane in the gas phase:[16] donor−acceptor interaction energies ($E^{(2)}$) 7.9 and 20.6 kcal mol^{-1}, respectively (Table S2). In fact, the observed dihedral angles C1−Br1−N1−S1 (99.84°) and Br1−N1−S1−C8 (90.11°) in the solid-state structure of **1** probably reflect these negative hyperconjugation.

Aziridines possess a strained ring and, thus, are susceptible to ring-opening reactions, which makes aziridines useful intermediates in organic synthesis.[17] The imino-λ^3-bromane **1** readily undergoes transfer of the sulfonylimido group to olefins even at room

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10.1021/ja075811i CCC: $37.00

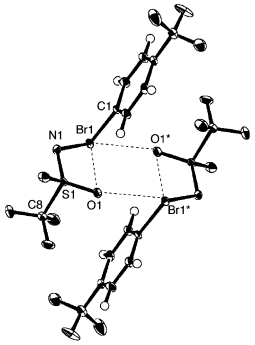


Figure 1. ORTEP drawing of the dimeric unit of **1** with thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg): Br1−N1 1.846(2), Br1−C1 1.931(2), C1−Br1−N1 100.94(11).

Table 1. Aziridination of Olefins with Imino-λ^3-bromane **1**[a]

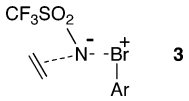
entry	olefin	solvent	time (h)	yield (%)[b]		*Z*:*E*
1	cyclohexene	MeCN	5	**2a**	67 (75)	
2	cyclohexene	CH_2Cl_2	5	**2a**	76 (85)	
3	cycloheptene	MeCN	3	**2b**	97	
4	*cis*-cyclooctene	MeCN	2	**2c**	90	
5	norbornene	MeCN	5	**2d**	72 (78)	
6	$Me_2C{=}CMe_2$	MeCN	9	**2e**	80	
7	*n*-$C_8H_{17}CH{=}CH_2$	CH_2Cl_2	18	**2f**	65 (68)	
8	*Z*-PhCH=CHPh	MeCN	12	**2g**	81	>99:1
9	*E*-PhCH=CHPh	MeCN	48	**2g**	0[c]	
10	*Z*-PhCH=CHMe	MeCN	3	**2h**	82 (97)	>99:1
11	*E*-PhCH=CHMe	MeCN	24	**2h**	(15)	7:93
12	*E*-PhCH=CHMe	CH_2Cl_2	8	**2h**	79 (84)	<1:99
13	*Z*-PrCH=CHPr	MeCN	1	**2i**	89 (98)	>99:1
14	*E*-PrCH=CHPr	MeCN	36	**2i**	(23)	5:95
15	*E*-PrCH=CHPr	CH_2Cl_2	6	**2i**	53 (88)	<1:99
16	$PhCH{=}CH_2$	CH_2Cl_2	12	**2j**	84 (91)	
17	*p*-$ClC_6H_4CH{=}CH_2$	CH_2Cl_2	36	**2l**	92 (95)[d]	

[a] Conditions: 1:1.2 olefin/bromane **1**, acetonitrile, room temperature, Ar. [b] Isolated yields. Numbers in parentheses are ^{1}H NMR yields. [c] *trans*-Stilbene (85%) was recovered. [d] Reaction was carried out at 0 °C.

temperature, yielding sulfonylaziridines. Preliminary results are shown in Table 1. Compared to the aziridination reaction with sulfonylimino-λ^3-iodanes, in which a transition-metal catalyst such as Cu or Rh(II) salt is indispensable to generate reactive metal imido species,[2,5] our imido transfer reaction does not require any metal additives. Furthermore, the aziridination proceeds using limiting amounts of starting olefins, in contrast to most of the reported reactions with preformed imino-λ^3-iodanes, which rely on excess amounts of substrate (3 or more equiv) to effect high product conversion.[18] Thus, exposure of cyclohexene to imino-λ^3-bromane **1** (1.2 equiv) in acetonitrile at room temperature for 5 h afforded *N*-triflylaziridine **2a** selectively in 67% yield, with no evidence for formation of an allylic amidation side product (entry 1). A wide array of cyclic and acyclic alkenes gave the corresponding aziridines in high yields. Among the challenging substrates, a terminal olefin 1-decene was found to afford a good yield of aziridine.

Our uncatalyzed aziridination appears to be quite sensitive to the geometry of olefins: aziridination of *cis*-1,2-disubstituted olefins occurs smoothly, and the isolated aziridines **2g**−**i** were found to be diastereomerically pure, with complete preservation of the original *cis* stereochemistry of the olefins. On the other hand, the aziridinations of *trans* isomers in acetonitrile were very sluggish. Finally, we found that use of dichloromethane as a solvent dramatically increases the rate and efficiency of the uncatalyzed reaction (compare entries 10−12 and 13−15). Acetonitrile probably coordinates to the positively charged bromine atom of imino-λ^3-bromane **1** and stabilizes it, which, in turn, will decrease the reactivity of **1**. Such an adduct is predicted to be more stabilized than the components by 7.8 kcal mol^{-1} (Figure S2). Most importantly, the olefin aziridination of both stereoisomers was found to be highly stereospecific, which is a relatively rare example of stereochemical retention in the aziridinations[19] and strongly suggests a concerted reaction mechanism.

Scheme 2



Rates for aziridination of *cis*-cyclooctene with imino-λ^3-bromane **1** were measured spectrophotometrically at 50 °C in acetonitrile solution. The observed rate constants k_{obsd} are proportional to concentration of the olefin and afforded k_2 value of 1.14×10^{-1} M^{-1} s^{-1} (Table S3). These results most likely suggest the involvement of a bimolecular transition state such as **3** (Scheme 2), in which an olefin attacks the σ^* N−Br orbital (LUMO) of **1** in the nitrenoid transfer process.

Supporting Information Available: Experimental details, Figures S1 and S2, Tables S1−S3, complete ref 14, and X-ray crystallographic data in CIF format for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Crystallographic data for iminobromane **1**: $C_8H_4BrF_6NO_2S$, $M = 372.08$, $T = 93$ K, monoclinic space group $P2_1/c$ (No. 14), $a = 13.0591(2)$ Å, $b = 9.8448(2)$ Å, $c = 8.9487(2)$ Å, $\beta = 93.0748(7)°$, $V = 1148.83(4)$ Å^3, $Z = 4$, $D_c = 2.151$ g cm^{-3}, μ (Cu Kα) = 74.063 cm^{-1}; 18535 reflections were collected; 2099 were unique; $R = 0.0315$, $R_w = 0.0734$.

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JA075811I