Metal-free C–H amination of unactivated hydrocarbons with sulfonylimino-λ3-bromanes generated in situ from diacetoxybromobenzene

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Metal-free C–H amination of unactivated hydrocarbons with sulfonylimino-λ^3-bromanes generated in situ from (diacetoxybromo)benzene

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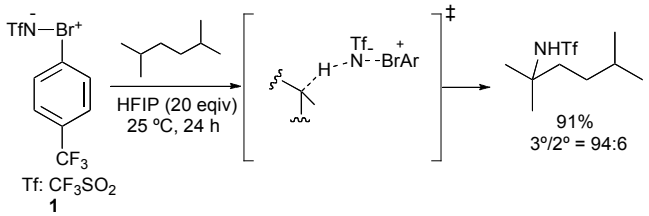
A simple method for direct metal-free C-H amination of unactivated hydrocarbons using easy-handling diacetoxy-λ^3-bromane and triflylamide or sulfamate esters, was developed. The high 2º/3º regioselectivities and deuterium isotope effects suggest a concerted organonitrenoid transition state, analogous to C-H amination with *N*-triflylimino-λ^3-bromane.

Highly selective C-H amination of ubiquitous alkanes under metal-free conditions has been an area of great interest over the past decade, because of its environmentally friendly nature and economic advantage.[1,2] These approaches use a combination of a suitable oxidant and a nitrogen source to generate active amination species such as PhI(OAc)$_2$/I$_2$/amines,[3] PhI=NTs/I$_2$,[4] diiodohydantoin/TsNH$_2$,[5] and chloramine-T/I$_2$.[2c] Although these reactions serve as excellent amination tools for relatively active benzylic C-H bonds, only limited success has been reported in unactivated simple alkyl C-H bonds. In contrast, thermally or photochemically generated free nitrenes insert into various hydrocarbons but they are generally nonselective and, thus, are of little synthetic value.[6] We have reported that *N*-triflylimino-λ^3-bromane **1** undergoes regio- and stereoselective amination of aliphatic unactivated C-H bonds under ambient temperature in the absence of transition metal catalysts.[7] A remarkable regioselectivity for methine over the methylene group was observed, while amination of the methyl group has never been observed. The high regioselectivity is probably because of a concerted bimolecular transition state with some hydride-transfer character (not *a nitrene mechanism*), for the C-H amination event with imino-λ^3-bromane **1** (Scheme 1). We report herein inter- and intramolecular metal-free C-H amination of aliphatic hydrocarbons with imino-λ^3-bromanes generated in situ from (diacetoxybromo)arene **2** and sulfonamides.

Recently, we reported the stereoselective aziridination of olefins with diacetoxybromane **2** in the presence of triflylamide, where *N*-triflylimino-λ^3-bromane **1** was generated in situ.[8] The one-pot procedure makes it possible to dispel the limitations of original aziridination methods: thus, only the highly electron deficient *N*-triflylimino group is available.[9] Other imino-λ^3-bromane with the less electron deficient sulfonyl group, for example, *N*-(2,2,2-trichloroethoxysulfonyl)imino-λ^3-bromane is highly labile and decomposes rapidly, even at 0 ºC in CD_2Cl_2.[10]

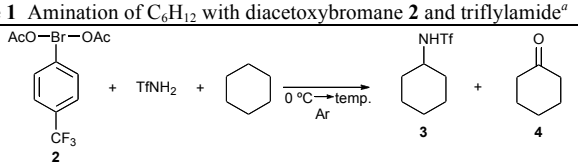


Scheme 1 Regioselective metal-free C-H amination of alkane with imino -λ^3-bromane **1**.

Although neither diacetoxybromane **2** nor triflylamide are soluble in alkanes, ligand exchange and the following C-H amination process occurs at ambient temperature without requiring a transition metal catalyst. To a stirred suspension of diacetoxybromane **2** (1.2 equiv, 0.01 M) in cyclohexane (925 equiv) was added triflylamide at 0 ºC under argon. After warming the mixture to room temperature, the formed white precipitate of λ^3-bromane gradually disappeared within 3 h, yielding cyclohexyl(triflyl)amide **3** in 87% yield (Table 1, entry 1). However, the conditions showed poor reproduciblility throughout five runs. The yields varied irregularly from 29% to 87%, and was accompanied by the formation of a small amount of cyclohexanone **4** (7-27%). Reproducible results were obtained when the reaction temperature were set to 7 ºC, 15 ºC, 25 ºC, and 35 ºC (entries 2-6). It is noteworthy that much lower yield of **3** was obtained at ≥25 ºC (entries 2, 3, and 6). In a nonpolar alkane, such as 2,2,4,4-tetramethylpentane, imino-λ^3-bromane **1** was highly unstable with a half-life time ($t_{1/2}$) of about 3.6 min and degraded to triflylamide and bromoarene quantitatively,[7] which partially accounts for the lower yield of **3**. The unexpected by-product, cyclohexanenone **4**, seemed to be produced by the reaction with diacetoxybromane **2** in the presence of molecular oxygen.[11] In fact, when the reaction was carried out in degassed cyclohexane, a slight increase in the yield of **3** was observed (entry 3). Interestingly, reactions carried out below 15 ºC result in much higher yields of **3**, but the rate slowed considerably at cooler temperature (entries 4 and 5). These reactions were carried out at least two times and

reproducible results were obtained. Imino-λ^3-bromane **1** shows very poor solubility in cyclohexane at 15 ºC (≤ 0.005 M), however, a reduced amount of cyclohexane was found to slow down the reaction rates (entries 7 and 8). From our preliminary experiments, the formation of cyclohexanone **4** probably involves the generation of cyclohexyl radical (Scheme S2). To prevent the formation of cyclohexanone, TEMPO free radical scavenger was used because this reagent immidiately traps carbon radical. The attempt, however, was found to be fruitless, probably due to the unwanted oxidation of TEMPO to the corresponding oxoammonium ion by diacetoxybromane **2** (entry 9).[12] Weakly acidic protic additives effectively stabilized imino-λ^3-bromane **1** and dramatically improved the C-H amination efficiencies.[7] However, in the present reaction, they were not effective (entries 10 and 11). The low efficiency observed in the reaction with hexafluoroisopropanol (HFIP) is probably due to the occurrence of a competing oxidation of this additive by diacetoxy-λ^3-bromane **2**. In fact, **2** promotes oxidation of HFIP yielding hexafluoroacetone monohydrate at 15 ºC in dichloromethane in the absence of triflylamide.[13] Notably, the use of (diacetoxyiodo)benzene, instead of **2**, afforded neither the desired product **3** nor cyclohexanone **4** under similar reaction conditions (entry 12).

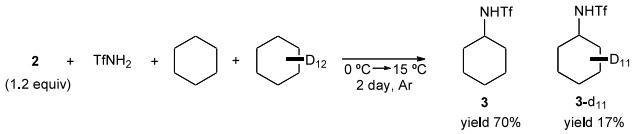
Table 1 Amination of C_6H_{12} with diacetoxybromane **2** and triflylamide[a]



Entry	CyH (equiv)	temp (ºC)	time (h)	yield[b] (%) **3**	**4**[b]
1	925	rt	7	87	27
2	925	25	7	29[c]	6[c]
3[d]	925	25	6	45[c]	3[c]
4[d]	925	15	26	94[c] (73)	6[c]
5[d]	925	7	144	93	4
6[d]	925	35	1	50	4
7[d]	372	15	67	98	6
8[d]	184	15	73	76	4
9[d, e]	925	15	23	65	7
10[d, f]	925	15	27	98	6
11[d,g]	925	15	24	5	-
12[d,h]	925	15	24	0	-

[a] Unless otherwise noted, reactions were carried out by mixing diacetoxybromane **2** (1.2 equiv) and $TfNH_2$ (1 equiv) in cyclohexane at 0 ºC, and then they were warmed to the desired temperature. [b] GC yields, isolated yield in parenthesis. [c] Values for two runs were averaged. [d] Degassed CyH was used. [e] TEMPO (0.1 equiv) was used. [f] AcOH (5 equiv) was used. [g] HFIP (20 equiv) was used. [h] (Diacetoxyiodo)benzene (1.2 equiv) was used.

To extend the applications of the present method, we examined C-H amination of various alkanes and the results are summarized in Table 2. Both cyclic and acyclic alkanes were efficiently transformed into *N*-triflylamides **5**-**10** under metal-free conditions. Five-, seven-, and eight-membered cyclic alkanes similarly afforded good to high yields of *N*-triflylamides at 15 ºC under metal-free conditions. Similar yields were obtained at 0 ºC, but these reactions required prolonged reaction time (entries 2 and 4). It is worth mentioning that the yields of *N*-triflylamides were comparable to that of imino-λ^3-bromane **1**.[7] Acyclic alkanes afforded moderate to good yields of amides **8**-**10** (entries 7-9). These reactions showed marked preference for tertiary C-H bonds over secondary C-H bonds, and the ratios were in fair agreement with the values observed in the reaction of imino-λ^3-bromane **1**. We observed no formation of any primary (methyl) C-H insertion products with any of the substrates examined. These regioselectivities suggest that the reaction mechanism probably involves a concerted asynchronous transition state, where a C-H σ bonding electron attacks the N–Br σ* orbital with some hydride transfer character.[7,14] We evaluated the deuterium kinetic isotope effect (KIE) by the competitive reaction of **2** and triflylamide with a 1:1 mixture of cyclohexane and cyclohexane-d_{12} at 15 ºC, which afforded the primary deuterium KIE ratio (k_H/k_D) of 4.07 for C-H amination, as determined by GC. The large isotope effects are very close to the previously observed KIE value (3.72) obtained with iminobromane **1**, supporting the concerted mechanism (Scheme 2).



Scheme 2. Deuterium kinetic isotope effect for C–H amination reaction.

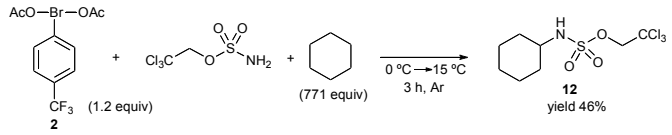
Table 2 Amination of alkanes with diacetoxybromane **2** and triflylamide[a]

Entry	alkane (equiv)	temp (ºC)	time (h)	Product	yield[b] (%)
1	(617)	15	25	**5**	91
2		0	120		93
3	(1190)	15	11	**6**	60
4		0	78		58
5	(427)	15	19	**7**	68
6	(85)[c]	15	30		57
7	(875)	15	26	**8**[d]	61[e]
8	(1110)	15	23	**9**[d]	78
9	(1030)	15	24	**10**	44

[a] Unless otherwise noted, reactions were carried out by mixing diacetoxybromane **2** (1.2 equiv, 0.01-0.05 M) and $TfNH_2$ (1 equiv) in degassed cyclohexane (0.01 M) at 0 ºC, and then they were warmed to desired temperature. [b] GC yields. [c] Bromane **2** (0.05 M). [d] *N*-Triflylaminoalkanes were obtained as a mixture of regioisomers: for entry 6, 3º/2º = 88:12; for entry 7, 3º/2º = 91:9. [e] Values for two runs were averaged.

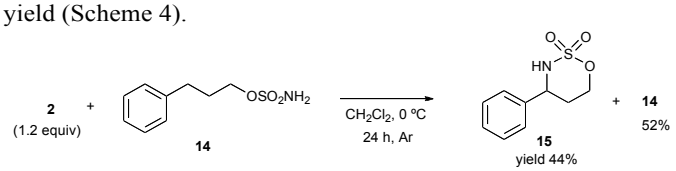
Direct C-H amination using (2,2,2-trichloroethoxy)-sulfonamide **11** is a fascinating process, because the product can be readily deprotected under mild reaction conditions, which may enable easy access to ubiquitous alkylamines from the parent alkanes.[15] The one-pot C-H amination procedure can be applied to the C-H amination using **11** (Scheme 3). Thus, amination of cyclohexane afforded *N*-(cyclohexyl)sulfonamide **12** in moderate yield. Interestingly, introduction of a sulfamate

ester to cyclohexane is faster than the comparable reaction with the triflylamide, possibly reflecting the high lability, and hence, the higher reactivity of *N*-(2,2,2-trichloroethoxysulfonyl)imino-λ^3-bromane.[10]



Scheme 3 C-H Amination with 2,2,2-trichloroethylsulfonylamide.

Recently, Du Bois *et al.* and some other research groups greatly extended efficient methods for oxidative intramolecular cyclization of sulfamate esters using diacetoxy-λ^3-iodanes.[16] In their reactions, Rh(II) catalyst plays an essential role: thus, the Rh nitrenoid generated in situ acts as an active intermediate. In contrast, diacetoxy-λ^3-bromane **2** promotes intramolecular cyclization of the sulfamate ester in the absence of a transition metal catalyst. For example, 3-phenylpropylsulfamate ester **14** could be converted into the 6-membered sultam **15** in moderate yield (Scheme 4).



Scheme 4 C-H amination of sulfamate ester **14**.

Conclusions

In conclusion, we have developed a simple method for direct C-H amination of unactivated hydrocarbons utilizing diacetoxy-λ^3-bromane **2** can be handled easily and triflylamide or sulfamate esters. The method provides a direct route for the regioselective synthesis of alkylamines.

Acknowledgement

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Experimental

General Information. IR spectra were recorded on JASCO FT/IR-420 spectrometers. ^{1}H NMR and ^{13}C NMR spectra were obtained on either a JEOL JNM-AL300, JNM-AL400, or Bruker AV400 spectrometers. Chemical shifts (d) are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on a 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). Kieselgel 60 (Merck, 230-400 mesh) was used for column chromatography.

Substrates. [*p*-(Trifluoromethyl)phenyl](diacetoxy)-λ^3-bromane (**2**) was synthesized by the reaction of *p*-(trifluoromethyl)phenyl-(difluoro)-λ^3-bromane,[17] with acetic anhydride and acetic acid in a Teflon PFA vessel.[8] *p*-(Trifluoromethyl)phenyl(difluoro)-λ^3-bromane was prepared from bromine trifluoride according to a literature method.[17] A Teflon PFA vessel was used because of the liberation of hydrogen fluoride in the reaction. Diacetoxy-λ^3-bromane **2** is fairly stable in the solid state and can be stored for more than two months without any decomposition at room temperature under argon. 2,2,2-Trichloroethylsulfamate and **14** were prepared by sulfamoylation of the corresponding alcohols according to the reported procedure.[18]

General Procedure for C-H Amination of Alkanes with Diacetoxy-λ^3-bromane 2 and Triflylamide. A Typical Example (Table 1, entry 4). To a suspension of diacetoxy-λ^3-bromane **2** (29.4 mg, 0.086 mmol) in degassed cyclohexane (8.6 mL) in a glass tube under argon at 0 ºC was added triflylamide (10.7 mg, 0.071 mmol) and the mixture was warmed to 15 ºC and vigorously stirred for 26 h. GC yield (94%) of *N*-(cyclohexyl)trifluoromethanesulfonamide (**3**) and (6%) cyclohexanone (**4**) were determined by capillary GC (FFS ULBON HR-1, 0.25 mm x 50 m, 60 ºC and 120 ºC) of the reaction mixture using *n*-nonane and *n*-tridecane as an internal standard. After filtration, the reaction mixture was evaporation under an aspirator vacuum to give a solid residue which was recrystallized from dichloromethane-hexane at -30 °C to give *N*-(cyclohexyl)trifluoromethanesulfonamide (**3**) (11.8 mg, 73%) as colorless prisms; IR (KBr) 3350-3250 (br), 2933, 1454, 1373, 1221, 1066, 1007, 931, 613 cm^{-1}; δ 4.62 (br s, 1H), 3.58 (m, 1H), 2.07-1.97 (m, 2H), 1.80-1.70 (m, 2H), 1.67-1.57 (m, 1H), 1.44-1.10 (m, 5H). Spectral data are in agreement with literature.[7]

***N*-(Cyclopentyl)trifluoromethanesulfonamide (5)** (32.2 mg of **2** was used): A colorless oil; IR (neat) 3330-3270 (br), 2971, 1446, 1375, 1232, 1192, 1146, 1022, 924, 609 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (br s, 1H), 3.97 (sext, *J* = 7.4 Hz, 1H), 2.14-1.99 (m, 2H), 1.79-1.48 (m, 2H). Sulfonamide **5** shows highly volatile nature which makes isolation difficult. Thus, **5** was characterized by comparison of the ^{1}H NMR and GCMS spectra with those of authentic sample, prepared by reported procedure.[19]

***N*-(Cycloheptyl)trifluoromethanesulfonamide (6)** (20.7 mg of **2** was used): A colorless oil (6.3 mg, 51%); IR (neat) 3330-3280 (br), 2932, 1435, 1377, 1230, 1192, 1147, 1039, 613 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (br s, 1H), 3.70 (m, 1H), 2.11-1.97 (m, 2H), 1.69-1.40 (m, 10H). Spectral data are in agreement with literature.[7]

***N*-(Cyclooctyl)trifluoromethanesulfonamide (7)** (24.8 mg of **2** was used): A colorless oil (9.8 mg, 63%); IR (neat) 3300-3270 (br), 2925, 1435, 1378, 1230, 1194, 1149, 1054, 1018, 615 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (br d, *J* = 8.6 Hz, 1H), 3.79 (m, 1H), 2.00-1.90 (m, 2H), 1.75-1.44 (m, 12H). Spectral data are in agreement with literature.[7]

***N*-(1,1,4-Trimethyl-1-pentyl)trifluoromethanesulfonamide (8)** (31.0 mg of **2** was used): A colorless oil (12.7 mg, 54%); IR (neat) 3300-3290 (br), 2960, 1427, 1373, 1196, 1144, 1000, 627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.51 (br s, 1H), 1.78 (nonet, *J* = 6.6 Hz, 1H), 1.55 (d, *J* = 6.6 Hz, 2H), 1.43 (s, 6H), 0.99 (d, *J* = 6.6 Hz, 6H). Spectral data are in agreement with literature.[7]

***N*-(1-Ethyl-1-methyl-1-propyl)trifluoromethanesulfonamide (9)**

(17.9 mg of **2** was used): A colorless oil (6.5 mg, 64%); IR (neat) 3300-3280 (br), 2918, 1431, 1367, 1228, 1192, 1140, 1014, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.45 (br s, 1H), 1.66 (q, J = 7.0 Hz, 4H), 1.36 (s, 3H), 0.94 (t, J = 6.9 Hz, 6H). Contaminated with a small amount of regioisomer. Spectral data are in agreement with literature.[7]

***N*-(1,1-Dimethyl-1-propyl)trifluoromethanesulfonamide (10)** (19.1 mg of **2** was used): A colorless oil (4.0 mg, 40%); IR (neat) 3310-3290 (br), 2979, 1431, 1366, 1228, 1196, 1141, 1068, 1003, 624 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.54 (br s, 1H), 1.67 (q, J = 7.1 Hz, 2H), 1.39 (s, 6H), 0.97 (t, J = 7.1 Hz, 3H). Spectral data are in agreement with literature.[7]

***N*-(Cyclohexyl)-2,2,2-trichloroethoxysulfonamide (12)** (24.6 mg of **2** was used): White solids (3.4 mg, 18%); IR (KBr) 3310-3290 (br), 2932, 2857, 1452, 1360, 1182, 1080, 1048, 1022, 998, 933, 890, 855, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.62 (s, 2H), 4.45 (br d, J = 8.9 Hz, 1H), 3.49-3.39 (m, 1H), 2.12-2.04 (m, 2H), 1.79-1.71 (m, 2H), 1.64-1.56 (m, 1H), 1.40-1.15 (m, 5H); ESIMS (positive) *m/z* 309 (M^+). Spectral data are in agreement with literature.[20]

4-Phenyl-[1,2,3]oxathiazinane-2,2-dioxide (15) (22.3 mg of **2** was used): White solids (2.7 mg, 24%); IR (KBr) 3280-3260, 3067, 2967, 1418, 1357, 1186, 1015, 913, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 4.92-4.83 (m, 2H), 4.67 (ddd, J = 10.7, 4.3, 2.2 Hz, 1H), 4.26-4.18 (m, 1H), 2.31-2.18 (m, 1H), 2.07-2.00 (m, 1H); ESIMS *m/z* 236 [$(M+Na)^+$]. Spectral data are in agreement with literature.[21]

Notes and references

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Electronic Supplementary Information (ESI) available: For Scheme S1 and S2. See DOI: 10.1039/b000000x/

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