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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 2°/3° regio-selectivities 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/I₂/amines,³ PhI = NTs/I₂,⁴ diiodohydantoin/TsNH₂,⁵ and chloramine-T/I₂.^{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 regioand stereoselective amination of aliphatic unactivated C-H bonds at 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 metalfree C-H amination of aliphatic hydrocarbons with imino- λ^3 bromanes generated in situ from (diacetoxybromo)arene 2 and sulfonamides.

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Scheme 1 Regioselective metal-free C–H amination of alkane with imino- $\lambda^3\text{-bromane 1.}$

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 °C in CD₂Cl₂.¹⁰

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 °C 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 reproducibility throughout five runs. The yields varied irregularly from 29% to 87%, and were accompanied by the formation of a small amount of cyclohexanone 4 (7-27%). Reproducible results were obtained when the reaction temperatures were set to 7 °C, 15 °C, 25 °C, and 35 °C (entries 2-6). It is noteworthy that a much lower yield of 3 was obtained at ≥ 25 °C (entries 2,

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Table 1 Amination of C₆H₁₂ with diacetoxybromane 2 and triflylamide^a

$\begin{array}{c} AcO-Br-OAc \\ \hline \\ CF_3 \\ 2 \end{array} + TfNH_2 + O \\ CF_3 \\ 2 \end{array} + TfNH_2 + O \\ Ar \\ CF_3 $										
Entry	CyH (equiv.)	Temp. (°C)	Time (h)	$\mathrm{Yield}^{b}\left(\%\right)3$	4^{b}					
1	925	rt	7	87	27					
2	925	25	7	29^c	6					
3^d	925	25	6	45^{c}	3					
4^d	925	15	26	$94^{c}(73)$	6					
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 TfNH2 (1 equiv.) in cyclohexane at 0 °C, 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. AcOH (5 equiv.) was used. ^gHFIP (20 equiv.) was used. ^{*h*} (Diacetoxyiodo)benzene (1.2 equiv.) was used.

3, and 6). In a nonpolar alkane, such as 2,2,4,4-tetramethylpentane, imino- λ^3 -bromane **1** was highly unstable with a halflife $(t_{1/2})$ 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, cyclohexanone 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 °C 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 °C (≤ 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 a cyclohexyl radical (Scheme S2⁺). To prevent the formation of cyclohexanone, TEMPO, a free radical scavenger, was used because this reagent immediately traps carbon radicals. 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 °C 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).

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 metalfree conditions. Five-, seven-, and eight-membered cyclic alkanes similarly afforded good to high yields of N-triflylamides at 15 °C under metal-free conditions. Similar yields were obtained at 0 °C, but these reactions required prolonged reaction time (entries 2 and 4). It is worth mentioning that the

Table 2 Amination of alkanes with diacetoxybromane 2 and triflylamide^a

Fntry	Alkane (equiv.)	Temp (°C)	Time (h)	Product	Vield ^b (%)
Lifely	Ankane (equiv.)	Temp: (C)	Time (ii)	Houdet	11clu (70)
1	$\bigcirc ((17))$	15	25	NHTF _	91
2	(617)	0	120	5	93
3	\bigcap	15	11	NHTf	60
4	(1190)	0	78	6	58
5	\bigcap	15	19	NHTf	68
6	(427)	15	30	7	57
	(85) ^c				
7		15	26	NHTf	61^e
	(875)			8 ^d	
8		15	22	\NHTf	70
	(1110)	15	25	9 ^d	70
9		15	24	\NHTf	44
	(1030)			~~ 10	

^{*a*} Unless otherwise noted, reactions were carried out by mixing diacetoxybromane 2 (1.2 equiv., 0.01–0.05 M) and TfNH₂ (1 equiv.) in degassed cyclohexane (0.01 M) at 0 °C, and then they were warmed to the desired temperature. ^{*b*} GC yields. ^{*c*} Bromane 2 (0.05 M). ^{*d*} N-Triflylaminoalkanes were obtained as a mixture of regioisomers: for entry 6, 3°/2° = 88 : 12; for entry 7, 3°/2° = 91 : 9. eValues for two runs were averaged.

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 did not observe 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 °C, which afforded the primary deuterium KIE ratio $(k_{\rm H}/k_{\rm D})$ 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).

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

Recently, Du Bois *et al.* and some other research groups have 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 2 Deuterium kinetic isotope effect for C-H amination reaction.



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



Scheme 4 C-H amination of sulfamate ester 14.

Conclusions

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

Experimental

General information

IR spectra were recorded on JASCO FT/IR-420 spectrometers. ¹H NMR and ¹³C NMR spectra were obtained on either a JEOL JNM-AL300, JNM-AL400, or Bruker AV400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me₄Si. Mass spectra (MS) were obtained on a Waters LCT Premier, or a 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 and 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 °C was added triflylamide (10.7 mg, 0.071 mmol) and the mixture was warmed to 15 °C and vigor-ously stirred for 26 h. GC yield (94%) of *N*-(cyclohexyl)trifluoro-methanesulfonamide (3) and (6%) cyclohexanone (4) were determined by capillary GC (FFS ULBON HR-1, 0.25 mm × 50 m, 60 °C and 120 °C) of the reaction mixture using

n-nonane and *n*-tridecane as an internal standard. After filtration, the reaction mixture was evaporated under vacuum using an aspirator 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 the 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; ¹H NMR (400 MHz, CDCl₃) 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 a highly volatile nature which makes its isolation difficult. Thus, 5 was characterized by comparison of the ¹H NMR and GCMS spectra with those of the authentic sample, prepared according to a 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; ¹H NMR (400 MHz, CDCl₃) 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 the 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; ¹H NMR (400 MHz, CDCl₃) 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 the 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; ¹H NMR (400 MHz, CDCl₃) 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 the 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, CDCl₃) 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 the 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, CDCl₃) 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 the 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, CDCl₃) 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 the 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, CDCl₃) 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 the literature.²¹

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