JOC The Journal of Organic Chemistry

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Reductive Detriflylation of *N*-Triflylamides with Red-Al

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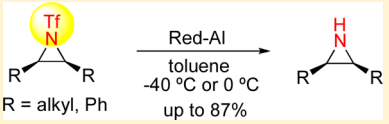
Supporting Information

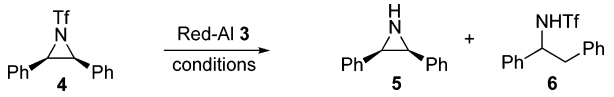
ABSTRACT: Reduction of *cis*-*N*-triflylaziridines with 10 equiv of Red-Al in toluene at −40 to 0 °C selectively afforded corresponding deprotected parent aziridines in good to high yields. *N,N*-Dialkyltriflylamides were also successfully cleaved under similar reaction conditions.



Aziridines, useful for the construction of complex organic molecules, are usually prepared by the direct aziridination of alkenes.[1] In the past decades, much attention has been paid to the stereoselective aziridination reaction with a combination of transition-metal catalysts and nitrenoid precursors.[2] In many cases, *N*-sulfonylimino-λ^3-iodanes **1** [$RSO_2N{=}IPh$] (where R = Me, *p*-tolyl, CCl_3CH_2O, etc.) served as nitrenoid progenitors because of high reactivity, stability, and nontoxic nature of the reagents.[3] Recently, we synthesized a group 17 congener aryl(trifluoromethanesulfonyl)imino-λ^3-bromane **2** which can serve as a versatile nitrenoid under metal-free conditions.[4] For example, reaction of various olefins with imino-λ^3-bromane **2** smoothly undergoes at 0 °C or room temperature and produces the corresponding aziridines in high yields with high stereoselectivity.[4a] Very recently, we have developed a one-pot methodology where imino-λ^3-bromane **2** is generated in situ from diacetoxyaryl-λ^3-bromane [p-$CF_3C_6H_4Br(OAc)_2$] and trifluoromethanesulfonamide ($TfNH_2$).[5] From a synthetic point of view, although these reactions potentially serve as a useful choice for stereoselective synthesis of aziridines, there is a difficult obstacle to overcome: triflylamides seem to be less susceptible to reductive deprotection compared to common arenesulfonamides. For example, the attempted reductive deprotection of *N*-(alkyl)triflylamides using SmI_2, which can successfully deprotect *N*-alkylarenesulfonamides, is fruitless.[6] There are only a limited number of methods available for deprotection of *N*-alkyltriflylamides, and they usually requires harsh reaction conditions (i.e., high temperature/excess powerful reductant).[7] Herein, we report a facile method for reductive deprotection of *N*-triflylaziridines using sodium bis(2-methoxyethoxy)aluminum dihydride (Red-Al) (**3**) under mild conditions (at −40 or 0 °C).[8] The reaction conditions were also successfully applied to the deprotection of *N,N*-dialkyltriflylamides.

Table 1 summarizes the initial attempts for reductive detriflylation of *cis*-*N*-triflylaziridine **4**. Exposure of aziridine **4** to excess Red-Al **3** in toluene resulted in a smooth cleavage of the N−S bond within 3 h at −40 °C and afforded parent *cis*-2,3-diphenylaziridine (**5**) in 88% yield, along with the formation of ring-cleaved triflylamide **6** (12%) (Table 1, entry 1). Changing the solvent to CH_2Cl_2 and THF resulted in a decrease in the yields of **5** (entries 2 and 3). Best selectivity was obtained when the reaction was carried out at 0 °C (entry 4). On the other hand, use of 3 equiv of Red-Al was found to be fruitless, yielding a low yield of **5** (entry 5).[9] In these reactions, no *cis*−*trans* isomerization of aziridine **5** was observed.

Table 1. Detriflylation of *cis*-2,3-Diphenyl-*N*-triflylaziridine (4)



				yield[a] (%)	
entry	Red-Al (equiv)	solvent	conditions	**5**	**6**
1	10	toluene	−40 °C, 3 h, Ar	88	12
2	10	CH_2Cl_2	−40 °C, 3 h, Ar	69	31
3	10	THF	−40 °C, 3 h, Ar	51	45
4	10	toluene	0 °C, 3 h, Ar	86 (82)	3
5	3	toluene	0 °C, 9.5 h, Ar	13[b]	9

[a] ^{1}H NMR yields. Isolated yield is shown in parentheses. [b] SM (43%) was recovered.

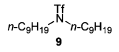
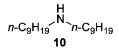
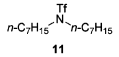
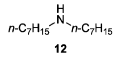
With optimized reaction conditions in hand, detriflylation of various triflylamides has been examined, and the results are listed in Table 2. The reductive deprotection of *cis*-2,3-disubstituted *N*-triflylaziridines **7a**−**c** with Red-Al **3** smoothly proceeded at 0 °C and afforded parent aziridines **8a**−**c** in good yields (entries 1−3). It should be noted that use of $LiAlH_4$ (87 equiv)/Et_2O/70 °C/14 h, instead of Red-Al **3**, produced only a ring-opended product for **7a** (31%). In marked contrast, the attempted deprotection of 2-octyl-*N*-triflylaziridine (**18**) with Red-Al **3** gave only a ring-opened *N*-(1-methyl-1-nonyl)-triflylamide (**19**), partly due to the smaller steric hindrance of less substituted carbon atom of aziridine ring (Scheme 1).[10]

Furthermore, a variety of *N,N*-dialkyltriflylamides gave the corresponding dialkylamines in high yields (entries 4−7). Interestingly, the reductive cleavage of *N,N*-dialkyltriflylamides is relatively slow and requires higher temperature and prolonged reaction time (50 °C/9 h). In fact, the reduction of *N,N*-dinonyltriflylamide (**9**) at room temperature gave only 53% of dinonylamine (**10**) after 5 h accompanied by the recovery of **9** (40%). The lower reactivity of *N,N*-dialkyltri-

Received: May 26, 2012
Published: August 9, 2012

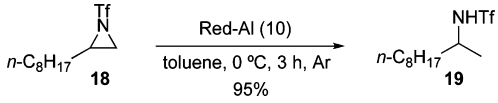
   dx.doi.org/10.1021/jo300947h | *J. Org. Chem.* 2012, 77, 8317−8320

Table 2. Detriflylation of *N*-Triflylaziridines with Red-Al.[a]

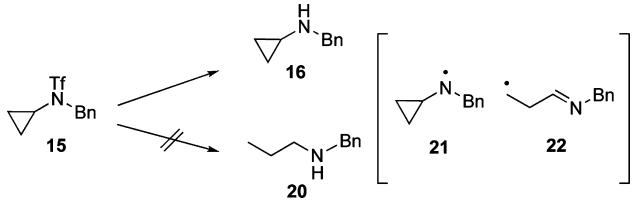
Entry	Substrate	Product	Yield (%)[b]
1	 **7a**	 **8a**	87[c]
2	 **7b**	 **8b**	60[c,d]
3	 **7c**	 **8c**	58
4	 **9**	 **10**	53 (93)[e]
5[e]	 **11**	 **12**	99
6[e]	 **13**	 **14**	78
7[e]	 **15**	 **16**	93

[a]Conditions: 1:10 triflylamide/Red-Al **3**, toluene, 0 °C, 3 h, Ar. [b]Isolated yields. [c]Isolated as trifluoroacetate. [d]*N*-(1-Phenylpropyl)-triflylamide (**17**) (25%) was obtained. [e]Yield of **10** at 50 °C for 9 h.

Scheme 1



Scheme 2



flylamides is responsible, at least in part, for the smaller leaving group ability of *N,N*-dialkylamino group than that of aziridino group.[11] Our conditions worked well when the adjacent protecting groups are base-labile benzyl group (entries 6 and 7).[12]

It should be noted that in the deprotection of *N*-cyclopropyltriflylamide **15**, no formation of β-fragmentation products such as **20** was detected, which probably suggests that the reactions do not involve a radical intermediate like **21** and/or **22** (Scheme 2).[13] A powerful thiol-like odor observed during workup process suggests the formation of hydrogen sulfide, which was confirmed by lead acetate paper test of acidified aqueous layer.[14] The formation of highly reduced sulfide ion (S^{2-}) is responsible, at least in part, for the requirement of excess amount of reductant Red-Al **3**.

In conclusion, Red-Al was shown to be an excellent deprotecting agent for *N*-triflylaziridines and *N,N*-dialkyltriflylamides.

EXPERIMENTAL SECTION

General Information. IR spectra were recorded on a FT-IR instrument. Nuclear magnetic resonance (^{1}H NMR and ^{13}C NMR) spectra were obtained on either a 300 or 400 MHz spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on either a ESIMS and GCMS instruments. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel with fluorescent. Kieselgel 60 (230−400 mesh) was used for column chromatography. Melting points were determined with melting points apparatus and are uncorrected. Sodium bis(2-methoxyethoxy)aluminum dihydride 65 wt % solution in toluene was purchased from commercial source.

Substrates. *N*-Triflylaziridines **4**, **7a−c** were prepared by aziridination of the corresponding olefins with imino-λ^3-bromane **2** according to the reported procedure.[4a] Triflylamides, **9**, **11**, **13**, **15**, and **17** were prepared from the corresponding amines by the reaction with trifluoromethanesufonic anhydride according to the reported procedure.[15]

General Procedure for Detriflylation of *N*-Triflylaziridines. A Typical Example (Table 1, Entry 4). To a stirred solution of *cis*-2,3-diphenyl-*N*-[(trifluoromethyl)sulfonyl]aziridine (5.3 mg, 0.016 mmol) in toluene (1.0 mL) was added sodium bis(2-methoxyethoxy)-aluminum dihydride 65 wt % in toluene (50 μL, 0.16 mmol) at 0 °C under argon, and the mixture was stirred for 3 h. After the addition of 5% aqueous ammonium chloride (5 mL) at 0 °C, the mixture was extracted with dichloromethane (each 7 mL, three times). The organic layer was dried over anhydrous sodium sulfate and concentrated under aspirator vacuum to give a white solid. ^{1}H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard showed the formation of *cis*-2,3-diphenylaziridine (**5**) in 86% yield and ring-opened triflylamide **6** in 3% yield. Purification by preparative TLC (ethyl acetate−hexane 3:7, R_f = 0.3) gave aziridine **5** (2.3 mg, 82%) as colorless needles:[5] mp 80−81 °C (lit.[5] mp 80−81 °C, recrystallized from hexane); IR (KBr) 3276, 3060, 2974, 1602, 1497, 1446, 1416, 1195, 1072, 1056, 1027, 869 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19−7.04 (m, 10H), 3.60 (s, 2H); EIMS *m*/*z* (relative intensity) 195 (43, M^+), 194 (42), 117 (13), 91 (100), 77 (5), 65 (22).

The authentic sample of triflylamide **6** was prepared from the corresponding amine by reaction with trifluoromethanesulfonic anhydride and triethylamine.[15]

*N-(1-Phenyl-2-phenethyl)trifluoromethanesulfonamide (**6**).* Purification by preparative TLC (ethyl acetate−hexane 3:7, R_f = 0.7): colorless prisms; mp 76−77 °C (recrystallized from dichloromethane−hexane at room temperature); IR (KBr) 3302, 3068, 3035, 1604, 1496, 1456, 1431, 1365, 1240−1160, 1144, 756, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39−7.29 (m, 4H), 7.29−7.22 (m, 2H), 7.16 (d, J = 7.5 Hz, 2H), 7.01−6.95 (m, 2H), 5.10 (d, J = 7.4 Hz, 1H), 4.90 (q, J = 7.4 Hz, 1H), 3.25−3.13 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6 (q), 135.5(q), 129.8 (t), 128.8 (t), 128.6 (t), 128.2 (t), 127.2 (t), 126.2 (t), 119.3 (q, $^1J_{CF}$ = 318.4 Hz), 60.8 (t), 44.2 (d); EIMS *m*/*z* (relative intensity) 238 [100%, $(M-Bn)^+$], 181 (3), 91 (27), 77 (16); HRMS (ESI, negative) *m*/*z* calcd for $C_{15}H_{13}F_3NO_2S$ $[(M-H)^-]$ 328.0619, found 328.0622.

Aziridine **8a** was converted to the corresponding trifluoroacetate salt by addition of excess trifluoroacetic acid to the combined organic layer before evaporation.

*cis-2,3-Dipropylaziridine (**8a**)·CF_3CO_2H:* colorless oil (7.7 mg, 87%); IR (neat) 3300, 2962, 2937, 2875, 1672, 1460, 1433, 1373, 1228, 1192, 1149, 1026, 617 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (br t, J = 4.4 Hz, 2H), 1.80−1.70 (m, 4H), 1.62−1.47 (m, 4H), 1.01 (t, J = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.2 (t), 26.1 (d), 20.4 (d), 13.4 (s); HRMS (ESI, positive) *m*/*z* calcd for $C_8H_{18}N$ $[(M - CF_3CO_2)^+]$ 128.1439, found 128.1442. After several attempts to measure the ^{13}C NMR spectrum, compound **8a**·TFA salt was found to be too labile to accumulate sufficient data to detect CF_3CO_2 group.

*cis-2-Methyl-3-phenylaziridine (**8b**):*[16] purification by preparative TLC (ethyl acetate−hexane 5:5, R_f = 0.5); colorless prisms (5.4 mg, 60%); mp 41 °C (lit.[16] mp 41−43 °C, recrystallized from dichloromethane); IR (neat) 3315, 2920, 2850, 1496, 1452, 1261, 737, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37−7.20 (m, 5H), 3.27 (d, J = 6.6 Hz, 1H), 2.43 (dq, J = 6.6, 5.9 Hz, 1H), 0.92 (d, J = 5.9 Hz, 3H); ESIMS (positive) *m*/*z* 134 $[(M + H)^+]$.

dx.doi.org/10.1021/jo300947h | J. Org. Chem. 2012, 77, 8317−8320

*cis-9-Azabicyclo[6.1.0]nonane (**8c**):*[17] purification by preparative TLC (methanol−dichloromethane 5:5, R_f = 0.4); colorless oil (1.2 mg, 58%); IR (neat) 3259, 2925, 2854, 1469, 1371, 1186, 924, 849, 781, 739 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.23−1.96 (m, 3H), 1.82−1.53 (m, 4H), 1.53−1.34 (m, 4H), 1.24−1.09 (m, 2H); ESIMS (positive) m/z 126 [$(M + H)^+$]. For **8c**, reactions were repeated three times to obtain reasonable amount of product.

*Dinonylamine (**10**):*[7f] white powder (17.8 mg, 93%); mp 34−35 °C (lit.[7f] mp 35−36 °C, recrystallized from dichloromethane); IR (neat) 3273, 3116, 2914, 2848, 1469, 1126, 901, 868, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.58 (t, J = 7.4 Hz, 4H), 1.47 (quint, J = 7.4 Hz, 4H), 1.35−1.18 (m, 24H), 0.88 (t, J = 7.2 Hz, 6H); EIMS m/z (relative intensity) 269 (3, M^+), 156 (100), 142 (4), 126 (2), 112 (5), 98 (7), 84 (7), 70 (9).

*Diheptylamine (**12**):*[7f] colorless oil (12.3 mg, 99%); IR (neat) 3286, 2925, 2854, 1466, 1377, 1130, 725 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.60 (t, J = 7.1 Hz, 4H), 1.48 (quint, J = 7.1 Hz, 4H), 1.37−1.17 (m, 16H), 0.88 (t, J = 6.7 Hz, 6H); EIMS m/z (relative intensity) 213 (5, M^+), 142 (16), 128 (100), 98 (6), 84 (6), 70 (9), 57 (24).

*N-Benzylcyclohexylamine (**14**):*[18] colorless oil (9.2 mg, 78%); IR (neat) 3307, 2925, 2852, 1495, 1362, 1348, 1122, 1028, 733, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.38−7.20 (m, 5H), 3.82 (s, 2H), 2.55−2.45 (m, 1H), 1.97−1.88 (m, 2H), 1.78−1.55 (m, 2H), 1.34−1.07 (m, 6H); EIMS m/z (relative intensity) 189 (21, M^+), 146 (78), 91 (100), 65 (14).

*N-Benzylcyclopropylamine (**16**):*[13b] colorless oil (12.5 mg, 93%); IR (neat) 3319, 3086, 3026, 2006, 2927, 2819, 1495, 1454, 1373, 1346, 1213, 1014, 733, 698 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35−7.20 (m, 5H), 3.83 (s, 2H), 2.19−2.11 (m, 1H), 0.48−0.41 (m, 2H), 0.41−0.35 (m, 2H); MS m/z (relative intensity) 147 (M^+, 7), 146 (22), 132 (16), 118 (7), 105 (6), 91 (100), 65 (17).

The authentic sample of triflylamide **17** was prepared from corresponding amine by the reaction with trifluoromethanesulfonic anhydride and triethylamine.[15]

*N-(1-Phenylpropyl)triflylamide (**17**):* colorless plates (2.4 mg, 25%, entry 2); mp 62−63 °C (recrystallized from dichloromethane); IR (KBr) 3286, 2972, 2879, 1441, 1371, 1356, 1230, 1186, 1151, 1028, 937, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43−7.29 (m, 3H), 7.29−7.22 (m, 2H), 5.08 (br d, J = 7.7 Hz, 1H), 2.01−1.84 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0 (q), 129.0 (t), 128.3 (t), 126.2 (t), 119.4 (q, $^1J_{CF}$ = 319.0 Hz), 61.5 (t), 30.8 (d), 10.5 (s); HRMS (ESI, negative) m/z calcd for $C_{10}H_{11}F_3NO_2S$ [$(M - H)^-$] 266.0463, found 266.0459.

*N-(1-Methyl-1-nonyl)trifluoromethanesulfonamide (**19**):* colorless oil (8.1 mg, 95%); IR (neat) 3303, 2929, 2858, 1460, 1431, 1230, 1194, 1151, 1024, 617 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.56 (br d, J = 8.5 Hz, 1H), 3.72−3.58 (m, 1H), 1.53 (q, J = 7.4 Hz, 2H), 1.44−1.17 (m, 15H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 115.4 (q, $^1J_{CF}$ = 318.3 Hz), 52.8 (t), 37.8 (d), 31.9 (d), 29.4 (d), 29.2 (d, 2C), 25.6 (d), 22.7 (d), 22.2 (s), 14.1 (s); HRMS (ESI, negative) m/z calcd for $C_{11}H_{21}F_3NO_2S$ [$(M - H)^-$] 288.1245, found 288.1236.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^1H NMR spectra of **5**, **6**, **8a**·TFA, **8b**, **8c**, **10**, **12**, **14**, **16**, **17**, and **19** and ^{13}C NMR spectra of **6**, **8a**, **17**, and **19**. This material is available free of charge via Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Young Scientists (B) (JSPS).

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dx.doi.org/10.1021/jo300947h | *J. Org. Chem.* 2012, 77, 8317−8320