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Highly Regio- and Stereoselective Asymmetric Bromoazidation of Chiral α,β-Unsaturated Carboxylic Acid Derivatives: Scope and Limitations

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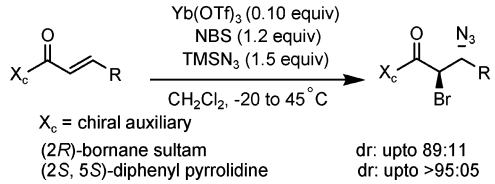

Lewis acid catalyzed asymmetric bromoazidation of chiral α,β-unsaturated carboxylic acid derivatives was performed using *N*-bromosuccinimide (NBS) and trimethylsilyl azide ($TMSN_3$) as the bromine and azide sources. Among the Lewis acids, $Yb(OTf)_3$ was found to be the best catalyst. Regio- and *anti*-selectivity of 100% and moderate to good diastereoselectivity (up to 89:11) with good yields were obtained when Oppolzer's bornane sultam chiral auxilairy was used. Diastereoselectivity of >95:05 was observed when (2*S*,5*S*)-2,5-diphenylpyrrolidine was used as the chiral auxiliary.

1,2-Haloazidation of alkenes is an important oxidative reaction in organic chemistry. These vicinal haloazides are versatile chemical intermediates for the synthesis of numerous functionalized compounds such as vinyl azides,[1] amines,[2] heterocycles,[3] and particularly aziridines.[4] The study of catalytic highly regio- and stereoselective haloazidation of alkenes, especially α,β-unsaturated carbonyl compounds, still remains a challenging task to organic chemists.

In the literature, 1,2-haloazides are usually prepared by addition of Br_2/NaN_3,[5] NBS/NaN_3,[4] I_2/AgN_3,[6] and ICl/NaN_3[7] onto alkenes. Although no problems have been reported, bromine azide and iodine azide are potentially explosive. There are also a few methods for the haloazidation of alkenes using $NBS/TMSN_3$/Nafion-H resin (cat.),[8] $PhI(OAc)_2/Et_4NX/TMSN_3$,[9] $CAN/NaI/NaN_3$,[10] $IPy_2BF_4/TMSN_3$,[11] and $Oxone/wet\text{-}Al_2O_3/KI/NaN_3$[12] mostly under noncatalytic conditions. The above methods except $IPy_2BF_4/TMSN_3$[11] have not been utilized for the haloazidation of α,β-unsaturated carbonyl compounds.

α,β-Unsaturated carbonyl compounds represent a synthetically useful class of substrate for various alkene oxidative reactions. In particular, haloazidation of α,β-unsaturated carbonyl compounds would provide the functionalized azidohalogenated compounds, which can be transformed to various useful organic compounds by replacing the halogen atom with a series of nucleophiles, where the azido functionality would serve as a protected amino group. However, little attention has been paid to haloazidation of α,β-unsaturated carbonyl compounds. Asymmetric haloazidation reaction has also not been explored. Herein, we report a Lewis acid catalyzed asymmetric bromoazidation of chiral α,β-unsaturated carboxylic acid derivatives using *N*-bromosuccinimide (NBS) and trimethylsilyl azide ($TMSN_3$) as the bromine and azide sources, in which 100% regioselectivity and high diastereoselectivity (>95:5) of the *anti*-α-bromo-β-azido carbonyl compounds are demonstrated with good yields.

A current interest in our laboratory is to develop asymmetric 1,2-halofunctionalization of alkenes, especially α,β-unsaturated carbonyl compounds.[13] A reliable possibility for exerting stereochemical control in the stereogenic centers is the use of the chiral auxiliary methodology. Recently we have found that Lewis acid activates NBS to facilitate the formation of bromonium ion intermediate from alkenes.[13a] Accordingly, we anticipated that a suitable Lewis acid might catalyze the bromoazidation of chiral α,β-unsaturated carboxylic acid derivatives containing a suitable chiral auxiliary with NBS and $TMSN_3$. Initially, asymmetric bromoazidation was investigated on cinnamic acid derivatives containing two well-known chiral auxiliaries such as Evans oxazolidinone[14] and Oppolzer's sultam.[15] *N*-Cinnamoyl-2-oxazolidinone **1a** was selected as a model substrate for the screening of the Lewis acids as catalysts for bromoazidation with NBS and $TMSN_3$ (Table 1). The metal halides and acetates, such as $CuCl_2$, $Co(OAc)_2$, $Cu(OAc)_2$, $Mn(OAc)_2$, and $Ni(OAC)_2$, showed poor to moderate catalytic effect for the bromoazidation of **1a** (entries 2−6). The metal triflates $Zn(OTf)_2$, $La(OTf)_3$, $Y(OTf)_3$, $Sm(OTf)_3$, and $Yb(OTf)_3$ as

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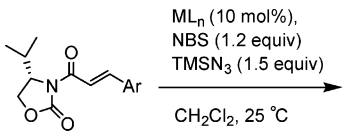
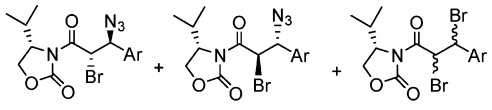
TABLE 1. Screening of Lewis Acids as Catalysts for the Bromoazidation of 1 with NBS and $TMSN_3$



1
1a: Ar = C_6H_5
1b: Ar = 4-$MeOC_6H_4$



2 **3** ***anti*-4/4'**

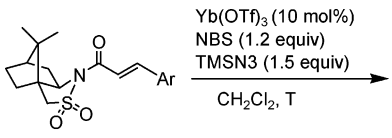
entry	sub-strate	MLn	*T* (h)	conv[a] (%)	ratio[a] (**2**+**3**):(**4**+**4′**)	dr of (**2**:**3**)[a]	yield[a] (%)
1	**1a**	none	24	<5	ND	ND	
2	**1a**	$CuCl_2$	24	60	71:29	57:43	70
3	**1a**	$Cu(OAc)_2$	24	75	88:12	55:45	47
4	**1a**	$Co(OAc)_2$	24	66	72:28	57:43	54
5	**1a**	$Mn(OAc)_2$	12	100	77:23	57:43	62
6	**1a**	$Ni(OAc)_2$	10	100	87:13	57:43	65
7	**1a**	$Mg(OTf)_2$	24	16	85:15	53:47	44
8	**1a**	$Cu(OTf)_2$	24	78	87:13	53:47	33
9	**1a**	$Zn(OTf)_2$	5.5	100	>95:5	56:44	77
10	**1a**	$La(OTf)_3$	12	100	>95:5	57:43	59
11	**1a**	$Y(OTf)_3$	3.5	100	>95:5	57:43	53
12	**1a**	$Sm(OTf)_3$	6	100	>95:5	55:45	52
13	**1a**	$Yb(OTf)_3$	4	100	>95:5	59:41	90 (87)
14	**1b**	$Yb(OTf)_3$	2	100	>95:5	55:45	97 (93)

[a] Determined by ^1H NMR spectrum analysis of the crude reaction mixture with succinic anhydride as an internal standard. Yields in the parentheses refer to the isolated yields. ND: not determined.

catalysts showed good results (entries 9−13). Among these, $Yb(OTf)_3$ was found to be the best catalyst. It should be noted that in the absence of Lewis acid the substrate **1a** did not undergo the bromoazidation reaction (entry 1). When **1a** was treated with $TMSN_3$ (1.5 equiv) and NBS (1.2 equiv) in CH_2Cl_2 in the presence of the $Yb(OTf)_3$ catalyst (10 mol %) and MS 4Å at room temperature (25 °C), within 4 h it gave the desired bromoazides **2a** and **3a** in good yield (entry 13). Without MS 4Å, 10−15% of halohydroxylated product[13a] was observed. The electron-rich cinnamoyl substrate **1b** also underwent the clean bromoazidation under the same reaction conditions. However, the diastereoselectivities of the above bromoazidation reactions were rather low.

$Yb(OTf)_3$-catalyzed bromoazidation of (2*R*)-*N*-cinnamoylbornanesultam **5a** did not occur at room temperature (Table 2; entry 1), but at 45 °C it provided the clean bromoazides **6a** and **7a** with moderate diastereoselectivity in good yield (entry 2). This $Yb(OTf)_3$-catalyzed bromoazidation reaction was further studied with other cinnamoyl substrates. Electron-rich cinnamoyl substrates **5b** and **5c** smoothly underwent the bromoazidation reaction at room temperature and afforded the bromoazides with good diastereoselectivity and yields (entries 3 and 5). Substrates **5b** and **5c** also responded to the bromoazidation reaction even at lower temperature such as −20 °C; however, diastereoselectivity went down (entries 4 and 6). The *ortho*-substituted electron-deficient cinnamoyl substrates **5d** and **5e** did not undergo the bromoazidation reaction even at 45 °C. However, substrates **5f** and **5g** containing the same electron-withdrawing groups at the *para* position underwent the bromoazidation reaction at 45 °C and provided a nonseparable mixture of

TABLE 2. $Yb(OTf)_3$-Catalyzed Bromoazidation of (2*R*)-*N*-Enoylbornanesultams 5



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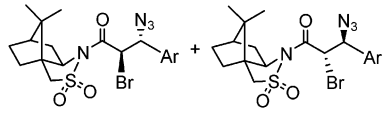

6 **7**

entry	substrate	Ar	*t* (h)	*T* (°C)	dr[a] (**6**:**7**)	yield[b] (%)
1	**5a**	C_6H_5	24	rt	NR	NR
2	**5a**	C_6H_5	4	45	70:30	86
3	**5b**	4-$MeOC_6H_4$	2	rt	86:14	85
4	**5b**	4-$MeOC_6H_4$	4	−20	60:40	87
5	**5c**	3,4-$MeOC_6H_3$	1	rt	89:11	88
6	**5c**	3,4-$MeOC_6H_3$	2	−20	65:35	84
7	**5d**	2-ClC_6H_4	24	45	NR	NR
8	**5e**	2-$NO_2C_6H_4$	24	45	NR	NR
9	**5f**	4-ClC_6H_4	36	45	75:25	85[c]
10	**5g**	4-$NO_2C_6H_4$	36	45	73:27	89[d]

[a] Determined by HPLC. NR: no reaction. [b] Combined isolated yields of **6** and **7** after column chromatography. NR: no reaction. [c] Combined isolated yield of **6f** and **7f** along with 17% of undesired compounds. [d] Combined isolated yield of **6g** and **7g** along with 24% of undesired compounds.

diastereomers[16] (entries 9 and 10). The bromoazidation of **5f** and **5g** required an excess of reagents (0.15 equiv of $Yb(OTf)_3$, 1.8 equiv of NBS, and 2.0 equiv of $TMSN_3$) and longer reaction time for 100% of conversion. Steric effect along with electronic effect might be responsible for substrates **5d** and **5e** not undergoing the bromoazidation reaction. Stereochemistry of the bromoazides **6** and **7** were assigned by analogy with our earlier work.[13a]

It was found that oxazolidinone chiral auxiliary provided poor diastereoselectivity (Table 1) and sultam showed moderate to good diastereoselectivity (Table 2) for the $Yb(OTf)_3$-catalyzed bromoazidation of **1** and **5**, respectively. We further investigated the bromoazidation reaction of α,β-unsaturated carboxylic acid derivatives possessing C_2-symmetry with 2,5-diphenylpyrrolidine[17] as a chiral auxiliary. When cinnamide **8a** was treated with $Yb(OTf)_3$ (0.10 equiv), $TMSN_3$ (1.5 equiv), and NBS (1.2 equiv) in CH_2Cl_2 at −20 °C, it provided *anti*-α-bromo-β-azido carbonyl compound **9a** with high diastereoselectivity (dr >95:05) and in good yield (Table 3; entry 1). However, bromoazidation of **8a** at room temperature or at 0 °C showed poor diastereoselectivity of 50:50 and 62:38, respectively.

This bromoazidation reaction was further studied using other cinnamoyl substrates containing electron-donating and -withdrawing substituents on the aromatic ring as well as alkenoyl substrates. It was found that the β-(2-naphthyl)-enoyl substrate **8b** smoothly underwent bromoazidation (entry 2) with high diastereoselectivity (94:06) at −20 °C. The more electron-rich cinnamoyl substrate **8c** also efficiently underwent bromoazidation reaction with slightly lower diastereoselectivity (85:15; entry 3). The electron-deficient cinnamoyl substrates **8d** and

(16) In addition, a minor amount (17−24%) of nonseparable undesired compounds was obtained.

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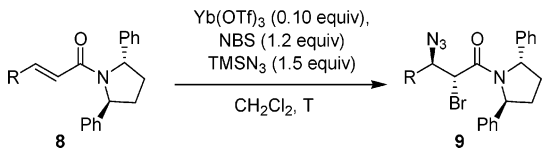
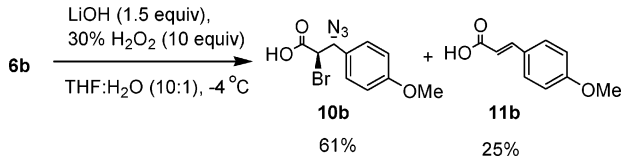
TABLE 3. Yb(OTf)$_3$-Catalyzed Bromoazidation of 8



entry	substrate	R	*t* (h)	*T* (°C)	dr[a]	yield[b] (%)
1	**8a**	C_6H_5	10	−20	>95:05	80
2	**8b**	2-naphthyl	8	−20	94:06	91
3	**8c**	3,4-$MeOC_6H_3$	2	−20	85:15	71
4[c]	**8d**	2-ClC_6H_4	24	25	NR	NR
5[c]	**8e**	2-$NO_2C_6H_4$	24	25	NR	NR
6	**8f**	4-ClC_6H_4	30	35	60:40	90[c]
7	**8g**	4-$NO_2C_6H_4$	30	35	50:50[d]	85[e]
8	**8h**	CH_3	6	−20	>95:05	87
9	**8i**	C_6H_{13}	24	25	>95:05	75

[a] Determined from the ^{1}H NMR spectrum of the crude reaction mixture. NR: no reaction. [b] Isolated yields of pure **9** after column chromatography. NR: no reaction. [c] Combined isolated yield of **9f** diastereomers along with 15% of undesired compounds. [d] Determined by HPLC. [e] Combined isolated yield of **9g** diastereomers along with 24% of undesired compounds.

SCHEME 1



8e, similar to **5f** and **5g**, did not undergo any bromoazidation reaction under the same reaction conditions, even with the use of excess reagents at room temperature (25 °C) and at 45 °C gave mixture of uncharacterized products. However, the substrates **8f** and **8g** containing the same electron-withdrawing groups at the *para* position yielded the bromoazides[18] **9f** and **9g** at 35 °C (entries 6 and 7). It is to be noted that bromoazidation of substrates **8f** and **8g** also required, similar to substrates **5f** and **5g**, an excess of reagents (0.15 equiv of Yb(OTf)$_3$, 1.8 equiv of NBS, and 2.0 equiv of $TMSN_3$) and longer reaction time for 100% of conversion. The crotonyl substrate **8h** underwent bromoazidation reaction at −20 °C and yielded the *anti*-α-bromo-*β*-azido carbonyl compound **9h** with >95:05 diastereoselectivity and 100% regioselectivity (entry 8). However, alkenoyl substrate **8i** showed the reactivity only at room temperature (25 °C) and provided the bromoazide compound **9i** with high diastereoselectivity and moderate yield (entry 9). The stereochemistry of **9** was confirmed from the single-crystal X-ray analysis of major compound **9c** (see Supporting Information).

Removal of the chiral auxiliary of the bromoazides would provide enantiomerically pure *anti*-α-bromo-*β*-azido carboxylic acids. As example, an aqueous THF (10:1) solution of compound **6b** was treated with LiOH (1.5 equiv) and 30% of H_2O_2 (10 equiv) at −4 °C. Within 6 h, it produced the *anti*-α-bromo-*β*-azido carboxylic acid **10b** in 61% yield along with a minor amount (25%) of parent cinnamic acid **11b** (Scheme 1), which might have been produced by retro-bromoazidation reaction under the alkaline condition. Sultam chiral auxiliary was recovered in 88% yield, and its optical purity was the same as that of the parent sultam.

(18) In addition, a minor amount (15−24%) of nonseparable undesired compounds was obtained.

In summary, we have developed a Lewis acid catalyzed asymmetric bromoazidation reaction of chiral α,*β*-unsaturated carbonyl compounds with NBS and $TMSN_3$ as the bromine and azide sources. The metal halides and acetates showed poor to moderate catalytic effect for the bromoazidation reaction, but metal triflates were found to be good catalysts. Among the metal triflates, Yb(OTf)$_3$ was found to be the best catalyst. Regio- and *anti*-selectivity of 100% and moderate to good diastereoselectivity (up to 89:11) with good yields were observed when bornanesultam was used as the chiral auxiliary. Use of the (2*S*,5*S*)-2,5-diphenylpyrolidine as a chiral auxiliary provided very high diastereoselectivity (>95:05) depending upon the reaction conditions. Alkenoyl, cinnamoyl, and electron-rich cinnamoyl substrates smoothly underwent the Yb(OTf)$_3$-catalyzed bromoazidation reactions with NBS and $TMSN_3$. The cinnamoyl substrates possessing electron-withdrawing substituents at the *para* position also responded to the reaction at higher temperature, but the cinnamoyl substrates containing electron-withdrawing substituents at the *ortho* position did not. This methodology offers an efficient method for the synthesis of chiral *anti*-α-bromo-*β*-azido carboxylic acid derivatives using commercially available NBS and $TMSN_3$ as the bromine and azide sources.

Experimental Section

General Procedure for the Bromoazidation of Compounds 1, 5, and 8. To a well-stirred suspended solution of substrate **1**, **5**, or **8** (0.50 mmol) and MS 4Å (0.100 g) in dry CH_2Cl_2 (2.5 mL; for the substrates **8**, 20% of THF was used when the reaction was performed at −20 °C) was added Yb(OTf)$_3$ (0.031 g, 0.05 mmol) under argon atmosphere. The temperature of the reaction mixture was maintaied as specified in Tables 1, 2, and 3. $TMSN_3$ (0.1 mL, 0.75 mmol) and NBS (0.107 g, 0.60 mmol) were successively added. Reaction was monitored by TLC, quenched with saturated $NaHCO_3$, and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated under vacuum. Flash column chromatography of the crude mixture using petroleum ether−EtOAc as an eluent gave pure α-bromo-*β*-azido carbonyl compounds **2**/**3**, **6**, and **9**. Minor isomers **7** and of **9** could not be isolated in pure form.

***anti*-(2*R*,2′*R*,3′*R*)-*N*-[3′-Azido-2′-bromo-3′-(4-methoxyphenyl)-propionyl]-bornanesultam (6b).** White solid, mp 144−146 °C; $[\alpha]^{25}_D$ = −116.57 (*c* 0.29, $CHCl_3$). IR (KBr, cm^{-1}): 500, 532, 547, 668, 831, 1026, 1116, 1136, 1177, 1215, 1255, 1294, 1314,-1329, 1384,1459, 1515, 1613, 1693 (CO), 2104 (N_3), 2342, 2361, 2961. ^{1}H NMR (200 MHz, $CDCl_3$): *δ* 0.99 (s, 3H), 1.17 (s, 3H), 1.20−1.55 (m, 3H), 1.85−2.05 (m, 2H), 2.10−2.25 (m, 2H), 3.55 (s, 2H), 3.82 (s, 3H), 4.04 (m, 1H), 4.90−5.10 (m, 2H), 6 94 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 19.8, 20.6, 26.4, 32.7, 37.5, 44.5, 45.2, 47.9, 48.8, 52.9, 55.2, 65.0, 65.9, 114.2 (2C), 127.1, 129.4 (2C), 160.3, 166.3. Anal. Calcd for $C_{20}H_{25}BrN_4O_4S$: C, 48.29; H, 5.07; N, 11.26. Found: C, 48.67; H, 5.06; N, 11.06. Diastereomeric ratio was determined by HPLC [ZORBAX Eclipse XBD-C18 column, acetonitrile/water (80/20 v/v), 1 mL/min, 250 nm].

***anti*-(2′*R*,3′*R*,2*S*,5*S*)-1-[3′-Azido-2′-bromo-3′-phenyl-propionyl]-2,5-diphenyl-pyrrolidine (9a).** White solid, mp 167−169 °C; $[\alpha]^{25}_D$ = −248.30 (*c* 0.94, $CHCl_3$). IR (KBr, cm^{-1}): 466, 536, 570, 604, 612, 668, 702, 755, 767, 802, 900, 1002, 1028, 1077, 1168, 1205, 1308, 1359, 1418, 1452, 1493, 1583, 1660 (CO), 2111 (N_3), 2342, 2361, 2961, 3028, 3057. ^{1}H NMR (200 MHz, $CDCl_3$): *δ* 1.60−2.05 (m, 2H), 2.35−2.75 (m, 2H), 4.12 (d, *J* = 10.5 Hz, 1H), 4.94 (d, *J* = 10.5 Hz, 1H), 5.36 (d, *J* = 7.7 Hz, 1H), 5.60 (d, *J* = 7.7 Hz, 1H), 6.75−6.90 (m, 2H), 7.00−7.65 (m, 13H). ^{13}C NMR (50 MHz, $CDCl_3$): *δ* 30.6, 32.9, 45.5, 62.4 (2C), 66.2, 125.1 (2C),

125.6 (2C), 126.9, 127.8 (2C), 128.0, 128.4 (2C), 128.5 (2C), 128.8, 129.2 (2C), 136.1, 142.1, 142.9, 166.0. Anal. Calcd for $C_{25}H_{23}BrN_4O$: C, 63.16; H, 4.88; N, 11.79. Found: C, 63.46; H, 5.25; N, 11.47.

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Supporting Information Available: General experimental details, characterization data of other bromoazides **2**/**3**, **6**, **9** and **10b**; ^{1}H, ^{13}C, and DEPT-135 NMR spectra of bromoazides **6**, **9**, and **10b**; HPLC traces of crude reaction mixture; ORTEP diagram and file for the single-crystal X-ray analysis of compound **9c** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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