Regioselective Bromocyclization of Unsaturated *N*-Tosylcarbamates Promoted by *N*,*N*-Dibromosulfonamides

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Abstract: Simple and highly regioselective bromo-N-cyclization and bromo-O-cyclization reactions of unsaturated *N*-tosylcarbamates have been developed. The use of *N*,*N*-dibromosulfonamides as brominating reagents plays an important role in these electrophilic cyclization reactions. This method is useful in organic synthesis. The desired products can be smoothly transformed into aziridines or epoxides.

Key words: alkenes, amides, cyclizations, electrophilic additions, regioselectivity

Electrophilic intramolecular halocyclizations of olefins are valuable synthetic transformations.[1] Various substrates, including unsaturated carboxylic acids, alcohols, amines, amides, and carbamates, have been widely used in syntheses of halogenated cyclic compounds.[2] Whereas halolactonization, haloetherification, and haloaminocyclization are efficient reactions,[1,3] halocyclizations of unsaturated substrates having ambident nucleophilic groups, such as amides or carbamates, can give mixtures of N- and O-cyclization products.[4] Generally, the O-selective products are obtained in preference to the N-selective products,[5] various methods have been developed to achieve regioselective halo-N-cyclization reactions, such as enhancement of the acidity of NH groups by the introduction of an electron-withdrawing group on the nitrogen atom[4d,6] conversion of the amide group into an imidate such as an *N*,*O*-disilyl imidate or thioimidate,[7] or the use of a strong base.[6b,8] However, under such conditions, the bromocyclization of the ambident substrate 2-phenylprop-2-en-1-yl tosylcarbamate (**1a**) resulted in low regioselectivities or yields (see below). Here, we describe an efficient, regioselective bromo-N- and -O-cyclization reactions of unsaturated *N*-tosylcarbamates by using *N*,*N*-dibromosulfonamides as brominating reagents.

We began our investigation by using tosylcarbamate **1a** as the substrate (Table 1).[9] After treatment of tosylcarbamate **1a** with *N*-bromosuccinimide in dichloromethane at 25 °C for four hours, thin-layer chromatography revealed the presence of two new spots with markedly different polarities. Column chromatography resulted in the isolation of the bromo-N-cyclization product, the oxazolidinone **2a**, and the bromo-O-cyclization product, the dioxolanimine **3a**, in 27% and 42% yields, respectively (Table 1, entry 1). We then examined the effects of stoichiometric amounts of various bases (entries 2–6). The regioselectivity was improved slightly by using potassium carbonate or sodium carbonate as the base (entries 2 and 3, respectively),[8,11] but when potassium *tert*-butoxide or triethylamine was used, oxazolidinone **2a** was obtained as the sole product in low yield (entries 4 and 6).

The structures of oxazolidinone **2a** and dioxolanimine **3a** were unambiguously confirmed by NMR spectroscopy and X-ray crystal studies (Figure 1).[10]

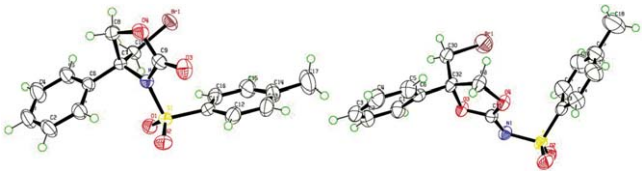

Figure 1 X-ray crystal structures of oxazolidinone **2a** (left) and dioxolanimine **3a** (right)

Electrophilic bromocyclizations catalyzed by Lewis or Brønsted acids or bases are well developed,[1,3] whereas catalytic regioselective bromocyclizations of ambident nucleophiles are less well understood.[12] We therefore attempted to optimize this cyclization by using various catalysts. Our preliminary results showed that the regioselectivity of bromo-O-cyclization could be improved by using a Lewis base (Table 1, entry 7), a Lewis acid (entries 9 and 10), or a Brønsted acid (entries 12–14) as a catalyst. However, a catalytic amount of 1,4-diazabicyclo[2.2.2]octane or scandium(III) triflate had less effect on the regioselectivity (entries 8 and 11).

We also examined the effects of various bromine sources (Table 1, entries 15–19) and, to our delight, we obtained the dioxolanimine **3a** as a single isomer in 89% yield when *N*,*N*-dibromo-4-nitrobenzenesulfonamide was used in the absence of a catalyst (entry 19). Moreover, the oxazolidinone **2a** was obtained exclusively in 88% yield when *N*,*N*-dibromo-4-toluenesulfonamide was used as brominating source in tetrahydrofuran containing a stoichiometric amount of potassium *tert*-butoxide (entry 21). As active reagents, *N*,*N*-dibromo sulfonamides can be used as bromine sources,[13,14] as amine sources,[15] as sources of both bromine and amine,[16] as oxidation reagents,[17] or as catalysts.[18] To the best of our knowledge, an improvement in the regioselectivity of bromocyclization reactions

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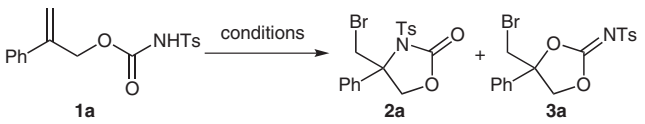
Table 1 Bromocyclization of 2-Phenylprop-2-en-1-yl Tosylcarbamate (**1a**)[a]



1a **2a** **3a**

Entry	Br source	Reagent or catalyst (equiv)	Solvent	Yield[b] (%) of **2a**	Yield[b] (%) of **3a**
1	NBS	–	CH_2Cl_2	27	42
2	NBS	K_2CO_3 (1.1)	MeCN	42	35
3	NBS	Na_2CO_3 (1.1)	MeCN	45	37
4	NBS	*t*-BuOK (1.1)	THF	29	–[c]
5	NBS	DBU (1.1)	CH_2Cl_2	32	35
6	NBS	Et_3N (1.1)	CH_2Cl_2	14	–[c]
7	NBS	Ph_3PS (0.1)	CH_2Cl_2	–[c]	65
8	NBS	DABCO (0.1)	CH_2Cl_2	27	60
9	NBS	$Cu(OTf)_2$ (0.1)	CH_2Cl_2	–[c]	11
10	NBS	$Y(OTf)_3$ (0.1)	CH_2Cl_2	–[c]	14
11	NBS	$Sc(OTf)_3$ (0.1)	CH_2Cl_2	36	26
12	NBS	TFA (0.1)	CH_2Cl_2	–[c]	43
13	NBS	HCO_2H (0.1)	CH_2Cl_2	–[c]	49
14	NBS	AcOH (0.1)	CH_2Cl_2	23	57
15	NBP[d]	–	CH_2Cl_2	5	54
16	NBA[e]	–	CH_2Cl_2	36	57
17	DBDMH[f]	–	CH_2Cl_2	28	63
18	$TsNBr_2$	–	CH_2Cl_2	56	41
19	$NsNBr_2$[g]	–	CH_2Cl_2	–[c]	89
20	DBDMH[f]	*t*-BuOK (1.1)	THF	54	–[c]
21	$TsNBr_2$	*t*-BuOK (1.1)	THF	88	–[c]

[a] Reaction conditions: **1a** (0.20 mmol), Br source (0.22 mmol), catalyst (0.02 mmol) or base reagent (0.22 mmol), solvent (3.0 mL), 25 °C, 4 h.
[b] Isolated yield.
[c] The desired product was not isolated by column chromatography.
[d] NBP = *N*-bromophthalimide.
[e] NBA = *N*-bromoacetamide
[f] DBDMH = 1,3-dibromo-5,5-dimethylhydantoin.
[g] $NsNBr_2$ = 4-$O_2NC_6H_4SO_2NBr_2$.

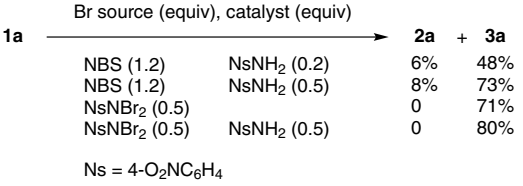
in the presence of *N*,*N*-dibromo sulfonamides has never previously been reported.

Having identified the optimal conditions,[19] we examined the reactions of other substrates (Table 2). With electron-deficient aryl-substituted unsaturated tosylcarbamates, the bromo-N-cyclization reactions proceeded smoothly with high regioselectivities and good yields (entries 2–4, 7, and 10). Substrates with electron-rich 3- or 2-tolyl substituents also gave high regioselectivities and good yields under the standard conditions (entries 8 and 11), whereas, substrates with 4-methoxyphenyl, 4-tolyl, or 3-methoxyphenyl substituents gave high regioselectivities and good yields when sodium carbonate was used as the base (entries 5–6 and 9). A substrate with an alkyl substituent also gave a good regioselectivity and yield (entry 13), as did a homoallylic tosylcarbamate (entry 14) and a trisubstituted alkene (entry 15).

Next, we examined the scope of the bromo-O-cyclization.[20] In general, the desired products were obtained with excellent regioselectivity and in good yields (Table 2). For aromatic substituted tosylcarbamates, this reaction worked well with both electron-deficient and electron-rich aryl substituents (entries 2–12), showing that the electronic character of the aromatic substituent has less effect on the regioselective bromo-O-cyclization reaction.

Note that *N*,*N*-dibromo sulfonamides play a crucial role in the regioselective cyclization reactions. Although the mechanism has not yet been clarified, the high regioselectivity of bromo-N-cyclization might result from the greater activity of *N*,*N*-dibromo-4-toluenesulfonamide as a brominating reagent.[14] A similar result was observed when 1,3-dibromo-5,5-dimethylhydantoin, a more active brominating reagent than *N*-bromosuccinimide, was used as a bromine source, and a high yield of a oxazolidinone **2a** was exclusively obtained in the presence of potassium *tert*-butoxide (Table 1, entry 20).

For the regioselective bromo-O-cyclization, we suspected that *N*,*N*-dibromo-4-nitrobenzenesulfonamide not only acts as an active brominating reagent, but that the resulting *N*-bromo-4-nitrobenzenesulfonamide byproduct catalyzes the reaction as a Brønsted acid.[21] To test this hypothesis, we treated tosylcarbamate **1a** with *N*-bromosuccinimide and a catalytic amount of 4-nitrobenzenesulfonamide and, indeed, both the regioselectivity and the yield were clearly improved (Scheme 1).



Scheme 1 Bromocyclization of tosylcarbamate **1a** in the presence of *N*-bromosuccinimide and 4-nitrobenzenesulfonamide

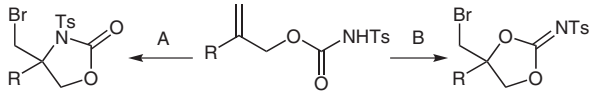
On the other hand, *N*-bromo-4-nitrobenzenesulfonamide might also act as a source of activated halogen. To test this hypothesis, we conducted the cyclization of tosylcarbamate **1a** in the presence of 0.5 equivalents of *N*,*N*-dibromo-4-nitrobenzenesulfonamide, and we obtained dioxolanimine **3a** exclusively in 71% yield, suggesting that both the bromine atoms in *N*,*N*-dibromo-4-nitrobenzenesulfonamide were used. Interestingly, when a catalytic amount of 4-nitrobenzenesulfonamide was added to the same mixture, the yield of the desired product **3a** was

slightly improved (Scheme 1). It appears that 4-nitrobenzenesulfonamide might also act as a Brønsted acid catalyst to promote the reaction. Furthermore, improvements in the regioselectivity of bromo-O-cyclization catalyzed by Brønsted acids were observed previously (entries 12–14). In these reactions, it is possible that a hydrogen bond is formed between the bromine source and the *N*-bromo-4-nitrobenzenesulfonamide or other Brønsted acid. Additionally, when *N*-bromosuccinimide was activated by a catalytic amount of a Lewis acid or base, the regioselectivity of the bromo-O-cyclization was improved (Table 1). These observations suggest that the regioselectivity of bromo-O-cyclization should be improved by the use of a more active bromine source.

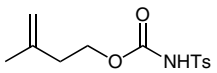
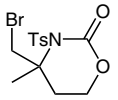
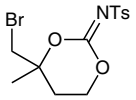
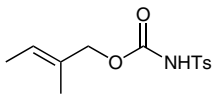
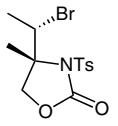
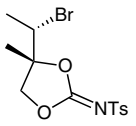
To demonstrate the synthetic utility of our method, we smoothly transformed the oxazolidinone **2a** and the dioxolanimine **3a** into the aziridine **4a** and the epoxide **5a**, respectively (Scheme 2); these products are useful building blocks in organic synthesis and medicinal chemistry.[22] Interestingly, the desired aziridine and epoxide were obtained with good overall yields from the single starting material **1a** after bromocyclization and reaction with potassium carbonate in methanol.

In summary, we have developed a general and efficient regioselective bromocyclization of unsaturated tosylcarbamates by using *N*,*N*-dibromosulfonamides as bromine sources. A wide range of oxazolidinone and dioxolanimine derivatives can be synthesized regioselectively. The

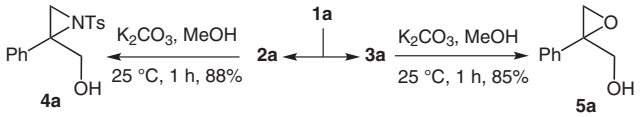
Table 2 Regioselective Bromocyclization of Unsaturated Tosylcarbamates[a]



2a–n **1a–n** **3a–n**

Entry	Substrate	R	Product	Yield[b] (%)	Product	Yield[b] (%)	*E*/*Z*[c]
1	**1a**	Ph	**2a**	88	**3a**	89	*E* only
2	**1b**	4-FC_6H_4	**2b**	88	**3b**	73	10:1
3	**1c**	4-ClC_6H_4	**2c**	77	**3c**	64	10:1
4	**1d**	4-BrC_6H_4	**2d**	65	**3d**	68	10:1
5	**1e**	4-$MeOC_6H_4$	**2e**[d]	83	**3e**	80	9:1
6	**1f**	4-Tol	**2f**[d]	74	**3f**	65	*E* only
7	**1g**	3-ClC_6H_4	**2g**	73	**3g**	66	11:1
8	**1h**	3-Tol	**2h**	82	**3h**	86	15:1
9	**1i**	3-$MeOC_6H_4$	**2i**[d]	59	**3i**	71	10:1
10	**1j**	3,5-$Cl_2C_6H_3$	**2j**	85	**3j**	67	16:1
11	**1k**	2-Tol	**2k**	71	**3k**	73	*E* only
12	**1l**	2-Naphthyl	**2l**	65	**3l**	63	*E* only
13	**1m**	Me	**2m**	81	**3m**	51	*E* only
14	 **1n**		 **2n**[d]	79	 **3n**	77	10:1
15	 **1o**		 **2o**[d]	87	 **3o**	56	*E* only

[a] Reaction conditions: A: **1** (0.20 mmol), $TsNBr_2$ (0.22 mmol), *t*-BuOK (0.22 mmol), THF (3.0 mL), 25 °C, 4 h. B: **1** (0.20 mmol), 4-$O_2NC_6H_4SO_2NBr_2$ (0.22 mmol), CH_2Cl_2 (3.0 mL), 25 °C, 1 h.
[b] Isolated yield.
[c] The ratio was determined by ^1H NMR analysis.
[d] Na_2CO_3 (0.22 mmol) was used instead of *t*-BuOK.
[e] Toluene (3.0 mL) was used instead of CH_2Cl_2.



Scheme 2 Synthesis of the aziridine **4a** and the epoxide **5a**

resulting products can be readily converted into synthetically useful building blocks. Further research on reactions with *N,N*-dibromosulfonamides as reagents is underway.

Acknowledgment

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(19) **4-(Bromomethyl)-4-phenyl-3-tosyl-1,3-oxazolidin-2-one (2a); Typical Procedure**
$TsNBr_2$ (72.4 mg, 0.22 mmol) was added in one portion to a stirred solution of *N*-tosylcarbamate **1a** (0.20 mmol) and *t*-BuOK (24.7 mg, 0.22 mmol) in anhydrous THF (3.0 mL) under N_2. The mixture was stirred at r.t. for 4 h then the reaction was quenched with sat. aq Na_2SO_3 (2.0 mL) and H_2O (2.0 mL). The mixture was extracted with EtOAc (3 × 5.0 mL) and the extracts were combined, washed with brine (10.0 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, PE–EtOAc) to give a white solid; yield: 72.2 mg (88%); mp 148–149 °C; IR (KBr): 1777, 1595, 1160, 811, 756, 618, 584 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.32 (m, 7 H), 7.11 (d, *J* = 8.2 Hz, 2 H), 4.65 (d, *J* = 9.2 Hz, 1 H), 4.50 (s, 2 H), 4.49 (d, *J* = 9.2 Hz, 1 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.0, 145.4, 137.5, 134.2, 129.4, 129.1, 128.9, 126.5, 124.3, 75.9, 67.7, 36.9, 21.6; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{16}BrNO_4SNa$: 431.9876; found: 431.9887.

(20) ***N*-[4-(Bromomethyl)-4-phenyl-1,3-dioxolan-2-ylidene]-4-toluenesulfonamide (3a); Typical Procedure**
$4\text{-}O_2NC_6H_4SO_2NBr_2$ (79.2 mg, 0.22 mmol) was added in one portion to a stirred solution of *N*-tosylcarbamate **1a** (0.20 mmol) in anhydrous CH_2Cl_2 (3.0 mL). The mixture was stirred at r.t. for 1 h and then the reaction was quenched with sat. aq Na_2SO_3 (2.0 mL) and H_2O (2.0 mL). The mixture was extracted with CH_2Cl_2 (3 × 5.0 mL) and the extracts were combined, washed with brine (10.0 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by flash column chromatography (silica gel, PE–EtOAc) to give a white solid; yield: 73.0 mg (89%); mp 125–126 °C; IR (KBr): 3126, 1778, 1160, 1093, 756, 584 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, *J* = 7.8 Hz, 2 H), 7.44–7.43 (m, 3 H), 7.32–7.28 (m, 4 H), 5.04 (d, *J* = 8.4 Hz, 1 H), 4.77 (d, *J* = 8.4 Hz, 1 H), 3.73 (d, *J* = 12.0 Hz, 1 H), 3.70 (d, *J* = 12.0 Hz, 1 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.5, 143.5, 138.1, 136.5, 129.8, 129.34, 129.25, 127.3 124.3, 88.2, 75.7, 37.3, 21.5; HRMS (ESI): *m*/*z* $[M + Na]^+$ calcd for $C_{17}H_{16}BrNO_4SNa$: 431.9876; found: 431.9881.

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