Letter

Stereoselective Synthesis of Enantioenriched 2-Chloro-2-aroylaziridines by Cascade Reaction between Aryl Nitriles, Silyldichloromethanes, and *tert*-Butanesulfinylimines

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Ⓢ *Supporting Information*

ABSTRACT: The cascade coupling of aryl nitriles, silyldichloromethanes, and *tert*-butanesulfinylimines is described, in which silyldichloromethyl-lithiums, generated from silyldichloromethanes in the presence of lithium diisopropylamide, undergo nucleophilic addition with aryl nitriles and subsequent [1,3]-aza-Brook rearrangement to give dichlorocarbanions bearing α-*N*-silyl imine (or their 1-azaenolate equivalents), which are then trapped by *tert*-butanesulfinylimines via an aza-Darzens-type transformation, affording enantioenriched 2-chloro-2-aroylaziridines after acidic hydrolysis of the *N*-silyl imine group. The stereochemistry of this cascade reaction can be tuned by selecting appropriate silyl groups on the silyldichloromethanes and altering the order of addition of the imines and the hexamethylphosphoramide additive.
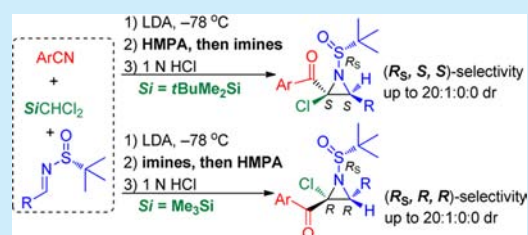
Aziridines are the smallest saturated aza-heterocycles that serve as key substructures in biologically active agents and useful precursors for the synthesis of other nitrogen-containing compounds via regioselective nucleophilic ring-opening reactions and other transformations.[1] *C*-Chloro-substituted aziridines are attracting increasing attention because of their characteristics and relatively broad reactivity,[2,3] as presented in more detail in a recent review.[2] Various synthetic protocols of aziridines have been developed, most of which involve transferring nitrogen to olefins or adding carbon to azomethines.[4] The aza-Darzens-type reaction is one of the oldest protocols for adding carbon to azomethines; it involves adding nucleophiles bearing α-leaving groups to imines followed by intramolecular nitrogen displacement.[5,6] This approach can be used to prepare *C*-chloro-substituted analogues.[7−11] For example, using enolates derived from dichloroacetates,[7] 3,3-dichloro-1-azaallylic anions,[8] or dichloromethyl anions generated from CH_2Cl_2[9] or $TMSCCl_2H$[10] as nucleophiles in the aza-Darzens-type transformation gives the corresponding 2-chloroaziridines. Despite these advances, methods are still needed to generate structurally diverse, functionalized 2-chloroaziridines using suitable nucleophiles.

Pioneering work by Oshima and co-workers showed that the reaction of lithium silyldichloromethane and aryl nitriles involves a nucleophilic addition/[1,3]-aza-Brook rearrangement[12] cascade, affording dichlorocarbanions bearing an α-*N*-silyl imine (or their 1-azaenolate equivalents, Scheme 1, **1 → 5** or **6**). The anions can subsequently be intercepted by alkyl halides, benzoyl chloride, or benzaldehyde, allowing construction of functionalized α,α-dichloroketones after acid hydrolysis of the *N*-silyl imine groups.[13] During our studies

Scheme 1. [1,3]-Aza-Brook Rearrangement-Mediated Coupling of Aryl Nitriles, Silyldichloromethanes, and *tert*-Butanesulfinylimines
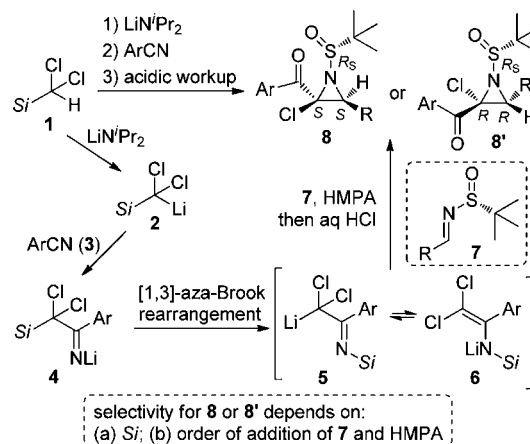
on Brook rearrangement reactions and their applications for the synthesis of nitrogen-containing compounds,[14] we speculated that the functionalized dichlorocarbanion intermediates generated from Oshima's protocol might serve as nucleophiles in an aza-Darzens-type transformation, resulting in an efficient pathway to access functionalized 2-chloroaziridines (Scheme 1, **5** or **6 → 8** or **8′**). Here, we present our study on this cascade reaction, which involves the coupling of aryl nitriles,

silyldichloromethanes, and *tert*-butanesulfinylimines.[15] We show that the one-pot coupling reaction provides rapid access to two enantioenriched *cis*-2-chloro-2-aroylaziridines[16] with high diastereocontrol. This diastereoselectivity is tuned by adjusting reaction conditions and the silyl groups on the silyldichloromethanes.

We began our studies by examining the ability of *tert*-butanesulfinylimine **7a** (R = Ph) to trap the nucleophilic intermediate arisen from the reaction between lithiated silyldichloromethane **1a** (TBSCHCl₂) and nitrile **3a** (Scheme 2, eq 1). As expected, the coupling reaction provided aza-

Scheme 2. Initial Results and Optimized Reaction Conditions (0.5 mmol Scale)
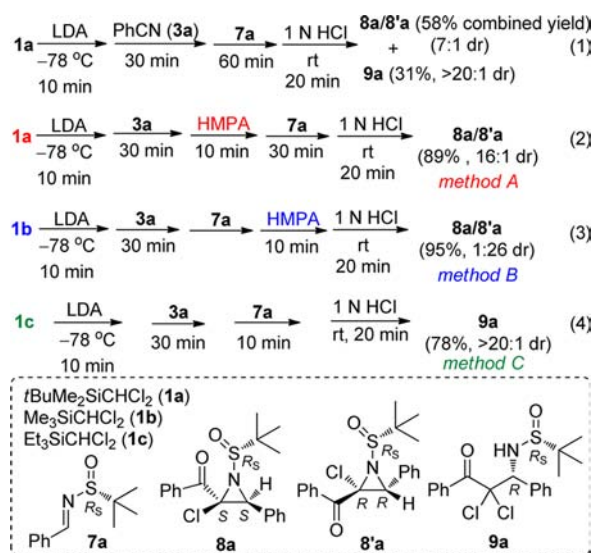
Darzens products **8a** and **8′a** in 58% yield with 7:1 diastereoselective ratio (**8a**:**8′a**, both *cis*) along with Mannich product **9a** in 31% yield with excellent diastereoselectivity (>20:1 dr) after acidic workup (1 N HCl). The stereochemistry of products **8a**, **8′a**, and **9a** was confirmed by X-ray crystallography.[17] The *trans*-aziridine diastereomers of aza-Darzens products, which have absolute configurations of (2R, 3S, RS) and (2S, 3R, RS) (not shown in Scheme 2), were not observed in these or any subsequent reactions. Adding hexamethylphosphoramide (HMPA) to the reaction accelerated the conversion of Mannich products to aziridines at low temperature. Thus, first adding imine **7a** and then HMPA to the reaction led to **8a** and **8′a** in 96% yield, albeit with low dr (1.5:1) (late addition of HMPA; reaction not shown in Scheme 2). Reversing the order of addition of HMPA and imine dramatically improved the diastereoselectivity to 16:1 (Scheme 2, eq 2, method A; early addition of HMPA).[18] Conversely, using silyldichloromethanes with less sterically hindered silyl groups reduced diastereoselectivity, as observed with TESCHCl₂ (**1c**, 9:1 dr) and TMSCHCl₂ (**1b**, 5:1 dr). Further investigation showed that using silyldichloromethane **1b** in the late-addition-of-HMPA protocol led to the cascade reaction to afford aziridines in 95% yield and excellent diastereocontrol favoring diastereomer **8′a** (1:26 dr, Scheme 2, eq 3, method B).[19] In contrast, performing the reaction in the absence of HMPA gave α,α-dichloro-β-amino ketone **9a** as the major product. Unfortunately, the **9a** produced in this way was contaminated with trace amounts of uncharacterizable silyl

group-containing byproducts that could not be separated by column chromatography. The contaminants were eliminated by replacing **1b** with **1c** (TESCHCl₂), giving **9a** as a pure compound (Scheme 2, eq 4, method C).[20] The three methods (A, B, and C) were scaled up 20-fold (>3.0 g scale) using optimized conditions and found to provide comparable yields and diastereoselectivities.

Under the optimized reaction conditions, we investigated substrate scope with respect to aryl nitrile and imine structures. Methods A and B were used to construct various aziridines, (2S, 3S, RS)-**8** and (2R, 3R, RS)-**8′**, respectively, with high yields and excellent diastereoselectivities in most cases (Table 1). Various *tert*-butanesulfinylimines derived from aryl and

Table 1. Diastereoselective Synthesis of 2-Chloro-2-aroylaziridines via Three-Component Coupling


			product (yield,[c] dr[d])	
entry	nitrile (3)	imine (7)	method A[a]	method B[b]
1	3a	7a	8a, 90%[e] (16:1)[e]	8′a, 96%[e] (>20:1)[e]
2	3a	7b	8b, 91% (11:1)	8′b, 99% (>20:1)
3	3a	7c	8c, 61% (>20:1); 82% (>20:1)[f]	g
4	3a	7d	8d, 92% (16:1)	8′d, 96% (>20:1)
5	3a	7e	8e, 89% (14:1)	8′e, 93% (>20:1)
6	3a	7f	8f, 95% (>20:1)	8′f, 97% (>20:1)
7	3a	7g	8g, 94% (18:1)	8′g, 95% (>20:1)
8	3a	7h	8h, 99% (>20:1)	8′h, 96% (>20:1)
9	3a	7i	8i, 89% (>20:1)	8′i, 92% (>20:1)
10	3a	7j	8j, 94% (19:1)	8′j, 99% (>20:1)
11	3a	7k	h	8′k, 91% (>20:1)
12	3b	7a	8l, 77% (6:1)	8′l, 41% (>20:1)
13	3c	7a	8m, 71% (3:1)	8′m, 81% (10:1)
14	3d	7a	8n, 91% (11:1)	8′n, 93% (>20:1)
15	3e	7a	8o, 60% (10:1)	8′o, 76% (8:1)
16	3f	7a	8p, 55% (10:1)	8′p, 78% (8:1)
17	3g	7a	8q, 80% (11:1)	8′q, 85% (12:1)
18	3h	7a	8r, 89% (13:1)	8′r, 93% (>20:1)
19	3i	7a	8s, 91% (11:1)	8′s, 98% (>20:1)

[a]Method A: TBSCHCl₂ (0.85 mmol), LDA (0.75 mmol), aryl nitrile (0.9 mmol), HMPA (3.0 mmol), and imine (0.50 mmol) in anhydrous THF under argon at −78 °C unless otherwise noted. [b]Method B: TMSCHCl₂ (1.0 mmol), LDA (1.00 mmol), aryl nitrile (1.10 mmol), imine (0.50 mmol) and HMPA (4.0 mmol) in anhydrous THF under argon at −78 °C unless otherwise noted. [c]Isolated yield of major diastereoisomer. [d]The ratios of **8**:**8′** were determined by ¹H NMR analysis of crude reaction mixtures. [e]Reaction at 10.0 mmol scale (>3.0 g scale). [f]Used 2.5 equiv of **3a**, 2.3 equiv of **1a**, 2.0 equiv of LDA, and 8.0 equiv of HMPA. [g]Product was unstable under standard workup and purification conditions. [h]Only trace amounts of aziridine were observed.

heteroaryl aldehydes were successfully applied to the cascade process with **3a** and **1a**/**1b** (entries 1–10). The reaction tolerated aryl imines bearing electron-withdrawing and -donating groups at the para position, as well as ortho- and meta-substituted aryl imines. Unsubstituted and substituted phenyl cyanides were suitable coupling partners (entries 12–19). However, the reaction was incompatible with heteroaryl nitriles, such as 2-furonitrile, 2-thiophenecarbonitrile, and 2-pyridinecarbonitrile, or with aliphatic nitriles, such as *t*BuCN, *n*PrCN, and BnCN. Reactions with these nitriles gave no three-component coupling products, leaving the imines intact. The substrate scope of method C for preparing α,α-dichloro-β-amino ketones **9** was also investigated (see Supporting Information).

Next, the dechlorination of 2-chloro-2-benzoylaziridine **8a** was examined (Scheme 3). When excess SmI$_2$ was used (5.0

Scheme 3. SmI$_2$-Mediated Dechlorination of 2-Chloro-2-aroylaziridine 8a and α,α-Dichloro-β-amino ketone 9a[a]
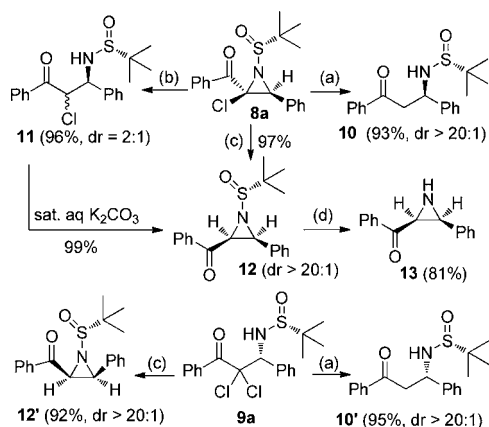

[a]Conditions: (a) 5.0 equiv SmI$_2$, THF/MeOH, −78 °C to rt, 1 h; (b) 2.5 equiv SmI$_2$, THF, −78 °C, 30 min; then, aq NH$_4$Cl; (c) 2.5 equiv SmI$_2$, THF, −78 °C, 30 min; then quenched with satd aq K$_2$CO$_3$, −78 °C to rt; (d) 4 N HCl, dioxane/MeOH, rt.

equiv),[21] ring-opening and subsequent dechlorination of **8a** proceeded efficiently to afford β-amino ketone **10** in 93% yield. This SET reagent-mediated reduction could be stopped at the stage of ring-opening of aziridine by reducing the amount of SmI$_2$ to 2.5 equiv, providing α-chloro-β-amino ketone **11**. In the presence of K$_2$CO$_3$, compound **11** could be further converted to *cis*-2-benzoylaziridine **12** in 99% yield with excellent diastereoselectivity (>20:1).[22] Conversion of **8a** to **12** was achieved in one pot with no loss of yield or dr. Similar conversions were also successful for α,α-dichloro-β-amino ketone **9a**: both β-amino ketone **10′** and *cis*-2-benzoylaziridine **12′** were obtained in high yield and excellent dr.[23]

We rationalized these stereochemical outcomes based on the well-known HMPA-mediated nonchelated open transition state (TS-1, method A)[24] as well as the lithium-chelated chairlike 6/4-membered bicyclic transition state (TS-2, method B).[25] On the basis of these transition states, a bulky silyl group, such as TBS, should strengthen the facial selectivity of 1-azaenolate in its approach toward the imine in TS-1, whereas a less bulky silyl group, such as TMS, should facilitate bonding of lithium to the nitrogen of the 1-azaenolate in TS-2. Following C−C bond formation, stereospecific 3-*exo-tet* ring closure of the initially formed adducts should occur via conformers-1 and -2. In these conformers, nonbonding interactions between the *N*-silyl imine

groups and the R groups are minimized, leading to the observed *cis*-aziridine diastereomers **8** and **8′**, respectively.

Scheme 4. Rationalization of the Diastereoselectivity of the Addition-Cyclization Cascade
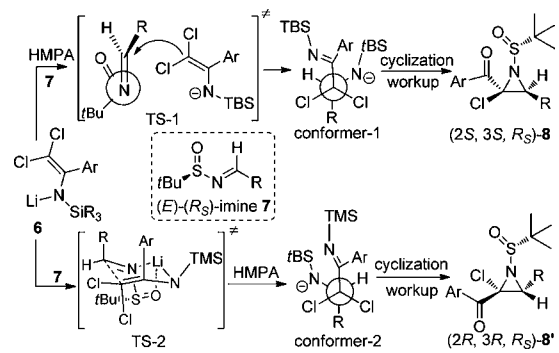
In summary, we have developed an efficient three-component coupling reaction for stereoselective synthesis of enantioenriched 2-chloro-2-aroylaziridines. The cascade transformation involving nucleophilic addition, [1,3]-aza-Brook rearrangement, and aza-Darzens-type transformation enables rapid construction of both *cis*-aziridine diastereomers from the same coupling partners through selection of suitable silyl groups on the silyldichloromethanes and appropriate timing of HMPA addition.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

and , **8′a**, and **9a**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01954.

　Experimental details and characterization data of all new compounds (PDF)
　X-ray crystal structure of compound **8a** (CIF)
　X-ray crystal structure of compound **8′a** (CIF)
　X-ray crystal structure of compound **9a** (CIF)

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Notes
The authors declare no competing financial interest.

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(17) See the Supporting Information for single-crystal structures of **8a**, **8′a**, and **9a**.

(18) Lewis acids that are normally used to activate imines and improve diastereoselectivity of Mannich-like reactions, such as BF$_3$-Et$_2$O, ZnCl$_2$, TiCl$_4$, or Ti(O*i*Pr)$_4$, completely inhibited imine coupling in the three-component conversion described herein.

(19) In contrast to **1b**, the reaction using **1c** provided coupling products **8a** and **8′a** in 92% combined yield with moderate dr (1:6).

(20) This reaction gave the aziridines **8a** and **8′a** in 17% yield with 7:1 dr, and the two compounds were easily separated during the purification of **9** by column chromatography.

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