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Asymmetric Substitution at the Tetrasubstituted Chiral Carbon: Catalytic Ring-Opening Alkylation of Racemic 2,2-Disubstituted Aziridines with 3-Substituted Oxindoles

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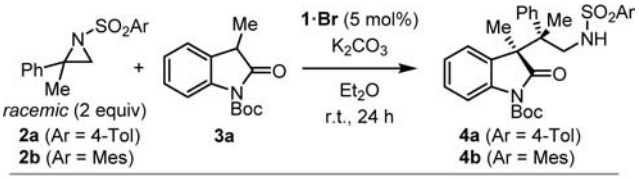
Supporting Information

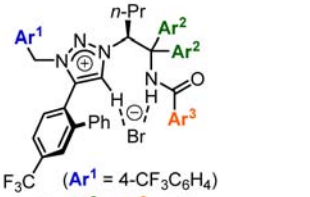
ABSTRACT: A highly diastereo- and enantioselective ring-opening alkylation of racemic 2,2-disubstituted aziridines with 3-substituted oxindoles is achieved under the catalysis of a chiral 1,2,3-triazolium salt. This reaction represents a hitherto unknown, catalytic stereoselective carbon−carbon bond formation through direct substitution at the tetrasubstituted chiral carbon.

Carbon−carbon bond formation through direct substitution at the chiral carbon center is one of the most fundamental and powerful transformations for constructing chiral organic molecular frameworks. In particular, stereospecific or stereoselective nucleophilic substitution at the trisubstituted chiral carbon of secondary (pseudo)halides, epoxides, and aziridines with carbon nucleophiles has been the subject of extensive research.[1,2] In contrast, asymmetric substitution at the tetrasubstituted chiral carbon remains a formidable pursuit, primarily because of the stringent difficulties associated with the preparation of enantiomerically pure tertiary (pseudo)halides and stereospecific carbon−carbon bond-forming substitution at their sterically congested chiral carbons. While several stereospecific reactions such as ring opening of optically active epoxides[3−5] and 1,2-metalate rearrangement of boronate complexes[6] have been reported, stereoselective direct substitution reactions at the tetrasubstituted chiral carbon are entirely unknown, and so are catalyst-controlled systems.[7] Here, we disclose the first successful example of such a transformation, that is, asymmetric ring-opening alkylation of racemic 2,2-disubstituted aziridines with 3-substituted oxindoles catalyzed by chiral 1,2,3-triazolium salts.[8] This catalytic protocol offers a robust strategy for the highly diastereo- and enantioselective construction of contiguous all-carbon quaternary stereocenters.[9,10]

N-Activated aziridines are regarded versatile pseudohalides, and their catalytic asymmetric ring-opening reactions with carbon nucleophiles provide useful tools for the synthesis of various nitrogen-containing biologically active compounds.[11−13] In consideration of the prominent reactivity of such aziridines, we attempted the reaction of racemic *N*-sulfonyl 2-methyl-2-phenylaziridine **2** with 3-methyloxindole **3a** (Table 1). Thus, **3a** was treated with 2 equiv of racemic *N*-tosyl aziridine **2a** in the presence of L-alanine-derived chiral 1,2,3-triazolium bromide

Table 1. Asymmetric Ring-Opening Alkylation of Racemic 2,2-Disubstituted Aziridines 2 with Oxindole 3a Catalyzed by Chiral 1,2,3-Triazolium Salt 1·Br[a]





entry	1	2	% yield[b]	dr[c]	% ee[d]
1	**1a**	**2a**	78	2:1	94/92
2	**1a**	**2b**	88	3.7:1	95/80
3	**1b**	**2b**	56	4.4:1	93/86
4	**1c**	**2b**	95	16:1	99/nd
5	**1d**	**2b**	99	>20:1	99/nd

[a]Reactions were carried out with 0.20 mmol of **2**, 0.10 mmol of **3a**, and 0.10 mmol of K_2CO_3 in the presence of **1** (5 mol %) in Et_2O (1.0 mL) at room temperature for 24 h. [b]Isolated yield based on the amount of **3a**. [c]Determined by ^1H NMR analysis of crude reaction mixture. [d]Determined by chiral HPLC analysis. nd = not determined.

1a·Br[14] (5 mol %) and K_2CO_3 (1 equiv) in Et_2O at room temperature for 24 h. The ring-opening substitution occurred exclusively at the fully substituted carbon to give alkylation product **4a**, which had adjacent quaternary chiral carbons, in 78% yield (entry 1). Although the diastereoselectivity was low, each diastereomer of **4a** was obtained in a highly enantioenriched form. Notably, the identity of the *N*-sulfonyl substituent was important for stereocontrol, and a slightly higher diastereoselectivity was attained in the reaction with *N*-mesitylsulfonyl aziridine **2b** without compromising on the enantioselectivity (entry 2). This preliminary information

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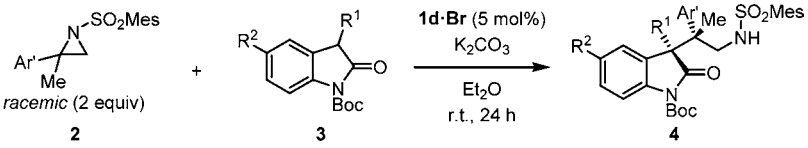
Table 2. Substrate Scope[a]



entry	2 (Ar′)	3 (R^1, R^2)	4	% yield[b]	dr[c]	% ee[d]
1	**2c** (3-MeC_6H_4)	**3a** (Me, H)	**4c**	92	>20:1	99
2	**2d** (3-MeOC_6H_4)	**3a**	**4d**	98	19:1	99
3[e]	**2e** (3-ClC_6H_4)	**3a**	**4e**	87	>20:1	99
4[e]	**2f** (3-BrC_6H_4)	**3a**	**4f**	81	11:1	98
5[e,f]	**2g** (4-MeC_6H_4)	**3a**	**4g**	82	14:1	99
6	**2h** (4-ClC_6H_4)	**3a**	**4h**	92	>20:1	99
7	**2i** (4-BrC_6H_4)	**3a**	**4i**	96	16:1	99
8	**2j** (4-*t*-BuO_2CC_6H_4)	**3a**	**4j**	87	>20:1	99
9	**2k** (2-Naph)	**3a**	**4k**	97	>20:1	99
10	**2b** (Ph)	**3b** (Et, H)	**4l**	71	>20:1	99
11[e,f]	**2b**	**3c** (Bn, H)	**4m**	80	>20:1	99
12	**2b**	**3d** (Me, Me)	**4n**	84	>20:1	99
13	**2b**	**3e** (Me, OMe)	**4o**	88	12:1	99
14[g]	**2b**	**3f** (Me, F)	**4p**	71	12:1	99

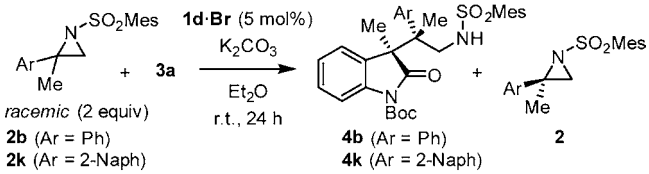
[a]Unless otherwise noted, reactions were carried out with 0.20 mmol of **2**, 0.10 mmol of **3**, and 0.10 mmol of K_2CO_3 in the presence of **1d·Br** (5 mol %) in Et_2O (1.0 mL) at room temperature for 24 h. [b]Isolated yield based on the amount of **3**. [c]Determined by ^{1}H NMR analysis of the crude reaction mixture. [d]Enantiomeric excesses of the major diastereomer were indicated, which were determined by chiral HPLC analysis. [e]Performed with 10 mol % of **1d·Br**. [f]Conducted at 10 °C for 48 h. [g]With 2.2 equiv of aziridine **2**.

prompted us to pursue structural modification of the modular chiral triazolium ion **1** in order to improve the catalytic efficiency and stereocontrolling ability. A systematic evaluation of the effect of individual substituent structures revealed that the L-norvaline-derived triazolium ion possessing strongly electron-withdrawing trifluoromethyl groups at the triazolium C(4) phenyl ring and the N(3) benzylic appendage (**1c**) allowed the reaction to proceed smoothly with a high level of diastereoselectivity as well as complete enantiocontrol (entries 3 and 4). Further tuning of the electronic and steric attributes of **1** led to the identification of triazolium bromide **1d·Br** as the optimal catalyst, which efficiently promoted bond formation between **3a** and **2b** to afford **4b** quantitatively with near-perfect diastereo- and enantioselectivity (entry 5). The relative and absolute stereochemistry of the alkylation product **4b** was unequivocally determined by X-ray crystallographic analysis.[15]

Experiments were then conducted to probe the substrate scope of this unprecedented catalytic, highly stereoselective ring-opening alkylation of 2,2-disubstituted aziridines. The representative results are summarized in Table 2. With regard to aziridine **2**, incorporation of both electron-donating and -withdrawing groups onto aryl substituents was tolerated, and good-to-excellent diastereo- and enantioselectivities were uniformly observed (entries 1−7). Moreover, functionalized and fused aromatic systems were also accommodated (entries 8 and 9). Not only 3-methyloxindole **3a** but also other alkyl-substituted oxindoles could be employed as the nucleophilic reacting partner, and the corresponding alkylation products were obtained with almost complete stereoselectivities, although a considerable decrease in the reactivity was inevitable, probably because of the increased steric hindrance (entries 10 and 11). This ring-opening alkylation was also applicable to oxindoles with substituents having different electronic properties on the aromatic nuclei (entries 12−14).

In the present catalytic asymmetric ring-opening substitutions, the starting aziridines **2** were recovered in optically active form. For instance, after the reaction of racemic aziridine **2b** with oxindole **3a** under the optimized conditions, **2b** was recovered with 76% ee (99% recovery yield based on the amount of **3a**) (Scheme 1). In the reaction of 2-naphthyl-

Scheme 1. Enantiomeric Excess of Recovered Aziridines 2[16]



4b: 99%, dr = >20:1, 99% ee, **2b**: 99% recovery, 76% ee, S = 17
4k: 97%, dr = >20:1, 99% ee, **2k**: 99% recovery, 76% ee, S = 17

substituted aziridine **2k** with **3a**, enantiomerically enriched **2k** (76% ee) was also obtained, and the absolute configuration of the major enantiomer was assigned to be *R* by single-crystal X-ray diffraction analysis (Figure 1). The relative and absolute stereochemistry of the corresponding alkylation product **4k** was established simultaneously. This information confirmed that (*S*)-aziridine was preferentially consumed and that the ring-

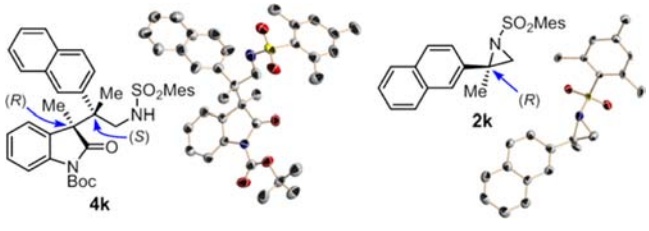


Figure 1. ORTEP diagrams of product **4k** and recovered **2k** (calculated hydrogens are omitted for clarity).

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opening substitution would mainly proceed in a stereoinvertive manner.[17,18]

To gain further insight into the reaction profiles, we performed kinetic experiments, which revealed that the present catalytic ring-opening alkylation had a pseudo-first-order dependence on the catalyst **1d·Br** and zero-order dependence on both aziridine **2** and oxindole **3**. When the amount of K_2CO_3 was increased, the reaction exhibited first-order kinetics.[15] In addition, the alkylation did not take place at all in the absence of **1d·Br**. These findings clearly indicate that the rate-limiting step is not carbon−carbon bond formation. In the phase-transfer reaction of the solid−liquid biphasic system without additional water, the process on the surface of the solid particle, that is the formation of potassium enolate in the present case, is usually slow compared to the processes in the organic phase.[19] As a consequence, ion exchange for the generation of the requisite chiral triazolium enolate **A** from the corresponding potassium enolate and either **1d·Br** (initial process) or the intermediary triazolium amide **B** (main process) becomes a turnover-limiting step of the catalytic cycle (Figure 2). We then examined the relationship between

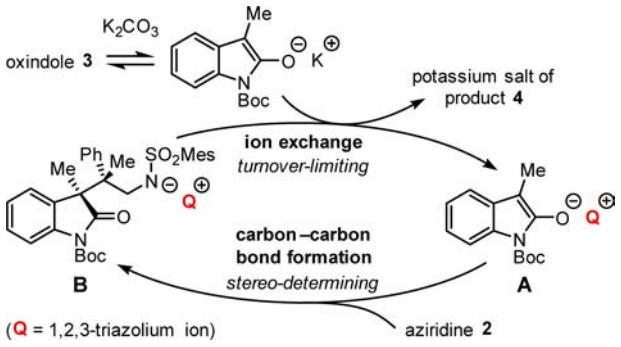


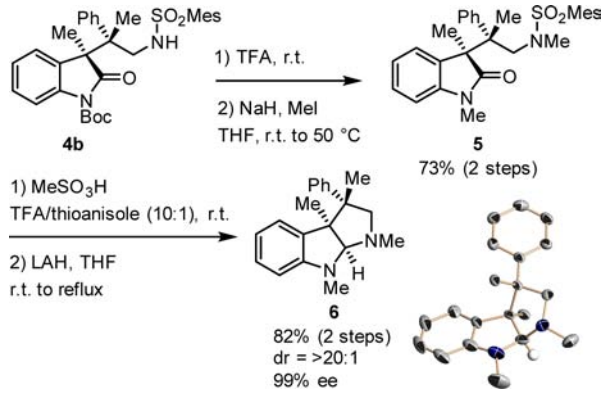
Figure 2. Main processes in catalytic cycle.

the ee of the catalyst **1d·Br** and the ee of the product **4b** and observed a pronounced positive nonlinear effect.[15,20] This phenomenon strongly suggests that more than one triazolium ion is involved in the stereo-determining alkylation transition state, although the precise structure remains open for discussion.

Finally, the synthetic utility of this catalytic protocol was clearly demonstrated by its application to the concise asymmetric synthesis of a pyrrolidinoindoline derivative, which is the ubiquitous core structure of a wide array of biologically relevant natural products.[21] As exemplified in Scheme 2, removal of the *N*-Boc group of **4b** (dr = >20:1, 99% ee) by treatment with trifluoroacetic acid, followed by the methylation of both oxindole and sulfonylamide nitrogens, furnished **5**. Subsequent desulfonylation was effected by the exposure of **5** to methanesulfonic acid in trifluoroacetic acid/thioanisole (10:1), and the following reductive cyclization gave rise to the stereochemically pure pyrrolidinoindoline **6** bearing vicinal all-carbon quaternary stereocenters in good yield.

In conclusion, we have developed a highly diastereo- and enantioselective ring-opening alkylation of racemic 2,2-disubstituted aziridines with 3-substituted oxindoles by using an appropriately modified chiral 1,2,3-triazolium salt as the requisite catalyst. This method represents the first catalytic, stereoselective carbon−carbon bond-forming reaction through direct substitution at a tetrasubstituted chiral carbon and should find fruitful applications in the rapid assembly of densely

Scheme 2. Derivatization of Alkylation Product 4b into Pyrrolidinoindoline 6



substituted chiral organic molecules, particularly those having contiguous all-carbon quaternary stereocenters. Further mechanistic studies to fully elucidate the transition state structure are the focus of ongoing investigations.

■ ASSOCIATED CONTENT

Supporting Information

Representative experimental procedures, additional experimental data, analytical data for new compounds, and crystallographic data for **1a·Cl**, **4b**, **4k**, **2k**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(14) The three-dimensional molecular structure of **1a·Cl** was unambiguously determined by single-crystal X-ray diffraction analysis. For detailes, see the Supporting Information.

(15) For details, see the Supporting Information.

(16) $S = k_{fast}/k_{slow} = \mathrm{In}[(1 - C/100)(1 - ee/100)]/\mathrm{In}[(1 - C/100)(1 + ee/100)]$ (C = conversion of **2**, ee = enantiomeric excess of recovered **2**).

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(18) As a control experiment, the reaction of **3a** with 1 equiv of **2b** under otherwise identical conditions with those described in Table 2 was conducted, which resulted in the formation of a diastereomeric mixture of **4b** (dr = 4:1) in 60% yield with 97% ee for the major diastereomer. This result also indicated that the kinetic resolution of aziridine **2** was operative in the present asymmetric ring-opening alkylation.

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