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The Concise Synthesis of Spiro-Cyclopropane Compounds via the Dearomatization of Indole Derivatives

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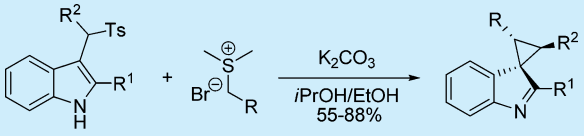
Supporting Information

ABSTRACT: A concise synthesis of spiro-cyclopropane compounds from indole derivatives and sulfur ylides has been developed via a dearomatization strategy. Moreover, the spiro-cyclopropane compounds could be conveniently transformed to rearomatized indole derivatives in the presence of acids.

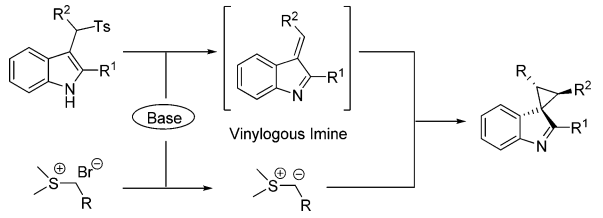


Dearomatization reactions are important transformations of aromatic compounds because they directly lead to a variety of ring systems.[1] Additionally, they are highly efficient for constructing quaternary carbon centers[2] and used as the key steps in the total synthesis of many natural products.[3] In this regard, dearomatization reactions of indoles,[4] pyridines,[5] phenols,[6] pyrroles,[7] etc., have been developed. Among them, compounds with an indole skeleton have attracted enormous attention because of the important biological activities of their derivatives.[8] Dearomatization reaction of indoles has been extensively studied over the past decades, with particular focuses on alkylative dearomatization[9] and oxidative dearomatization.[10] In addition, the Diels−Alder pathway with various dienophiles[11] and organocatalyzed Michael/Mannich cyclization cascade reactions were also demonstrated in dearomatization reactions of indoles.[12] Besides, several transition-metal-catalyzed dearomatization reactions of indoles were also documented.[13] Although great progress has been made in the dearomatization reaction of indoles, most of the methods required harsh conditions and designed catalysts that are currently commercially unavailable. Thus, to develop a facile and efficient method for a dearomatization reaction of indole derivatives from readily available starting materials would be of considerable significance in organic chemistry.

Spiro-cyclopropane structure motifs are ubiquitous and prevalent in various anticancer agents and pharmaceuticals.[14] In addition, they also serve as valuable synthetic intermediates for a wide range of organic compounds.[15] Therefore, the construction of spiro-cyclopropane skeletons has achieved extensive attention, and a plethora of efficient methods have been developed for the synthesis of these important structures, including from alkenes by Simmons−Smith and related reactions or with ylides, transition-metal-catalyzed carbene transfer, Michael-initiated ring closure (MIRC), and organocatalytic cyclopropanation, which have been described in the literature.[16,17]

The use of an arylsulfonyl group as an auxiliary group is still a prominent synthetic strategy in organic synthesis.[18] Recently, the utilization of the arylsulfonyl group in connection with indole has attracted intriguing interests. The sulfonyl moiety at the benzylic position of 3-substituted indoles acts as a good leaving group, which enables the generation of vinylogous imines intermediates under basic conditions. The generating vinylogous imines intermediates are equal to α,β-unsaturated imines, which are able to react with numerous nucleophiles.[19] Considering that sulfur ylides act as a nucleophile under the basic condition,[20] the vinylogous imine intermediates can be generated from arenesulfonylindole under the mild basic conditions. We envisioned that ylides could react with the vinylogous imine intermediates to furnish the spiro-cyclopropane compounds (Scheme 1). Herein, we report an efficient

Scheme 1. Synthesis of Spiro-Cyclopropane Compounds via the Dearomatization of Indoles



dearomatization reaction of indole derivatives in which arylsulfonyl group acts as a leaving group with sulfonium salts under mild conditions to synthesize spiro-cyclopropane compounds.

Initially, our investigation was launched with 2-methyl-substituted arenesulfonylindole **1a** (1.0 equiv), sulfonium salt **2a** (1.5 equiv), K_2CO_3 (3.0 equiv) as the base in CH_2Cl_2

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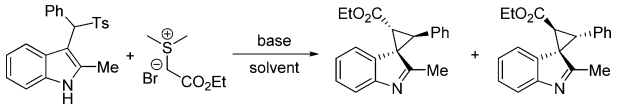
(Table 1). Delightfully, the spiro-cyclopropane products **3a** and **3a′** were obtained with 71% yield and a ratio of 3:1. Next, a

Table 1. Optimization for the Reaction of 2-Methylarenesulfonylindole 1a with Sulfonium Salt 2a[a]



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

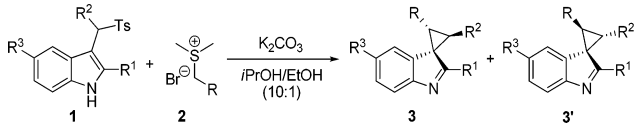
entry	solvent	base	yield (%)[b]	dr[c]
1	CH_2Cl_2	K_2CO_3	74	3:1
2	toluene	K_2CO_3	<5	–
3	CH_3OH	K_2CO_3	26	4:1
4	EtOH (E)	K_2CO_3	87	6:1
5	*i*PrOH (P)	K_2CO_3	55	19:1
6	E/P (1:1)	K_2CO_3	83	7:1
7	E/P (1:5)	K_2CO_3	84	8:1
8	E/P (1:10)	K_2CO_3	83	13:1
9	E/P (1:10)	Cs_2CO_3	66	6:1
10	E/P (1:10)	DIPEA	75	7:1
11	E/P (1:10)	Na_2CO_3	61	15:1
12	E/P (1:10)	KO^{t}Bu	<5	–

[a]Condition: 0.25 mmol **1a**, 0.375 mmol **2a**, 0.75 mmol base, 3.3 mL of solvent, room temperature, 12 h. [b]Isolated yields of the mixture of **3a** and **3a′**. [c]All of the dr (**3a**/**3a′**) were determined by ^{1}H NMR spectroscopy. E/P: EtOH/*i*PrOH.

series of solvents were examined, and to our delight, high yield was obtained from EtOH (87%, Table 1, entry 4), and *i*PrOH gave the excellent 19:1 of diastereoselectivity (Table 1, entry 5). Thus, the next screening was focused on the mixed solvents. When the ratio of *i*PrOH/EtOH was 10:1, the yield could be retained, and the diastereoselectivity could be raised up to 13:1 (Table 1, entry 8); several other bases were also examined, and moderate yields and diastereoselectivities were obtained (Table 1, entries 9−11). So, the optimal conditions were established, K_2CO_3 as the base and *i*PrOH/EtOH (10:1) as the solvent.

With the optimized conditions in hand, we explored the reaction scope using a variety of 2-substituted arenesulfonylindoles **1** and sulfonium salts **2** as listed in Table 2. A range of sulfonium salts were examined, and medium to good yields and excellent diastereoselectivitives were achieved (55−78% yields, dr = 13:1 to >20:1, Table 2, entries 2−5). Especially, when R was aryl carbonyl, up to >20:1 diastereoselectivity were obtained. The steric and electronic property of the aryl substituents had little effect on the yield and diastereoselectivity for substituents R^2 (Table 2, entries 7−13); all of them could get satisfactory yields and diastereoselectivity. The electronic nature of the indole core had little influence on the outcome of the reactions; when the sulfonylindoles with fluorine or methyl as substituent at the 5-position of the indole ring, both gave excellent yields and satisfactory diastereoselectivities (Table 2, entries 14−15). It is worthy of note that when the 2-position of the indole ring was phenyl, the diastereoselectivity was reversed (Table 2, entry 16), which may ascribe to the change of geometry of C═C bond and relative stability of vinylogous imine intermediate due to steric hindrance of phenyl group. To our delight, the 2-position unsubstituted sulfonyl indoles were also suitable reaction partners using ethanol as solvent and provided the desired products in good yields and excellent diastereoselectivities (Table 2, entries 17−20).[21]

Table 2. Scope for the Reaction of Arenesulfonylindoles 1 with Sulfonium Salts 2[a]



1 **2** **3** **3'**

2a, R = CO_2Et **2d**, R = $CO(4\text{-}MeC_6H_4)$
2b, R = $CONEt_2$ **2e**, R = $CO(4\text{-}MeOC_6H_4)$
2c, R = COC_6H_5

entry	$R^1/R^2/R^3$	2	3, yield[b] (%)	dr[c]
1	Me/Ph/H	**2a**	**3a**, 83	13:1
2	Me/Ph/H	**2b**	**3b**, 78	13:1
3	Me/Ph/H	**2c**	**3c**, 60	>20:1
4	Me/Ph/H	**2d**	**3d**, 55	>20:1
5	Me/Ph/H	**2e**	**3e**, 71	>20:1
6	Me/*n*-Pentyl/H	**2a**	**3f**, 56	>20:1
7	Me/4-MeC_6H_4/H	**2a**	**3g**, 88	14:1
8	Me/3-MeC_6H_4/H	**2a**	**3h**, 86	13:1
9	Me/2-MeC_6H_4/H	**2a**	**3i**, 84	13:1
10	Me/4-ClC_6H_4/H	**2a**	**3j**, 82	14:1
11	Me/3-ClC_6H_4/H	**2a**	**3k**, 75	12:1
12	Me/4-BrC_6H_4/H	**2a**	**3l**, 81	15:1
13	Me/3-$MeOC_6H_4$/H	**2a**	**3m**, 69	11:1
14	Me/Ph/5-Me	**2a**	**3n**, 88	12:1
15	Me/Ph/5-F	**2a**	**3o**, 83	10:1
16	Ph/4-BrC_6H_4/H	**2a**	**3p**, 70	1:5
17[d]	H/Ph/H	**2a**	**3q**, 82	>20:1
18[d]	H/4-ClC_6H_4/H	**2a**	**3r**, 81	>20:1
19[d]	H/4-BrC_6H_4/H	**2a**	**3s**, 83	>20:1
20[d]	H/*n*-Pentyl/H	**2a**	**3t**, 85	>20:1

[a]Condition: 0.25 mmol **1**, 0.375 mmol **2**, 0.75 mmol K_2CO_3, 3.0 mL of *i*PrOH, 0.3 mL of EtOH, room temperature, 12 h. [b]Isolated yields of the mixture of **3** and **3′**. [c]All of the dr (**3**/**3′**) were determined by ^{1}H NMR spectroscopy. [d]3.3 mL of EtOH was used.

The structure and stereochemistry of spiro-cyclopropanes **3a** (Figure 1), **3p**, and **3p′** were verified by the combination of

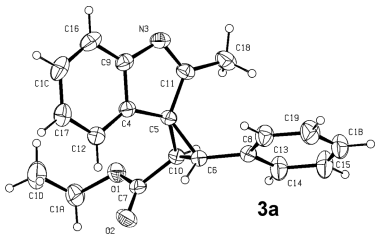


Figure 1. X-ray crystal structure of compound **3a**.

NMR, HRMS spectroscopy, and single-crystal X-ray diffraction anaysis (for X-ray crystal structure of **3p** and **3p′**, see the Supporting Information).[22]

Furthermore, a preliminary study on the enantioselective version of this dearomatization reaction was also tried. Using the known chiral sulfonium salts[23] originally developed by Aggarwal, only moderate enantioselectivity 64% ee and low yield (29%) were obtained (Scheme 2). These promising results demonstrated the potential for synthesis of the chiral spiro-cycopropane derivatives, although more efficient catalytic systems need to be developed.

It is noted that the model substrates **1a** and **2a** could also be carried out at a gram scale. As illustrated in Scheme 3, the target

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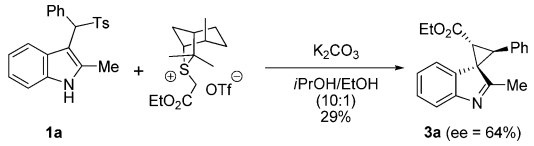
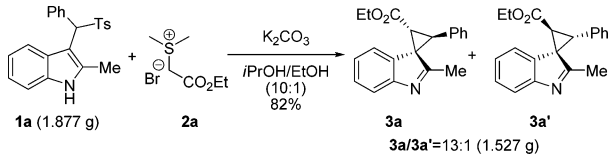
Scheme 2. Synthesis of Chiral Spiro-Cyclopropane with the Chiral Sulfonium Salt



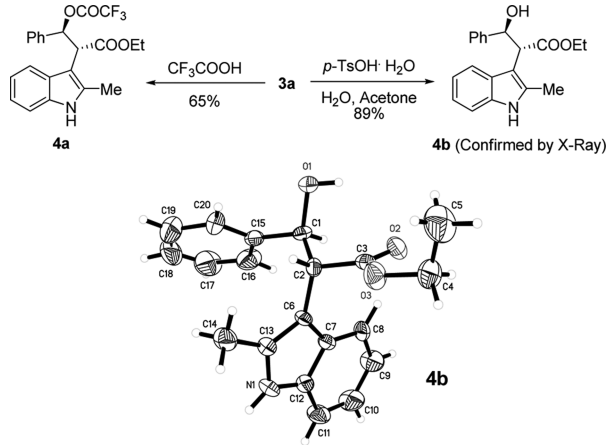
products **3a** and **3a′** could be obtained in 82% yield and the diastereoselectivity could be kept with 13:1.

Scheme 3. Scale-up of Model Substrates



In order to explore the application of our methodology, we tried to transform them to rearomatized 2,3-disubstituted indole derivatives (Scheme 4). Pleasingly, when trifluoroacetic

Scheme 4. Selective Transformations of 3a to Rearomatized Indole Derivatives



acid was added, the expected rearomatized product **4a** was obtained in 65% yield with excellent diastereoselectivity; trifluoroacetic acid served as both acid and nucleophile in this reaction. When water was chosen as nucleophile, the product hydroxyl ester **4b** could also be obtained with 89% yield with excellent diastereoselectivity. The single-crystal of **4b**[24] was successfully obtained and confirmed the relative configuration (see the Supporting Information).

In conclusion, we have developed a concise and efficient dearomatization method for the rapid and facile synthesis of spiro-cyclopropane compounds via the vinylogous imine intermediates generated from readily available arenesulfonylindoles and sulfonium salts under mild basic conditions. This methodology provides a succinct access to substituted spiro-cyclopropane derivatives. Moreover, the spiro-cyclopropanes could be conveniently transformed to rearomatized indole derivatives with excellent yields in the presence of acids. Our ongoing studies are focused on an asymmetric version of this reaction.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, X-ray structures, data for the determination of enantiomeric excess, and NMR spectra. 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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