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$POCl_3$-Promoted Trifluoromethylthiolation-based Vicinal Bifunctionalization of Indoles with CF_3SO_2Na

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Keywords: trifluoromethylthiolation, indole, bifunctionalization, perfluoromethylthiolation, sodium trifluoromethanesulfinate

An efficient trifluoromethylthiolation-based vicinal bifunctionalization of indoles with sodium trifluoromethanesulfinate in the presence of phosphorus oxychloride were achieved to introduce a chlorine atom into the 2-position under transition-metal-free and mild conditions. The protocol could also extend to other sodium perfluoroalkanesulfinates or phosphorus oxybromide. The possible pathway was proposed based on the experimental results.

Introduction

The importance of organofluorine compounds, especially in the area of material and life sciences,[1] has recently attracted increasing attention since fluorine or fluoroalkyl groups in organic molecules can change their physical and biochemical properties.[2] One of the fluorine-containing groups, trifluoromethylthio (CF_3S), has led to a resurgence of interest in organofluorine chemistry due to its electron-withdrawing effect and good lipophilicity.[3]

In recent years, numerous methods involving transition metal catalysis or transition-metal-free conditions for the introduction of trifluoromethylthio group into aromatic compounds have been developed.[4] In early times, more reactive and practical trifluoromethanesulfenyl chloride (CF_3SCl) was used as electrophilic trifluoromethylthiolating reagents,[5] but its corrosive and toxic properties limited its use. Although shelf-stable and easy-to-handle CF_3S-N or CF_3S-O based electrophilic trifluoromethylthiolating reagents[6] and a series of highly efficient nucleophilic trifluoromethylthiolating reagents (such as $AgSCF_3$,[7] Me_4NSCF_3 [8] and $CuSCF_3$[9]) were established and demonstrated high efficiency in a range of trifluoromethylthiolation reaction in the past decades, the preparation of these reagents required multiple steps before the reaction, and expensive reagents could be required.

Therefore, it's greatly necessary to explore the cheap and readily accessible trifluoromethylthiolating reagents. For this purpose, CF_3SO_2-based trifluoromethylthiolating reagents have aroused great interest of organic and medicinal chemists in the range of trifluoromethylthiolation reaction.[10] In 2009, the group of Magnier isolated a small quantity of trifluoromethylthiolation product in the preparation of Umemoto reagent using CF_3SO_2K and biphenyl derivatives.[11] In addition, trifluoromethanesulfonyl hypervalent iodonium ylide was used for copper-catalyzed trifluoromethylthiolation reaction reported by the group of Shibata, and afforded the desired CF_3S-substituted products. [12] Recently, various methods have emerged involving the combination of trifluoromethanesulfonyl chloride (CF_3SO_2Cl) and different phosphorus reagent, such as CF_3SO_2Cl/PMe_3,[13] $CF_3SO_2Cl/(EtO)_2P(O)H$,[14] and CF_3SO_2Cl/PPh_3.[15]

As we all know, sodium trifluoromethanesulfinate (CF_3SO_2Na, Langlois reagent) is a cheap and easily available commercial chemical. In 2015, Li, Zhang et al reported a direct trifluoromethylthiolation of $C(sp^2)$-H bonds with $CF_3SO_2Na/(EtO)_2P(O)H$ system catalyzed by CuCl.[16] And transition-metal-free fluoroalkylthiolation reaction was achieved using the similar reagent system very recently.[17] Meanwhile, Cai and coworkers also developed a direct trifluoromethylthiolation of indole derivatives with CF_3SO_2Na/PPh_3 system, but an additional X^+ source such as *N*-chlorophthalimide was essential for this reaction.[18] Recently, Lu's group and our group have simultaneously reported a selective trifluoromethylthiolation and trifluoromethylsulfinylation of indoles with sodium trifluoromethanesulfinate promoted by different phosphorus reagent under transition-metal-free conditions.[19] However, above methods are trifluoromethylthiolation-based monofunctionalization of indoles. So far, there is no report about the bifunctionalization of indoles with sodium trifluoromethanesulfinate. With our continuing to study the CF_3SO_2Na/[P] system, we surprisingly found that 2-chloro-3-((trifluoromethyl)thio)-indole derivatives as bifunctionalization products could be obtained. Herein, the results are reported in this paper.

Results and Discussion

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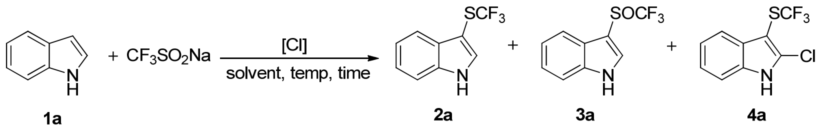
In our previous research, when indole (**1a**) was treated with 1.2 equivalent of sodium trifluoromethanesulfinate (CF_3SO_2Na) and 1.0 equivalent of phosphorus oxychloride in *N, N*-dimethyl formide (DMF) at room temperature in 0.5 hour, ^{19}F NMR monitoring indicated that trifluoromethylsulfinylation product (**3a**) was obtained in 89% yield along with trace amount of trifluoromethylthiolated compound (**2a**) (Table 1, entry 1). But interestingly enough, if we continued to extend the reaction time to 12 hours, compound **2a** and 2-chloro-3-((trifluoromethyl)thio)-1*H*-indole (**4a**) were obtained in 27% and 20% yield, respectively, and the yield of **3a** reduced to 38% (entry 2). Inspired by this result, we commenced searching for a suitable condition to improve the yield of bifunctionalization product (**4a**). Through investigating the ratio of the reactants, we found that the increasing the amount of phosphorus oxychloride or sodium trifluoromethanesulfinate was benefitful for bifunctionalization reaction (entries 3-11). The yield of **4a** was improved to 66% and 22% yield of **2a** was still observed by employing a 1:1.2:3 ratio of indole/CF_3SO_2Na/$POCl_3$ (entry 6). Subsequently, we tested the effect of the reaction temperature, when the reaction was employed at 50 °C, a higher yield (78%) was obtained and reaction time could be shorten to 3 hours (entry 12). Further increasing the reaction temperature did not improve the yield of **4a** (entry 13). Other solvents, such as acetonitrile, tetrahydrofuran (THF), 1,4-dioxane, toluene, dimethyl sulfoxide (DMSO) and dimethylamide (DMA), were not suitable for this reaction (entries 14−19). We also attempted to examine the effect of different chlorination reagents. When $POCl_3$ was replaced by oxalyl chloride [$(COCl)_2$] or thionyl chloride ($SOCl_2$), the yield of **4a** was decreased to 42% and 35%, respectively, and a large amount of **2a** were produced (entries 20-21). Therefore, the optimal reaction conditions were set to 1.2 equivalent of CF_3SO_2Na, 3.0 equivalent of $POCl_3$ in DMF at 50 °C.

Table 1: Optimization of conditions for the bifunctionalization reaction of **1a** with CF_3SO_2Na.

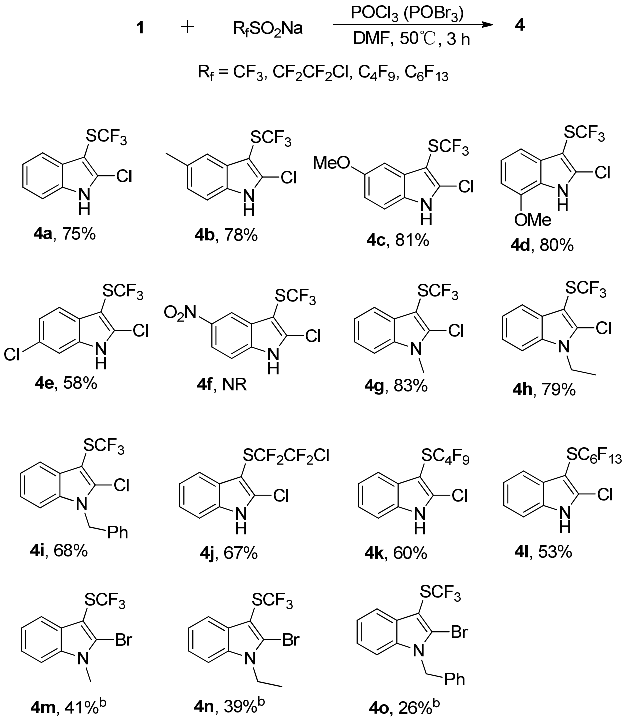


entry[a]	[Cl]	**1a**:CF_3SO_2Na:[Cl]	solvent	temp/°C	time/h	**2a**/%[b]	**3a**/%[b]	**4a**/%[b]
1	$POCl_3$	1:1.2:1	DMF	Rt	0.5	trace	89	0
2	$POCl_3$	1:1.2:1	DMF	Rt	12	27	38	20
3	$POCl_3$	1:1.2:1.5	DMF	Rt	12	32	12	32
4	$POCl_3$	1:1.2:2	DMF	rt	12	27	trace	43
5	$POCl_3$	1:1.2:2.5	DMF	rt	12	21	trace	47
6	$POCl_3$	1:1.2:3	DMF	rt	12	22	trace	66
7	$POCl_3$	1:1.2:3.5	DMF	rt	12	16	trace	44
8	$POCl_3$	1:1.5:1	DMF	rt	12	19	29	21
9	$POCl_3$	1:1.5:1.5	DMF	rt	12	25	15	37
10	$POCl_3$	1:1.5:2	DMF	rt	12	24	20	54
11	$POCl_3$	1:1.5:3	DMF	rt	12	trace	trace	53
12	$POCl_3$	1:1.2:3	DMF	50	3	trace	trace	78
13	$POCl_3$	1:1.2:3	DMF	80	3	23	trace	51
14	$POCl_3$	1:1.2:3	CH_3CN	50	3	20	trace	65
15	$POCl_3$	1:1.2:3	THF	50	3	18	14	57
16	$POCl_3$	1:1.2:3	1.4-Dioxane	50	3	NR	NR	NR
17	$POCl_3$	1:1.2:3	Toluene	50	3	13	trace	62
18	$POCl_3$	1:1.2:3	DMSO	50	3	NR	NR	NR
19	$POCl_3$	1:1.2:3	DMA	50	3	11	trace	70
20	$(COCl)_2$	1:1.2:3	DMF	50	3	38	trace	42
21	$SOCl_2$	1:1.5:3	DMF	50	3	40	trace	35

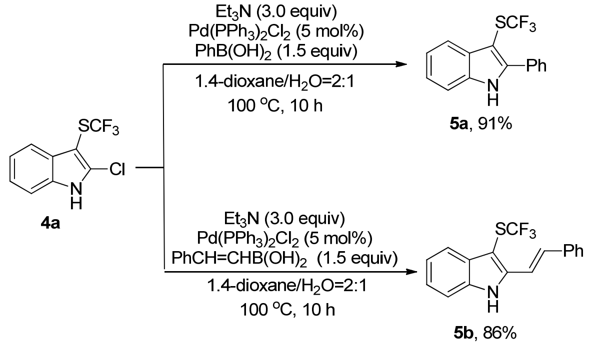
a) Reaction conditions: **1a** (0.4 mmol), CF_3SO_2Na (0.48-0.6 mmol), [Cl] (0.4-1.4 mmol), solvent (1.0 mL). b) Determined by ^{19}F NMR using $PhCF_3$ as internal standard.

With the optimized conditions in hand, we explored the substrate scope of the $POCl_3$-promoted bifunctionalization reaction. Both electron-rich and electron-deficient indoles were evaluated and the results are summarized in Scheme 1. The electronic property of the indoles had light effect on the reaction. Indoles **1b-1d** bearing methyl or methoxy-substitution produced 2-chloro-3-((trifluoromethyl)thio)-1*H*-indole derivatives **4b-4d** in higher yields. Chlorine substituted indole could also react with CF_3SO_2Na, but only 58% yield of **4e** was obtained. The reaction of nitro-substituent indole (**1f**) under standard conditions was also investigated. Unfortunately, no product was observed and all of indole was recovered. It is worth mentioning that the reaction of *N*-methyl, *N*-ethyl and *N*-benzyl indoles proceeded well and afforded the expected products (**4g-4i**) in moderate to good yields. In addition, we have also extended this protocol to sodium perfluoroalkanesulfinates (R_fSO_2Na), such as $ClCF_2CF_2SO_2Na$, *n*-$C_4F_9SO_2Na$ and *n*-$C_6F_{13}SO_2Na$. Gratefully, perfluoromethylthiolation-based bifunctionalization took place smoothly to give expected products (**4j-4l**) in moderate yields. In order to further expend the scope of this reaction, phosphorus oxybromide ($POBr_3$) was also tried instead of phosphorus oxychloride as phosphorous reagent, and 2-bromo-3-((trifluoromethyl)thio)-indole derivatives (**4m-4o)** were successfully isolated although yields were low, while acetonitrile was used as solvent.

Scheme 1. The bifunctionalization reaction of indoles and R_fSO_2Na [a]



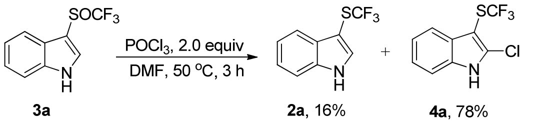
a) Reaction conditions: **1** (0.4 mmol), R_fSO_2Na (0.48 mmol), $POCl_3$ or $POBr_3$ (1.2 mmol), DMF (1 mL) under N_2 at 50 °C, isolated yields. b) Reaction was carried out in CH_3CN.



Scheme 2. The transformation of **4a**.

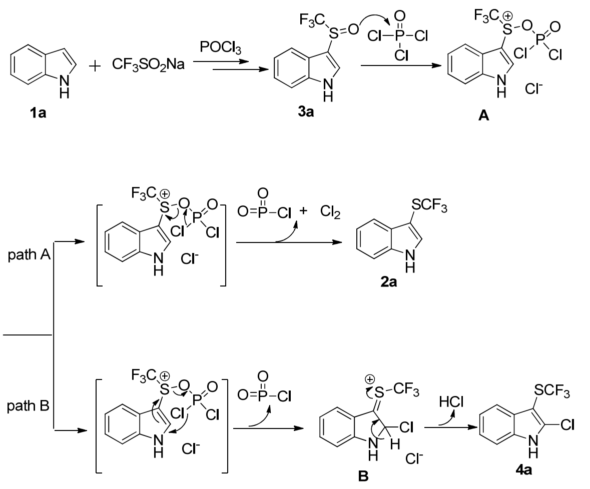
The bifunctionalization products **4** obtained in Scheme 1 allowed modification of the trifluoromethylated compounds due to the existence of chloro and bromo substitutions. To demonstrate their synthetic potentials, **4a** was reacted with phenylboronic acid and *E*-styrylboronic acid in the presence of 5 mol% $Pd(PPh_3)_2Cl_2$ as catalyst gave their Suzuki coupling products **5a** and **5b** in 91% and 86% isolated yields, respectively (Scheme 2).

To explore the reaction mechanism of the transformation, trifluoromethylsulfinylation compound **3a** was employed with 2.0 equivalent of $POCl_3$ at 50 °C in DMF, trifluoromethylthiolated compound **2a** and bifunctionalization products **4a** were obtained in 16% and 78% yields, respectively (Scheme 3). Therefore, it is indicated that bifunctionalization products **4a** could be tranformed from **3a**.



Scheme 3. Reaction of **3a** with $POCl_3$

In light of literature reports and our experimental results,[19,20] a plausible mechanism for this reaction was proposed in Scheme 4. Initially, trifluoromethylsulfinylation of indole with sodium trifluoromethanesulfinate in the presence of phosphorus oxychloride rapidly takes place to give compound **3a**, which could continue to react with another phosphorus oxychloride to form the intermediate **A**. Decomposition of intermediate **A** afford the trifluoromethylthiolation product **2a** (path A). At the same time, intermediate **A** also could be attacked by chlorine anion (Cl^-) to produce intermediate **B**. Subsequent loss of a proton in intermediate **B** gives bifunctionalization product **4a** (path B). According to the reaction result in Scheme 3, both path A and path B exist as completing reactions in the transformation and Path B takes place dominantly to produce bifunctionalization product 2-chloro-3-((trifluoromethyl)thio)-indole **4a** as major product.



Scheme 4. Proposed mechanism.

Conclusions

In conclusion, we have demonstrated an efficient method for the trifluoromethylthiolation-based vicinal bifunctionalization of indoles with cheap and easily available reagents sodium trifluoromethanesulfinate in the presence of phosphorus oxychloride or phosphorus oxybromide, which affords another functional group (chloro or bromo) for further transformation. This reaction was employed under transition-metal-free and mild conditions in one pot. Furthermore, we have extended this protocol to perfluoromethylthiolation-based bifunctionalization reaction with sodium perfluoroalkanesulfinates.

Experimental Section

Experimental Section

General procedure for trifluoromethylthiolation-based vicinal bifunctionalization reaction: To a solution of indole **1a** (0.4 mmol) and CF_3SO_2Na (0.48 mmol) in DMF (1.0 mL) was added $POCl_3$ (1.2 mmol). The mixture was stirred at 50 ℃ for 3 hours. After the completion of the reaction, the mixture was quenched with water. The resulting mixture was extracted with EtOAc three times and the organic layers were combined, dried over $MgSO_4$ and concentrated. The resulting crude product was purified by column chromatography on silica gel to give the corresponding products **4a** (petroleum ether/ethyl acetate=10/1 v/v).

General procedure for the Suzuki coupling reaction of 4a: To a solution of 2-chloro-3-((trifluoromethyl)thio)-1*H*-indole **4a** (0.4 mmol), $Pd(PPh_3)_2Cl_2$ (0.05 equiv) and $PhB(OH)_2$ (1.5 equiv) in 1.4-dioxane/H2O (v_1:v_2=2:1, 3 mL) was added NEt_3 (3.0 equiv), The mixture was stirred at 100℃ for 10h. After the completion of the reaction, the reaction mixture was cooled to room temperature and filtered by diatomaceous earth. The resulting mixture was extracted with dichloromethane three times and the organic layers were combined, dried over $MgSO_4$ and concentrated. The resulting crude product was purified by column chromatography on silica gel to give the corresponding products **5a** (petroleum ether/ethyl acetate=8/1 v/v).

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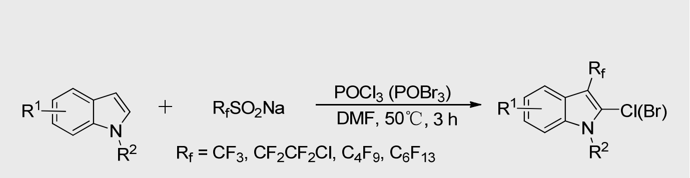

Direct trifluoromethylthiolation-based vicinal bifunctionalization of indoles with sodium trifluoromethanesulfinate in the presence of phosphorus oxychloride were achieved, which affords another functional group (chloro or bromo) for further transformation.

Bifunctionalization
Trifluoromethylthiolation

*Dong-Wei Sun, Xu Jiang, Min Jiang, Yun Lin and Jin-Tao Liu**

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$POCl_3$-Promoted Trifluoromethylthiolation-based Vicinal Bifunctionalization of Indoles with CF_3SO_2Na

Trifluoromethylthiolation, Indole, Bifunctionalization, Perfluoromethylthiolation, Sodium trifluoromethanesulfinate