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Sulfination of alcohols with sodium sulfinates promoted by $BF_3{\cdot}OEt_2$: an unexpected access

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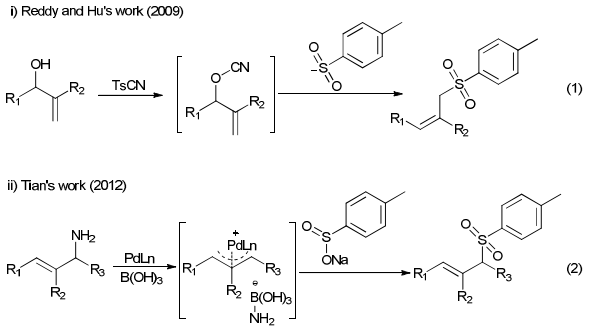
A $BF_3{\cdot}OEt_2$-promoted direct substitution of various levels of alcohols with sodium sulfinates affording sulfinates under mild conditions has been developed. Further elaboration of the hydroxysteroids reaches the highly complex sulfinates in good yields, two potential pharmacophores routinely encountered in drug discovery.

Alcohols are one of the most common and versatile compounds for natural products and key precursors for other classes of chemicals in organic synthesis.[1] Because of the lower leaving ability of hydroxyl group in alcohols, nucleophilic substitution of it is generally difficult.[2] Requisite preactivation of hydroxyl group to afford good leaving groups including halide or mesylate were generally used previously.[3] As a subject of consistent interest for organic chemistry, our group have demonstrated several direct substitutions of alcohols to afford ethers, sulfonamides and diarylalkanes.[4] In this context, we wished to obtain sulfones by direct substitution of sodium sulfinates utilizing the nucleophilicity of sulfur. Earlier researches reported on the direct sulfonylation of alcohols with sulfinic acids by using Brønsted acids including HCl, AcOH and HCOOH to afford sulfones.[5] An overview of previously relevant works on the sulfonylation of alcohols to form sulfone moiety could be produced by sodium sulfinate, sulfide, sulfinic acid, sulfonyl chloride, potassium metabisulfite and arenesulfonyl cyanides,[6] of which sodium sulfinate is the most favorable reagent, due to its superior stability and ease of handling.

Continuous attractivity lies in a facile synthesis of sulfones via a Baylis-Hillman adduct of *p*-toluenesulfonyl cyanide with allylic alcohols in the presence of diisoproylethylamine was reported by Reddy and Hu (eq. 1, Scheme 1).[7] Tian developed a direct substitution of primary allylic amines with sodium sulfinate using boric acid to activate the NH_2 group where the NH_2 group served as an effective leaving group to obtain stable allylic carbocation (eq. 2, Scheme 1).[8] Sulfinate salts also served as the nucleophiles to attack the allylic carbon activated by palladium catalyst, and obtained allyl sulfones. Inspired by these works about sodium sulfinate, we summarized relevant mechanism[9] and envisioned that S-attack of sodium sulfinate onto the stable carbocation is capable of generating the desired sulfones (toward left, Fig. 1).



Scheme 1 Reported direct sulfonylation.

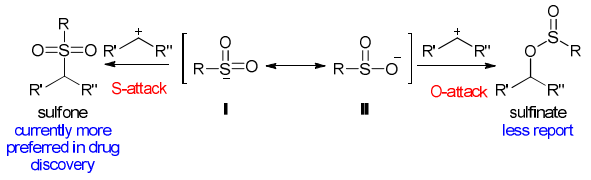


Fig. 1 Two ways for nucleophile of carbocation toward sulfone and sulfinate.

On the basis of our recent works, we assumed the initiation of direct substitution of alcohols with sodium sulfinates by means of boron trifluoride diethyl ether ($BF_3{\cdot}OEt_2$) resulting in carbocation. $BF_3{\cdot}OEt_2$ is a special species: it serves as a Brønsted acid in the presence of water and sometimes it acts

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

as Lewis acid due to its empty *p*-orbital. As a Brønsted acid, in our former work, mixing $BF_3{\cdot}OEt_2$ with H_2O resulted in the formation of BF_3-H_2O which has promoted benzylation reaction of arenes via a carbonium intermediate.[4c,10] As a Lewis acid, it has been found a very efficient catalyst in a large amount of reactions. Our former studies have demonstrated the $BF_3{\cdot}OEt_2$ catalytic synthesis of bis(indolyl)methanes from indoles and carbonyl compounds[11] and etherification of alcohols[4a], where catalyst loading can be lowered to 5‰ and recoverable utilization was in high yield. Moreover, $BF_3{\cdot}OEt_2$ participated cyanation of silyl enol ethers[12] and direct N-benzylation of sulfonamides with benzyl alcohols[4b] were also reported by our group. As an extension of these works, herein we wish to report a direct sulfonylation of alcohols with sodium arenesulfinate.

To probe the feasibility of this hypothesis, we first evaluated our investigations on the model reaction of benzyl alcohol (**1a**) with sodium *p*-toulenesulfinate (**2a**) in the presence of 20 mol% of $BF_3{\cdot}OEt_2$ in dichloromethane at 45 °C for 3 h (Table 1, entry 1). As expected, the reaction took place. When the product was analyzed based on NMR spectroscopy, we found two peaks in doublet for benzyl hydrogen atoms indicating different chemical environment (Fig. 2). It could be preliminarily interpreted by the influence of chiral sulfur center of the unexpected sulfinate **3a** not the envisioned sulfone. Through the structure of sulfinate **3a**, it seemed that sodium sulfinate was not converted to sulfinate anion **I**, and only kept the form of sulfinic acid nucleophile **II** (see Figure 1). During our manuscript preparation, we found a relevant synthetic report firstly falling in same puzzles.[13] Considering the importance and bifunction of sulfinate anion in organic synthesis,[14] we kept going to accomplish this work (toward right, Fig. 1).

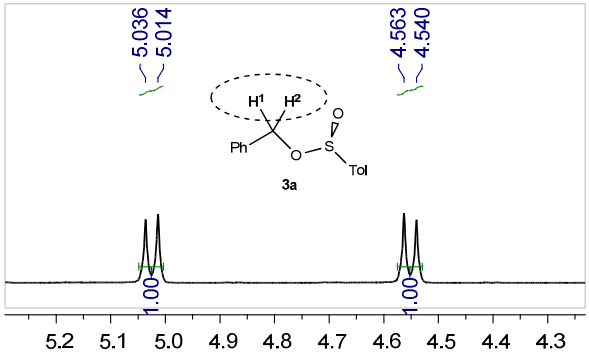
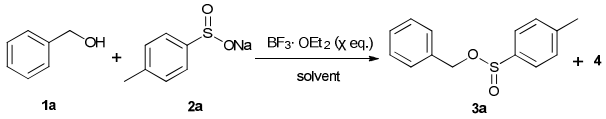


Fig. 2 ^{1}H NMR doublet peaks for two benzyl hydrogen atoms of sulfinate.

We initially concentrated on the optimization of the reaction conditions for the synthesis of sulfinate **3a**. The treatment of benzyl alcohol (**1a**) with 1.0-2.0 equivalents of $BF_3{\cdot}OEt_2$ yielded 26-80% of desired product **3a**, accompanied with 4-methylphenyl *p*-toluenesulfinate **4** (Table 1, entries 2-6), and 1.8 equivalents of $BF_3{\cdot}OEt_2$ was found to be the best. The effect of different temperatures was studied; as a result, the reaction was temperature-sensitive and the temperature of 50 °C gave rise to the product in the best NMR yield of 87% (82% for separation) (Table 1, entries 7-9). Moreover, it can be deduced that at 50 °C, less side reaction took place, by comparing the conversion with yield. Reaction times were investigated; as a result, increasing the reaction time from 4 h to 8 h led to successively decreasing yields caused by increasing side reactions (Table 1, entries 10-12). Various strong polar and non-polar solvents were then screened, subsequently, no desire products were detected in DMSO or THF (Table 1, entries 13 and 14), while 57% yield was obtained in chloroform (Table 1, entry 15). With cyclohexane as solvent, the **3a** was afforded in yield of 41% (Table 1, entry 16). Upon exposure to CH_3NO_2 or $C_2H_5NO_2$, the lower activities were observed with yields of 36% and 48%, respectively (Table 1, entries 17 and 18).

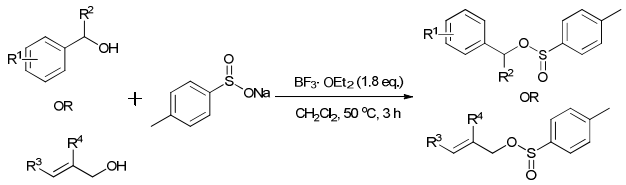
Table 1. Optimization of reaction conditions[a]



Entry	χ	Solvent	*T* (°C)	*t* (h)	**3a** Conv.[b] (%)	**3a** Yield[b] (%)	**4** Yield[c] (%)
1	0.2	CH_2Cl_2	45	3	15	15	< 1
2	1.0	CH_2Cl_2	45	3	30	26	9
3	1.4	CH_2Cl_2	45	3	42	41	11
4	1.6	CH_2Cl_2	45	3	69	68	14
5	1.8	CH_2Cl_2	45	3	83	80	12
6	2.0	CH_2Cl_2	45	3	82	73	19
7	1.8	CH_2Cl_2	35	3	66	63	15
8	1.8	CH_2Cl_2	50	3	88	87(82)[d]	5
9	1.8	CH_2Cl_2	55	3	90	81	10
10	1.8	CH_2Cl_2	50	4	88	74	13
11	1.8	CH_2Cl_2	50	5	89	70	19
12	1.8	CH_2Cl_2	50	8	95	69	34
13	1.8	DMSO	50	3	0	0	0
14	1.8	THF	50	3	0	0	0
15	1.8	$CHCl_3$	50	3	67	57	11
16	1.8	CYH	50	3	93	41	< 1
17	1.8	CH_3NO_2	50	3	66	36	< 1
18	1.8	$C_2H_5NO_2$	50	3	63	48	10

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.65 mmol), $BF_3{\cdot}OEt_2$ (specified), solvent (1.5 mL). The amount of **2a** and the volume of CH_2Cl_2 were optimized (for the details, see Table S1 in the Supporting Information). [b] Determined by ^{1}H NMR spectroscopy using anisole as an internal standard on the basis of **1a**. [c] Determined by ^{1}H NMR spectroscopy using anisole as an internal standard on the basis of **2a**. [d] Isolated yield.

Table 2 Sulfination of different activated alcohols with sodium *p*-toluenesulfinate salt[a]



1 2a 3

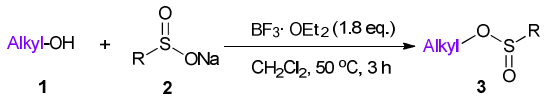
Entry	**1**, R^1, R^2, R^3, R^4	**3**	Conv.[b] (%)	Yield[b] (%)
1	**1a**, R^1 = H, R^2 = H	**3a**	88	87 (82)[c]
2	**1b**, R^1 = 4-Me, R^2 = H	**3b**	84	83 (73)
3	**1c**, R^1 = 4-NO_2, R^2 = H	**3c**	74	73 (69)
4	**1d**, R^1 = 4-CN, R^2 = H	**3d**	73	65 (61)
5	**1e**, R^1 = 4-OH, R^2 = H	**3e**	37	37 (36)
6	**1f**, R^1 = 2-Cl, R^2 = H	**3f**	82	82 (75)
7	**1g**, R^1 = 4-Cl, R^2 = H	**3g**	98	95 (92)
8	**1h**, R^1 = 2-F, R^2 = H	**3h**	80	78 (71)
9	**1i**, R^1 = 4-F, R^2 = H	**3i**	92	90 (80)
10	**1j**, R^1 = 3,4-F, R^2 = H	**3j**	49	49 (44)
11	**1k**, R^1 = 4-CF_3, R^2 = H	**3k**	53	52 (45)
12	**1l**, R^1 = 1-naphthyl, R^2 = H	**3l**	93	22 (21)
13	**1m**, R^1 = H, R^2 = Me	**3m**	95	39 (34)
14	**1n**, R^1 = H, R^2 = Ph	**3n**	92	92 (85)
15	**1o**, R^1 = 4-F, R^2 = Ph	**3o**	80	80 (74)
16	**1p**, R^3 = H, R^4 = H	**3p**	83	83 (79)
17	**1q**, R^3 = Ph, R^4 = H	**3q**	90	24 (21)
18	**1r**, R^3 = Ph, R^4 = Me	**3r**	94	33 (30)

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.65 mmol), BF_3·OEt_2 (1.8 equiv), dichloromethane (1.5 mL) at 50 °C for 3 h. [b] Determined by ^{1}H NMR spectroscopy using anisole as an internal standard. [c] Yield of isolated products shown within parentheses.

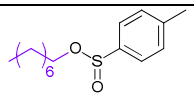
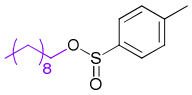
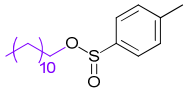
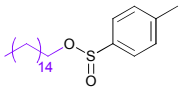
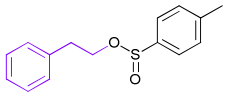
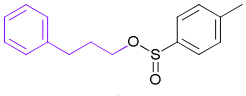
With the optimized reaction conditions in hand, the scope of structurally various benzylic and allylic alcohols with sodium *p*-toluenesulfinate was explored and the results were summarized in Table 2. We firstly focused on the generality of various benzyl alcohols (Table 2, entries 1-12). A series of primary benzyl alcohols **1a-l** were examined in the reaction with **2a**. It was found that benzyl alcohols with methyl, nitro and cyano substitutions at the *para*-position presented appreciable activities, giving the products **3a-d** in good yields (65-87%) (Table 2, entries 1-4). The sulfination with 4-methoxybenzyl alcohol was unsuccessful, however, in the case of *p*-hydroxybenzyl alcohol (**1e**) without OH-protection, a moderate yield of the corresponding sulfinate **3e** was obtained (Table 2, entry 5). Benzyl alcohols with halogen substitutions underwent the reaction smoothly giving the desired products in good to excellent yields (Table 2, entries 6-10). *o*-Chloro (**1f**), *p*-chloro (**1g**), *o*-fluoro (**1h**), *p*-fluoro (**1i**) and 3,4-difluoro (**1j**) substituents generated the corresponding sulfinates up to 95% yield. Due to the steric hindrance, **1f** and **1h** gave lower yields, compared to their *para* isomer (Table 2, entries 6 vs 7, and 8 vs 9, respectively), and dihalogen substituent led to the lowest yield (Table 2, entry 10). Trifluoromethyl substituted benzyl alcohol gave rise to the desired product in moderate yield (Table 2, entry 11). Due to heavy side reaction, the reaction of 1-naphthalenemethanol (**1l**) afforded corresponding sulfinate **3l** in yield of 22% (Table 2, entry 12).

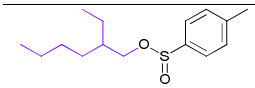
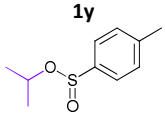
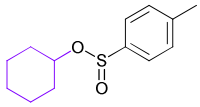
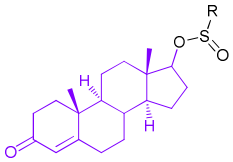
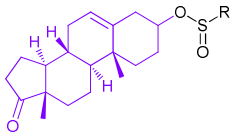
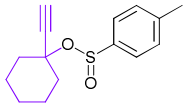
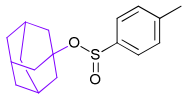
Routinely, we set out to explore various secondary alcohols as well as allylic alcohols (Table 2, entries 13-18). The benzylic secondary alcohols, such as α-phenethyl alcohol (**1m**), benzhydrol (**1n**) and *p*-fluorobenzhydrol (**1o**) provided the desired products in 39-92% yields and in the case of **1m** no significant formation of olefins was generated from elimination of β-H, respectively (Table 2, entries 13-15). We investigated the substitutions on different allylic alcohols as well, the desired products were obtained in 24-83% yields and γ-sulfinated products were not detected, resulted from the π-bond shift (Table 2, entries 16-18).

Table 3 Sulfination of different unactivated alcohols with sodium sulfinate salts[a]



1 2 3

Product **3**		Conv.[b] (%)	Yield[b] (%)
 **1s**	**3s**	93	92 (86)[c]
 **1t**	**3t**	92	91 (85)
 **1u**	**3u**	87	84 (81)
 **1v**	**3v**	83	80 (79)
 **1w**	**3w**	82	76 (74)
 **1x**	**3x**	85	83 (78)

 1y	**3y**		95	94 (87)
 1z	**3z**		91	91 (85)
 1A	**3A**		64	63 (59)
 1B	**3B**	**2a**, R = *p*-Tolyl	83	82 (81)
	3C	**2b**, R =Ph	82	82 (80)
 1C	**3D**	**2a**, R = *p*-Tolyl	81	81 (78)
	3E	**2b**, R =Ph	81	80 (78)
 1D	**3F**		96	48 (41)
 1E	**3G**		55	52 (51)

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.65 mmol), $BF_3{\cdot}OEt_2$ (1.8 equiv), dichloromethane (1.5 mL) at 50 °C for 3 h. [b] Determined by ^1H NMR spectroscopy using anisole as an internal standard. [c] Yield of isolated products shown within parentheses.

Compared with benzyl carbocation, less stability exists for aliphatic carbocation, especially for primary and secondary ones. We explored the substrate scope of several structurally various aliphatic alcohols with sodium sulfinates in this sulfination, and the results are summarized in Table 3. We first focused on substituted primary fatty alcohols. Interestingly, linear aliphatic alcohols such as octanol, decanol, dodecanol, hexadecanol and branched aliphatic alcohol proceeded cleanly with sodium *p*-toluenesulfinate in the presence of $BF_3{\cdot}OEt_2$ to the corresponding sulfinates **3s-y** in high to excellent yields (76-94%). Inspired by these results with primary aliphatic alcohols, we turned our attention to secondary fatty alcohols. The sulfinations of isopropyl alcohol and cyclohexanol with sodium *p*-toluenesulfinate also afforded the sulfinates effectively (91% for **3z**, 63% for **3A**). Hydroxysteroids molecules are broadly distributed in nature and induce a wide variety of biological processes, such as proliferation, development, and differentiation of cell. We investigated the substitution of testosterone and dihydroepiandrosterone with sodium *p*-toluenesulfinate and sodium benzenesulfinate,[15] and the desired steroidal sulfinates **3B-3E** were obtained in high yields without by-products. The structure of sulfinate **3D** was confirmed convincingly through single-crystal X-ray diffraction analysis (Fig. 3). Fortunately, tertiary alcohols worked well as expected. Due to the presence of acetylenic bond, in the case of 1-ethynyl-1-cyclohexanol, the product **3F** was given in yield of 48% along with some unidentified by-products. In the reaction of bulkyl 1-adamantanol with sodium *p*-toluenesulfinate, the reaction efficiency was diminished reasonablely, and solely gave the desired product in 52% yield (**3G**).

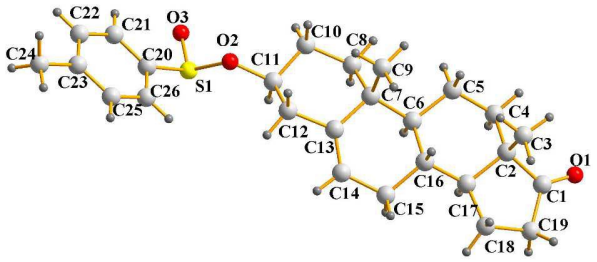
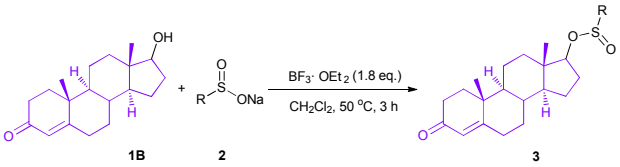
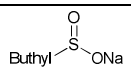
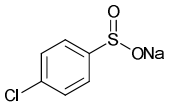


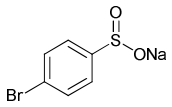
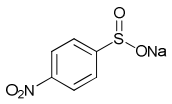
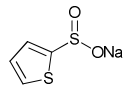
Fig. 3 X-ray crystal structure of **3D.**

Upon the structure of testosterone **1B**, the scope of the reaction was also investigated by varying sodium sulfinates and the results were given in Table 4. Sulfinate **3H** was obtained in 40% yield from sodium butyl sulfinate **2c**. Chlorine and bromine substituted sodium sulfinates (**2d** and **2e**) provided the corresponding sulfinates **3I** and **3J** in 72% and 69% yields, respectively. The sodium sulfinate **2f** bearing an electron-withdrawing group required much more reaction time, compared to the sodium sulfinate **2a**, giving **3K** in moderate yield of 45%. The sodium heteroaryl sulfinate **2g** went smoothly to furnish the desired steroidal sulfinates **3L** in 87% yield.

Table 4 Sulfination of testosterone **1B** with various sodium sulfinate salts[a]



Entry	2	3	Conv.[b] (%)	Yield[b] (%)
1	 **2c**	**3H**	42	40 (38)[c]
2	 **2d**	**3I**	72	72 (70)

3	 **2e**	**3J**	72	69 (66)
4	 **2f**	**3K**	47	45 (41)[d]
5	 **2g**	**3L**	88	87 (85)

[a] Reaction conditions: **1B** (0.5 mmol), **2** (0.65 mmol), $BF_3{\cdot}OEt_2$ (1.8 equiv), dichloromethane (1.5 mL) at 50 °C for 3 h. [b] Determined by ^1H NMR spectroscopy using anisole as an internal standard. [c] Yield of isolated products shown within parentheses. [d] 5 h.

To glean insights into the mechanism, two control experiments were performed. In the presence of catalytic amount (20 mol%) of $BF_3{\cdot}OEt_2$, *p*-toulenesulfinic acid was chosen as sulfination reagent to react directly with benzyl alcohol **1a** in dichloromethane at 50 °C for 3 h; as a result, **3a** was obtained in 84% yield. Under the protection of nitrogen, the model reaction was executed and no reaction took place, which suggested that moisture from air of open-flask conditions were requisite for formation of superacid BF_3-H_2O and promoted conversion of sodium *p*-toluenesufinate into corresponding nucleophile sulfinic acid. So $BF_3{\cdot}OEt_2$ plays a dual role in this transformation: a) catalyzing the sulfination; b) forming BF_3-H_2O to neutralize the sodium sulfinate. Accordingly, a plausible mechanism is proposed as shown in Fig. 4. Firstly, hydroxyl moiety of benzyl alcohol is effectively activated by the Lewis acid $BF_3{\cdot}OEt_2$ through the strong coordination to boron center. To obtain **3a**, this procedure may undergo two different pathways. Following the S_N2 pathway, the nucleophilic O-attack of the *p*-toulenesulfinic acid onto activated benzyl alcohol generates a transition state (**TS**) with the bond C-OH weakened. Alternatively, benzyl alcohol can give rise to stable carbocation more favorably due to *p*-*π* super conjugation, thus sufination undergoes S_N1 process to reach protonated target molecule, and then via a deprotonation, sulfination product is assembled. The released BF_3-H_2O is recycled to enter either transformation of sodium sufinate or activation of starting material.

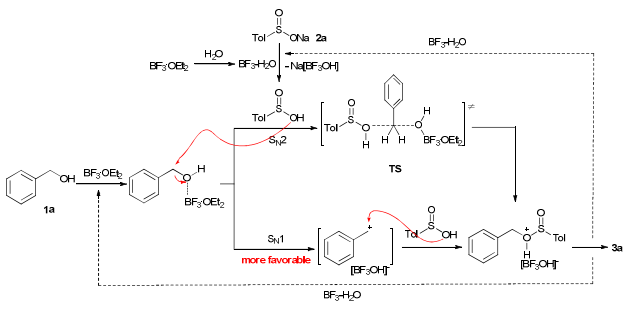


Fig. 4 A plausible mechanism.

Conclusions

In summary, $BF_3{\cdot}OEt_2$ participated sulfination of various levels of alcohols with sodium sulfinates has been developed, which provided an convenient method for the synthesis of structurally various functionalized sulfinates. We have advanced our understanding on $BF_3{\cdot}OEt_2$ participated reaction special for reactivity of alkyl carbocation. Several highly complex and medicinally relevant compounds have been shown in sulfination, and series of steroidal alcohols could be elaborated hopefully into more complex sulfinates of broad interest.

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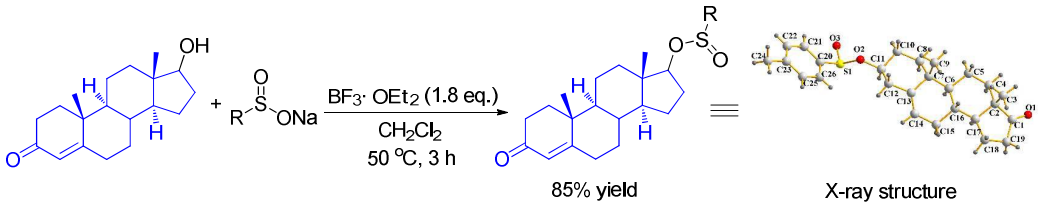

A convenient and efficient method for the synthesis of structurally various functionalized sulfinates shows good substrate generality of alcohols and sodium sulfinates.