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Bismuth(III) Bromide-Catalysed Substitution of Benzyl Alcohols with Arylsulfonylmethyl Isocyanides: An Unexpected Access to Sulfinates

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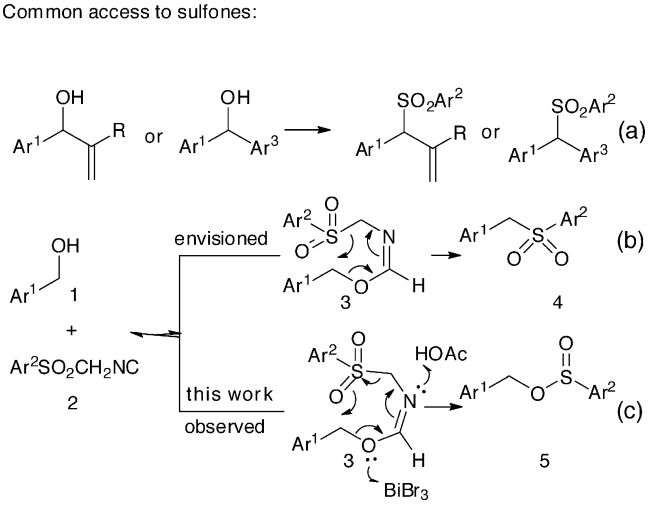
Abstract: A bismuth(III) bromide-catalysed direct substitution of benzyl alcohols with arylsulfonylmethyl isocyanides affords sulfinates under mild acidic conditions. An unforeseen reversed reactivity was observed in this highly selective formation of sulfinates instead of the formation of the usually favoured sulfones. Cytotoxicity tests (*in vitro*) indicated that the sulfinates exhibit antibiotic activity against a human leukaemia cell line HL-60, which would widen the structural diversity of this antitumour target and confirm the perspectives of further investigations.

Keywords: benzyl alcohols; bismuth; selectivity; substitution; sulfonates

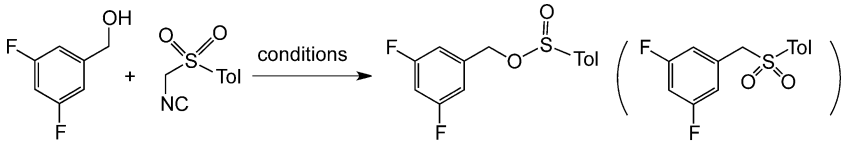
Substitution of alcohols is an important and widespread chemical reaction in organic synthesis. As the hydroxy group is a poor leaving group, substitution of an alcohol traditionally consists of functionalisation of the hydroxy group to furnish a latent leaving group, and subsequently substitution of the resulting alcohol derivative with an appropriate nucleophile.[1] The realisation of a direct substitution of various alcohols is a long-standing challenge and has been a subject of consistent interest for organic chemists.[2,3] Direct sulfonylation of strongly activated alcohols,[4] such as Baylis–Hillman alcohols and diarylmethanols, with sulfonyl nucleophiles, such as sulfinate salts[4a,b,f] and *para*-toluenesulfonylmethyl isocyanide,[4d] has been well developed (Scheme 1a). Unfortunately, benzyl alcohols, as relatively less activated alcohols, were found not to be appropriate substrates in these transformations.[4d] Considering that an intramolecular process is usually easier than the corresponding intermolecular process, the sulfonylation of benzyl alcohols with arylsulfonylmethyl isocyanides might be practical *via* a facile reversible isocyanide insertion into the O–H bond of benzyl alcohols,[5] followed by a potential intramolecular ring rearrangement[6] (Scheme 1b).

To probe the feasibility of this hypothesis, we first evaluated the reaction using 3,5-difluorobenzyl alcohol (**1a**) with *para*-toluenesulfonylmethyl isocyanide (TosMIC, **2a**) as the model substrates (Table 1). Reaction of **1a** with **2a** in the presence of 10 mol% of $Bi(OTf)_3$ in nitromethane (CH_3NO_2) at 60 °C for 1 day did not afford sulfone **4a**. Surprisingly, sulfinate **5a** instead was unexpectedly obtained, albeit in only



Scheme 1. Possibilities for direct substitution of some alcohols.

Table 1. Optimization of reaction conditions for the substitution of 3,5-difluorobenzyl alcohol (**1a**) with TosMIC (**2a**).[a]



1a **2a** **5a** **4a** not observed

Entry	Catalyst	Additive	Solvent	Temperature	Yield [%]
1	$Bi(OTf)_3$		CH_3NO_2	60 °C	38
2	$Sc(OTf)_3$		CH_3NO_2	60 °C	24
3	$In(OTf)_3$		CH_3NO_2	60 °C	17
4	$Hf(OTf)_4$		CH_3NO_2	60 °C	22
5	$Fe(OTf)_3$		CH_3NO_2	60 °C	13
6	$Cu(OTf)_2$		CH_3NO_2	60 °C	14
7	$Zn(OTf)_2$		CH_3NO_2	60 °C	7
8	$Yb(OTf)_3$		CH_3NO_2	60 °C	15
9	$Bi(NO_3)_3$		CH_3NO_2	60 °C	54
10	$BiCl_3$		CH_3NO_2	60 °C	43
11	BiI_3		CH_3NO_2	60 °C	42
12	$BiBr_3$		CH_3NO_2	60 °C	59
13	$BiBr_3$		CH_3NO_2	40 °C	31
14	$BiBr_3$		CH_3NO_2	r.t.	22
15	$BiBr_3$		CH_3NO_2	r.t.	11
16	$BiBr_3$		THF	r.t.	20
17	$BiBr_3$		DMF	r.t.	trace
18	$BiBr_3$		CH_3CN	r.t.	trace
19	$BiBr_3$		CH_3OH	r.t.	trace
20	$BiBr_3$	KPF_6	CH_3NO_2	r.t.	trace
21	$BiBr_3$	H_3PO_4	CH_3NO_2	r.t.	9
22	$BiBr_3$	AcOH	CH_3NO_2	r.t.	71
23	$BiBr_3$	AcOH	CH_3NO_2	40 °C	69
24		AcOH	CH_3NO_2	r.t.	0
25[b]	$BiBr_3$	AcOH	CH_3NO_2	r.t.	51
26[c]	$BiBr_3$	AcOH	CH_3NO_2	r.t.	0

[a] *General conditions:* **1a** (1.0 equiv.), **2a** (1.5 equiv.) and catalyst (10 mol%) in solvent ($c = 0.2$ M) for 1 day.
[b] $BiBr_3$ (5 mol%) was used.
[c] Sodium *para*-toluenesulfinate (1.5 equiv.) was used instead of TosMIC.

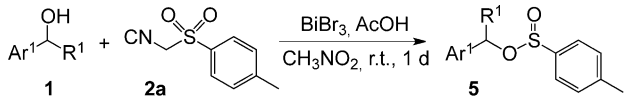
38% yield (entry 1). From the structure of sulfinate **5a**, it seemed that instead of undergoing the envisioned intramolecular six-membered ring rearrangement (Scheme 1b), a potential intramolecular seven-membered ring rearrangement[7] (Scheme 1c) arguably took place and thereby exhibited a reversed selectivity.[4d] The spatial arrangement in the latter rearrangement minimised indeed the unfavourable steric hindrance, and thus facilitated the seven-membered ring rearrangement. Considering the importance of sulfinates in synthetic chemistry,[8,9] we then turned to optimising the reaction conditions for the synthesis of sulfinate **5a**.

With the use of other triflate salts in comparison to $Bi(OTf)_3$, relatively lower yields were observed under otherwise the same conditions (Table 1, entries 1–8). Further parameter optimisation identified $BiBr_3$ as the most effective bismuth catalyst (entries 1 and 9–12). Decreased yields were observed when the reaction temperatures were decreased from 60 °C to room temperature (entries 12–14). The reaction could take place in dichloromethane or tetrahydrofuran (THF) at room temperature, while nitromethane appeared to be the most appropriate solvent (entries 14–19). Addition of potassium hexafluorophosphate (KPF_6, 1.0 equiv.) or phosphoric acid (H_3PO_4, 1.0 equiv.) as the additive did not provide any better results (entry 14 and entries 20 and 21). Fortuitously, with acetic acid (AcOH, 1.0 equiv.) as the additive, the reaction proceeded smoothly at room temperature to afford sulfinate **5a** with an excellent yield (entry 22). No better result was obtained when this reaction was performed at a higher temperature (entries 22 and 23). The reaction did not work in the absence of $BiBr_3$, indicating that acetic acid itself is not an effective promoter (entries 22 and 24). The yield of **5a** was decreased to 51% when the loading of $BiBr_3$ was decreased from 10 mol% to 5 mol% (entry 25). The re-

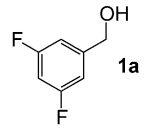
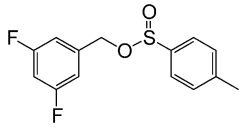
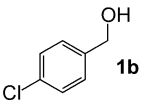
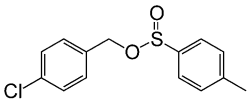
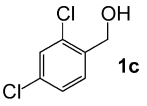
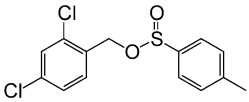
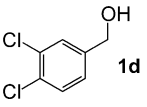
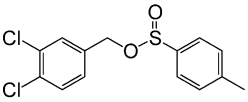
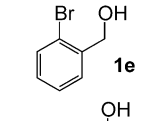
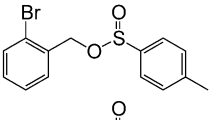
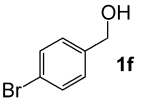
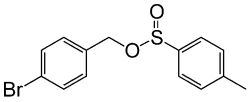
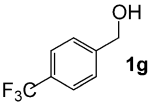
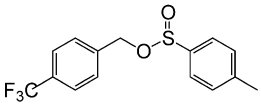
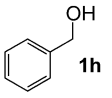
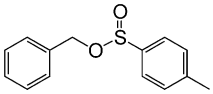
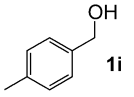
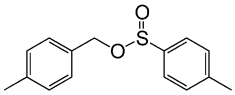
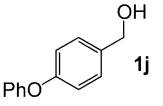
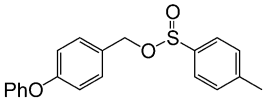
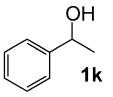
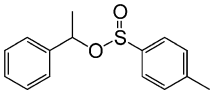
action did not take place when sodium *para*-toluenesulfinate was used instead of TosMIC (**2a**) under otherwise the same conditions, indicating that sulfinate anions are not effective sulfinate nucleophiles for this reaction (entries 22 and 26). Usually, sulfinate salts were used as common weak sulfonyl nucleophiles for the substitution of benzyl bromides,[10] allylic amines,[11] allylic alcohols,[4] alcohol derivatives[12] under harsh conditions. To our delight, sulfinate **5a** can be accessed by substitution of benzyl alcohol **1a** with arylsulfonylmethyl isocyanide **2a** under mild acidic conditions. Although we are not able at this time to accurately explain the underlying mechanism of this reaction, the mild conditions might help to prevent the departure of the hydroxy group of benzyl alcohol **1a** in the presence of $BiBr_3$ that helped to activate the benzylic C–O bond of intermediate **3a** (Scheme 1c). Moreover, acetic acid appeared to serve the role of activating the imine moiety of intermediate **3a** (Scheme 1c).

With the optimized reaction conditions in hand, the scope of the reaction was subsequently investigated, and the representative results are summarised in Table 2. With the aromatic ring of benzyl alcohols bearing weak electron-withdrawing groups such as fluoro, chloro and bromo, benzyl alcohols **1a--f** reacted smoothly with arylsulfonylmethyl isocyanide **2a** in the presence of $BiBr_3$ (10 mol%) and AcOH (1.0 equiv.) at room temperature to afford sulfinates **5a–f** in good to excellent yields within 1 day (entries 1–6). With a strong electron-withdrawing group such as a trifluoromethyl group at the aromatic ring of the benzyl alcohol, benzyl alcohol **1g** reacted equally well with arylsulfonylmethyl isocyanide **2a** under the standard conditions to give sulfinate **5g** in 70% yield (entry 7). Sulfination of an unsubstituted benzyl alcohol (**1h**) with arylsulfonylmethyl isocyanide **2a** under the standard conditions generated sulfinate **5h** in 56% yield (entry 8). With electron-donating groups, such as methyl (a weak electron-donating group) and phenoxy (a strong electron-donating group), at the aromatic ring of benzyl alcohols, substitution of benzyl alcohols **1i** and **j** with arylsulfonylmethyl isocyanide **2a** under the standard conditions afforded sulfinates **5i** and **j** in moderate yields (entries 9 and 10). Reaction of 1-phenylethanol (**1k**) with arylsulfonylmethyl isocyanide **2a** under the standard conditions generated sulfinate **5k** in 47% yield (entry 11). By treating (*S*)-(−)-1-phenylethanol with arylsulfonylmethyl isocyanide **2a** under otherwise identical conditions, chiral sulfinate **5k** was obtained with an excellent enantioselectivity (>99% *ee*, see the Supporting Information for the HPLC traces). The isolation of chiral sulfinate **5k** indicates that this reaction occurs by an S_N2 mechanism, supporting the proposed intramolecular ring rearrangement, which involves an S_N2-type nucleophilic substitution.

Table 2. Sulfination of benzyl alcohols with TosMIC.[a]



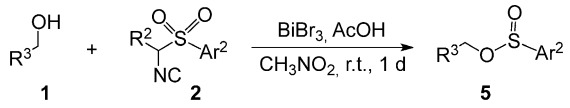
1 2a 5

Entry	1	Product 5 and Yield [%]
1	 **1a**	 **5a**: 71
2	 **1b**	 **5b**: 60
3	 **1c**	 **5c**: 68
4	 **1d**	 **5d**: 65
5	 **1e**	 **5e**: 57
6	 **1f**	 **5f**: 58
7	 **1g**	 **5g**: 70
8	 **1h**	 **5h**: 56
9	 **1i**	 **5i**: 51
10	 **1j**	 **5j**: 55
11	 **1k**	 **5k**: 47

[a] *General conditions:* **1** (0.2 mmol), **2a** (59.7 mg, 0.3 mmol), $BiBr_3$ (9.1 mg, 0.02 mmol) and AcOH (3.7 μL, 0.2 mmol) in CH_3NO_2 (1 mL) at room temperature for 1 day.

Sulfination of different alcohols with arylsulfonylmethyl isocyanides were next investigated (Table 3). Sterically hindered arylsulfonylmethyl isocyanide **2b** reacted with benzyl alcohol **1a** in the presence of $BiBr_3$ (10 mol%) and AcOH (1.0 equiv.) at room temperature to afford sulfinate **5a** in 60% yield within 1 day (entry 1). By treatment of arylsulfonylmethyl isocyanide **2c** with benzyl alcohol **1g** under the stan-

Table 3. Sulfination of alcohols with arylsulfonylmethyl isocyanides.[a]



1 2 5

Entry	1	2	Product 5 and Yield [%]
1	1a	2b	5a: 60
2	1g	2c	5l: 70
3	1l	2a	5m: 71
4	1m	2a	5n: 69
5	1n	2a	5o: 53

[a] *General conditions:* **1** (0.2 mmol), **2** (0.3 mmol), $BiBr_3$ (9.1 mg, 0.02 mmol) and AcOH (3.7 μL, 0.2 mmol) in CH_3NO_2 (1 mL) at room temperature for 1 day.

dard conditions, sulfinate **5l** was obtained in 70% yield (entry 2). Methallyl alcohol (**1l**) and cinnamyl alcohol (**1m**) have also been investigated; they reacted with arylsulfonylmethyl isocyanide **2a** under the standard conditions to afford sulfinates **5m** and **n** in good yields (entries 3 and 4). Furthermore, phenethyl alcohol (**1n**), a non-activated alkyl alcohol, reacted with arylsulfonylmethyl isocyanide **2a** uneventfully to give sulfinate **5o** in 53% yield (entry 5).

Cytotoxicity tests (*in vitro*) indicated that sulfinate **5c** exhibits antibiotic activity against a human leukaemia cell line HL-60 (IC_{50} = 7.5 μM), which would widen the structural diversity of this antitumour target and confirm the perspectives of further investigations in this area.

In summary, $BiBr_3$-catalyzed sulfination of benzyl alcohols with arylsulfonylmethyl isocyanides went smoothly under mild acidic conditions, which provided an unprecedented method for the synthesis of functional aryl benzyl sulfinates, potent selective antitumour targets for human leukaemia. Mechanistic investigations of this sulfinate synthesis as well as the structural-activity relationship studies are in progress.

Experimental Section

Procedure for the Sulfination of Benzyl Alcohols with Arylsulfonylmethyl Isocyanides

The mixture of 3,5-difluorobenzyl alcohol (**1a**, 23.8 μL, 0.2 mmol), *para*-toluenesulfonylmethyl isocyanide (TosMIC, **2a**, 59.7 mg, 0.3 mmol), bismuth bromide ($BiBr_3$, 99%, 9.1 mg, 0.02 mmol) and acetic acid (AcOH, 3.7 μL, 0.2 mmol) in nitromethane (CH_3NO_2, 1 mL) under argon was stirred at room temperature for 1 day, and added with water (5 mL) and ethyl acetate (10 mL). The two layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were washed by brine, dried over anhydrous sodium sulfinate, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (100–200 mesh) to afford sulfinate **5a** as a yellow liquid; yield: 40 mg (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.78–6.70 (m, 3H), 4.95 (d, J = 12.3 Hz, 1H), 4.49 (d, J = 12.3 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (dd, $J_{C,F}$ = 330.2, 16.7 Hz, 1C), 143.3, 141.2, 139.6 (t, $J_{C,F}$ = 12.2 Hz, 1C), 129.8, 125.3, 110.8 (dd, $J_{C,F}$ = 23.0, 10.8 Hz, 1C), 103.6 (t, $J_{C,F}$ = 33.4 Hz, 1C), 63.6, 21.5; FT-IR (film): ν = 1629, 1599, 1464, 1368, 1323, 1137, 1119, 946, 854, 813, 759, 673 cm^{-1}; HR-MS (ESI): m/z = 305.0416, calcd. for $C_{14}H_{12}F_2NaO_2S$ $[M+Na]^+$: 305.0418.

Acknowledgements

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