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# Chiral-Auxiliary-Controlled Diastereoconvergent Dehydrative Nucleophilic Substitutions of Diarylmethanol Diastereomixtures with 1,3-Dicarbonyls Catalyzed by SnBr<sub>4</sub>

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Abstract: Diastereoconvergent direct dehydrative nucleophilic substitutions of diastereomixtures of diarylmethanols with 1,3-dicarbonyls in the presence of SnBr<sub>4</sub> as a Lewis acid catalyst are reported. Excellent diastereoselectivities and high yields were achieved by a chiral-auxiliary-controlled process. The reaction proved applicable to a wide range of substrates, irrespective of aromatic ring substituents tested, and several 1,3-diketones, and  $\beta$ -ketoesters were utilized as nucleophilic partners. Efficient transformation of selected alkylated products to pyrazoles was achieved by treatment with NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O. A plausible reaction pathway for the nucleophilic substitution was proposed.

#### Introduction

In recent years, direct dehydrative nucleophilic substitution reactions of alcohols have drawn considerable attention in organic synthesis.<sup>[1]</sup> The reaction proceeds without the need to convert the hydroxyl group into a leaving group, making it an atom-efficient process. Furthermore, ideally, the only reaction by-product is water, another desirable aspect in terms of environmental considerations. Within this class of reaction, the use of 1,3-dicarbonyl compounds as nucleophiles is a wellknown successful methodology for C-C bond formation. Numerous characteristic reactions using Lewis acids and Brønsted acids as catalysts have been reported to date (Scheme 1 (a)).<sup>[2]</sup> However, almost all previously reported methods deliver products as racemates, and extension to an asymmetric version remains a difficult task. On the other hand, many related organocatalytic enantioselective syntheses utilizing quinone methides<sup>[3]</sup> have been developed, but they are often restricted to substrates containing electron donating groups. Preceding this research, we developed a chiral auxiliary and applied it to Lewis acid-catalyzed chiral inductive diastereoconvergent couplings diarylmethanol of diastereomixtures 3, employing nucleophiles such as 2naphthols,<sup>[4]</sup> allyltrimethylsilane,<sup>[5]</sup> benzamides,<sup>[6]</sup> and sodium sulfinates.<sup>[7]</sup> It was revealed that these reactions were applicable to a variety of substrates to give products 4, 5, 6, and 7, respectively (Scheme 1 (b)). In addition, by using different Lewis acid catalysts, chiral inductive diastereodivergent sulfonamidation<sup>[8]</sup> of 3 was developed to produce diastereomeric

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sulfonamides **8a** and **8b** (Scheme 1 (b)). Thus, we hypothesized that 1,3-dicarbonyl compounds could be applied to our chiral inductive methodology and thus extended this to the development of a new asymmetric C–C bond forming methodology (Scheme 1 (c)).

Herein, we describe an auxiliary-controlled direct diastereoconvergent dehydrative nucleophilic substitution of diarylmethanol diastereomixtures with 1,3-dicarbonyl compounds, catalyzed by Lewis acids.



**Scheme 1.** (a) Related previous study; direct substitution of diarylmethanols with 1,3-dicarbonyl compounds, (b) our previous study, and (c) this study; diastereoconvergent asymmetric substitution of alcohols.

#### **Results and Discussion**

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# COMMUNICATION

To find optimal reaction conditions, we commenced by exploring different Lewis acids (Table 1). As a model reaction, diarylmethanol diastereomers  $3a^{[4]}$  [diastereomeric ratio (dr) = approximately 60:40] were chosen as substrates for nucleophilic substitution with 1,3-dicarbonyls 10 or 11 using FeCl<sub>3</sub> as the Lewis acid. FeCl<sub>3</sub> is an efficient Lewis acid catalyst for dehydrative nucleophilic substitutions,<sup>[9]</sup> and a number of coupling reactions of benzhydrol derivatives with 1,3-dicarbonyls using FeCl<sub>3</sub> as a catalyst have been reported to date.<sup>[2g,2h,2l,2u,2v]</sup> The FeCl<sub>3</sub>-calalyzed reaction of 3a with 10 was initially carried out in MeNO<sub>2</sub> at 0 °C. The reaction was complete within 1 h, and the desired product 12a was obtained in 83% yield and with a 97:3 dr (entry 1). We have already reported on the applicability of tin salts as Lewis acids for the diastereoconvergent coupling reactions of 3a with several nucleophiles.[4-8] Thus, the same reaction was conducted in the presence of several tin salts, namely, SnCl<sub>2</sub>, SnBr<sub>2</sub>, SnCl<sub>4</sub>, and SnBr<sub>4</sub>. Good results were obtained in all cases (entries 2-5), and it was found that the reaction afforded high yields and selectivities, regardless of the type of Lewis acid used (entries 1-5). However, when the reaction was carried out using 11 as the nucleophile, reactivity was found to be influenced by the choice of Lewis acid catalyst. Reactions using  $FeCI_3$ ,  $SnCI_4$ , and  $SnBr_4$  were complete within 1 h, and good diastereoselectivities were achieved (entries 6, 11, and 12). On the contrary, prolonged reaction times were required in the case of SnCl<sub>2</sub> and SnBr<sub>2</sub> in order to consume the starting material, although comparable diastereoselectivities were obtained (entries 7 versus 8, and 9 versus 10). On the basis of thin-layer chromatography (TLC) analysis and diastereoselectivity results, reaction conditions shown in entry 12 were selected for further studies, where SnBr4 was selected as the Lewis acid catalyst.

 Table 1. Examination of the effect of Lewis acids on the diastereoconvergent substitutions of 3a with 1,3-dicarbonyls 10 and 11.

	MeO Ph O O H 3a	R1 (1.5 [10; R1 = Ph Lewis aci MeNO 0 °C, 7	$R^{1}$ equiv) t, <b>11</b> ; R <sup>1</sup> = Me] d (5 mol-%) 2 (0.1 M) Time [h]	$MeO \xrightarrow{Ph} \\ \downarrow \\ Ph \\ \downarrow \\ Ph \\ \downarrow \\ Ph \\ 12a; R^1 = Ph \\ 13; R^1 = Me$	R <sup>1</sup>
Entry	Lewis acid	Reagent	Time [h]	Yield [%]	dr <sup>[a]</sup>
1	FeCl₃	10	1	83 <sup>[b]</sup> ( <b>12a</b> )	97:3
2	SnCl <sub>2</sub>	10	1	87 <sup>[b]</sup> ( <b>12a</b> )	97:3
3	SnBr <sub>2</sub>	10	1	92 <sup>[b]</sup> ( <b>12a</b> )	97:3
4	SnCl <sub>4</sub>	10	1	90 <sup>[b]</sup> ( <b>12a</b> )	95:5
5	SnBr <sub>4</sub>	10	1	87 <sup>[b]</sup> ( <b>12a</b> )	97:3
6	FeCl₃	11	1	99 <sup>[c]</sup> ( <b>13</b> )	88:12
7	SnCl <sub>2</sub>	11	1	51 <sup>[b]</sup> ( <b>13</b> )	89: 11
8	SnCl <sub>2</sub>	11	24	72 <sup>[c]</sup> ( <b>13</b> )	89:11

9	SnBr <sub>2</sub>	11	1	72 <sup>[b]</sup> ( <b>13</b> )	89: 11
10	SnBr <sub>2</sub>	11	24	93 <sup>[c]</sup> ( <b>13</b> )	89:11
11	SnCl <sub>4</sub>	11	1	89 <sup>[c]</sup> ( <b>13</b> )	88:12
12	SnBr <sub>4</sub>	11	1	89 <sup>[c]</sup> ( <b>13</b> )	89:11

[a] Diastereomeric ratio (*dr*) was determined by <sup>1</sup>H NMR analysis. [b] Determined by <sup>1</sup>H NMR analysis of the crude reaction mixture using 2-acetylnaphthalene as an internal standard. [c] Yield of isolated mixtures of diastereomers.

To explore substrate scope and possible limitations thereof, a series of diarylmethanols 3a-31 bearing various aromatic ring substituents were reacted with 1,3-dicarbonyl 10, applying the above-mentioned conditions (Table 2). Reactions of substrates containing methyl-substituted aromatic rings 3b-3d proceeded with high levels of diastereoselectivity, and although good yields were obtained with 3c and 3d (entries 4 and 5), a moderate yield was achieved in the case of 3b (entry 2). Because the reaction of 3b resulted in a complex mixture, in order to control the reactivity, reaction temperature was decreased from 0 °C to -10 °C. Pleasingly, both the yield and selectivity were improved (entry 3 versus 2). A good yield and diastereoselectivity was achieved for 3f, where the MeO substituent is in the metaposition (entry 7); however, when the MeO substituents are in ortho- and para-positions, as in 3e and 3g, respectively, reaction profiles were again complicated at 0 °C. This is likely a consequence of these reactions proceeding via the active orthoand para-quinone methides, which are stabilized by the electron donating ability of the MeO moiety. However, both gave good results when the reaction temperature was decreased to -15 °C (entries 6 and 8). Low reactivities of CI-substituted aryls were anticipated as the electron withdrawing properties of CI, which result in the formation of unstabilized cation intermediates. However, reactions of 3i and 3j with CI substituents at meta- and para-positions afforded good results (entries 11 and 12), while low reactivity was observed for the ortho-isomer, 3h, under the standard conditions. By prolonging the reaction time to 24 h or by increasing the catalyst loading to 10 mol%, the reactivity of 3h was satisfactorily improved (entries 9 and 10, respectively).  $\alpha$ - and  $\beta$ -Naphthyl-substituted aryls, **3k** and **3l**, afforded good results, irrespective of the substitution pattern (entries 13 and 14).

	MeO Ph	Ph F 0 0 (10; 1.5 equiv SnBr <sub>4</sub> (5 mol-	v) W) Ph Ph Ar Ph	Ph
	OH 3a–3I	MeNO <sub>2</sub> (0.1 M 0 °C, Time [h	M) 1] 12a–12I	
Entry	Ar	Time [h]	Yield of <b>12</b> <sup>[a]</sup> [%]	<i>dr</i> <sup>[b]</sup>
1	Ph ( <b>a</b> )	1	90	97:3

2	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub> ( <b>b</b> )	1	66	92:8
3 <sup>[c]</sup>	$o\operatorname{-MeC}_{6}\operatorname{H}_{4}(\mathbf{b})$	1	82	97:3
4	$m-MeC_6H_4$ (c)	1	83	95:5
5	$p\text{-MeC}_{6}\text{H}_{4}\left(\textbf{d} ight)$	1	87	95:5
6 <sup>[d]</sup>	$o ext{-MeOC}_6H_4$ ( $e$ )	1	74	91:9
7	<i>m</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>f</b> )	1	89	97:3
8 <sup>[d]</sup>	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub> ( <b>g</b> )	1	88	97:3
9	o-CIC <sub>6</sub> H <sub>4</sub> ( <b>h</b> )	24	81	96:4
10 <sup>[e]</sup>	o-CIC <sub>6</sub> H <sub>4</sub> ( <b>h</b> )	4	88	95:5
11	<i>m</i> -ClC <sub>6</sub> H <sub>4</sub> (i)	2	70	97:3
12	<i>p</i> -CIC <sub>6</sub> H <sub>4</sub> ( <b>j</b> )	1	91	96:4
13	α-Np ( <b>k</b> )	1	89	94:6
14	β-Np (I)	1	86	96:4

[a] Isolated yield of major diastereomer. [b] Diastereomeric ratio (*dr*) was determined by <sup>1</sup>H NMR analysis. [c] Reaction temperature was -10 °C. [d] Reaction temperature was -15 °C. [e] Using 10 mol% SnBr<sub>4</sub>.

Next, to test the scope and limitations of nucleophiles, reactions of 3a with β-ketoesters 14-17 were carried out (Scheme 2). Reactivity was slightly decreased in all cases, when compared to results obtained with 1,3-dicarbonyl 10. However, reactions of 14, 15, and 17 afforded the corresponding targets 18, 19, and 21 in high yields when catalyst loading was increased and/or by prolonging the reaction time. β-Ketoester 16 afforded the desired product 20 in a moderate yield, probably owing to steric repulsion of the isopropyl group. Since products 18-21 were mixtures of keto-enol tautomers, in order to estimate diastereoselectivities of the nucleophilic substitution step, they were decarboxylated by treatment with NaOH. Decarboxylation of 18 and 19 was complete within 1-2 h, whereas a reaction time of 24 h was necessary for intermediates 20 and 21. In all cases, good diastereoselectivities were obtained. Unfortunately, malonic esters were unreactive, in agreement with our previous analogous report.[2e]



Scheme 2. Diastereoconvergent nucleophilic substitutions of 3a with various 1,3-ketoesters, followed by decarboxylation. [a] Yield of isolated mixtures of diastereomers.

Next, we undertook to transform single diastereomer **24** into the 1-benzopyran derivative **25**, a motif frequently present in biologically active compounds<sup>[10]</sup> (Scheme 3). When **24** was treated with BBr<sub>3</sub> at -40 °C for 2 h, cleavage of the chiral auxiliary followed by cyclization afforded the pyran **25** in 72% yield without erosion of optical purity. The absolute configuration of **25** was determined by comparison with a previously reported optical rotation value.<sup>[11]</sup> In addition, absolute configurations of other alkylated products **12a–12I**, **22**, **23** and **24** were assigned based on the result.



Scheme 3. Transformation of 24 into 1-benzopyran 25, and determination of the absolute configuration.

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To further transform alkylated products **12a**, **b**, **d**, **g** and **j**, we attempted to construct the corresponding pyrazoles. The pyrazole scaffold has versatile applicability in many fields, such as pharmaceuticals, agricultural chemicals, and functional materials.<sup>[12]</sup> To explore the effect of different substituents on the aromatic rings of the substrates, single diastereomers of abovementioned alkylated products **12** were treated with NH<sub>2</sub>NH<sub>2</sub>·H<sub>2</sub>O in MeOH (Scheme 4).<sup>[13]</sup> All *para*-substituted intermediates afforded corresponding pyrazoles **26** in high yields after 48 h, irrespective of the electronic nature of substituents. However, the reaction of **12b** bearing a methyl substituent in the *ortho* position proceeded slowly, and a prolonged reaction time of 72 h was required to give **26b** in 78% yield. In every case, products **26** were obtained as single diastereomers without epimerization.



Scheme 4. Transformation of the alkylated 12 into the pyrazoles 26.

A plausible reaction mechanism for the Lewis acid-catalyzed dehydrative nucleophilic substitution of diarylmethanol A (= 3a) with 1,3-dicarbonyl compound 10 is depicted in Scheme 5. Diarylmethyl cation int-2 is generated by activation of the hydroxy group on the diarylmethanol **A** with SnBr<sub>4</sub>, as shown in step (a), followed by subsequent elimination of the hydroxy group in step (b). It is expected that int-2 is stabilized by chelation of the oxygen atom of the MeO group on the chiral auxiliary, and its conformation is controlled to form a sevenmembered ring transition state.<sup>[4,5]</sup> TLC analysis shows that there is a partial equilibrium between int-2 and homoether AA, derived from 2 equivalents of A.[2c,14] In step (d), SnBr4 coordinates to the two oxygen atoms of 1,3-dicarbonyl 10 to generate int-3. The activated int-3 is subsequently enolized by deprotonation with hydroxy tetrabromostannate to generate int-4, along with the release of H<sub>2</sub>O and the regeneration of SnBr<sub>4</sub> in step (e). In the final step, step (c), int-4 attacks int-2 to afford desired 12a.

To confirm the above described reaction mechanism, we carried out the reaction of isolated homoether **AA** with 1,3dicarbonyl compound **10** under the optimal reaction conditions (Scheme 6). Treatment of diarylmethanol **A** (= **3a**) with SnBr<sub>4</sub> as a catalyst without a nucleophile gave homoether **AA** in 85% yield (*dl*, *meso* = 55:28:17, stereochemistries not assigned). When homoether **AA** was reacted with **10** in the presence of SnBr<sub>4</sub> as a catalyst, the results were almost identical to those of the reaction of diarylmethanol **3a** (see Table 2, entry 1). These results indicate that alcohol **A** (= **3a**) is partially in equilibrium with homoether **AA**.







Scheme 6. Synthesis of homoether AA, and the reaction of AA with 1,3dicarbonyl 10, catalyzed by SnBr<sub>4</sub>.

#### Conclusions

We have developed a diastereoconvergent methodology for dehydrative substitutions of diastereomixtures of diarylmethanols bearing a chiral auxiliary, carried out with 1,3dicarbonyls and catalyzed by SnBr4 as a Lewis acid. It was revealed that the efficacy of the reaction is dependent on the stability of carbocation intermediates. Where optimization was necessary, desired products were obtained in high yields with high diastereoselectivities in the case of substrates bearing an electron donating group, by lowering the temperature; in the case of substrates bearing an electron withdrawing group, by increasing the catalyst loading or prolonging the reaction time. Thus, the reaction is applicable to a broad range of substrates, and several 1,3-dicarbonyl compounds and β-ketoesters can be utilized. Further studies are currently underway in our laboratory to discover other nucleophiles and establish a more general utility of the present method.

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#### **Experimental Section**

Typical Procedure for the Diastereoconvergent Nucleophilic Substitutions of Diarylmethanols Diastereomixtures with 1,3-Dicarbonyl Compounds (Table 2, entry 1): To a solution of SnBr4 (4.2 mg, 9.58 µmol) in MeNO<sub>2</sub> (0.4 mL) at 0 °C were successively added diarylmethanol 3a<sup>[4]</sup> (63.9 mg, 0.191 mmol) in MeNO<sub>2</sub> (0.5 mL + 0.5 mL + 0.5 mL rinse) and (PhCO)<sub>2</sub>CH<sub>2</sub> (64.7 mg, 0.289 mmol). The reaction mixture was stirred for 1 h at 0 °C and then it was guenched with saturated aqueous NaHCO3 at 0 °C and the mixture diluted with CH2Cl2. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration of the mixture and evaporation of the solvent, the crude product was semi-purified by thin-layer chromatography on silica (hexane/EtOAc = 4:1 x2) to afford the diastereomer mixtures 12a, whose ratio was determined by <sup>1</sup>H NMR analysis (dr = 97:3). The both diastereomers were separated by thin-layer chromatography on silica (toluene/EtOAc = 20:1 x2) to afford the major diastereomer 12a (93.2 mg, 90% yield) as a white solid.

The 1 mmol-scale Synthesis of 12a: To a solution of SnBr<sub>4</sub> (23.0 mg, 52.5 µmol) in MeNO<sub>2</sub> (6.5 mL) at 0 °C were successively added diarylmethanol  $3a^{[4]}$  (352.0 mg, 1.05 mmol) in MeNO<sub>2</sub> (2 mL + 1 mL + 1 mL rinse) and (PhCO)<sub>2</sub>CH<sub>2</sub> (353.1 mg, 1.57 mmol). The reaction mixture was stirred for 1 h at 0 °C and then it was quenched with saturated aqueous NaHCO<sub>3</sub> at 0 °C and the mixture diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. After filtration of the mixture and evaporation of the solvent, the crude product was semi-purified by column chromatography on silica (hexane/EtOAc = 4:1 x2) to afford the diastereomer mixtures 12a, whose ratio was determined by <sup>1</sup>H NMR analysis (*dr* = 97:3). The both diastereomers were separated by thin-layer chromatography on silica (toluene/EtOAc = 20:1 x2) to afford the major diastereomer 12a (517.8 mg, 91% yield) as a white solid.

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Layout 2:



Synthetic Methods\*

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Chiral-Auxiliary-Controlled Diastereoconvergent Dehydrative Nucleophilic Substitutions of DiaryImethanol Diastereomixtures with 1,3-Dicarbonyls Catalyzed by SnBr4

\*one or two words that highlight the emphasis of the paper or the field of the study