The Effect of Lewis Acids on the Pinacol Homocoupling Reaction of Aldehydes Promoted by Samarium Diiodide

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The effect of various Lewis acids on the samarium diiodide promoted pinacol homocoupling of aldehydes was investigated. The reaction of benzaldehyde proceeded with fair to good 1,2-*anti*-stereoselectivity, while in the case of other aromatic and aliphatic aldehydes *syn*-stereoselectivity was generally observed. Chiral α-alkylaldehydes allowed for an almost complete stereocontrol favoring *syn*-1,2-diols.

Introduction

The pinacol coupling reaction is receiving renewed attention because of the recent availability of mild and selective reducing agents.[1] Among these, samarium diiodide has been successfully employed in the synthesis of several natural and nonnatural products.[1][2] While the intramolecular coupling procedure is well established, less is known about the intermolecular reaction: since the pioneering work of Kagan et al.,[3] only a few studies have dealt with the stereochemical outcome of the pinacol homocoupling of aldehydes promoted by Sm^{II} species.[1,2,4]

A great deal of effort has been devoted to make SmI_2-promoted reactions more convenient.[2] Interesting procedures have recently been proposed for the generation of SmI_2 from metallic samarium.[5] SmI_2 can be regenerated from Sm^{III} species employing electrochemical procedures[6a] or metallic species as coreductants,[6b,6c] and in the presence of metallic magnesium a catalytic cycle was proposed.[6b,7] Sm(Hg) was very recently shown to promote pinacol homocoupling of aromatic aldehydes.[8] Metal ketyl complexes have been characterized by X-ray techniques,[9] while the reducing power of SmI_2 in THF in the presence of cosolvents such as HMPA has been measured.[10][11]

An increasing amount of studies also deals with the effect of added Lewis acids on the intermolecular pinacol coupling.[4,12–14] The stereoselection of the pinacol coupling is often attributed to the capability of the metal to complex both reactants in the transition state; the use of Lewis acids more coordinating than the samarium(III) species is thus likely to influence the *syn*/*anti* ratio. Very recently, we published some preliminary results on the SmI_2-promoted homocoupling of imines in the presence of $Yb(OTf)_3$,[15] and wish now to report on our studies on the effect of Lewis acids on the homocoupling reaction of aldehydes to give *syn* and *anti* 1,2-diols.

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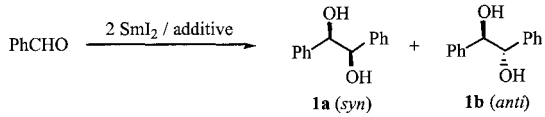
Results and Discussion

SmI_2-Promoted Homocoupling of Benzaldehyde in the Presence of Lewis Acids

The SmI_2-promoted homocoupling reaction of benzaldehyde was chosen to screen the behavior of different Lewis acids. All reactions were run in THF under an argon atmosphere; two molar equivalents of a 0.1M THF solution of SmI_2 were added dropwise to a 0.1M THF solution of benzaldehyde and the required additive (reaction conditions, additives, chemical yields and diastereoisomeric ratios are collected in Table 1). Assignment of the relative configuration to the known diols **1a**,**b** was based on the chemical shift values of the C*H*OH proton that resonates at 4.65 and 4.80 ppm in the *syn* and *anti* isomer, respectively.[16]

Table 1. SmI_2-promoted homocoupling of benzaldehyde



1a (*syn*) **1b** (*anti*)

#	T (°C)	t	additives (eq)[a]	yield %	*syn/anti*
1	–78	2 h30′	–	90	50/50
2	–78	2 h30′	CF_3COOH (2.2)	58	50/50
3	–78	2 h30′	MeOH (2.2)	45	50/50
4	–78	1 h15′	BF_3Et_2O (2.2)	90	50/50
5	–78	5h	$Ti(OiPr)_4$ (1)	–	–
6	–30	12h	$Ti(OiPr)_4$ (1)	55	25/75
7	0	12h	$Ti(OiPr)_4$ (1)	62	27/73
8	20	12h	$Ti(OiPr)_4$ (1)	94	27/73
9	60	18h	$Ti(OiPr)_4$ (1)	61	25/75
10	20	12h	$TiCl_2(OiPr)_2$ (1)	60	33/67
11	20	20h	$Ti(TADDOL)_2$ (1)	57	30/70
12	–78/0	18h	$NiCl_2$ (1)	–	–
13	20	12h	$NiCl_2$ (1)	70	30/70
14	–78 up to 20	18h	$NiCl_2$ (1)	85	25/75
15	–78	1 h30′	$Yb(OTf)_3$ (1)	79	40/60
16	–30	5h	$Yb(OTf)_3$ (1)	55	38/62
17	–78	5h	$ZnCl_2$ (1)	90	30/70
18	–30	12h	$ZnCl_2$ (1)	70	36/64
19	–78	5h	$MgBr_2$ (1)	96	31/69
20	–78	5h	$Cu(OTf)_2$ (1)	96	33/67
21	20	18h	$Ti(OiPr)_4$ (1) + HMPA (8)	27	34/66
22	–78	2 h30′	HMPA (8)	[b]	–
23	–78	2 h30′	HMPA (4)	80	40/60

[a] Molar equivalents with respect to benzaldehyde. – [b] Only benzyl alcohol was isolated.

  1434–193X/99/1212–3369 $ 17.50+.50/0

As can be seen from the literature,[1−3] the coupling reaction also proceeds smoothly at −78°C in the absence of additives with excellent chemical yields, but with no stereoselection (entry 1). The addition of proton donors (entries 2,3) did not affect the stereoselection, but lowered the chemical yield,[3] leading to the formation of benzyl alcohol as the only by-product. On passing from protic acids to $BF_3{\cdot}Et_2O$, the diols **1a**,**b** were obtained in good yields, but the reaction was completely stereorandom (entry 4). More interestingly, in the presence of titanium(IV) a predominance of the *anti* diastereoisomer was observed.[5a] Addition of $Ti(OiPr)_4$ slowed the reaction and higher temperatures were required for the coupling to proceed (entries 5−9), the best results being achieved at 20°C (entry 8). The stereoselection was independent of the reaction temperature. More acidic Ti^{IV} species, such as $Ti(OiPr)_2Cl_2$, led to less satisfactory results (entry 10). The use of the more hindered $Ti(TADDOL)_2$ did not allow for significant improvements (entry 11); unfortunately, only racemic *syn*-**1a** was observed.

The reaction performed in the presence of $NiCl_2$[12] showed an analogous behavior to the one observed when $Ti(OiPr)_4$ was employed: higher temperatures (20°C) were required for the reaction to proceed, and *anti* selectivity was observed (entries 12−14).[17] All the other Lewis acids we tested allowed for modest to good *anti* stereoselectivity, but with no significant improvement (entries 15−20).

HMPA is indeed the most commonly used cosolvent in SmI_2-promoted reactions, including pinacol coupling,[1][2] and influences both the chemical yield and the stereoselectivity of the reaction.[11] Addition of HMPA to SmI_2 solutions is known to lead to the formation of species with an increased reducing power. In fact, the oxidation potential of a 0.5M solution of SmI_2 in THF (−1.33 V) rises to −1.46 V for $SmI_2(HMPA)_2$, and to −2.05 V for $SmI_2(HMPA)_4$.[10] The combined use of 2 molar equivalents of $SmI_2(HMPA)_4$ (generated in situ from SmI_2 and HMPA) together with one equivalent of $Ti(OiPr)_4$ allowed for the formation of only a small quantity of diols (27%) with a modest *anti* stereoselectivity (entry 21). As by-products, benzyl alcohol and various deoxygenated and unsaturated compounds were observed.[18]

This disappointing result prompted us to investigate the effect of HMPA alone as an additive. In fact, the reaction performed with $SmI_2(HMPA)_4$ led to the formation of benzyl alcohol as the only product (entry 22). With 2 molar equivalents of HMPA per SmI_2, **1a**,**b** were recovered in good chemical yield, but the reaction was almost stereorandom (entry 23).

A few comments can be added concerning the SmI_2/Lewis acid-promoted pinacol coupling of benzaldehyde (Table 1, entries 5−20). First of all, the significant decrease of the reaction rate observed when Ti^{IV} (entries 5−11) or Ni^{II} (entries 12−14) species were added, could be due to the presence of complexation equilibria in solution. Before addition of SmI_2, benzaldehyde is complexed with the Lewis acid; decomplexation and complexation with Sm^{II} is probably needed for the reaction to take place.[2][19] If a direct reduction by SmI_2 of the Lewis acid-complexed benzaldehyde was possible, the reaction rate should be increased due to the more electrophilic character of the complexed C=O bond. However this was not the case (Table 1, entries 5−9).

In Figure 1 we indicate two possible transition structures to account for the observed stereoselectivity. In the presence of Ti^{IV} or Ni^{II} species, the Sm^{III}-ketyl radical complex reacts immediately with the strongly electrophilic Lewis acid-complexed aldehyde before the chelation equilibrium takes place. In TS **A**, leading to the *anti* diol, steric and electrostatic interactions are minimized. The *syn* isomer, on the other hand, may be derived from the chelated TS **B**. The intervention of different reducing agents, generated in situ from the Lewis acid by SmI_2, can be ruled out. Sm^{II} is not likely to reduce all the added metal species. Moreover, several low-valent titanium species are known to promote the coupling reaction, but with significant *syn* selectivity.[1][19]

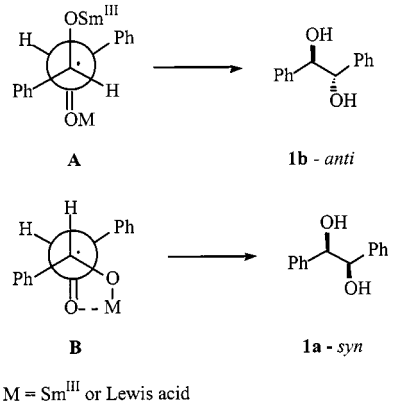


Figure 1. Proposed TS for the formation of **1a,b**

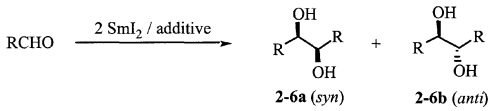
SmI_2-Promoted Coupling of Aldehydes in the Presence of Ti^{IV} Species

The homocoupling reaction of aldehydes other than benzaldehyde in the presence of SmI_2 and Lewis acids was then investigated. These aldehydes, however, were either nonreactive, or reacted with low selectivity, and only $Ti(OiPr)_4$ was an efficient additive in this reaction. As for the coupling of benzaldehyde, the presence of the Ti^{IV} species slowed the reaction, so that higher temperatures and sometimes longer reaction times were required for the reaction to proceed. Some significant data are collected in Table 2.

Both in the absence or in the presence of $Ti(OiPr)_4$, *ortho*-substituted electron-rich aromatic aldehydes did not couple to give the corresponding diols (entries 1,2), with the significant exception of salicylaldehyde.[20] In the absence of a Lewis acid the coupling is stereorandom, while when $Ti(OiPr)_4$ was added an 80:20 selectivity was observed, favoring the *syn* isomer.

2-Thienylcarboxaldehyde led to decomposition products in the presence of SmI_2; upon addition of $Ti(OiPr)_4$ only

Table 2. SmI_2-promoted homocoupling of aldehydes



2-6a (*syn*) **2-6b** (*anti*)

#	R	T (°C)	t	additives (eq)[a]	diol	yield%	*syn/anti*
1	2-MeOPh	–78 or 20	15h	–	–	–	–
2	2,4-$(MeO)_2$Ph	20	15h	$Ti(OiPr)_4$ (1)	–	–	–
3	2-HOPh	–78	3h	–	**2a,b**	55	50/50
4	2-HOPh	20	15h	$Ti(OiPr)_4$ (1)	**2a,b**	91	80/20
5	2-thiophenyl	–30 or 20	15h	–	–	–	–
6	2-thiophenyl	20	15h	$Ti(OiPr)_4$ (1)	**3a,b**	10	n.d.
7	2-furyl	–30	15h	–	**4a,b**	63	60/40
8	2-furyl	20	15h	$Ti(OiPr)_4$ (1)	**4a,b**	31	55/45
9	$PhCH_2$	20	15h	–	**5a,b**	40	86/14
10	$PhCH_2$	20	15h	$Ti(OiPr)_4$ (1)	–	[b]	–
11	*c*-C_6H_{11}	20	15h	$Ti(OiPr)_4$ (1)	**6a,b**	25	60/40[c]
12	*c*-C_6H_{11}	20	40h	$Ti(OiPr)_4$ (1)+HMPA (8)	**6a**	21	>98/2[c]
13	*c*-C_6H_{11}	60	40h	$Ti(OiPr)_4$ (1)+HMPA (8)	**6a**	27	>98/2[c]
14	*c*-C_6H_{11}	20	15h	HMPA (8)	**6a,b**	27	61/39
15	*c*-C_6H_{11}	60	15h	HMPA (8)	**6a**	61	>98/2[c]

[a] Molar equivalents with respect to benzaldehyde. – [b] Only 2-phenylethanol was isolated. – [c] Determined by ^{13}C NMR spectroscopy, see ref.[22]

traces of diols **3a**,**b** were recovered (entries 5,6).[2][21] 2-Furylcarboxaldehyde, on the other hand, underwent the pinacol reaction in both cases affording diols **4a**,**b**, but with no significant stereoselectivity (entries 7,8).

The behavior of aliphatic aldehydes was less puzzling. 2-Phenylacetaldehyde in the presence of SmI_2 gave diols **5a**,**b** with good *syn* selectivity, while in the presence of $Ti(OiPr)_4$ only the corresponding alcohol was isolated (entries 9,10). Aliphatic aldehydes, such as cyclohexancarboxyaldehyde, were known to give the corresponding pinacols in good yields and with no selectivity by reaction with SmI_2.[1][3] Addition of $Ti(OiPr)_4$ slowed the reaction, and even at higher temperatures diols **6a**,**b** were isolated in low yields and with little *syn* selectivity (entry 11). When performed in the presence of $SmI_2(HMPA)_4$ and $Ti(OiPr)_4$ the reaction was completely *syn* selective, although in low chemical yield, and was independent of the reaction temperature (entries 12,13). The stereoselectivity is due to $SmI_2(HMPA)_4$: in the absence of added Lewis acid, pinacol **6a** was formed with complete stereoselection at 60°C, while at room temperature the reaction is stereorandom (entries 14,15). Addition of $Ti(OiPr)_4$ allows complete stereoselectivity also at room temperature, but at the expense of longer reaction times.[22][23]

From the data reported in Table 2, it can clearly be seen that the reaction conditions need to be tuned to the particular substrate. However, we preferred to use standard reaction conditions in order to compare the behavior of different substrates. When the coupling was stereoselective (entries 9,12,13,15), a preference for the *syn* isomer was observed in all cases, while for benzaldehyde reactions *anti* diol was favored. Complexation equilibria can take place before the actual coupling reaction occurs; in these conditions, TS **B** (Figure 1) is the most favored and well accounts for the preferential *syn* stereoselectivity.[24] The reactions of salicylaldehyde to give **2a**,**b** probably proceed through chelated TS′s **C** and **D**, depicted in Figure 2.

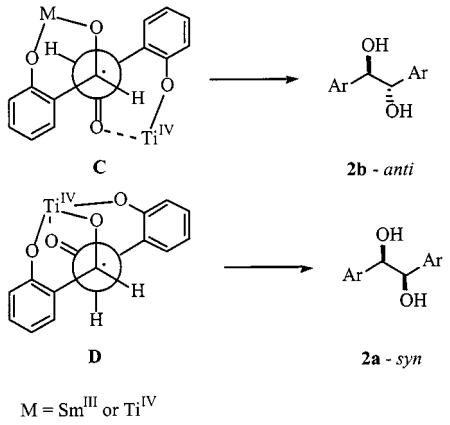
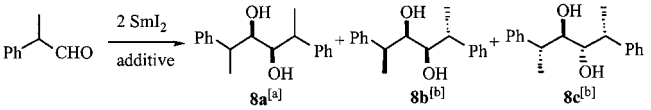


Figure 2. Proposed TS for the formation of **2a,b**

SmI_2-Promoted Coupling of Chiral Aldehydes

Despite its major drawbacks, we tested this procedure to the pinacol coupling of chiral aldehydes. Reaction of optically active α-alkoxy-aldehydes in the presence of SmI_2, with or without $Ti(OiPr)_4$, led only to deoxygenation of the substrates,[2] while the reaction performed on α-amino-aldehydes gave only the corresponding α-amino alcohols. Better results were obtained with α-methylaldehydes such as *rac*-2-phenylpropanal (Table 3). The coupling reaction performed in the presence of 2 molar equivalents of SmI_2 at 0°C led to the formation of only three out of the six (two *meso* and four *d,l* couples) possible diastereoisomers of diol **8** (entry 1; cf. Figure 3), namely 3,4-*syn*-**8a** and **8b** and 3,4-*anti*-**8c** in a 56:22:22 ratio (see below for structural assignment). Upon raising the reaction temperature to 20°C, both chemical yield and reaction stereoselectivity improved, and only **8a** and **8b** (in a 90:10 ratio) were formed in 55% chemical yield (entry 2). At this temperature and in the presence of 1 molar equivalent of $Ti(OiPr)_4$, only **8b** was detected and isolated in 77% yield (entry 3). Other reaction conditions, i.e. higher reaction temperature (entry 4), addition of HMPA (entries 5,6) and of $Ti(OiPr)_4$ and HMPA (entry 7) were detrimental to yield but not to stereoselection. Interestingly, in the presence of HMPA the reaction temperature seems to exert a major influence (entries 5,6), but

Table 3. SmI_2-promoted homocoupling of *rac*-2-phenylpropanal



8a[a] **8b**[b] **8c**[b]

#	T(°C)	t	additives (eq)[c]	yield%	8a	8b	8c	3,4-*syn/anti*
1	0	15h	–	45	56	22	22	78/22
2	20	15h	–	55	90	10	–	>98/2
3	20	15h	$Ti(OiPr)_4$ (1)	77	–	>98	–	>98/2
4	60	15h	–	[d]	–	–	–	–
5	20	15h	HMPA (8)	18	>98	–	–	>98/2
6	60	40h	HMPA (8)	25	–	>98	–	>98/2
7	20	15h	$Ti(OiPr)_4$ (1) + HMPA (8)	10	7	93	–	>98/2

[a] *rac*-diol **8a** possesses C_2 symmetry; relative configuration at C-2 and C-3 was not assigned (see text). – [b] Only one enantiomer is indicated for sake of simplicity. – [c] Molar equivalents with respect to benzaldehyde. – [d] Only 2-phenyl-1-propanol was isolated.

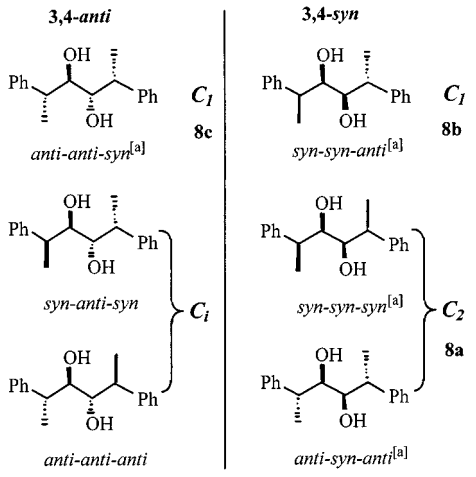


Figure 3. All possible diastereomeric structures for diols **8**

the extremely low chemical yields don't allow for further speculation.

The assignment of the relative configuration at C-3 and C-4 of compounds **8a**−**c** was carried out on converting **8** to acetonides **9** and then using a combination of spectroscopic evidence and symmetry considerations.[25] The reduced number of signals observed in both the ^1H and ^{13}C spectra of **8a** suggested a C_2 or C_S symmetry for this compound. Acetonide **9a**, readily obtained from **8a** (2,2-DMP, $BF_3{\cdot}Et_2O$) also showed ^1H and ^{13}C NMR spectra compatible with these symmetries (Figure 4). The observed isochronicity of the two geminal methyls (homotopic in the C_2-symmetric structure, diastereotopic in the C_S one) strongly supported the 4,5-*trans* configuration of **9a**, and hence the

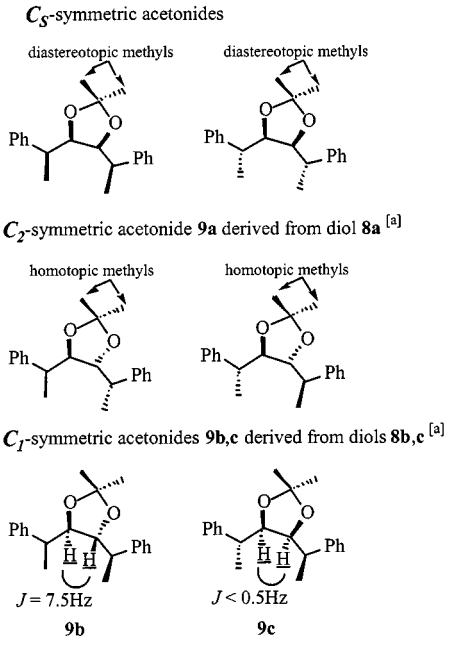


Figure 4. All possible diastereomers for acetonides **9**

3,4-*syn* configuration of **8a**. Assignment of the relative configuration at C-2 and C-5 (which can be either 2,3-*syn*/4,5-*syn* or 2,3-*anti*/4,5-*anti*) was not possible.

Conversion of an 80:10 mixture of **8b** and **8c** into the corresponding acetonides gave the asymmetric (C_1) compounds **9b** and **9c** (Figure 4). The coupling constant values observed for the hydrogens at C-4 and C-5 of the dioxolanyl moiety (J = 7.5 and < 0.5 Hz for **9b** and **9c**, respectively) supported the *trans* configuration for **9b** and the *cis* configuration for **9c**. On the basis of these observations and of the asymmetric (C_1) structure of **9b** and **9c** the 2,3-*syn*-3,4-*syn*-4,5-*anti* configuration was assigned to diol **8b**, and the 2,3-*anti*-3,4-*anti*-4,5-*syn* configuration to diol **8c**.

It is tempting to discuss the stereochemical outcome of the homocoupling of 2-phenylpropanal; however, reliable suggestions can be advanced only for the reaction performed in the presence of $Ti(OiPr)_4$ as additive (Table 3, entry 3).[26] Only in this case could the stereoselectivity be unambiguously assigned as 2,3-*syn*-3,4-*syn*-4,5-*anti* − only **8b** was formed − and chemical yields were satisfactory (77%). A rationale is tentatively depicted in Figure 5.

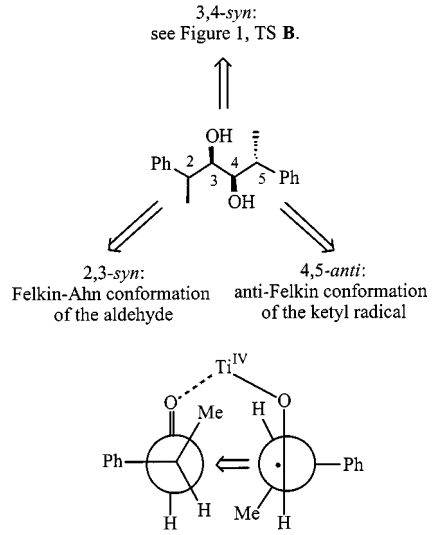


Figure 5. Proposed TS for the formation of **8b**

The complete 3,4-*syn* stereoselectivity arises from coordination of both reagents to the Ti^{IV} species, as shown in Figure 1 (TS **B**). The well-known tendency of 2-phenylpropanal to react with nucleophiles in a Felkin-Ahn mode can account for the 2,3-*syn* relative stereochemistry.[27] In the corresponding radical-anion species, however, the increased steric requirements of the alkoxide changes its reactivity to an *anti*-Felkin mode,[28] thus a 4,5-*anti* relative stereochemistry is favored. In the proposed TS, moreover, all steric interactions are minimized.[24]

Conclusion

The major pitfall of the SmI_2-based pinacolic homocoupling lies in the great versatility of this reagent: the reaction conditions need to be tuned carefully for each substrate in

order to achieve the best results each time. The intermolecular homocoupling reaction of benzaldehyde upon addition of Lewis acids stronger than Sm^{III} allows for synthesis of the *anti* diol, while *syn* diastereoisomers are always favored with different, achiral aldehydes.

The presence of chiral substituents on the aldehyde has a major influence on the reaction selectivity. The intermolecular coupling of chiral α-methylaldehydes is extremely stereoselective, and *syn* stereoselectivity is often complete. Further investigation is needed in order to extend this methodology to substrates of greater synthetic interest.

Experimental Section

CHN Analyses: Perkin−Elmer 240 instrument. ^1H and ^{13}C NMR: Bruker AM300 at 300.133 and 75.47 MHz, respectively; $CDCl_3$ as solvent; ^1H chemical shifts are reported in δ relative to TMS; ^{13}C chemical shifts and J_{H-H} coupling constants are reported in Hz. Silica gel (230−400 mesh) was used for flash chromatography. Organic extracts were dried over Na_2SO_4 and filtered before removal of the solvent. Dry solvents were distilled as follows: THF from Na and benzophenone (twice), CH_2Cl_2 from CaH_2; HMPA from CaH_2 (in vacuo). Distilled HMPA was stored under a nitrogen atmosphere over 4A molecular sieves. All reactions employing dry solvents were performed under an argon atmosphere. $Ti(OiPr)_4$ and all aldehydes were distilled before use. $ZnCl_2$ was dried by subsequent fusions in vacuo. $TiCl_2(OiPr)_2$ was prepared from $TiCl_4$ (1 mol. equiv.) and $Ti(OiPr)_4$ (1 mol. equiv.); $Ti(TADDOL)_2$ from $Ti(OiPr)_4$ (1 mol. equiv.) and TADDOL (2 mol. equiv.). Commercially available (Aldrich) 0.1M solution of SmI_2 in dry THF was used in the coupling procedure.

General Procedure for the Homocoupling Reaction of Aldehydes: Synthesis of Diols 1, 6a−b and 8a−c: To a stirred 0.1M solution of the required aldehyde in dry THF, kept at the desired temperature (see Tables 1−3), were added the appropriate additive (see Tables 1−3) and SmI_2 (0.1M solution in THF, 2 equiv.). The reaction was monitored by TLC, and quenched with 10% aqueous HCl. The two phases were separated, and the water layers were extracted twice with Et_2O. The crude product was purified by flash chromatography (Et_2O/ hexanes 50:50 → 80:20). Reaction conditions, chemical yields and diastereoisomeric ratios are reported in Tables 1−3.

Diols **1**, **3−6a**,**b** are known compounds.[16,22,23]

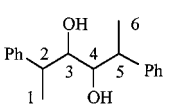
2a,**b:** $C_{14}H_{14}O_4$ (246.262): calcd. C 68.28, H 5.73; found C 68.35, H 5.70. − ^1H NMR: δ = 7.13 (dt, *J* = 7.6, 1.7 Hz, 2 H), 6.86 (dd, *J* = 7.1, 1.1 Hz, 2 H), 6.60 (dt, *J* = 7.1, 1.1 Hz, 2 H), 6.45 (dd, *J* = 7.6, 1.7 Hz, 2 H), 5.05 (s, 2 H, **2b**), 5.02 (s, 2 H, **2a**).

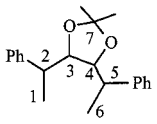
8a−c: $C_{18}H_{22}O_2$ (270.372): calcd. C 79.96, H 8.20; found C 79.91, H 8.24. For significant ^1H and ^{13}C NMR resonances, see Table 4.[25]

Synthesis of 7a,b From 2a,b: To a stirred solution of **2a**,**b** (1 mmol) in dry THF (10 mL) was added K_2CO_3 (5 mmols) at room temperature. After 45 min., methyl iodide (3 mmols) was added dropwise; the mixture was stirred overnight, then diluted with water (10 mL) and Et_2O (10 mL). The two phases were separated, and the aqueous layers extracted twice with Et_2O. The crude product was purified by flash chromatography (Et_2O/hexanes 90:10), affording known **7a**,**b**[23] in 70% yield.

Synthesis of 9a−c From 8a−c: To a stirred solution of **8** (1 mmol) in dry CH_2Cl_2 (10 mL) were added 2,2-dimethoxypropane (3 mmols) and $BF_3{\cdot}Et_2O$ (0.1 mmols) at 0°C, and the reaction kept at that temperature for 2 h. The reaction was quenched with saturated aqueous NH_4Cl, and extracted twice with Et_2O. The crude product was purified by flash chromatography (Et_2O/hexanes 90:10). Compound **9a** was obtained from **8a** in 81% yield; **9b**,**c** were obtained from **8b**,**c** in 95% yield. $C_{21}H_{26}O_2$ (310.437): calcd. C 81.25, H 8.44; found C 81.31, H 8.46. Significant ^1H and ^{13}C NMR resonances are reported in Table 4.

Table 4. Significant ^1H and ^{13}C NMR spectroscopic data for compounds **8a−c** and **9a−c**





		1	6	2	5	3	4	Me-7	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
8a	^1H	1.23		2.88		3.33		–	–	–	–
	^{13}C	18.05		42.8		75.6		–	–	–	–
8b	^1H	1.32		2.97		3.72		–	–	–	–
	^{13}C	18.4		43.2		74.9		–	–	–	–
8c[a]	^1H	1.37		2.97		3.33		–	–	–	–
9a	^1H	1.28		2.33		3.90		1.47	–	–	–
	^{13}C	16.8		43.2		84.0		27.9	–	–	–
9b	^1H	1.35	1.13	2.77	2.09	3.64	3.98	1.27; 1.42	7.5	7.5	4.0
	^{13}C	18.3[b]	19.3[b]	45.0[c]	41.8[c]	83.1[d]	84.7[d]	28.0; 27.8	–	–	–
9c	^1H	1.42[b]	1.18[b]	3.00		3.37	3.73	1.28; 1.43	7.0	< 0.5	7.0
	^{13}C	18.5[b]	18.8[b]	43.2[c]	43.9[c]	76.0	75.0	28.0	–	–	–

[a] ^{13}C NMR spectrum not measured. − [b] Resonances cannot be assigned unambiguously to C(H)-1 or C(H)-6. − [c] Resonances cannot be assigned unambiguously to C-2 or C-5. − [d] Resonances cannot be assigned unambiguously to C-3 or C-4.

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[21] Desulfurization was the major (or only) reaction path allowed in this case. While working on a different research project, we tested the reactivity of aromatic aldehydes *ortho*-substituted with sulfur-bearing residues in the presence of SmI_2: we never observed diol formation, but only desulfurization products together with substitution reaction at the aromatic ring in some particular substrates.
[22] Diols **3a**, **4a**, **5a**,**b** and **6a** are known compounds.[23] Diols **2a**,**b** were chemically correlated to the known *o*-methoxyderivatives **7a**,**b**.[23] Stereochemical assignment to diols **2−6a**,**b** was performed on the basis of both ^1H and ^{13}C NMR spectra and chemical correlation. The C*H*(OH) resonance of the *syn* products often overlapped with the CH_2OH singlet of the corresponding alcohol (the most common by-product of these reactions).
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