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Facile pinacol coupling of aliphatic ketones by Brook rearrangement in the presence of samarium species



Xincan Wang^{a,b}, Guanqun Xie^b, Yanfei Zhao^b, Ke Zheng^b, Yanxiong Fang^{a,*}, Xiaoxia Wang^{b,*}

^a School of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou, Guangdong 510006, China
^b School of Materials Science and Engineering, Dongguan University of Technology, Dongguan 523808, China

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ABSTRACT

Herein we report a practical pinacol coupling reaction, in which ketones (aldehydes) react smoothly with Sm and TMSBr to afford the diol products with Sm(II) or (III) siliyl species generated *in situ*. This reported method affords poor yields for aromatic ketone substrates and good yields for aliphatic ketones. Therefore, it distinguishes from most reductive coupling approaches that are more effective for aromatic carbonyl compounds and provides a facile and robust approach for the pinacol coupling of aliphatic ketones. Mechanistic studies also indicated the pinacolization probably proceeded via an anionic instead of radical coupling pathway involving the Brook rearrangement in the presence of samarium (II or III) silyl species.

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Introduction

Pinacol coupling of carbonyl compounds is one of the most important C-C forming reactions that has been widely used in the construction of versatile important compounds, especially as a key step for the synthesis of natural products [1]. It could also be used as a probe reaction for the assessment of reductive C--C bond formation potential of emerging reagents. Most routine pinacolization methods involve the generation of keyl radicals and followed by the radical homo-dimerization [2,3]. Among the various methods, the homo-coupling of aromatic carbonyl compounds, including photoredox- and electrochemcial protocols reported recently, have been well developed [4]. However, despite the available reports of intramolecular couplings of aliphatic aldehydes and ketones [5], efficient reagent systems that could achieve the readily intermolecular pinacolization of aliphatic carbonyls are relatively fewer. The high reductive potential of aliphatic carbonyls makes the generation of aliphatic ketyl difficult. On the other hand, the ketvl intermediates of the aliphatic carbonyls are highly unstable, thereby possessing a strong tendency to undergo H abstraction to form simple alcohols.

Sm(II) reagents has been well applied in promoting a variety of coupling reactions [6], among which SmBr₂ has showed more powerful reactivity than SmI₂ [6f,g]. However, the generation of SmBr₂ is not as convenient as SmI₂, which limits its popularity to certain extent. The available preparative methods include: (1) reduction of SmBr₃ with Li metal; [7a] (2) the reaction between Sm and 1,2-dibromoethane [7b] or 1,1,2,2-tetrabromoehane; [7c] (3) addition of four-fold excess of LiBr in the SmI₂ solution [7d,e] The Ishii group has attempted the preparation of Sm(II) regent from Sm/TMSBr in CH₃CN [7f], where 5 h under reflux conditions were required and the exact Sm(II) species has not been addressed. It is worth mentioning that large excess Sm and related bromocontaining reagents were usually employed to ensure good coupling efficiency.

In continuation of our investigation on developing bromo containing Sm(II) species such as allyISmBr [8], we incidentally found the simple mixing of Sm, TMSBr and the carbonyl substrate (molar ratio: 1:1:1) in THF under N₂ atmosphere afforded a facile method for the effective coupling of aliphatic ketones, and probe of the mechanism indicates the possible involvement of samarium (II or III) silyl species.

Results and discussion

* Corresponding authors.

2-Heptanone (**1a**, 1.0 mmol) was used as a model substrate, which was added to a mixture of Sm (1.0 equiv.) and TMSBr (1.0 equiv.) in THF (3 mL) at r.t. under N₂ atmosphere. The reaction pro-



E-mail addresses: fangyx@gdut.edu.cn (Y. Fang), wangxx@dgut.edu.cn (X. Wang).

Table 1

Examination of Sm/additive on the pinacol coupling of 2-heptanone 2a.^a



Entry	Sm (equiv.)	Additive (equiv.)	Reaction time	Yield % ^b
1	1.0	TMSBr (1.0)	0.5 h	78%
2	1.0	TMSCI (1.0)	10 h	0
3	1.0	TMSI (1.0)	2.5 h	71%
4	1.0	BBr ₃ (1.0)	Over night	20%
5	1.0	PBr ₃ (1.0)	Over night	0%
6	1.0	Et ₃ N•HBr (1.0)	Over night	0
7	0.33	TMSBr (1.0)	6 h	63%
8	1.0	TMSBr (0.1)	0.5 h	16% ^c
9	1.0	TMSBr (0.5)	0.5 h	60%
10	1.0	TMSBr (2.0)	0.5 h	37%

^a Reaction conditions: Sm 1.0 mmol (0.15 g), 2-heptanone (1.0 mmol, 0.114 g) and the additive in dry THF 3 mL under N₂ at the room temperature. The reaction mixture was quenched with Bu_4NF (1.0 M in THF, 1.2 mL) and allowed to be stirred for 1 h followed by usual workup (see SI).

^b Isolated yields.

^c With 71% of the starting material recovered.

cess was monitored by GC-MS. It is satisfying that 78% of isolated yield of the desired aliphatic diol 2a was obtained in 30 min. under the mild conditions (Table 1, entry 1). A blue slurry was gradually formed in the reaction indicating the formation of Sm(II) species. For comparison, the reaction promoted by Sm/TMSCl and Sm/TMSI were examined. No color change could be observed using Sm/ TMSCl system and GC-MS analysis showed no formation of the desired diol even in 10 h except a small amount of the 2-heptanol (~5% yield). The result is consistent with the report by Yu and Zhang [9], where aliphatic ketones are sluggish substrates in Sm/ TMSCl. Slightly lower yield of the diol was obtained using Sm/TMSI (Table 1, entries 2 and 3), and in this case, the reaction mixture also took on blue color. Besides, BBr₃, PBr₃ and Et₃N•HBr were also examined as the bromo source. The reaction with Sm/BBr3 was sluggish as most starting ketone remained unreacted and only 20% yield of the desired pinacol was detected even by prolonging the time overnight (Talbe 1, entries 4). No desired reaction could be observed at all using Sm/PBr3 or Sm/ Et3N·HBr (Talbe 1, entries 5 and 6).

From the viewpoint of atom economy, 1/3 mmol of Sm, with its complete transformation into Sm(III) oxidation state, would be enough to achieve the complete coupling of 1 mmol of the ketone. Thus the substoichiometric amount of Sm was attempted and it was found relatively good yield was afforded (Table 1, entry 7). Screening on the loading of TMSBr showed 0.5 equiv. of TMSBr could afford reasonable yields, while 0.1 equiv. or 2.0 equiv. of TMSBr gave unsatisfactory yields (Table 1, entries 8–10). The decrease in the yield of diol with excess TMSBr could be rationalized by the competitive formation of hexamethyl disilante, as has been monitored by GC–MS.

Considering the simplicity of the condition and the good yield (entry 1, Table 1), no further optimization of the reaction was conducted and the ratio of Sm/TMSBr/substrate (1:1:1) was established as the standard condition. Subsequently, the scope of the reaction was examined by extending the substrates to a variety of ketones and aldehydes. The results are shown in Table 2.

It is noteworthy the Sm/TMSBr system afforded good to high yields of the diols rapidly for aliphatic ketones (in 30 min.). In con-

trast, aromatic ones are less efficient. For acetophenone 1k 65% of the starting material remained in 30 min. together with the diol in 22% yield (Table 2, entries 1-10 vs entry 11). Sterically hindered ketone **11** is not a suitable substrate and only trace amount of the diol was detected (Table 2, entry 12). As far as we know, the available reductive coupling methods always realize the pinacolization of aromatic ketones and aldehydes better than that of their aliphatic counterparts [10]. Therefore, the above results can not be satisfactorily explained by initiation via the reduction of the carbonyl to form ketyl since the reduction of aliphatic carbonyls is more difficult than aromatic ones. The same phenomenon was observed between aliphatic and aromatic aldehydes (Table 2, entries 13-19 vs entries 20-21). Unfortunatley, aldehydes usually afforded lower yields under the standard conditions, where simple reduced products was the main side reaction together with several minor by-products mixture. For aromatic aldehydes, 1u with the electro-withdrawing F group afforded better yield of the diol than 1t with an electro-donating methyl group.

Measurement of cyclic voltammetry of TMSCI, TMSBr and TMSI found the reductive potentials were *ca.* -2.58, -1.67 and -0.488 V respectively (*vs* Ag/AgCl with Fc/Fc⁺ as internal standard, see supporting information), which could account for the facts that Sm reacts with TMSBr and TMSI to give a green suspension of Sm(II) species while the reaction between Sm and TMSCI is sluggish.

In view of the more negative reductive potentials of carbonyl compounds (-2.05 to -2.23 V vs Ag/AgCl) and aliphatic carbonyl compounds (~3.00 V) [11], it is reasonable that Sm may reduce TMSBr preferentially in the coexistence of ketones and aldehydes. Furthermore, the more negative reductive potentials of aliphatic carbonyls could not rationale why the reaction of aliphatic carbonyls is more readily than aromatic ones in the system. A mechanism rather than ketyl related coupling should exist.

According to the research on the pinacolization with Yb/TMSBr by Takaki and Fujiwan et al. [12], where YbBr₂ was proposed to be the active species, it seems reasonable to propose the key Sm(II) species produced here maybe $SmBr_2$ (Scheme 1, path a). However, treatment of 2-heptanone with $SmBr_2$ (1.0 equv.) or $SmBr_2$ (1.0

Table 2

Sm/TMSBr promoted pinacol coupling of carbonyl compounds.^a

Entry	Substrate 1	Product 2	Yield (%) of 2 ^b	Dl : meso ^c
1) 1a	n-C ₅ H ₁₁ HO	78%	52:48
2		$\stackrel{OH}{\xrightarrow{n-C_3H_7}} h_{C_3H_7} \mathbf{2b}$	58%	58:42
3		∕ ÖH n-C₀H₁9 HO → 	54%	49:51
4		OH 2d	61%	52:48
5	1e		78%	56:44
6	↓ 1f	\downarrow У он HO n-C ₃ H ₇ n-C ₃ H ₇ — (-n-C ₃ H ₇ 2f	74%	-
7	$r - C_3 H_7$ $r - C_3 H_7$	$\begin{array}{c} {}_{n-C_{3}H_{7}} \text{OH} \\ HO \qquad C_{2}H_{5} \\ C_{2}H_{5} \end{array} C_{4}H_{9} \mathbf{2g} \end{array}$	76%	50:50
8		C_4H_9 OH	63%	-
9	° 1i		70%	-
10	^ 1j	OH 2j	75%	-
11	لي الم		22%	57:43
12	ب ۲ ا		1% ^d	_
13	$\int_{\mathbf{n}-\mathbf{C}_{5}\mathbf{H}_{11}}^{\mathbf{O}}\mathbf{H}$ 1m	$HO \rightarrow -C_5H_{11}$ 2m	49%	48:52
14	0 n-C ₆ H ₁₃	$\stackrel{n-C_6H_{11}}{\xrightarrow{HO}} \stackrel{n-C_6H_{13}}{\xrightarrow{2n}} \mathbf{2n}$	50%	68:32
15	0 □-C+Her H 10	$\stackrel{\text{HO}}{\longrightarrow} \stackrel{\text{n-C}_{7}H_{15}}{\swarrow} 20$	51%	60:40
16	о н 1р	п-С ₇ Н ₁₅ ОН онон 2 р	60%	60:40
17	,н 1q	онон 2q	64%	56:13:12:19 ^e
18	H Ir	OH 2r	48%	0:100
19	⊖ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ ↓ S	́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́ ́	46%	51:49
20	∫ 1t		16%	49:51
21	1u	OH OH 2u	25%	43:57

^a Reaction conditions: Sm 1.0 mmol (0.15 g), the carbonyl compound (1.0 mmol), TMSBr (1.0 mmol) in dry THF 3 mL under N₂ at the room temperature. The reaction mixture was quenched with Bu₄NF (1.0 M in THF, 1.2 mL) and allowed to be stirred for 1 h followed by usual workup (see SI).

^b Isolated yields.
 ^c Determined by GC-MS.
 ^d Together with simple reduced alcohol (12%) and the starting ketone (87%) as determined by GC-MS.
 ^e Four diastereomers were detected.



Scheme 1. Proposed generation of Sm(II) species from Sm and TMSBr.

equiv.)/TMSBr (1.0 equiv.) afforded the desired diol only in 16% and 20%, respectively. Therefore, the reaction between Sm and TMSBr should proceed in an alternative way. The samarium(II) species A (Me₃SiSmBr) may be involved (Scheme 1, path b).

Accordingly, the mechanism shown in Scheme 2 is proposed for the Sm/TMSBr system mediated pinacol coupling.

Thus Sm may reduce the Si-Br bond to form Me₃SmBr **A**, which then undergoes nuecleophilic addition [13] to the carbonyl of the ketone to produce an organosiliyl intermediate **I**, which would undergo samarium Brook rearrangement [14] to form organosamarium(II) reagent **II**. Subsequently, **II** attacked another ketone molecule to afford the momosamarium(II) pinacolate **III**. By exchange of the trimetylsily with samarium cation, the disilyl pinacolate **IV** was produced and at the same time releasing SmBr₂. Although SmBr₂ is a powerful reducing agent and could achieve the

pinacolization efficiently [6a,c], however, in the co-existenc of Sm, SmBr₂ may reduce TMSBr more efficiently [15] to generate Me₃-SmBr₂ V and SmBr₃, rather than reduce the carbonyl into a ketyl to give the pinacols. Me₃SmBr₂ could undergo the same nuecleophilic addition to the carbonyl of the ketone to produce an organosiliyl intermediate VI. Brook rearrangement of VI transforms into organosamarium(III) reagent VII. In a similar way, the momosamarium(III) pinacolate VIII would be produced. Cation exchange with TMSBr gives disilyl pinacolate IV and regenerates SmBr₃, which is then reduced by Sm readily to regenerate SmBr₂. With such a cycle, the piancol coupling of aliphatic carbonyls with Sm metal will be more efficient, since the formation of organosamarium intermediate and the key coupling process both involved the nucleophilic addition to the carbonyls. It is well known that alihphatic carbonyls are more electrophilic and sterically less hindered than their aromatic counterparts, therefore the former are more active towards nucleophiles.

In conclusion, a novel and efficient protocol for the pinacol coupling of aliphatic ketones has been developed with readily available reagents. The in-advance preparation of the active Sm(II) species is avoided, and the amount of the reagents and solvent could be significantly decreased [16]. A unique Me₃SiSmBr species was proposed, and an anionic pinacol coupling pathway *via* samarium Brook rearrangement was suggested. Further studies concerning the catalytic version of the novel reductive system with proper ligand to further improve the diastereoselectivities of the coupling reaction would be underway.



Scheme 2. Proposed mechanism for the generation of diols.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2021.153069.

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