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An Unexpected Transformation of Aldehydes into Benzoins with Copper(I)/Samarium

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Abstract

The reductive coupling of aldehydes to afford pinacolic alcohols is well-known by using all kinds of reducing agents involving samarium. In this report, however, treatment of aromatic aldehydes with Cu(I)/Sm system produces benoins and/or benzils in good yields. A possible mechanism is proposed where Cu(I) not only activates the Sm metal but also promotes the dehydrogenation of the intermediates, during which a Cu(III) species is proposed to be involved.

[Supplementary materials are available for this article. Go to the publisher's online edition of *Synthetic Communications*® for the following free supplemental resource(s): Full experimental and spectral details.]

$$Ar-CHO \xrightarrow{Sm/CuX}_{THF} \begin{bmatrix} O & OH \\ Ar-C-CH-Ar \end{bmatrix} \longrightarrow Ar-C-C-Ar$$

$$CuX = CuI, CuBr/KI, CuCI/KI$$

Ar = phenyl, fused aromatic rings, heterocyclic aromatic rings

KEYWORDS: Samarium; copper; iodides; aldehydes; benzoins

Copper mediated coupling reactions have played important roles for constructing organic molecules with a large variety of structures.^[1] Besides, the incorporation of copper salts into other metals for the achievement of specific purposes is also impressive. With the incorporation into sec-alkyl Grignard reagent, copper salt was recenlty reported to achieve the challenging cross-coupling^[2b] of nonactivated sec-alkyl halides and pseudohalides. By using copper salt as a catalyst, zinc mediated conjugate addition reaction was able to proceed in water smoothly.^[2c] while in the presence of CuI a cyclopropylzinc species can be afforded by the diastereoselective addition of diorganozinc reagents to cyclopropene derivatives.^[2d] The combination of copper and titanium catalyzes the three-component coupling of unactivated ketones with amines and terminal alkynes to form tetrasubstituted propargylamines under solvent-free conditions.^[2e] In addition to the classic Sonogashira reaction, palladium has been explored with the corporation of copper salts for many exclusive coupling reactions in most recent reports.^[2f,i] In these typical reactivity patterns of organocuprates, the formation of the key carbon-carbon or carbon-heteroatom bond was often mediated by a Cu(III) intermediate, which has long been proposed to be involved during the catalytic process of copper salts.^[3]

Samarium reagents have drawn much attention due to their particular importance in reductive coupling reactions.^[4] Although the applications of samarium diiodide are obviously efficient due to its advantages in organic transformations, the direct use of metallic samarium as a reducing agent showed certain advantages as of being more practical and electron-economical than the use of samarium diiodide.^[5] The reactions promoted by samarium metal generally requires the presence of an auxiliary^[5,6] such as iodine, hydrochloric acid, alkyl halides and TMSCl, etc. so as to activate the surface of the samarium metal and thus improve the reactivity.^[6]

Our studies on the direct use of samarium^[7] have directed our efforts into exploiting a copper / samarium system. Inspired by the extraordinary effect resulting from the combination of copper salt with other metal and organometallic reagents,^[3] we assume that the incorporation of copper salts into samarium metal may possess unique reactivity. Herein we report the coupling of aldehydes into benzoins and/or benzils with Cu(I)/Sm system. It should be noted that although aldehydes underwent Pinacolic coupling in the presence of samarium reagents,^[6e,8] no piancols were detected with the Cu(I)/Sm system.

Benzaldehyde was chosen as the model substrate (Scheme 1) and the reaction conditions for the coupling was optimized.

Table 1 summarized the results of the investigation on screening a variety of copper salts for this condensation. No reaction occurred by using copper(I) chloride, while copper(I) iodide gave good yield of benzoin (Table 1, entry 2). Improvement of the yield as well as acceleration of the reaction rate was observed when KI or NaI was added as an auxiliary catalyst to CuI or CuBr (Table 1, entries 4 and 5). Divalent Cu(II) salts, such as (AcO)₂Cu or CuSO₄, were also examined but found unsuccessful (Table 1, entries 7 and 8). Although CuCl₂ can promote the self-condensation of benzaldehyde into benzoin in the presence of potassium iodide, the higher temperature and longer time it required together with the relatively lower yield make it less attractive (Table 1, entry 6). The results also showed that either benzaldehyde or samarium alone is unreactive to copper(I) iodide even under reflux for 5 hours.

Finally, Sm/CuCl/KI was established as the standard conditions. To explore the scope of the reaction, a series of aromatic aldehydes were examined. Gratifyingly, most substrates afforded the desired benzoins smoothly. In certain cases, unexpectedly, benzils were also obtained as the byproducts (Scheme 2). The results of the reactions are summarized in Table 2.

In the presence of Sm, CuCl and KI (compared with CuI alone), the reaction proceeded more readily and afforded higher yields (Table 2, make a comparison between entries 1 and 1', 5 and 5', 10 and 10', 13 and 13', 19 -21 and 19' - 21'). Even remarkable concerning

Sm/CuCl/KI is that 4-cyanobenzaldehyde (1m) can undergo the condensation smoothly to afford the corresponding benzil, while no reaction occur under CuI/Sm alone (Table 2, entries 13 and 13'). The condensations of 1a, 1f, 1g, 1h, 1j, 1k, 1l, 1o and 1p possessing electron-donating groups afforded the bezoins in good yields (Table 2, entries 1, 6-8, 10-12, 15 and 16). In contrast, the condensations of 1b, 1c, 1d and 1e possessing electron-withdrawing groups require relatively longer reaction time and give lower total yields (Table 2, entries 2-5). Nevertheless, the formation of either 2h, 2o, 3i or 3m is noteworthy since the vitamin B₁ catalyzed benzoin condensation was not applicable for the aromatic aldehyde substrates with strong electron-withdrawing or electron-donating groups attached on the aryl,^[9] while other methods could not afford the benzoins from aldehydes in such a direct way.

The reaction of *o*-substituted aromatic aldehyde such as 2-chlorobenzaldehyde (1d) only afforded 2,2'-chlorobenzil 3d (Table 2, entry 4). The same results were observed with heterocyclic aldehydes (1s, 1t) and fused-ring aromatic aldehyde (1u), which underwent the condensation successfully (Table 2, entries 19-21) and afforded benzil as the only products after work-up. The reaction of aliphatic aldehyde (1r), however, resulted in a complex mixture and the desired benzoin was not isolated in this case (Table 2, entry 18). The condensations of 4-nitrobenzaldehyde (1n, Table 2, entry 14) and 1,4-phthalaldehyde (1q, Table 2, entry 17) failed to generate benzoins. However, it was surprising that the nitro group, labile to most samarium regeants, was tolerated

under the reaction conditions. Attempts to expand the condensation to 4-hydroxybenzaldehyde or 2-hydroxybenzaldehyde were not successful, which may indicate the process is incompatible with proton donor.

Elucidation of the condensation mechanism is challenging since apparently no reducing process occurs during the transformation from benzaldehydes to benzions. Considering the reaction was operated under inert nitrogen atmosphere, we propose a dehydrogenation step may be involved during the condensation process since copper salts are efficient catalysts for dehydrogenation.^[10] Moreover, based on the experimental results and other studies on the copper catalyzed reactions,^[2,3] we suggest a Cu(III) species may be involved in the reaction. Thus, aromatic aldehydes firstly obtain an electron from samarium to form ketyl **A**, which then transforms into a six-membered Cu(III) species^[3d] with the cooperation of iodine ion to increase its stability and solubility. Subsequently a complicated dehydrogenation of the intermediate may occur thus affords enol **B**, which would tautermerizes to give benzoin **2** in the work-up.

An alternative mechanism may also be proposed, which could rationale the formation of benzoin by dehydrogenation of hydrobenzoin in the presence of copper salts. A controlled experiment was conducted, where 1,2-diphenylethane-1,2-diol was also subjected to the same reaction conditions. It was only to find no reaction occurred at

all. Thus the dehydrogenation of hydrobenzoin under the conditions was excluded. Besides, aldehydes were found inert to either samarium metal or CuI, which indicates a possible synergistic effect among aldehyde, samarium and copper salt.

The formation of benzils may result from auto-oxidation of benzoins. The reports that some metal salts such as copper(I)^[11a] and Ce(IV)^[11b] can easily catalyze the autoxidation of benzoins to the corresponding benzils make it reasonable to deduce that during the work-up, the presence of copper(I) and samarium salts may accelerate the formation of benzils from benzoins. An experiment was also designed to confirm the auto-oxidation process. Thus when the condensation reaction of benzaldehyde was complete, the reaction mixture was placed in air at room temperature and then monitored by TLC in regular intervals. The results showed the content of benzoins became less and less, while that of benzils increased as the standing time prolonged. Finally, the benzoins almost disappeared in 10-20 hours, thus validating the auto-oxidation process (Scheme 3). The results are summarized in Table 3.

In conclusion, Cu(I) salts were used to combine with samarium metal to construct a new system and its reactivity was preliminarily examined. With aromatic aldehydes as the substrates, the system did show unique reactivity and afforded benzoins and benzils as the products instead of pinacols. Further investigation concerning clarification of the

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mechanism and search for more applications of the system in organic synthesis are currently underway in our lab.

EXPERIMENTAL

General

All NMR spectra were measured in CDCl₃ and recorded on Bruker Avance-500 (500 MHz) spectrometer with TMS as the internal standard. Chemical shifts are expressed in ppm and J values are given in Hz. IR spectra were recorded on a Bruker Tensor-27 spectrometer. Melting points are uncorrected. All the reactions in this paper were performed under nitrogen atmosphere. THF was refluxed and got rid of water before use.

Typical Procedure For The Self-Condensation Of Aromatic Aldehydes

To a mixture of Sm powder (0.3 g, 2 mmol), CuCl (0.2 g, 2 mmol) and KI (0.33 g, 2 mmol) in anhydrous tetrahydrofuran (THF, 10 mL), benzaldehyde (0.4 mL, 4 mmol) was added at room temperature under a nitrogen atmosphere with magnetic stirring. After completion of the reaction (about 2 h, monitored by TLC), dilute hydrochloric acid (2 M, 5 mL) was added and the resulting mixture was extracted with ethyl acetate (3×20 mL). The combined organic layer was washed with brine and saturated sodium thiosulfate solution, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The crude product were purified with flash chromatography (silica/hexane - ethyl acetate 5 : 1 v/v) to afford 0.36 g of the corresponding benzoin (**2a**) with 84 % yield.

2-Hydroxy-1,2-diphenylethanone (2a): white solid; mp 135-136°C, lit.^{7f} 134-136°C; ¹H NMR: δ 7.92 - 7.93 (m, 2 H), 7.52 -7.55 (m, 1 H), 7.39 -7.42 (m, 2 H), 7.29 -7.34 (m, 5 H), 5.96 (d, 1 H, *J* = 6.0 Hz), 4.56 (d, 1 H, *J* = 6.0 Hz); IR (KBr): 3416, 3028, 2931, 1680, 1596, 1491, 1449 cm⁻¹; ¹³C NMR: δ 76.3, 127.9, 128.7, 128.8, 129.2, 133.5, 134.0, 139.1, 199.0.

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entry ^a	metal salts	temp.	time (h)	isolated yield
				of benzoin
1	CuI	rt	5	72
2	CuCl	reflux	5	^b
3	CuCl ₂	reflux	5	^{b,c}
4	CuCl/KI	rt	2	84
5	CuBr/NaI	rt	2	81
6	CuCl ₂ /KI	reflux	5	12 ^b
7	(AcO) ₂ Cu/KI	reflux	5	b,c
8	CuSO ₄ /KI	reflux	5	^{b,c}

Table 1. Reaction Results of Benzaldehyde in the Presence of Samarium / Copper Salts
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^{a.} The ratio of aldehyde : samarium : Cu (I) is 2 : 1 : 1. ^b No reaction. ^c The ratio of

aldehyde : samarium : Cu (II) is 2 : 2 : 1.

entry ^a	Ar in substrate 1	temp.	time	isolated yield of 2	isolated yield of 3
		(°C)	(h)	(%)	(%)
1	$C_{6}H_{5}$ - (1a)	rt	2	84 (2a)	
1'	(1 a)	rt	5	72 (2 a)	
2	<i>p</i> -F-C ₆ H ₄ - (1b)	rt	3	68 (2b)	
3	<i>p</i> -Cl-C ₆ H ₄ - (1c)	rt	2	66 (2c)	
4	<i>o</i> -Cl-C ₆ H ₄ - (1d)	rt	3		60 (3d)
5	p-Br-C ₆ H ₄ - (1e)	reflux	2	64 (2e)	
5'	(1e)	reflux	4	48 (2e)	
6	<i>p</i> -Me-C ₆ H ₄ - (1f)	rt	3	76 (2f)	13 (3f)
7	<i>m</i> -Me-C ₆ H ₄ - (1g)	reflux	3	77 (2 g)	
8	<i>p</i> -MeO-C ₆ H ₄ -(1 h)	rt	3	78 (2h)	15 (3h)
9	p-EtO-C ₆ H ₄ - (1i)	rt	2		54 (3i)
10	$p-Me_2N-C_6H_4-(1j)$	rt	3	67 (2j)	
10'	(1 j)	rt	5	53 (2j)	
11	p- <i>i</i> -Pr-C ₆ H ₄ - (1k)	rt	2	81 (2 k)	
12	p- t -Bu-C ₆ H ₄ - (11)	rt	2	86 (2l)	
13	p-CN-C ₆ H ₄ - (1m)	reflux	4		52 (3 m)
13'	(1 m)	reflux	6	^b	^b
14	p-NO ₂ -C ₆ H ₄ -(1 n)	reflux	24	20 ^c	

Table 2.	Reactions	of Aromatic	Aldehydes	Promoted by	Sm/CuCl/KI in TH	F
			2			

15		rt	2	76 (20)	
	0-(10)				
16	Me	rt	3	87 (2p)	
	Me (1p)				
17	онс-(1q)	reflux	20	12 ^b	
18	CH ₂ CH ₂ ⁻	reflux	3	^b	^b
	(1r)				
19	(1s)	rt	3		63 (3s)
19'	(1s)	reflux	6		40 (3s)
20		rt	3		82 (3t)
	S (It)				
20'	(1t)	reflux	5		67 (3 t)
21		rt	3		71 (3u)
	(1u)				
21'	(1u)	reflux	5		53 (3u)

^{a.}Entries 1', 5', 10', 13', 19', 20', 21' are performed in the presence of CuI alone without potassium iodide. ^{b.} A complex mixture was obtained. ^{c.} 4-Nitrobenzyl alcohol was afforded.

Entry	R	Time (h)	Isolated yield of $2 (\%)^a$	Isolated yield of 3 (%) ^{<i>a</i>}
1	Н	12	15 (2a)	68 (3a)
2	<i>p</i> -F	10	6 (2b)	61 (3b)
3	<i>p</i> -Cl	10	_ ^b	67 (3c)
4	<i>p</i> -Br	10	_b	65 (3 e)
5	<i>p</i> -Me	20	16 (2f)	60 (3f)

Table 3 The auto-oxidation of the benzoins to benzils under	air
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^{a.} Based on aryl aldehydes. ^b Not detected.

Scheme 1 Reaction of benzaldehyde promoted by CuI/Sm



Scheme 2 Reactions of aromatic aldehydes promoted by Cu(I)/Sm



Scheme 3 Possible mechanism for the formation of benzoin



Scheme 4 Oxidation of benzoins to benzils in condensation mixture under air

3

о он -с—сн-- R R

(condensation mixture in the presence of samarium and copper salts)

2