

Intramolecular cyclization and disilylation of 1,1-dicyano-2,2-diarylethenes promoted by samarium/TMSCl in DMF: a new approach to the syntheses of polysubstituted indenenes

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Abstract—Promoted by samarium metal in DMF and in the presence of TMSCl, 1,1-diaryl-2,2-dicyanoethylenes undergo an unexpected kind of reductive cyclization, thus affording a new approach to the construction of indene core. Simultaneously, disilylation occurred at the amino moiety resulting from the reduction of the cyano group.

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As important synthetic intermediates, the use of indenenes have been widely exploited in pharmaceuticals, catalysis, metal complexes, polymer chemistry, and the syntheses of natural products.¹ A number of synthetic methodologies for indenenes have appeared.² Semmelback et al. reported the cyclopropene rearrangements for benzannulation to synthesize indene compounds catalyzed by Mo(CO)₆ or Cr(CO)₆.^{2a} 3-Vinylcyclopropenes were also reported to undergo photochemical rearrangement to form indenenes.^{2b} The addition of vinyl Grignard reagents with aromatic ketones followed by annulation and dehydration catalyzed by methyl sulfonic acid is also a useful method for indenenes syntheses.^{2c} Besides, a variety of catalysts, such as SOCl₂/AlCl₃,^{1a} H₂SO₄/AlCl₃,^{1b} P₂O₅,^{2d} BF₃/(C₂H₅O)₂O,^{2e} NBS,^{2f} TiCl₄,^{2g} CrCl₂/NiCl₂,^{2h} and Mn(CO)_n,²ⁱ were exploited for different substrates for the synthesis of indenenes. However, in most cases, the formation of indene skeleton requires laborious operational procedure and relatively harsh reaction conditions. Therefore, further investigation to explore new ways for the construction of indene core is still in need.

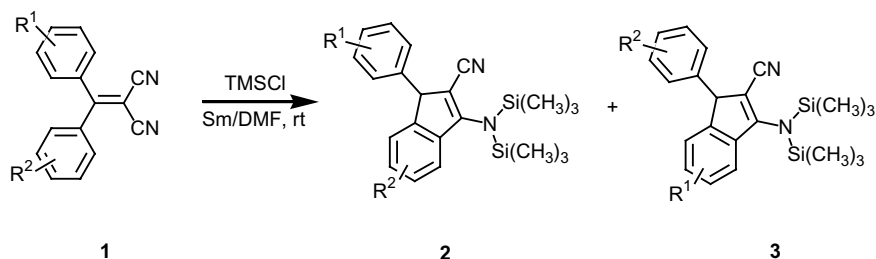
Recently, direct use of metallic samarium as a reducing agent in organic transformations has attracted the attention of many organic chemists.³ Though THF was in most cases favored as the reaction media for the organic reactions promoted by Sm,^{4,5} we have found some drastically interesting characteristics of metallic samarium as a reducing agent when *N,N*-dimethylformamide (DMF) was used as a solvent.⁶

1-Aryl-2,2-dicyanoethylenes were reported to undergo intermolecular reductive cyclodimerization to afford cyclopentenamines promoted by SmI₂.^{7a} To clarify the effect of hindrance on the reactivity of such compounds, we set out to investigate the reaction of the sterically more hindered structure, namely, the structurally analogues 1,1-diaryl-2,2-dicyanoethylenes, promoted by samarium metal.

1,1-Diaryl-2,2-dicyanoethylenes, like diaryl ketones, were reported to be able to form radical anions due to the similarity between the C=C(CN)₂ and C=O groups.⁸ Based on this property, the reductive cross-coupling reaction of 1,1-diaryl-2,2-dicyanoethylenes or 1,1-diaryl-2-cyano-2-ethoxycarbonylethylenes with aromatic nitriles mediated by samarium diiodide⁷ were successfully realized to prepare polysubstituted 3*H*-pyrroles. Herein, we wish to report that 1,1-diaryl-2,2-dicyanoethylenes undergo intramolecular cyclization to form indene compounds promoted by samarium metal. When 1,1-diaryl-2,2-dicyanoethylenes (**1**) were treated

Keywords: Samarium; DMF; 1,1-Dicyano-2,2-diarylethene; TMSCl; Indene.

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Scheme 1.

with samarium metal in the presence of TMSCl in DMF, polysubstituted indenenes (**2** and **3**) were obtained in moderate to excellent yields (Scheme 1 and Table 1).

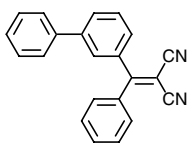
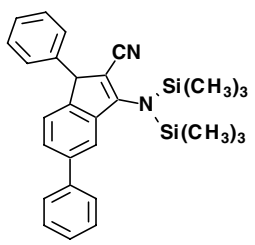
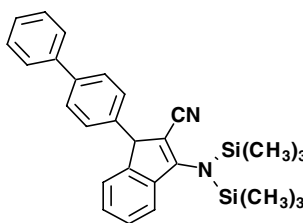
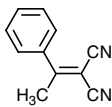
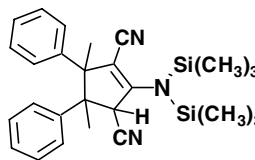
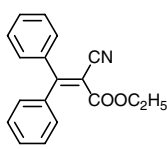
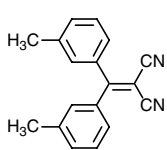
Though two kinds of indenenes were produced, the reaction was in fact regioselective. With all the substrates tested, the indenenes with a relatively electron-rich aromatic indene ring were preferentially formed and therefore predominated in the products (the ratio of **2/3**, Table 1).⁹ When 2-(1-phenyl-ethylidene)-malononitrile (**1f**) was used in this reaction, however, the intermolec-

ular coupling cyclization product was obtained. This may be attributed to the lower hindrance of methyl group and thus it behaves like 1-aryl-2,2-dicyanoethylenes, which undergo intermolecular coupling cyclization when treated with SmI₂.^{7a} Another interesting phenomenon is that one of the cyano groups was eliminated (entry 6) during the reaction process. The removal of cyano group here is extraordinary considering that decyanation reaction is usually difficult to occur and only few examples are available for the successful decyanation.¹⁰ Attempts to extend the intramolecular cyclization to 1,1-diphenyl-2-cyano-2-ethoxycarbonyl-

Table 1. Regioselective intramolecular cyclization and disilylation of 1,1-dicyano-2,2-diarylethenes promoted by samarium in DMF in the presence of TMSCl¹¹

Entry	Substrate 1	Time (min)	Products		Yield (%) ^a
			2	3	
1		40			87 (2a)
2		35			92 (2b)
3		30			90 (2c/3c = 74/26) ^b
4		25			64 (2d/3d = 5/95) ^b

Table 1 (continued)

Entry	Substrate 1	Time (min)	Products		Yield (%) ^a
			2	3	
5	 (1e)	40			47 (2e/3e = 100/0) ^b
6	 (1f)	40			81 (2f) ^c
7	 (1g)	30			— ^d
8	 (1b)	40			— ^{d,e}

^a Isolated yields based on substrates **1**.

^b The ratio was determined by ¹H NMR.

^c Isolated product.

^d A complex mixture was obtained.

^e DMSCl was used instead of TMSCl.

ethylene (entry 7) were not successful and a complex mixture was obtained.

It should be pointed out that the adoption of TMSCl is necessary here since the reaction did not occur in the absence of TMSCl. When DMSCl (entry 8) were used instead of TMSCl, the reaction could not give any encouraging results. The use of DMF is also important to this reaction. When THF was used as a solvent, the reaction failed to give the desired indenenes and only the C=C bonds in the 1,1-dicyano-2,2-diarylethenes were reduced.

Since the NMR, IR, and MS spectral data was not enough for the structure identification of products **2a**, single-crystal X-ray diffraction of **2a** was performed. It was determined unambiguously that product **2** has an indene core and the two trimethylsilyl groups were attached to the nitrogen atom (Fig. 1). The fact that all products **2** share the same NMR patterns suggests the stereochemistry of these compounds should be identical.

The mechanism of this reaction is not clear enough at present stage. According to the experimental results, the

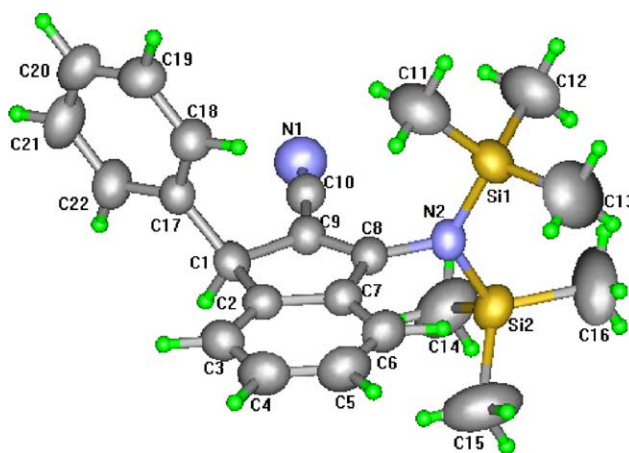
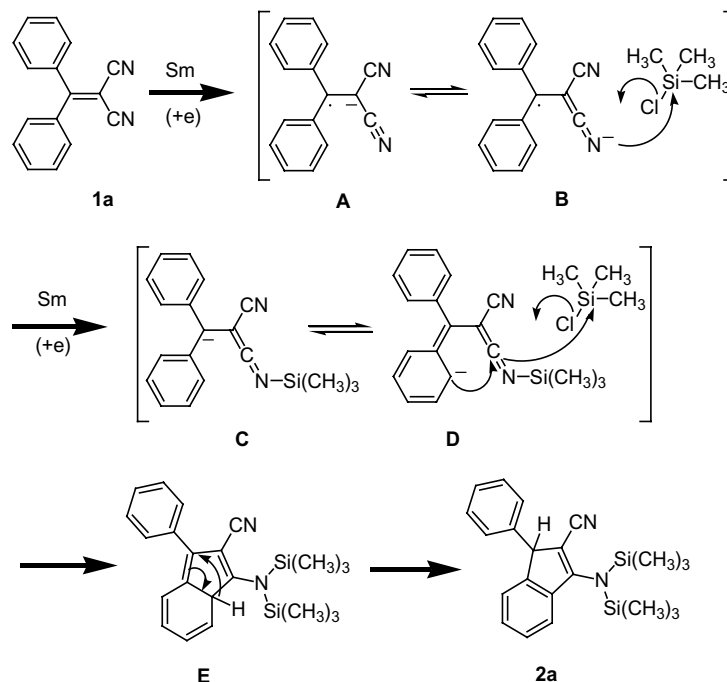


Figure 1. The crystal structure of **2a**.

following reaction pathway is proposed as one of the most plausible mechanisms (Scheme 2). Firstly, a radical anion intermediate **A** is formed via the electron transfer from samarium to substrate **1**.⁸ **A** rearranges to intermediate **B**, which reacts with the electrophile TMSCl



Scheme 2.

and then accepts another electron from samarium to afford intermediate C. Intermediate C rearranges to intermediate D, which the carbon anion attacks the C=N bond and subsequent silylation of the resulting nitrogen anion by another molecule of TMSCl forms intermediate E. Intermediate E rearranges in a 1,3-H migration manner to give the final product **2a**.

On the other hand, as an efficient ligand, indenenes can form metal complexes with transition metals.^{1a–c,12} Like the cyclopentadiene–samarium complex known in previous reports,¹² it is possible, due to the strong complex ability of samarium cation, that the similar indene–samarium complex forms during the process so as to assist the reaction to proceed smoothly.

In conclusion, in the presence of TMSCl in DMF, metallic samarium can promote a new kind of intramolecular cyclization. The reaction proceeds both efficiently and regioselectively and provides an efficient protocol for the syntheses of polysubstituted indenenes. With mild reaction conditions, short reaction time, facile operational procedure and easily available materials, it offers a promising method for the construction of indene cores. The simultaneous disilylation of the resulting amino moiety is also unexpected.

Acknowledgements

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9. A typical procedure is as follows: To a mixture of Sm powder (2 mmol), 1,1-dicyano-2,2-diphenylethene (2 mmol) in freshly distilled *N,N*-dimethylformamide (DMF, 10 mL), trimethylsilyl chloride (TMSCl, 5 mmol, freshly distilled) was added at room temperature with magnetic stirring under a nitrogen atmosphere. The resulting solution turned brown within 10 min and an exothermic reaction was observed. After the completion of the reaction (about 40 min), a routine workup of the reaction mixture followed by column chromatography afforded **2a** in 87% yield.
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11. All of the products obtained in this study were characterized (¹H NMR, ¹³C NMR, MS, IR, EA). For example, 3-(1,1,1,3,3,3-hexamethyl-disilazan-2-yl)-1-phenyl-1*H*-indene-2-carbonitrile (**2a**): Crystal structure deposition number: CCDC 234282. Colorless prism, mp 129–130 °C. ν_{\max} (KBr)/cm⁻¹: 3065, 2956, 2207, 1587, 1557, 1498. δ_{H} (DMSO-*d*₆): 7.29–7.49 (6H, m), 7.21–7.23 (1H, m), 7.12–7.13 (2H, m), 5.13 (1H, s), 0.22 (9H, s), 0.19 (9H, s). ¹³C NMR δ (CDCl₃): 161.9, 144.9, 140.7, 134.8, 126.82, 126.80, 125.8, 125.5, 125.4, 122.3, 119.3, 115.1, 111.1, 52.2, 0.21. *m/z* (%): 377 (M⁺+1, 5.09), 376 (M⁺, 13.69), 361 (31.27), 303 (3.33), 288 (2.38), 287 (4.19), 77 (2.55), 73 (100). Anal. Calcd for C₂₂H₂₈N₂Si₂: C, 70.16; H, 7.49; N, 7.44. Found: C, 70.34; H, 7.50; N, 7.42. 2-(1,1,1,3,3,3-Hexamethyl-disilazan-2-yl)-4,5-dimethyl-4,5-diphenyl-cyclopent-1-ene-1,3-dicarbonitrile (**2f**): Colorless crystal, mp 180–181 °C. ν_{\max} (KBr)/cm⁻¹: 2969, 2218, 1616, 1498, 1256. δ_{H} (CDCl₃): 7.35–7.46 (6H, m), 7.23–7.24 (2H, m), 7.13–7.15 (2H, m), 4.60 (1H, s), 1.29 (3H, s), 1.16 (3H, s), 0.51 (9H, s), 0.42 (9H, s). *m/z* (%): 458 (M⁺+1, 3.87), 457 (M⁺, 9.54), 442 (11.74), 384 (0.74), 73 (100). Anal. Calcd for C₂₇H₃₅N₃Si₂: C, 70.84; H, 7.71; N, 9.18. Found C, 70.71; H, 7.72; N, 9.20.
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