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A Novel Cyclodimerization of Arylidene-Cyanoacetate Promoted by Samarium Diiodide

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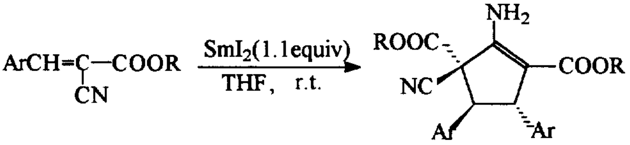
Abstract: The intermolecular reductive coupling reaction of arylidenecyanoacetate induced by SmI_2 was studied. The configuration of cyclodimerization product was confirmed by X-ray and a possible reaction mechanism was proposed. © 1997 Elsevier Science Ltd.

The chemistry of samarium diiodide (SmI_2) is of current interest in organic synthesis. SmI_2 has been developed as a mild, neutral, and versatile single electron transfer reductant. A wide range of reductions and coupling reactions have been reported[2]. The reactivity of samarium diiodide towards various nitrogen compounds including nitro compounds[3], azocompounds[4], hydrazones[3b,5], oximes[3b], imines[3b] and azides[6] has already been examined and shown to be of synthesis interest especially in the conversion of nitroarenes and nitroalkanes to hydroxylamines and/or amines. Recently, Hong and Kang[7] reported the decyanation of α-alkoxycarbonyl substituted nitrile derivatives by samarium diiodide. Howerever, no cyclization products were observed when the side chains had a carbon-carbon double bond . Yacovan[8] published 1,1-diphenyl-2,2-dicyanoethylene can be quantitatively reduced to diphenylmethyl malononitrile without any dimeric products. There are, to our knowledge, no literature examples for the reduction of cyano group to produce amine with this reagent. Here, we wish to describe our preliminary results on a novel cyclodimerization via an intermolecular reductive cross coupling of arylidenecyanoacetate by SmI_2, which differ from alkoxycarbonyl substituted nitrile dervatives to give substituted cyclopentenamines.

When arylidenecyanoacetates **1** were treated with SmI_2, the cyclodimerization products 3,4-trans-4,5-trans isomers of 2-amino-3-cyano-1,3-dialkoxy carbonyl-4,5-diaryl cyclopentenes **2** were obtained.



1 **2**

Table 1 SmI_2 induced the cyclodimerization of arylidenecyanoacetate

Entry	Ar	R	Yield(%)[a,b]	Entry	Ar	R	Yield(%)[a,b]
a	4-ClC$_6$H$_4$	C_2H_5	88	i	4-CH$_3$OC$_6$H$_4$	CH_3	80
b	4-ClC$_6$H$_4$	CH_3	84	j	4-CH$_3$OC$_6$H$_4$	C_2H_5	82
c	4-ClC$_6$H$_4$	i-C$_3$H$_7$	83	k	4-CH$_3$C$_6$H$_4$	CH_3	75
d	2-ClC$_6$H$_4$	C_2H_5	81	l	4-CH$_3$C$_6$H$_4$	C_2H_5	80
e	C_6H_5	C_2H_5	72	m	4-CH$_3$C$_6$H$_4$	i-C$_3$H$_7$	78
f	4-BrC$_6$H$_4$	C_2H_5	87	n	3,4-OCH$_2$OC$_6$H$_3$	CH_3	75
g	3-BrC$_6$H$_4$	C_2H_5	82	o	3,4-OCH$_2$OC$_6$H$_3$	C_2H_5	79
h	3-BrC$_6$H$_4$	i-C$_3$H$_7$	84	p	3,4-OCH$_2$OC$_6$H$_3$	i-C$_3$H$_7$	78

a) Yield of isolated products b) Reaction time is about 10 minutes

Table 1 summarizes our results on the cyclodimerization of a number of substrates. In all the reactions, the cleavage takes place between the C≡N bond, rather than the C=O bond. At the same time, chloro, bromo, alkoxyl groups could not be reduced under the reaction conditions and have no influence on the rate of cyclodimerization. The all reactions complete rapidly in a few minutes and give good to excellent yields . These reactions are highly regio and steroselective as only one isomer was obtained and the careful analysis of the reaction mixture indicated the absence of the other regioisomer. This was confirmed by the X-ray crystal structure of the product **2a**[9], which clearly illustrates the trans stereochemistry of the product. (Fig. 1)

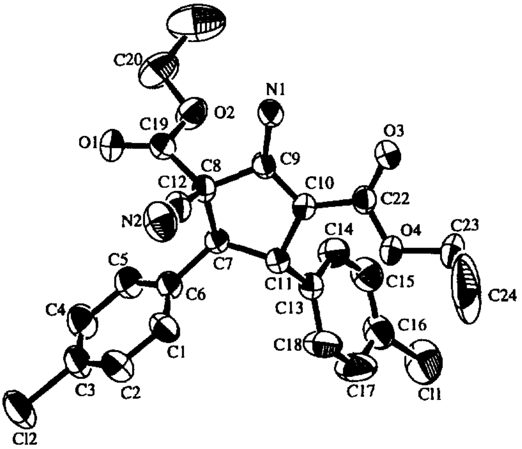
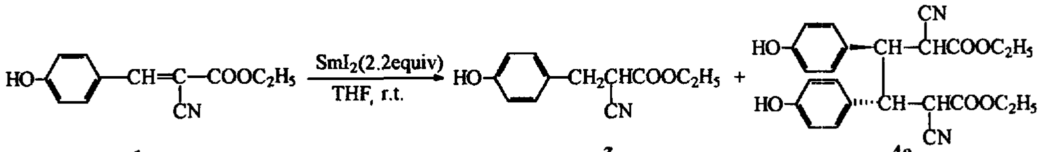


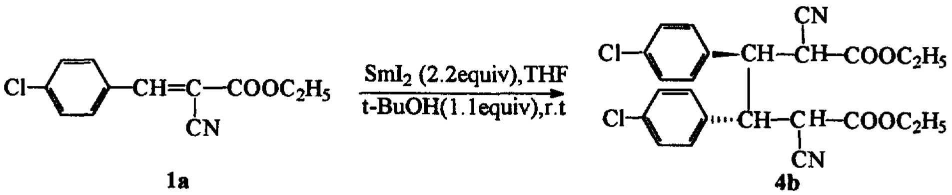
Fig. 1 the X-ray crystal structure of compound **2a**

Howerever, the hydroxyl group of the substrate changes the reductive product. Treatment of substrate **1q** with SmI_2 in THF under the same reaction condition afforded carbon-carbon double bond reductive product **3** (75%) along with dimerization product **4a** (11%). the cyclodimerization product **2** was not obtained.

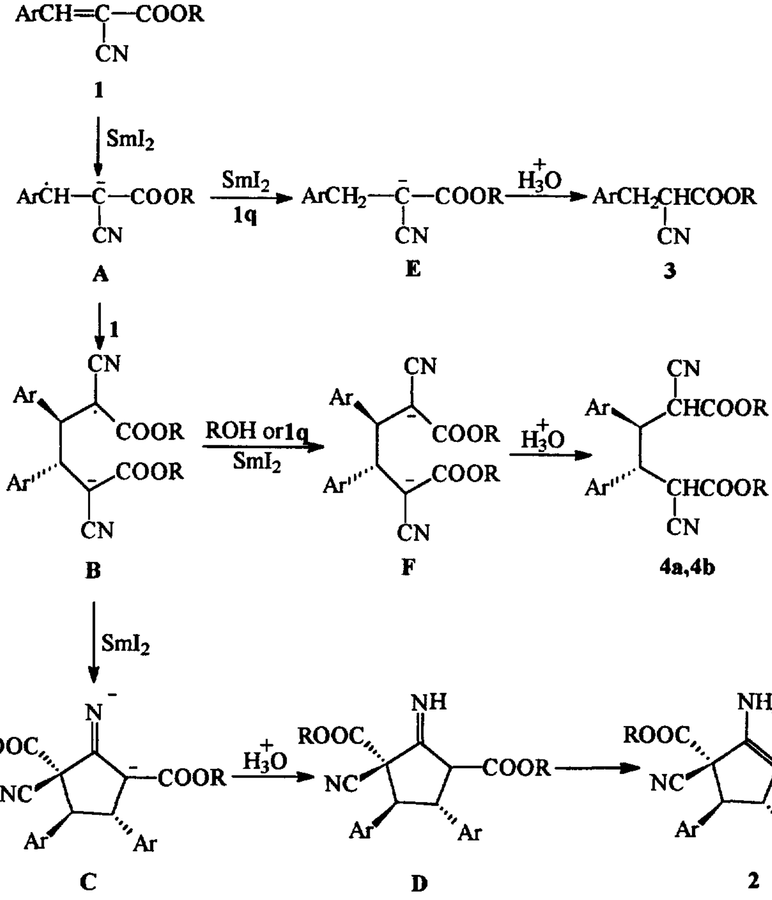


1q **3** **4a**

On the other hand, the reaction of compound **1a** with the same reagent in THF–tert-BuOH only produced dimerization product **4b** in 89% yield. The simple carbon-carbon double bond reductive product or cycodimerization product was not found.



The possible mechanism of the reaction may be postulated as Scheme I.



Scheme I

In the initial step, an electron is transferred from SmI_2 to substrate **1** results in the formation of radical aninon **A**, the radical anion **A** then attacks the another substrate to form the carbon-carbon bond and generates **B**. The latter reacts in intramolecularly to result in the formation of another carbon-carbon bond and produce intermediate C. Then the form C would be transformed to **D** and then isomerized to product **2**. In the presence of good proton doner, the radical aniones A and **B** would be transformed to **3** as major and **4** as minor through intermediate **E** and **F**, respectively. Employing t-BuOH as proton source, only dimerization product **4b** was obtained through intermediate **F**.

Typical procedure: A solution of substrate **1** (1mmol) in THF (3ml) was added to SmI_2 (1.1mmol) at room temperature under nitrogen atomsphere. The reaction was completed in a few minutes and the colour of samarium diiodide changed to a brownish yellow. The reaction was quenched with dilute HCl (0.1M, 1ml) and extracted with ether. After usual work-up, the crude product purified by preparative TLC or column chromatography (ethyl acetate: petroleum (30-60 ℃), 1:4).

In summary , SmI_2 promotes the cyclodimerization of arylidenecyanoacetate, which has not been achieved previously by other reductive agents. Further studies to develop other new reactions using SmI_2 are now in progress.

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References and Notes:

1. Permanent address :Department of Chemistry, Xuzhou Normal University, Jiangsu, 221009, China
2. a. Namy, J.L.; Girard, P. ; Kagan, H.B. *New J. Chem.* **1977**, 1, 5; b. Kagan, H.B. ; Namy, J.L. *Tetrahedron* **1986**, 42, 6573; c. Kagan, H.B. ; Sasaki, M. ; Collin, J. *Pure Apple. Chem.* **1988**, 60, 1725; d. Kagan, H.B. *New J. Chem.* **1990,** 14, 453; e. Soderquist, J.A. *Aldrichim. Acta* **1991**, 24, 15; f. Molander, G.A. *Chem. Rev.* **1992**, 92, 29; g. Hasegawa, E. ; Curran, D.P. *J. Org. Chem.* **1993**, 58, 5008; h. Molander, G.A. *Organic Reactions* **1994**, 46, 211; i. Molander, G.A. ; Harris, C.R. *Chem. Rev.* **1996**, 96, 307.
3. a. Zhang, Y. ; Lin, R. *Synth. Commun.* **1987**, 17, 329; b. Souppe, J. ; Danon, L.; Namy, J.L. ; Kagan, H.B. *J. Organometal. Chem.* **1983**, 250, 227; c. Mukaiyama, T. ; Yoyozu, K. ; Kato, K. ; Yamada, T. *Chem. Lett.* **1992**, 181.
4. Kende, A.S. ; Mendoza, J.S. *Tetrahedron Lett.* **1991**, 32, 1699.
5. Burk, M.J.; Feaster, J.E. *J. Am. Chem. Soc.* **1992,** 114, 6266.
6. Natale, N.R. *Tetrahedron Lett.* **1982**, 23, 5009.
7. Kang, H.Y. ; Hong, W.S. *Tetrahedron Lett.* **1995**, 36, 7661.
8. a. Yacovan, A. ; Hoz, S. *J. Org. Chem.* **1997**, 62, 771; b. Yacovan, A. ; Hoz, S. *J. Am. Chem. Soc.* **1996**, 118, 261.
9. Crystal data: for 2a: $C_{24}H_{22}O_4N_2Cl_2$, M=473.35, coloreless prismatic crystals, 0.20 × 0.20 × 0.30 mm, monoclinic, space group $P2_1/c$, a=6.923 (1), b=33.178(5), c=10.644(3)Å, β=99.86(2)°, U=2408.8(8)$Å^3$, Z=4, D_c=1.305 gcm^{-3}, F(000)=984.00, $\mu(M_0K_\alpha)$=3.01cm^{-1}. Intensity data were collected on Rigaku AFC7R diffractometer with graphite-monochromated M_0-K_α radiation (λ=0.71069Å) using ϖ-2θ scan mode with $2\theta_{max}$=49.8°. 3308 unique reflections were measured and 2147 reflections with I>3.00 σ (I) were used in the refinement. Refinement of positional and anisotropic thermal parameters fot all non-hydrogen atoms (290 variables) converged to R=0.052 and R_w=0.067.

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