



A Novel Cyclodimerization of Arylidene-Cyanoacetate Promoted by Samarium Diiodide

Longhu Zhou¹ and Yongmin Zhang*

Department of Chemistry, Hangzhou University, Hangzhou, 310028, P. R. China

Abstract: The intermolecular reductive coupling reaction of arylidenecyanoacetate induced by SmI₂ 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 (SmI₂) is of current interest in organic synthesis. SmI₂ has been developed as a mild, neutral, and versatile single electron transfer reductant. A wide range of reductions and coupling reactions have been reported². The reactivity of samarium diiodide towards various nitrogen compounds including nitro compounds³, azocompounds⁴, hydrazones^{3b,5}, oximes^{3b}, imines^{3b} and azides⁶ 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 Kang⁷ reported the decyanation of α -alkoxycarbonyl substituted nitrile derivatives by samarium diiodide. However, no cyclization products were observed when the side chains had a carbon-carbon double bond. Yacovan⁸ 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 SmI₂, which differ from alkoxycarbonyl substituted nitrile derivatives to give substituted cyclopentenamines.

When arylidenecyanoacetates **1** were treated with SmI₂, the cyclodimerization products 3,4-trans-4,5-trans isomers of 2-amino-3-cyano-1,3-dialkoxy carbonyl-4,5-diaryl cyclopentenenes **2** were obtained.

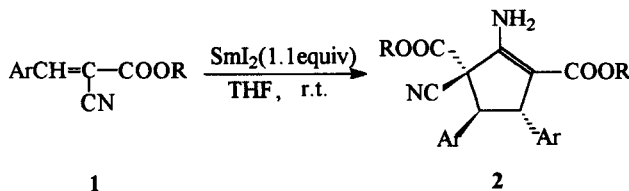
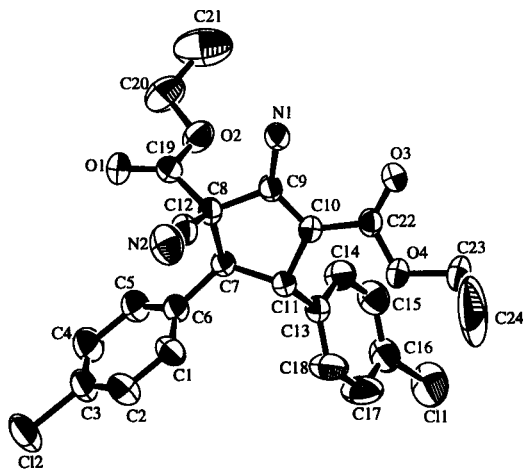


Table 1 SmI₂ induced the cyclodimerization of arylidenecyanoacetate

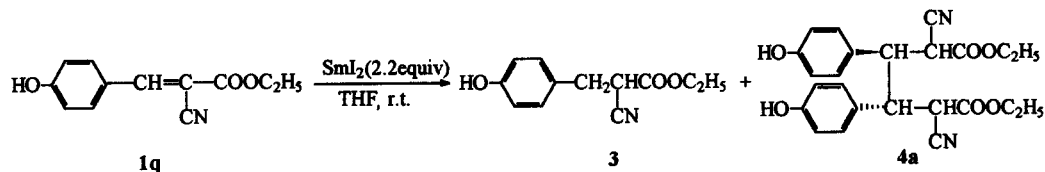
Entry	Ar	R	Yield(%) ^{a,b}	Entry	Ar	R	Yield(%) ^{a,b}
a	4-ClC ₆ H ₄	C ₂ H ₅	88	i	4-CH ₃ OC ₆ H ₄	CH ₃	80
b	4-ClC ₆ H ₄	CH ₃	84	j	4-CH ₃ OC ₆ H ₄	C ₂ H ₅	82
c	4-ClC ₆ H ₄	i-C ₃ H ₇	83	k	4-CH ₃ C ₆ H ₄	CH ₃	75
d	2-ClC ₆ H ₄	C ₂ H ₅	81	l	4-CH ₃ C ₆ H ₄	C ₂ H ₅	80
e	C ₆ H ₅	C ₂ H ₅	72	m	4-CH ₃ C ₆ H ₄	i-C ₃ H ₇	78
f	4-BrC ₆ H ₄	C ₂ H ₅	87	n	3,4-OCH ₂ OC ₆ H ₃	CH ₃	75
g	3-BrC ₆ H ₄	C ₂ H ₅	82	o	3,4-OCH ₂ OC ₆ H ₃	C ₂ H 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

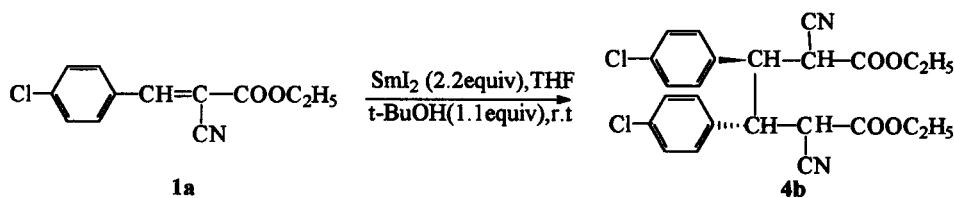
Table 1 summarizes our results on the cyclodimerization of a number of substrates. In all the reactions, the cleavage takes place between the C≡N bond, rather than the C=O bond. At the same time, chloro, bromo, alkoxy groups could not be reduced under the reaction conditions and have no influence on 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 stereoselective 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**

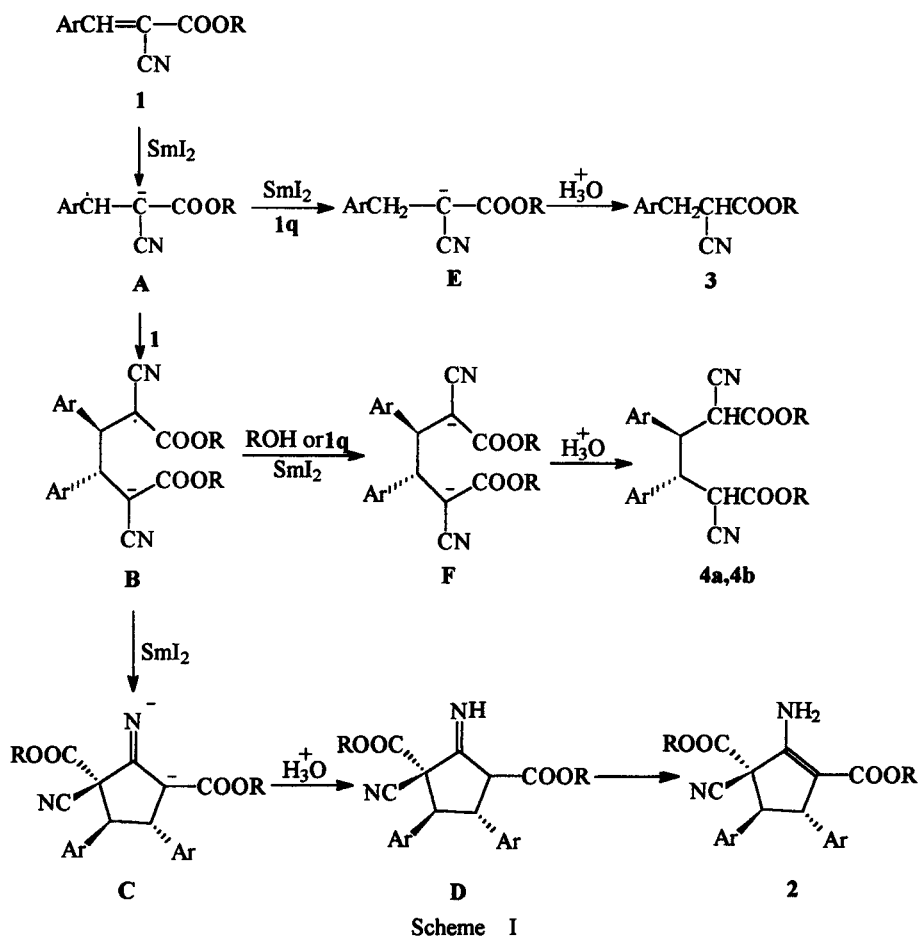
However, the hydroxyl group of the substrate changes the reductive product. Treatment of substrate **1q** with SmI₂ in THF under the same reaction condition afforded carbon-carbon double bond reductive product **3** (75%) along with dimerization product **4a** (11%). the cyclodimerization product **2** was not obtained.



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.



In the initial step, an electron is transferred from SmI_2 to substrate **1** results in the formation of radical anion **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 donor, 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 SmI₂ (1.1mmol) at room temperature under nitrogen atmosphere. 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 °C), 1:4).

In summary, SmI₂ promotes the cyclodimerization of arylidenecyanoacetate, which has not been achieved previously by other reductive agents. Further studies to develop other new reactions using SmI₂ are now in progress.

Acknowledgements: We are grateful to the National Natural Science Foundation of China and the Open Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry of Chinese Academy of Science for financial support.

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9. Crystal data: for 2a: C₂₄H₂₂O₄N₂Cl₂, M=473.35, colorless prismatic crystals, 0.20 × 0.20 × 0.30 mm, monoclinic, space group P2₁/c, a=6.923 (1), b=33.178(5), c=10.644(3) Å, β=99.86(2)°, U=2408.8(8) Å³, Z=4, D_c=1.305 g cm⁻³, F(000)=984.00, μ(MoKα)=3.01 cm⁻¹. Intensity data were collected on Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ=0.71069 Å) using ω-2θ scan mode with 2θ_{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 for all non-hydrogen atoms (290 variables) converged to R=0.052 and R_w=0.067.

(Received in China 23 June 1997; accepted 6 August 1997)