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Metallic Samarium Promoted Reductive Dimerization Cyclization of *gem*-Diactivated Alkenes, Reductive Debromination of *vic*-Dibromides, and Reduction of Sodium Alkyl Thiosulfates in Aqueous Media

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Abstract: In saturated NH_4Cl (aq.)-THF solution at room temperature, metallic samarium promoted reductive dimerization cyclization of *gem*-diactivated alkenes, reductive debromination of *vic*-dibromides, and reduction of sodium alkyl thiosulfates occur to afford corresponding functionalized cyclopentenes, (*E*)-alkenes, and disulfides, respectively in good yield. Only sub-stoichiometric quantities of samarium are employed in the former reactions and the *trans*- or *trans,trans*-form isomer is the majority product of the polysubstituted cyclopentene products.

INTRODUCTION

Recently metallic samarium, its salts and organosamarium compounds have been widely **employed** as useful reagents or catalysts in organic synthesis.[1] Since pioneering studies by H. B. Kagan and co-workers demonstrated the particular effectiveness of samarium(II) iodide as a powerful one-electron transfer **reductant,**[2] the utilization of SmI_2 in synthetic organic synthesis has been documented, such as: radical cyclizations,[3] ketyl-olefin coupling reactions,[4] pinacolic coupling reactions,[5] Barbier-type reactions,[6] aldol-type reactions,[7] Reformatsky-type reactions,[8] reductive coupling cyclizations,[9] etc.. Though SmI_2 is a useful **reagent,** some problems are encountered when it is used as a reductant. For example, it is expensive, needs delicate treatment, careful storage because it is very sensitive to air oxidation and has been invariably used in stoichiometric amounts. On the other hand, metallic samarium is stable in air and has stronger reducing power (Sm^{3+}/Sm = -2.41 V) and it has been noted recently that cheaper and more convenient metallic samarium can be used directly as a reductant instead of SmI_2 in organic synthesis.[10] To the best of our knowledge, only one paper reported that water could accelerate the reaction of alkyl and aryl iodides with SmI_2 and there were few reports on the

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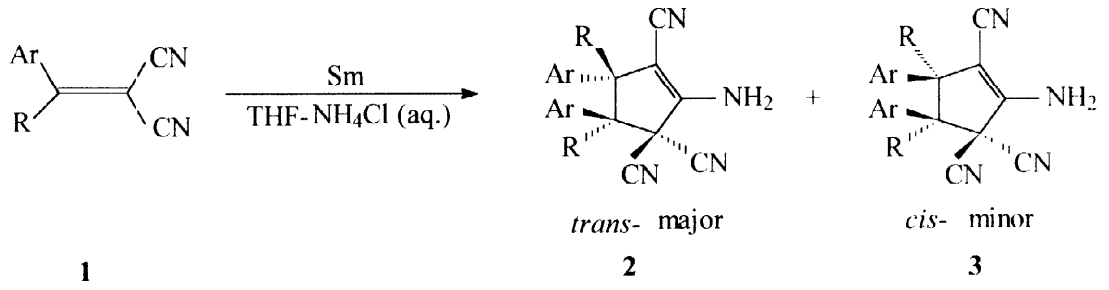
organic reaction mediated by samarium in aqueous media.[11]

In the last decade, metal-mediated organic reactions in aqueous media have received considerable attention.[12] Such aqueous reactions offer a number of advantages over conventional organometallic reactions in organic solvent. They are the practically convenient, environmentally friendly and do not require anhydrous organic solvents. Recently, metal Al(Hg),[13] Cp_2TiCl,[14] $TiCl_3$,[15] Zn-$ZnCl_2$[16] and Mn[17] have been reported to be effective for the reductive dimerization of aldehydes or ketones under aqueous conditions. In our primarily communication, we reported that metallic samarium was used for the reductive dimerization cyclization of 1, 1-dicyanoalkenes in aqueous media.[18] In order to extend the application of samarium as a mediator in aqueous media, herein, we wish to report that metallic samarium powder mediated reductive dimerization cyclization of ethyl arylmethylidenecyanoacetates and *N*-methyl-*N*-phenylaminocarbonylalkenes, reductive debromination of *vic*-dibromides, and reduction of sodium alkyl thiosulfates occur to afford corresponding functionalized cyclopentenes, (*E*)-alkenes, and disulfides, respectively in good yield under THF-NH_4Cl (aq.) conditions.

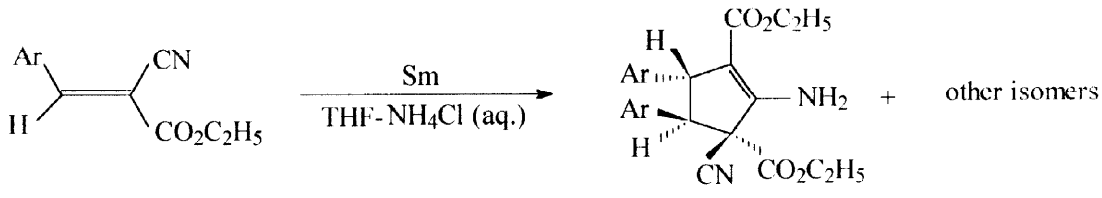
RESULTS AND DISCUSSION

Reductive Dimerization Cyclization of gem-Diactivated Alkenes Mediated by Samarium in Aqueous Media



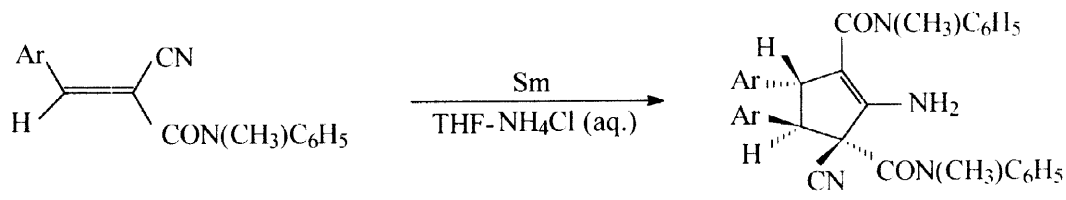
trans- major *cis-* minor

1 2 3



trans,trans- major minor

4 5



trans,trans- only product

6 7

The results of reductive dimerization cyclization of *gem*-diactivated alkenes mediated by samarium are summarized in **Tables 1, 2** and **3**. The *gem*-diactivated alkenes have enough reactivity to complete the **reductive** dimerization cyclization in the presence of metallic samarium powder under saturated aqueous NH_4Cl-THF (1 : 4) conditions due to their carbon-carbon double bonds being activated by attached electron withdrawing cyano group, ethoxycarbonyl or *N*-methyl-*N*-phenylaminocarbonyl group, and the stability of the five-membered ring in cyclic hydro-dimers. From **Table 1**, we found that substrates **1** derived from aromatic aldehydes **or** ketones and malononitrile gave the products in 50-88% yields within 1 h at room temperature. From **Table 2**, we found that substrates **4** derived from aromatic or heteroaromatic aldehydes and ethyl cyanoacetate gave the products in 60-85% yield within 4 h at room temperature, and from **Table 3**, we found that substrates **6** derived from aromatic aldehydes and cyanoacetophenylmethylamide gave the products in 42-54% yields within 9 h at room temperature. We also found that the major product from **1** is the *trans*-form isomer (*trans/cis* ratio is in the range of 60 : 40 to 80 : 20), substrates **4** gave products, in which the major product was the *trans, trans*-form isomer (the range of **5** : other isomers ratio is 80/20 to 95/5), and substrates **6** gave only *trans, trans*-form products.

It is noteworthy that reactivity of *gem*-diactivated alkenes decreases in the order, 1,1-dicyanoalkenes > 1-cyano-1-ethoxylcarbonylalkenes > 1-cyano-1-(*N*-methyl-*N*-phenylaminocarbonyl)alkenes. The reason may be the difference of the electron withdrawing ability of cyano, ethoxylcarbonyl and *N*-methyl-*N*-phenylaminocarbonyl groups. Moreover, the *trans,trans*-form isomer is the only product from **6**, since the *N*-methyl-*N*-phenylaminocarbony group is bulky.

Table 1 Reductive Coupling Cyclization of *gem*-Diactivated Alkenes **1** [a]

Entry	Ar	R	Temp.(℃)	Time (h)	Yield (%) [b]	**2** : **3** [c]
a	C_6H_5	H	r. t.	1	80	80 : 20
b	*p*-$CH_3OC_6H_4$	H	r. t.	1	63	76 : 24
c	*p*-ClC_6H_4	H	r. t.	1	88	80 : 20
d	C_6H_5	CH_3	r. t.	2	50	60 : 40

[a] Reactions were carried out in THF-NH_4Cl (aq.) (4 : 1, 5 cm^3) using substrate (1 mmol) and metallic samarium (0.75 mmol).
[b] Combined isolated yields. [c] Ratio determined by ^1H NMR.

Table 3 Reductive Coupling Cyclization of *gem*-Diactivated Alkenes **6** [a]

Entry	Ar	Temp.(℃)	Time (h)	Yield (%) [b]
a	C_6H_5	r. t.	9	45
b	*p*-$CH_3C_6H_4$	r. t.	9	42
c	*p*-ClC_6H_4	r. t.	9	53
d	*p*-FC_6H_4	r. t.	9	50
e	*m*-BrC_6H_4	r. t.	9	54

[a] Reactions were carried out in THF-NH_4Cl (aq.) (4 : 1, 5 cm^3) using substrate (1 mmol) and metallic samarium (0.75 mmol).
[b] Isolated yields.

Table 2 Reductive Coupling Cyclization of *gem*-Diactivated Alkenes **4** [a]

Entry	Ar	Temp.(℃)	Time (h)	Yield (%) [b]	**5** : other isomers [c]
a	C_6H_5	r. t.	4	75	83 : 17
		r. t.	8	0,[d] 0,[e] 0,[f]	--
		50	10	0,[g] 0,[h] 0,[i]	--
b	*p*-$CH_3C_6H_4$	r. t.	4	70	90 : 10
c	*p*-$CH_3OC_6H_4$	r. t.	4	63	91 : 9
d	*p*-ClC_6H_4	r. t.	4	80	89 : 11
e	*p*-FC_6H_4	r .t.	4	82	87 : 13
		r. t.	4	83,[j] 82[k], 83[l]	87 : 13
f	*p*-BrC_6H_4	r. t.	4	81	88 : 12
g	*p*-$CF_3C_6H_4$	r. t.	4	85	93 : 7
h	*m*-BrC_6H_4	r. t.	4	76	85 : 15
i	*o*-BrC_6H_4	r. t.	4	74	83 : 17
j	3,4-$OCH_2OC_6H_3$	r .t.	4	83	90 : 10
k	*p-tert*-$C_4H_9C_6H_4$	r. t.	4	68	95 :5
l	2-Furyl	r. t.	4	60	80 : 20

[a] Reactions were carried out in THF-NH_4Cl (aq.) (4 : 1, 5 cm^3) using substrate (1 mmol) and metallic samarium (0.75 mmol). [b] Combined isolated yields. [c] Ratio determined by RF-HPLC analysis. [d] THF (anhydrous, 5 cm^3) was used as solvent instead of THF-NH_4Cl (aq.) (4 : 1, 5 cm^3). [e] CH_3CN (dry, 5 cm^3) was used as solvent instead of THF-NH_4Cl (aq.) (4 : 1, 5 cm^3). [f] Et_2O (dry, 5 cm^3) was used as solvent instead of THF-NH_4Cl (aq.) (4 : 1, 5 cm^3). [g] THF-H_2O (4 : 1, 5 cm^3) was used as solvent instead of THF-NH_4Cl (aq.) (4 : 1, 5 cm^3). [h] H_2O (5 cm^3) was used as solvent instead of THF-NH_4Cl (aq.) (4 : 1, 5 cm^3). [i] THF-HCl (1.0 mol/L) (4 : 1, 5 cm^3) was used as solvent instead of THF-NH_4Cl (aq.) (4 : 1, 5 cm^3). [j] Metallic samarium (1 mmol) was used. [k] Metallic samarium (2 mmol) was used. [l] Metallic samarium (0.5 mmol) was used .

The mixtures of stereoisomeric cyclic hydro-dimers from **1** or **4** could not be separated by TLC. For substrate **1**, two products were given and the configuration and the *trans/cis* ratio of product was determined by ^1H NMR and NOE spectra.[18] Meanwhile, four products were given from substrate **4** and the ratio of product was determined by HPLC under reverse conditions. Fortunately, *trans*-form product **2**, and *trans, trans*-form product **5** could be separated as pure compounds from the mixture of its *cis/trans* isomers by the fractional crystallization method. The assignments of structure are based on the spectroscopic evidence, NOE and X-ray crystal diffraction result. The strong IR absorption at *ca.* 1660 cm^{-1} is evidence for the C=C-NH_2 ↔ C-C=NH entity. Characteristic N-H stretching bands are also present and, in the NMR experiments, NH protons were observed in the range of 5.00-6.50 ppm and exchanged in D_2O. Molecular formulae were derived from MS spectra on molecular ions and CHN elemental analysis. The stereochemistry of the *trans*-form structure was determined by NOE, and the *trans, trans*-form structure was confirmed by the X-ray crystal diffraction.

Since metallic samarium is stable to the water and neutral organic solvents, when the reaction was carried out in THF (anhydrous), CH_3CN (dry), Et_2O (dry), THF-H_2O (4 : 1) or H_2O, no product was formed, even after

longer reaction times (see entry **a** in **Table 2**). When the reaction was performed in THF-NH_4Cl (aq.) solution, reductive coupling cyclization products were isolated in high yields in a short reaction time. However, when the reaction was carried out in dilute hydrochloric acid-THF solution, no cyclic hydro-dimer product was given (also see entry **a** in **Table 2**). On the other hand, when we used other metal powders, such as tin or indium to replace samarium, no reaction took place.

We have tried to change the quantities of samarium used in the reaction. The results indicated that when the substoichiometric amounts of Sm (substrate/Sm = 2/1～4/3) were used, the reaction could finish within 4 h in high yield, and when stoichiometric or superstoichiometric quantities of Sm (substrate/Sm = 1/1～1/2) were used, the yield of product did not increase.

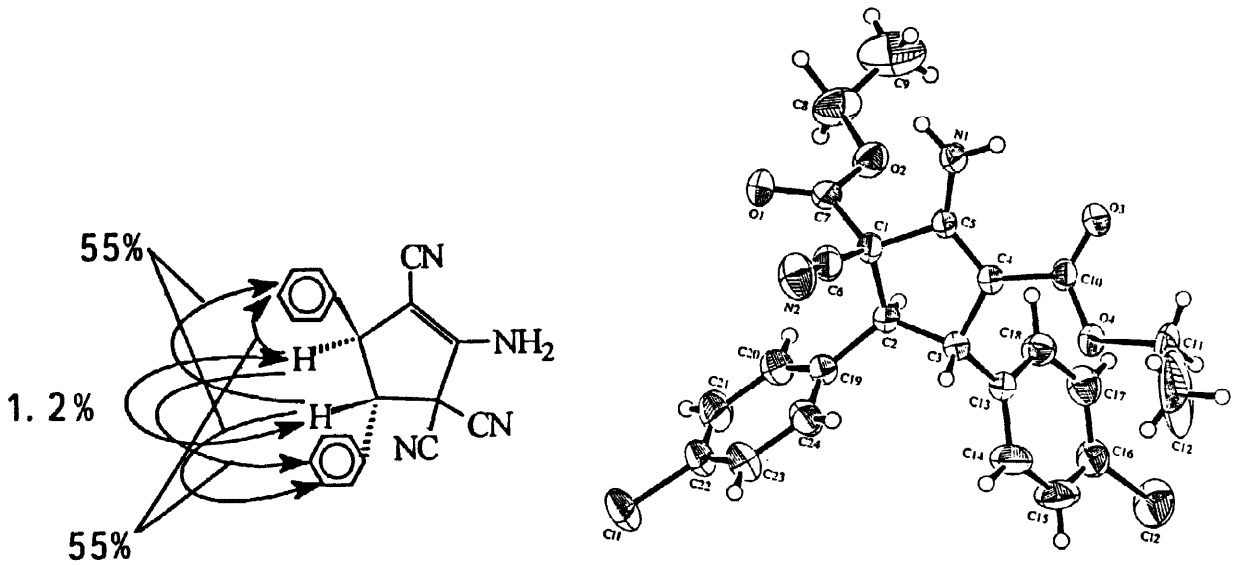
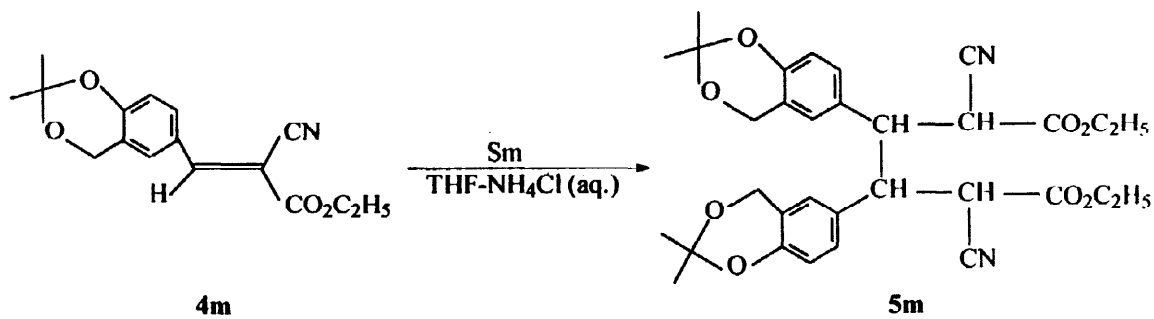


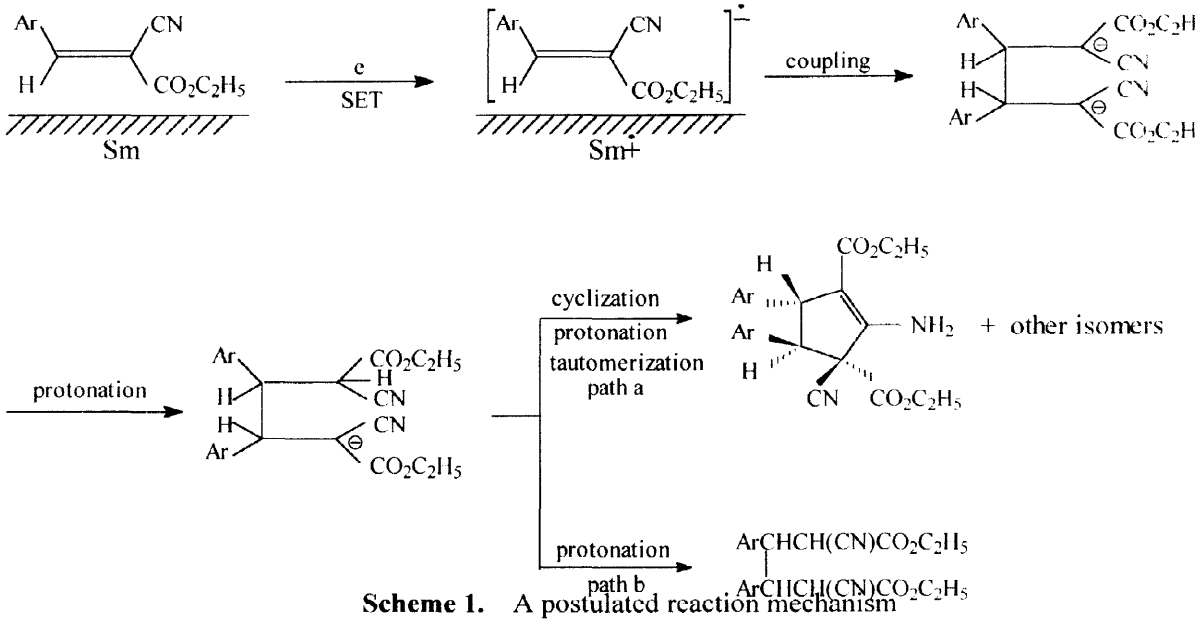
Fig. 1 Observed NOE of **2a** and X-ray crystal structure of diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-chlorophenyl)-1,3-cyclopentenedicarboxylate **5d**

Interestingly, treatment of substrate **4m** with samarium powder under the same reaction conditions only gave the reductive dimerization product (60% yield), and no reductive dimerization cyclization product. The effect of the substituted groups in benzene ring is not fully clear and it may be that this results from bulky *m*- and *p*- position substitutes (in detail, see the following reaction mechanism).



4m **5m**

A possible mechanism for the formation of substituted cyclopentene is described in **Scheme 1**. A radical anion of the electron deficient olefin may be formed by a single-electron transfer (SET) process under the reaction conditions. Here the carbon bearing the negative charge should be flanked by the electron withdrawing cyano and ethoxycarbonyl groups which are capable of stabilizing the carbanion, and the free radical should be shared by the neighboring aromatic ring, so that the radical anion is easy to form and has enough time to react with another radical anion of the substrate to produce a dianion (coupling process). Eventually, there are two possible pathways competing with each other, generating either reductive dimerization cyclization product (path a) or reductive coupling product (path b). The presence of NH_4Cl (aq.) could clean and activate the metallic samarium surface to effect further reactions.



Scheme 1. A postulated reaction mechanism

However, when substrates derived from aliphatic aldehydes or ketones were used, no reductive coupling cyclization product was isolated. It is probable that this result may be attributed to the difference in stability of the radical anion intermediate. A benzyl radical anion intermediate from *gem*-diactivated alkenes derived from aromatic aldehyde or ketone is stabilized by the neighboring aromatic ring. The radical anion intermediate from substrate derived from an aliphatic aldehyde or ketone is less stable and difficult to form, so that the starting material was recovered. At the same time, other electron-deficient olefin, such as 1,1-diacetylstyrene, 1-acetyl-1-ethoxycarbonylstyrene, 1-ethoxycarbonylstyrene, 1,1-diethoxycarbonylstyrene or cinnamyl cyanide failed to react under identical conditions.

Reduction of Sodium Alkyl Thiosulfates Mediated by Samarium in Aqueous Media

Disulfides are important reagents in organic synthesis,[19-21] and many methods for the synthesis of disulfides have been recommended, for example, the oxidation of thiols[22] and nucleophilic substitution of

sulfenylthiocyanates,[23] thiolsulfonates,[24] sulfenylhydrazo compounds,[25] and sulfenimides[26] with thiols, the reduction of sulfonic acids and sodium sulfonates,[27] and sulfenyl, sulfinyl and sulfonyl derivatites,[28] etc. The drawback of the former method is the foul smell of thiols, while the later method requires rather long reaction time, reflux and anhydrous conditions and usually results in only moderate yields. It is desirable to develop milder methods of disulfide preparation. In order to expand the scope of the Sm/THF-NH_4Cl (aq.) reduction system, we have examined the reduction of sodium alkyl thiosulfates. The results are listed in **Table 4.**

$$\underset{\mathbf{8}}{RSSO_3Na} \xrightarrow[THF\text{-}NH_4Cl\ (aq.)]{Sm} \underset{\mathbf{9}}{RSSR}$$

Table 4 The Reduction of Sodium Alkyl Thiosulfates to Disulfides by Sm/THF-NH_4Cl (aq.)

Entry	R	Temp. (℃)	Time (h)	Product	Yield(%)[a]
a	$C_6H_5CH_2$	r. t.	4	$C_6H_5CH_2SSCH_2C_6H_5$	95
b	$C_{12}H_{25}$	r. t.	4	$C_{12}H_{25}SSC_{12}H_{25}$	90
c	$C_{10}H_{21}$	r. t.	4	$C_{10}H_{21}SSC_{10}H_{21}$	85
d	C_8H_{17}	r. t.	4	$C_8H_{17}SSC_8H_{17}$	87

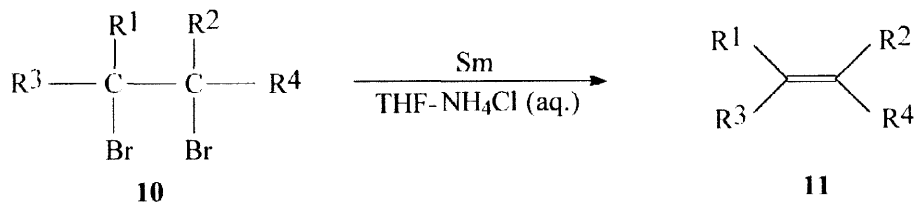
[a] Isolated yields.

Table 4 shows that sodium alkyl thiosulfates can easily be reduced to the corresponding symmetrical disulfides by metallic samarium in good to excellent yields under aqueous conditions at room temperature, and as starting materials, the sodium alkyl thiosulfates are readily prepared from the reaction of sodium thoisulfate with suitable alkyl bromide under mild and phase transfer catalysis conditions.[29]

Reductive Debromination of vic-Dibromides with Metallic Samarium in Aqueous Media

The debromination of *vic*-dibromides to alkenes is of some importance in organic synthesis, especially in the purification of steroides through their dibromides, and a variety of methods have been devised to accomplish this transformation.[30] Among the many possible debromination agents are sodium,[31] magnesium,[32] zinc,[33] sodium selenide,[34] lithium aluminium hydride,[35] sodium sulfide,[36] titanium(III),[37] cobalt(II),[38] DMF[39] and Sm/methanol,[40] etc.

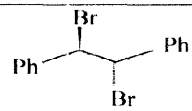
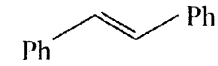
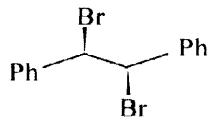
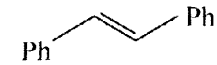
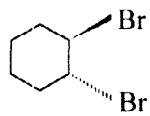
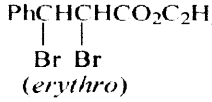
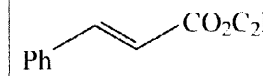
In order to verify the reductive ability of Sm/THF-NH_4Cl (aq.) system and extend its application in organic synthesis further, we have found that *vic*-dibromides on treatment with metallic samarium in THF-NH_4Cl (aq.) solution are smoothly converted into the corresponding (*E*)-alkenes in good yields. The reaction occurs at room temperature, thus minimizing side reactions.



10 **11**

Table 5 summarized the results concerning the debromination of *vic*-dibromides. *trans*-Stilbene was produced from *meso*-1,2-dibromo-1,2-diphenylethane in a excellent yield (entry **a**), as well as from *dl*-1,2-dibromo-1,2-diphenylethane (entry **b**) within 2 h at room temperature. The other benzylic *vic*-dibromides, such as ethyl 1,2-dibromophenylpropinate(*erythro*), similarly gave the corresponding(*E*)-alkene in a high yield (entry **d**). In the case of aliphatic *vic*-dibromide *trans*-1,2-dibromocyclohexane, longer reaction time (4h) was needed to obtain cyclohexene (94% GC yield, entry **c**). The reactivity of *vic*-dibromides decreases in the order, *meso*-1,2- dibromo-1,2-diphenylethane ≅ *dl*-1,2-dibromo-1,2-diphenylethane > ethyl 1,2-dibromophenylpropinate > *trans*-1,2-dibromocyclohexane, due to the radical or anion intermediate of aliphatic *vic*-dibromide being less stable than that of the aromatic analogues.

Table 5 Reductive Debromination of *vic*-Dibromides by Sm in Aqueous Media

Entry	Substrate	Temp.(℃)	Time (h)	Product	Yield (%) [a]
a		r. t.	2		98
b		r. t.	2		95
c		r. t.	4		80(94) [b]
d	 (*erythro*)	r. t.	3		92

[a] Isolated yields. [b] The number in parenthesis is GC yield.

CONCLUSION

In summary, it has been found that metallic samarium powder is a useful metal to mediate the reductive dimerization cyclization of *gem*-diactivated alkenes, reductive debromination of *vic*-dibromides, and reduction of sodium alkyl thiosulfates in aqueous media at room temperature. The remarkable advantages of this reaction are its mild, neutral and environmentally friendly reaction conditions, simple operation, and good yields. It may open a new way for using metallic samarium instead of samarium(II) diiodide in organic synthesis.

EXPERIMENTAL

General details

Melting points were determined with X-4 microscope melting point apparatus and are uncorrected. IR

spectra were measured with a Nicolet 560-FTIR spectrophotometer as KBr discs. The ^1H NMR spectra were obtained on a Bruker AC 300 or a Bruker AC 80 spectrometers. All NMR samples were measured in $CDCl_3$ using TMS as internal standard. *J* values are given in Hz. Elemental analyses were performed on a Carlo Erba 1106 instrument. Mass spectra were obtained on a HP 5989A mass spectrometer using electron impact mode (70 eV). HPLC determinations were done on a Shimadzu LC-6A chromatographic instrument by using tetrahydrofuran -methanol-water (2 : 6 : 2) as mobile phase under reversed phase conditions. GC determinations were carried out on a Perkin Elmer Autosystem XL gas chromatograph. Thin layer chromatography (TLC) was performed on 0.5 mm silica gel (GF 254) pre-coated microscope slides and visualised with UV light (254 nm). Preparative TLC was carried out on 1.5 mm silica gel (GF 254) pre-coated plate glass (20 cm×20 cm) and visualised with UV light (254 nm).

Metallic samarium, aldehydes, malononitrile, ethyl cyanoacetate, and all solvents were purchased from commercial sources and used without purification. Cyanoacetophenylmethylamide was prepared from the reaction of ethyl cyanoacetate with N-methylaniline under reflux. The *gem*-diactivated alkenes were synthesized by the reaction of aromatic aldehydes or ketones with malononitrile, ethyl cyanoacetate or cyanoacetophenylmethylamide using piperidine as catalyst following the usual procedure.[41]

General Procedure for the Syntheses of Functionalized Cyclopentenes by Samarium Mediated Reductive Dimerization Cyclization of gem-Diactivated Alkenes in Aqueous Media

Under an inert atmosphere of nitrogen, powdered samarium (113 mg, 0.75 mmol) and *gem*-diactivated alkene (1.0 mmol) were placed in a round bottomed flask, and THF (5 cm^3) was added in one portion. After saturated NH_4Cl (aq.) (1 cm^3) was added dropwise to the mixture *via* syringe within 1 h, the mixture was stirred at room temperature for the time indicated in **Tables 1, 2** and **3**. A dilute HCl (0.5 mol/L, 4 cm^3) solution was added and the mixture then extracted with ether (2×30 cm^3), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue was then purified by preparative thin layer chromatography on silica gel with cyclohexane-ethyl acetate as eluent to afford the product. After fractional crystallization of the mixture with suitable solvents(the mixture of ether, chloroform and petroleum ether), pure compounds **2** or **5** were obtained.

2-Amino-1,3,3-tricyano-*trans*-4,5-diphenylcyclopentene 2a

Colorless crystals, mp 132-134℃; υ_{max} (KBr)/cm^{-1} 3378, 3217 (NH_2), 3052 (ArH), 2940 (CH), 2212 (CN), 1678 (C=C-NH_2), 1660, 1630, 1503, 1460 (Ar); δ_H ($CDCl_3$) 3.75 (1H, d, *J* 9.4, CH), 4.59 (1H, d, *J* 9.4, CH), 5.45 (2H, br s, NH_2), 6.90 - 7.52 (10H, m, ArH); m/z 311 (M^++1, 25%), 310 (M^+, 100), 283 (13), 156 (16), 155 (39), 128 (16), 102 (13), 101 (13), 78 (15), 77 (27), 52 (24), 51 (49). Anal. for $C_{20}H_{14}N_4$: Cal.(found) C, 77.40 (77.67); H, 4.55 (4.72); N, 18.05 (17.80) %.

2-Amino-1,3,3-tricyano-*trans*-4,5-di(4-methoxyphenyl)cyclopentene 2b

Colorless crystals. mp 98-100℃; υ_{max} (KBr)/cm^{-1} 3370, 3220 (NH_2), 3050 (ArH), 2945 (CH), 2221 (CN), 1683 (C=C-NH_2), 1648, 1618, 1500, 1460 (Ar); δ_H ($CDCl_3$) 3.66 (s, 3H, CH_3O), 3.76 (s, 3H, CH_3O), 4.09 (1H, d, *J* 9.4, CH), 4.42 (1H, d, *J* 9.4, CH), 5.40 (2H, br s, NH_2), 6.80 - 7.32 (8H, m, ArH); m/z 371 (M^++1, 28), 370 (M^+, 100%), 369 (34), 355 (22), 339 (35), 255 (20), 199 (30), 184 (32), 171 (65), 155 (51), 142 (32), 114 (34), 77 (38), 63 (32), 51 (36). Anal. for $C_{22}H_{18}N_4O_2$: Cal.(found) C, 71.34 (71.57); H, 4.90 (4.66); N, 15.13 (15.01) %.

2-Amino-1,3,3-tricyano-*trans*-4,5-di(4-chlorophenyl)cyclopentene 2c

Colorless crystals. mp 160-162℃; υ_{max} (KBr)/cm^{-1} 3375, 3200 (NH_2), 3070 (ArH), 2950 (CH), 2220 (CN), 1685 (C=C-NH_2), 1660, 1630, 1500, 1460 (Ar); δ_H ($CDCl_3$) 3.75 (1H, d, *J* 9.1, CH), 4.53 (1H, d, *J* 9.1, CH), 5.42 (2H, br s, NH_2), 6.93 - 7.56 (8H, m, ArH); m/z 382, 380, 378 (M^+, 13, 58, 100%), 345 (36), 344 (29), 343 (52), 156 (23), 155 (58), 127 (21), 101 (17), 77 (26), 76 18), 75 (33), 63 (17), 52 (15), 51 (25). Anal. for $C_{20}H_{12}Cl_2N_4$: Cal.(found) C, 63.34 (63.57); H, 3.19 (3.02); N, 14.77 (14.90)%.

2-Amino-1,3,3-tricyano-4,5-dimethyl-diphenylcyclopentene (2d and **3d)**

υ_{max} (KBr)/cm^{-1} 3380, 3225 (NH_2), 3050 (ArH), 2950 (CH), 2225 (CN), 1685 (C=C-NH_2), 1660, 1600, 1500, 1460 (Ar); δ_H ($CDCl_3$) 1.21 (s, 0.40×3H, *cis*-CH_3), 1.46 (s, 0.60×3H, *trans*-CH_3), 1.88 (s, 0.40×3H, *cis*-CH_3), 2.01 (s, 0.60×3H, *trans*-CH_3), 5.37 (2H, br s, NH_2), 6.93 - 7.45 (10H, m, ArH); m/z 339 (M^++1, 73%), 338 (M^+, 73), 328 (18), 170 (19), 169 (42), 157 (20), 156 (45), 155 (100), 128 (18), 115 (28), 103 (18), 102 (15), 78 (25), 77 (42), 52 (27), 51 (48). Anal. for $C_{22}H_{18}N_4$: Cal.(found) C, 78.08 (77.87); H, 5.36 (5.12); N, 16.56 (16.80)%.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-diphenyl-1,3-cyclopentenedicarboxylate 5a

Colorless crystals. mp 173-175℃; υ_{max} (KBr)/cm^{-1} 3424, 3332, 3253, 3200 (NH_2), 3026 (ArH), 2986, 2934, 2900 (CH), 2250 (CN), 1738 (C=O), 1672 (C=C-NH_2), 1637, 1578, 1455 (Ar); δ_H ($CDCl_3$) 0.86 (3H, t, *J* 6.6, CH_3), 1.30 (3H, t, *J* 6.9, CH_3), 3.73 - 4.20 (3H, m, CH_2 and CH), 4.26 - 4.63 (3H, m, CH_2 and CH), 5.98 (2H, br s, NH_2), 7.04 - 7.82 (10H, m, ArH); m/z 404 (M^+, 27%), 403 (100), 402 (34), 374 (35), 332 (24), 331 (85), 312 (23), 311 (46), 286 (33), 285 (82), 258 (37), 257 (57), 181 (18), 131 (22), 130 (25). Anal. for $C_{24}H_{24}N_2O_4$: Cal.(found) C, 71.27 (71.31); H, 5.98 (5.99); N, 6.93 (6.71) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-methylphenyl)-1,3-cyclopentenedicarboxylate 5b

Colorless crystals. mp 189-191℃; υ_{max} (KBr)/cm^{-1} 3415, 3322, 3238, 3190 (NH_2), 3038 (ArH), 2985, 2931, 2885 (CH), 2250 (CN), 1737 (C=O), 1665 (C=C-NH_2), 1631, 1565, 1460 (Ar); δ_H ($CDCl_3$) 0.90 (3H, t, *J* 7.0, CH_3), 1.30 (3H, t, *J* 6.9, CH_3), 2.22 (3H, s, CH_3), 2.28 (3H, s, CH_3), 3.71 - 4.10 (3H, m, CH_2 and CH), 4.18 - 4.55(3H, m, CH_2 and CH), 5.90 (2H, br s, NH_2), 6.90 - 7.42 (8H, m, ArH); m/z 432 (M^+, 100%), 433 (M^++1, 28), 431 (21), 402 (29), 385 (15), 359 (20), 358 (69), 340 (27), 339 (63), 314 (27), 313 (68), 312 (17), 286 (26), 285 (43), 221 (14), 145 (21), 144 (24). Anal. for $C_{26}H_{28}N_2O_4$: Cal.(found) C, 72.20 (72.05); H, 6.52 (6.54); N,

6.48 (6.19) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-methoxyphenyl)-1,3-cyclopentenedicarboxylate 5c

Colorless crystals. mp 160-162℃; υ_{max} (KBr)/cm^{-1} 3408, 3323, 3242, 3190 (NH_2), 3025 (ArH), 2999, 2980, 2935, 2838 (CH), 2251 (CN), 1737 (C=O), 1664 (C=C-NH_2), 1638, 1611, 1567, 1460 (Ar); δ_H ($CDCl_3$) 0.92 (3H, t, *J* 6.7, CH_3), 1.31 (3H, t, *J* 7.0, CH_3), 3.71 - 4.22 (9H, m, CH_2, CH and 2×CH_3O), 4.28 - 4.56 (3H, m, CH_2 and CH), 6.08 (2H, br s, NH_2), 6.76 - 7.84 (8H, m, ArH); m/z 464 (M$^+$, 45%), 418 (11), 390 (30), 372 (11), 371 (34), 344 (28), 317 (18), 237 (10), 233 (13), 232 (56), 186 (10), 161 (24), 160 (100), 159 (15). Anal. for $C_{25}H_{28}N_2O_6$: Cal.(found) C, 67.23 (67.09); H, 6.08 (5.82); N, 6.03 (6.17) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-chlorophenyl)-1,3-cyclopentenedicarboxylate 5d

Colorless crystals. mp 178-180℃; υ_{max} (KBr)/cm^{-1} 3425, 3331, 3257, 3202 (NH_2), 3035 (ArH), 2980, 2935, 2910 (CH), 2250 (CN), 1737 (C=O), 1675 (C=C-NH_2), 1638, 1583, 1493 (Ar); δ_H ($CDCl_3$) 0.90 (3H, t, *J* 7.0, CH_3), 1.30 (3H, t, *J* 7.0, CH_3), 3.73 - 4.25 (3H, m, CH_2 and CH), 4.30 - 4.75(3H, m, CH_2 and CH), 6.27 (2H, br s, NH_2), 6.80 - 7.28 (8H, m, ArH); m/z 476, 474, 472 (M$^+$, 13, 67, 100%), 445 (29), 443 (36), 427 (20), 400 (64), 399 (34), 398 (96), 381 (27), 379 (35), 354 (54), 352 (69), 324 (43), 291 (22), 215 (21), 189 (23), 165 (39). Anal. for $C_{24}H_{22}N_2O_4Cl_2$: Cal.(found) C, 60.90 (61.07); H, 4.68 (4.49); N, 5.92 (5.71) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-fluorophenyl)-1,3-cyclopentenedicarboxylate 5e

Colorless crystals. mp 170-172℃; υ_{max} (KBr)/cm^{-1} 3423, 3330, 3248, 3201 (NH_2), 3070 (ArH), 2987, 2941, 2905 (CH), 2256 (CN), 1741 (C=O), 1671 (C=C-NH_2), 1637, 1571, 1509 (Ar); δ_H ($CDCl_3$) 0.91 (3H, t, *J* 7.8, CH_3), 1.30 (3H, t, *J* 6.8, CH_3), 3.53 - 4.15 (3H, m, CH_2 and CH), 4.25 - 4.63(3H, m, CH_2 and CH), 6.09 (2H, br s, NH_2), 6.73 - 7.91 (8H, m, ArH); m/z 440 (M$^+$, 39%), 410 (15), 366 (40), 347 (26), 320 (40), 294 (21), 293 (32), 220 (25), 199 (10), 173 (10), 149 (31), 148 (100). Anal. for $C_{24}H_{22}N_2O_4F_2$: Cal.(found) C, 65.45 (65.61); H, 5.03 (4.97); N, 6.36 (6.15) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-bromophenyl)-1,3-cyclopentenedicarboxylate 5f

Colorless crystals. mp 192-194℃; υ_{max} (KBr)/cm^{-1} 3424, 3328, 3251, 3201 (NH_2), 3045 (ArH), 2995, 2945, 2908 (CH), 2255 (CN), 1737 (C=O), 1674 (C=C-NH_2), 1636, 1582, 1490 (Ar); δ_H ($CDCl_3$) 0.93 (3H, t, *J* 6.7, CH_3), 1.32 (3H, t, *J* 7.0, CH_3), 3.65 - 4.10 (3H, m, CH_2 and CH), 4.18 - 4.63 (3H, m, CH_2 and CH), 6.06 (2H, br s, NH_2), 6.73 - 7.82 (8H, m, ArH); m/z 564, 562, 560 (M$^+$, 52, 100, 50%), 533 (39), 491 (46), 489 (91), 487 (49), 445 (37), 443 (64), 435 (46), 334 (29), 255 (30), 210 (41), 208 (45). Anal. for $C_{24}H_{22}N_2O_4Br_2$: Cal.(found) C, 51.27 (51.37); H, 3.94 (3.81); N, 4.98 (4.80) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-trifluoromethylphenyl)-1,3-cyclopentenedicarboxylate 5g

Colorless crystals. mp 184-186℃; υ_{max} (KBr)/cm^{-1} 3425, 3332, 3254, 3200 (NH_2), 3042 (ArH), 2985, 2932, 2905 (CH), 2245 (CN), 1739 (C=O), 1674 (C=C-NH_2), 1638, 1577, 1467 (Ar); δ_H ($CDCl_3$) 0.85 (3H, t, *J* 7.0, CH_3), 1.31 (3H, t, *J* 7.0, CH_3), 3.70 - 4.20 (3H, m, CH_2 and CH), 4.25 - 4.68(3H, m, CH_2 and CH), 6.07 (2H, br

s, NH_2), 7.00 - 7.83 (8H, m, ArH); m/z 540 (M^+, 74%), 539 (26), 511 (28), 495 (27), 468 (31), 467 (100), 448 (29), 422 (36), 421 (82), 393 (51), 392 (49), 324 (14), 249 (16), 203 (24), 199 (27). Anal. for $C_{26}H_{22}N_2O_4F_6$: Cal.(found) C, 57.78 (57.58); H, 4.10 (4.07); N, 5.18 (4.97) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (3-bromophenyl)-1,3-cyclopentenedicarboxylate 5h

Colorless crystals. mp 150-152℃; υ_{max} (KBr)/cm^{-1} 3420, 3331, 3255, 3204 (NH_2), 3065 (ArH), 2988, 2939, 2904 (CH), 2246 (CN), 1739 (C=O), 1673 (C=C-NH_2), 1639, 1580, 1477 (Ar); δ_H ($CDCl_3$) 0.91 (3H, t, *J* 7.0, CH_3), 1.32 (3H, t, *J* 7.2, CH_3), 3.72 - 4.13 (3H, m, CH_2 and CH), 4.25 - 4.70 (3H, m, CH_2 and CH), 6.23 (2H, br s, NH_2), 6.85 - 7.75 (8H, m, ArH); m/z 564, 562, 560 (M^+, 44, 86, 45%), 533 (40), 516 (28), 491 (51), 489 (100), 487 (54), 445 (55), 443 (85), 415 (44), 362 (23), 255 (39), 209 (29), 154 (22), 102 (20). Anal. for $C_{24}H_{22}N_2O_4Br_2$: Cal.(found) C, 51.27 (51.06); H, 3.94 (3.89); N, 4.98 (4.78) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (2-bromophenyl)-1,3-cyclopentenedicarboxylate 5i

Colorless crystals. mp 192-194℃; υ_{max} (KBr)/cm^{-1} 3420, 3320, 3251, 3192 (NH_2), 3055 (ArH), 2984, 2943, 2908 (CH), 2244 (CN), 1753 (C=O), 1671 (C=C-NH_2), 1640, 1571, 1469 (Ar); δ_H ($CDCl_3$) 0.92 (3H, t, *J* 7.0, CH_3), 1.20 (3H, t, *J* 6.0, CH_3), 3.98 - 4.60 (3H, m, CH_2 and CH), 4.74 - 5.15 (3H, m, CH_2 and CH), 6.30 (2H, br s, NH_2), 7.10 - 8.22 (8H, m, ArH); m/z 564, 562, 560 (M^+, 10, 19, 10%), 489 (30), 483 (100), 481 (99), 443 (17), 408 (13), 362 (26), 334 (12), 283 (20), 255 (41), 240 (15), 181 (10), 102 (12). Anal. for $C_{24}H_{22}N_2O_4Br_2$: Cal.(found) C, 51.27 (51.08); H, 3.94 (3.85); N, 4.98 (5.09) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4,*cis*-5-di(3,4-methylenedioxyphenyl)-1,3-cyclopentenedicarboxylate 5j

Colorless crystals. mp 186-188℃; υ_{max} (KBr)/cm^{-1} 3422, 3321, 3247, 3185 (NH_2), 3070 (ArH), 2987, 2918, 2882 (CH), 2248 (CN), 1739 (C=O), 1660 (C=C-NH_2), 1632, 1562, 1489 (Ar); δ_H ($CDCl_3$) 0.94 (3H, t, *J* 7.0, CH_3), 1.30 (3H, t, *J* 7.2, CH_3), 3.90 - 4.40 (3H, m, CH_2 and CH), 4.52 - 4.98 (3H, m, CH_2 and CH), 6.25 (2H, s, OCH_2O), 6.33 (2H, s, OCH_2O), 6.38 (2H, br s, NH_2), 6.93 - 7.72 (6H, m, ArH); m/z 492 (M^+, 86%), 463 (10), 419 (35), 399 (42), 372 (41), 344 (23), 297 (11), 268 (14), 246 (53), 202 (13), 174 (100), 144 (27). Anal. for $C_{26}H_{24}N_2O_8$: Cal.(found) C, 63.41 (63.62); H, 4.91 (4.76); N, 5.69 (5.56) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-*tert*-butylphenyl)-1,3-cyclopentenedicarboxylate 5k

Colorless crystals. mp 174-175℃; υ_{max} (KBr)/cm^{-1} 3424, 3320, 3261, 3204 (NH_2), 3038 (ArH), 2965, 2906, 2870 (CH), 2248 (CN), 1744 (C=O), 1672 (C=C-NH_2), 1638, 1585, 1459 (Ar); δ_H ($CDCl_3$) 0.86 (3H, t, *J* 7.2, CH_3), 1.25 (9H, s, *t*-C_4H_9), 1.29 (9H, s, *t*-C_4H_9), 1.42 (3H, t, *J* 7.0, CH_3), 3.62 - 4.15 (3H, m, CH_2 and CH), 4.26 - 4.53(3H, m, CH_2 and CH), 5.90 (2H, br s, NH_2), 6.73 - 7.60 (8H, m, ArH); m/z 516 (M^+, 100%), 487 (32), 459 (22), 443 (70), 413 (23), 396 (35), 369 (33), 341 (22), 311 (15), 156 (15), 57 (65). Anal. for $C_{32}H_{40}N_2O_4$: Cal.(found) C, 74.39 (74.12); H, 7.80 (8.07); N, 5.42 (5.22) %.

Diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (2-furyl)-1,3-cyclopentenedicarboxylate 5l

Colorless crystals. mp 131-133℃; υ_{max} (KBr)/cm^{-1} 3408, 3327, 3260, 3204 (NH_2), 2983, 2938, 2902, 2875

(CH), 2247 (CN), 1743 (C=O), 1677 (C=C-NH_2), 1633, 1583, 1465 (Ar); δ_H ($CDCl_3$) 0.80 (3H, t, *J* 6.8, CH_3), 1.26 (3H, t, *J* 7.0, CH_3), 3.70 - 4.15 (3H, m, CH_2 and CH), 4.28 - 4.48(3H, m, CH_2 and CH), 5.93 (2H, br s, NH_2), 6.12 - 6.45 (2H, m, ArH), 7.10 - 7.52 (1H, m, ArH); m/z 384 (M^+, 21%), 383 (100), 354 (28), 337 (30), 310 (95), 292 (23), 266 (24), 265 (97), 243 (24), 238 (29), 237 (100), 209 (27), 164 (14), 121 (36). Anal. for $C_{29}H_{20}N_2O_6$: Cal.(found) C, 62.49 (62.31); H, 5.24 (5.40); N, 7.29 (7.18) %.

Compound 5m

Colorless crystals. mp 215-217℃; υ_{max} (KBr)/cm^{-1} 3021 (ArH), 2960, 2924, 2880 (CH), 2260 (CN), 1749 (C=O), 1630, 1600, 1510 (Ar); δ_H ($CDCl_3$) 1.03 (6H, t, *J* 7.0, 2×CH_3), 1.50 (12H, s, 4×CH_3), 3.27 - 4.24 (8H, m, 2×CH_2, 2×CH and 2×CH), 4.82(4H, s, 2×CH_2O), 6.57 - 7.53 (6H, m, ArH); m/z 576 (M^+, 2%), 518 (27), 460 (45), 386 (35), 347 (37), 340 (92), 314 (45), 288 (100), 230 (28), 158 (71). Anal. for $C_{32}H_{30}N_2O_8$: Cal.(found) C, 66.65 (66.55); H, 6.29 (6.44); N, 4.86 (4.67) %.

2-Amino-1,3-di(*N*-methyl-*N*-phenylaminocarbonyl)-*r*-3-cyano-*trans*-4,5-diphenylcyclopentene 7a

Colorless crystals. mp 188-190℃; υ_{max} (KBr)/cm^{-1} 3385, 3321 (NH_2), 3040 (ArH), 2960, 2934 (CH), 2238 (CN), 1642 (C=C-NH_2), 1598, 1532, 1490 (Ar); δ_H ($CDCl_3$) 2.93 (1H, d, *J* 9.2, CH), 3.07 (3H, s, CH_3), 3.25 (3H, s, CH_3), 3.63 (1H, d, *J* 9.0, CH), 5.25 (2H, br s, NH_2), 6.57 (2H, d, *J* 6.4, ArH), 6.68 (2H, d, *J* 6.0, ArH), 7.00 ~ 7.30 (16H, m, ArH); m/z 526 (M^+, 2%), 419 (10), 352 (6), 264 (6), 263 (5), 135 (10), 134 (100), 107 (71), 106 (50), 77 (21). Anal. for $C_{34}H_{30}N_4O_2$: Cal.(found) C, 77.54 (77.81); H, 5.74 (5.50); N, 10.64 (10.78) %.

2-Amino-1,3-di(*N*-methyl-*N*-phenylaminocarbonyl)-*r*-3-cyano-*trans*-4,5-di(4-methylphenyl)cyclopentene 7b

Colorless crystals. mp 207-209℃; υ_{max} (KBr)/cm^{-1} 3395, 3318 (NH_2), 3010 (ArH), 2980, 2923 (CH), 2245 (CN), 1638 (C=C-NH_2), 1595, 1548, 1494 (Ar); δ_H ($CDCl_3$) 2.22 (3H, s, CH_3), 2.32 (3H, s, CH_3), 2.99 (1H, d, *J* 8.8, CH), 3.08 (3H, s, CH_3), 3.22 (3H, s, CH_3), 3.51 (1H, d, *J* 9.0, CH), 5.28 (2H, br s, NH_2), 6.45 (2H, d, *J* 7.8, ArH), 6.71 (2H, d, *J* 6.0, ArH), 6.82 ~ 7.32 (14H, m, ArH); m/z 554 (M^+, 3%), 449 (6), 448 (22), 447 (25), 421 (9), 313 (11), 135 (10), 134 (100), 107 (90), 106 (53), 77 (21). Anal. for $C_{36}H_{34}N_4O_2$: Cal.(found) C, 77.95 (78.09); H, 6.18 (6.02); N, 10.10 (10.38) %.

2-Amino-1,3-di(*N*-methyl-*N*-phenylaminocarbonyl)-*r*-3-cyano-*trans*-4,5-di(4-chlorophenyl)cyclopentene 7c

Colorless crystals. mp 201-203℃; υ_{max} (KBr)/cm^{-1} 3401, 3314 (NH_2), 3057 (ArH), 2975, 2940 (CH), 2220 (CN), 1631 (C=C-NH_2), 1591, 1548, 1491 (Ar); δ_H ($CDCl_3$) 2.95 (1H, d, *J* 9.1, CH), 3.09 (3H, s, CH_3), 3.24 (3H, s, CH_3), 3.53 (1H, d, *J* 9.0, CH), 5.41 (2H, br s, NH_2), 6.45 (2H, d, *J* 8.3, ArH), 6.69 (2H, d, *J* 6.1, ArH), 6.90 (2H, d, *J* 8.0, ArH), 7.03 (2H, d, *J* 8.3, ArH), 7.22 ~ 7.37 (10H, m, ArH); m/z 596, 594 (M^+, 6. 9%), 490 (11), 489 (27), 488 (18), 487 (36), 460 (9), 297 (9), 134 (72), 107 (100), 106 (48), 77 (22), 44 (21). Anal. for $C_{34}H_{28}N_4O_2Cl_2$: Cal.(found) C, 69.79 (70.03); H, 4.56 (4.50); N, 9.04 (9.28) %.8

2-Amino-1,3-di(*N*-methyl-*N*-phenylaminocarbonyl)-*r*-3-cyano-*trans*-4,5-di(4-fluorophenyl)cyclopentene 7d

Colorless crystals. mp 195-197℃; υ_{max} (KBr)/cm^{-1} 3407, 3305 (NH_2), 3045 (ArH), 2960, 2927 (CH), 2335 (CN), 1640 (C=C-NH_2), 1596, 1509, 1440 (Ar); δ_H ($CDCl_3$) 2.97 (1H, d, *J* 9.0, CH), 3.09 (3H, s, CH_3), 3.26 (3H, s, CH_3), 3.58 (1H, d, *J* 9.2, CH), 5.39 (2H, br s, NH_2), 6.47 ~ 7.37 (18H, m, ArH); m/z 562 (M$^+$, 1%), 280 (11), 279 (13), 187 (3), 185 (5), 177 (13), 174 (29), 146 (17), 134 (46), 121 (22), 117 (18), 107 (100), 106 (45), 85 (31), 77 (32), 44 (60), 41 (30). Anal. for $C_{34}H_{28}N_4O_2F_2$: Cal.(found) C, 73.71 (73.95); H, 4.81 (4.77); N, 9.55 (9.21) %.

2-Amino-1,3-di(*N*-methyl-*N*-phenylaminocarbonyl)-*r*-3-cyano-*trans*-4,5-di(3-bromophenyl)cyclopentene 7e

Colorless crystals. mp 208-210℃; υ_{max} (KBr)/cm^{-1} 3425, 3325 (NH_2), 3040 (ArH), 2980, 2936 (CH), 2320 (CN), 1645 (C=C-NH_2), 1590, 1550, 1450 (Ar); δ_H ($CDCl_3$) 2.95 (1H, d, *J* 9.1, CH), 3.05 (3H, s, CH_3), 3.23 (3H, s, CH_3), 3.56 (1H, d, *J* 8.6, CH), 5.45 (2H, br s, NH_2), 6.48 (2H, d, *J* 7.0, ArH), 6.76 (2H, d, *J* 7.2, ArH), 6.65 ~ 7.34 (14H, m, ArH); m/z 686, 684, 682 (M$^+$, 0.5, 1, 0.5%), 577 (9), 255 (2), 178 (3), 134 (58), 108 (11), 107 (100), 106 (49), 77 (18). Anal. for $C_{34}H_{28}N_4O_2Br_2$: Cal.(found) C, 61.03 (61.20); H, 3.98 (4.18); N, 7.91 (7.68) %.

Crystal data for diethyl 2-amino-*r*-3-cyano-*trans*-4, *cis*-5-di (4-chlorophenyl)-1,3-cyclopentenedicarboxylate 5d

$C_{24}H_{22}N_2O_4Cl_2$, *M* = 473.35, Monoclinic, space group $P2_1/c$ (#14), crystal dimensions 0.20×0.20×0.30 mm, colorless prismatic crystal, a = 6.924(1), b = 33.176(8), c = 10.647(3) Å, β = 99.93(2)° , *U* = 2409(1) Å^3, by least-squares refinement using the setting angles of 21 carefully centered reflections in the range 18.18° < 2θ < 21.57° , *Z* = 4, *Dc* = 1.305 g cm^{-3}, *F*(000) = 984.00. Data collection and processing. Rigaku AFC7R diffractometer, graphite monochromated M_o - K_α radiation (λ = 0.71069 Å), μ(Mo - K_α) = 3.01 cm^{-1}, 4139 reflections measured, maximum 2θ value of 50.0° , 3767 unique reflections measured (R_{int} = 0.027), 2400 of these with $I > 2.00\ \sigma(I)$ used in refinement. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 5.94528e - 0.7). The intensities of three representative reflections were measured after every 200 reflections. Over the course of data collection, the standard decreased by -0.4%. A linear correction factor was applied to the data to account for this phenomenon. Structure solution and refinement. The structure was solved by direct methods using SHELXS-86[42] and expanded using Fourier technique.[43] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not

refined. The final cycle of full-matrix least-squares refinement was based on 2400 observed reflections and 290 variable parameters. Refinement converged at a final R = 0.051 and R_w = 0.063. Max/min peaks in final difference map 0.37/-0.30. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.[44]

General Procedure for the Syntheses of Disulfides by Samarium Mediated Reduction of Sodium Alkyl Thiosulfates in Aqueous Media

Under an inert atmosphere of nitrogen, powdered samarium (180 mg, 1.2 mmol) and sodium alkyl thiosulfate (1.0 mmol) were placed in a round bottomed flask, and THF (5 cm^3) was added to it in one portion. After saturated NH_4Cl (aq.) (1 cm^3) was added dropwise to the mixture *via* syringe within 1 h, the mixture was stirred at room temperature for the time indicated in **Table 5**. After usual workup, the residue was then purified by preparative thin layer chromatography on silica gel with petroleum ether as eluent to afford the product **9**.

Dibenzyldisulfide 9a

mp 70℃ (lit.[45] 71℃); υ_{max} (KBr)/cm^{-1} 3080, 3040 (ArH), 2980, 2940, 2870 (CH), 1610, 1590, 1500 (Ar); δ_H (CCl_4) 3.50 (4H, s, CH_2), 6.87 - 7.33 (10H, m, ArH).

Didodecyldisulfide 9b

mp 30℃ (lit.[45] 30℃); υ_{max} (KBr)/cm^{-1} 2980, 2960, 2880, 1470, 1385, 720; δ_H (CCl_4) 0.86 (6H, t, *J* 7.2, 2 $\times CH_3$), 1.21-1.76 [40H, m, $2\times(CH_2)_{10}$], 2.61 (4H, t, *J* 7.0, $2\times SCH_2$).

Didecyldisulfide 9c

oil (lit.[45]); υ_{max} (KBr)/cm^{-1} 2970, 2950, 2880, 1460, 1380, 720; δ_H (CCl_4) 0.85 (6H, t, *J* 7.1, $2\times CH_3$), 1.10-1.73 [32H, m, $2\times(CH_2)_8$], 2.60 (4H, t, *J* 7.1, $2\times SCH_2$).

Dioctyldisulfide 9d

oil (lit.[45]); υ_{max} (KBr)/cm^{-1} 2975, 2960, 2880, 1460, 1380, 720; δ_H (CCl_4) 0.88 (6H, t, *J* 7.0, $2\times CH_3$), 1.20-1.76 [24H, m, $2\times(CH_2)_6$], 2.63 (4H, t, *J* 7.0, $2\times SCH_2$).

General Procedure for the Syntheses of Alkenes by Samarium Mediated Reductive Debromination of vic-Dibromides in Aqueous Media

Under an inert atmosphere of nitrogen, powdered samarium (180 mg, 1.2 mmol) and *vic*-dibromide (1.0 mmol) were placed in a round bottomed flask, and THF (5 cm^3) was added to it in one portion. After saturated NH_4Cl (aq.) (1 cm^3) was added dropwise to the mixture *via* syringe within 1 h, the mixture was stirred at room temperature for the time indicated in **Table 6**. After usual workup, the residue was then purified by preparative thin layer chromatography on silica gel with cyclohexane-ethyl acetate as eluent to afford the product **11**.

***trans*-Stilbene 11a**

mp 123-124℃ (lit.[46] 123-124℃); υ_{max} (KBr)/cm^{-1} 3080, 3060, 3040 (ArH), 1610, 1500, 1460 (Ar); δ_H (CCl_4) 7.10 (2H, s, Vinyl-H), 7.15-7.60 (10H, m, ArH).

Cyclohexene 11c

Oil. bp 81-83℃ (lit.[47] 81-83℃); υ_{max} (film)/cm^{-1} 3030, 2980, 2840, 1650, 1440, 720; δ_H (CCl_4) 1.47-2.48 (8H, m, 4×CH_2), 5.40 (2H, m, Vinyl-H).

***trans*-Ethyl cinnamate 11d**

Oil. bp 130-132℃ (lit.[48] 128-130℃); υ_{max} (film)/cm^{-1} 3030 (ArH), 2980 (CH), 1710 (C=O), 1640, 1580, 1500, 1460 (Ar); δ_H (CCl_4) 1.30 (3H, t, *J* 7.3, CH_3), 4.18 (2H, q, *J* 6.8, CH_2), 6.33 (1H, d, *J* 15.8, Vinyl-H), 7.20-7.73 (6H, m, ArH and Vinyl-H).

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