Pergamon

Tetrahedron 54 (1998) 11129–11140

TETRAHEDRON

# Water Accelerated Sm/TMSCl Reduction System: Pinacolic Coupling of Aromatic Carbonyl Compounds and Reductive Dimerization Cyclization of 1,1-Dicyanoalkenes

**Lei Wang and Yongmin Zhang***

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

Received 25 January 1998; revised 23 March 1998; accepted 28 May 1998

***Abstract***: By action of Sm/TMSCl in THF at room temperature, aromatic carbonyl compounds produce the corresponding 1,2-diols *via* reductive coupling reaction and 1,1-dicyanoalkenes produce the functionalized cyclopentenes through reductive dimerization followed by intramolecular cyclization in one-pot. The former gives approximately equal amounts of (*dl*)- and (*meso*)-1,2-diols and the later gives the major *trans*-form products. Added micro amounts of water to the system not only can accelerate the reaction, but also increase the yields of products. Moreover, only substoichiometric quantities of metallic samarium are employed. 

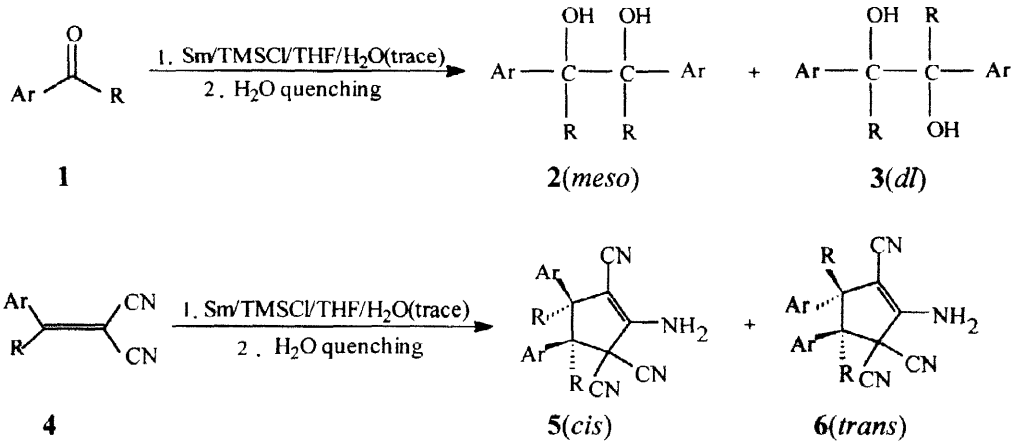
## INTRODUCTION

The chemistry of samarium(II) iodide($SmI_2$) is of current interest in organic synthesis.[1] Since pioneering studies by Kagan and his group demonstrate the particular effectiveness of $SmI_2$ as a mild, neutral, and ether-soluble one-electron transfer reducing agent,[2] the utilization of $SmI_2$ reagent in synthetic organic chemistry has been extensively documented, such as the deoxygenation of sulfoxides[3] and epoxides,[4] the reduction of organohalo compounds,[5] the homocoupling allylic or benzylic halides,[6] acid chlorides,[7] carbonyl compounds,[8] the Barbier reaction,[9] and the Reformatsky reaction,[10] etc.. However, some problems are encountered when it is used as a reductant. Though $SmI_2$ is a useful reagent, storage is difficult because it is very sensitive to air oxidation and in general, it has been used invariably in stoichiometric amounts. On the other hand, metallic samarium is stable in air and its strong reducing power ($Sm^{3+}/Sm$ = -2.41V) is similar to that of magnesium ($Mg^{2+}/Mg$ = -2.37V), and superior to that of zinc ($Zn^{2+}/Zn$ = -0.71V). These properties prompted us to use the more convenient and cheaper samarium directly as a reductant instead of samarium(II) iodide. Recently, there

0040-4020/98/$ - see front matter 
*PII:* S0040-4020(98)00666-8

are some reports on the direct use of Sm in organic synthesis.[11] Unfortunately, to the best our knowledge, only one paper reported that water could accelerate the reaction of alkyl and aryl iodides with $SmI_2$.[12]

Ishii and co-workers have shown that metallic tin reacts with allylic alcohols in the presence of iodotrimethylsilane ($Me_3SiI$) derived from chlorotrimethylsilane and sodium iodide ($Me_3SiCl/NaI$) to form an allylic iodotin species, which subsequently undergoes the α-selective coupling reaction with aldehydes to give the corresponding homoallylic alcohols in good yields under ambient temperature.[13] Most recently, $Sm/Me_3SiCl/NaI$ and $Sm/Me_3SiBr$ system have been used for intermolecular carbon-carbon bond formation reactions of carbonyl compounds.[14] Here, we report that $Sm/Me_3SiCl$ promotes pinacolic coupling of aromatic carbonyl compounds to form pinacols **2** and **3**, and reductive dimerization cyclization of 1,1-dicyanoalkenes to afford functionalized cyclopentenes **5** and **6** in one-pot at room temperature.




## RESULTS AND DISCUSSION

### *Effects of Additives on the Sm/TMSCl Reduction System*

Various additives were used in the Sm/TMSCl reduction system and the results are summarized in **Table 1**. We have found that, in the absence of any additive, aromatic carbonyl compounds can be reduced to the corresponding 1,2-diols, and 1,1-dicyanoalkenes to the functionalized cyclopentenes, but the reactions need longer times for completion and the yields are moderate. As water or a low molecular weight alcohol is added to the system, it not only accelerates the reaction, but also increases the yield. Among these additives, water is the most effective, economical and environment-friendly.

We also examined the effect of water on the Sm/TMSCl reduction system. The results are shown in **Fig. 1**. We find that the optimum quantity of added water is in the range of 10 ~ 30 μl in 1 mmol scale reaction conditions.

**Table 1.** Effects of Additives on the Sm/TMSCl Reduction System Using 4-Chlorobenzaldehyde and 1,1-Dicyano-2-(4-chlorophenyl)ethene as Model Substrate Respectively[a]

| Entry | Additive | Pinacolic Coupling | | Reductive Dimerization Cyclization | |
|---|---|---|---|---|---|
| | | Time(h) | Yield(%)[b] | Time(h) | Yield(%)[b] |
| 1 | no | 15 | 40 | 15 | 50 |
| 2 | t-BuOH[c] | 12 | 64 | 12 | 62 |
| 3 | i-PrOH[c] | 9 | 74 | 9 | 80 |
| 4 | MeOH[c] | 6 | 75 | 6 | 78 |
| 5 | $H_2O$[d] | 3 | 83 | 3 | 90 |
| 6 | NaI[e] | 9 | 57 | 9 | 60 |
| 7 | HMPA[f] | 9 | 54 | 9 | 55 |

a. Reaction conditions: substrate 1 mmol, Sm 0.75 mmol, TMSCl 0.5 ml, THF 4 ml, r. t.. b. Isolated yields.
c. ROH : substrate = 4 : 1. d. $H_2O$ : substrate = 1 : 1. e. NaI : substrate = 1 : 1. f. HMPA 0.2 ml.

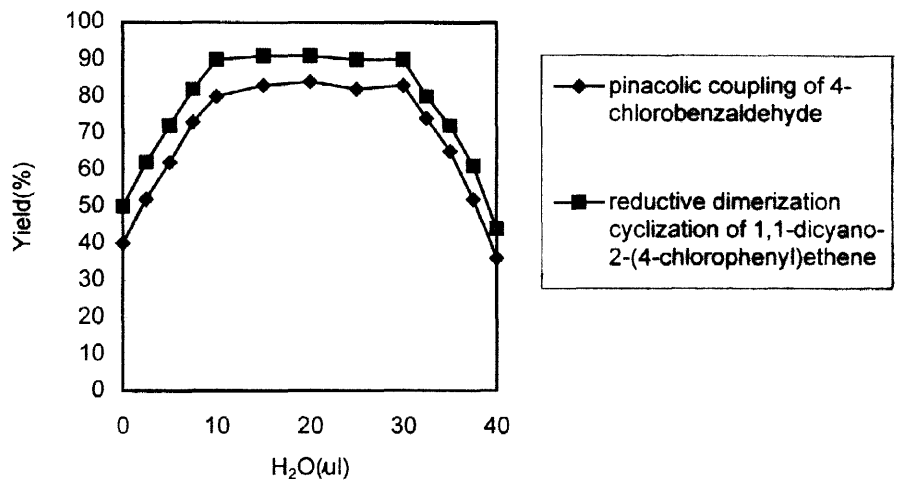



**Fig. 1.** The effect of added of water on the Sm/TMSCl reduction system

Reaction conditions: substrate 1 mol, Sm 0.75 mmol, TMSCl 0.5 ml, THF 4 ml, r.t.

***The Effect of the Amount of Metallic Samarium on the Reduction System***

**Table 2** summarizes the results. To samarium(II) iodide reduction or metallic samarium directly as a reductant, excess or stoichiometric amounts of samarium were used, in general. When Sm/TMSCl/$H_2O$(trace) system was the reductant in the pinacolic coupling of aromatic carbonyl compounds and in the reductive dimerization cyclization of 1,1-dicyanoalkenes, only substoichiometric amounts of Sm (Sm/substrate = 1/2 ~ 3/4) were used to complete the reaction. When the stoichiometric or superstoichiometric quantities of Sm (Sm/substrate = 1/1 ~ 2/1) were used, the yield of product was not increased.

**Table 2.** The Effect of the Amount of Metallic Samarium on the Reduction System Using 4-Chlorobenzaldehyde and 1,1-Dicyano-2-(4-chlorophenyl)ethene as Model Substrate[a]

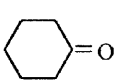
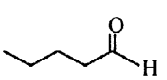
| Sm/Substrate | Yield(%)[b] | |
|---|---|---|
| | Pinacolic Coupling Reaction | Reductive Dimerization Cyclization |
| 1/1 | 81 | 90 |
| 0.75/1 | 83 | 89 |
| 0.5/1 | 83 | 88 |
| 1.5/1 | 84 | 89 |
| 2/1 | 82 | 88 |

a. Reaction conditions: substrate 1 mmol, TMSCl 0.5 ml, THF 4 ml, $H_2O$ 18 μl, r. t.. b. Isolated yields.

***Reductive Coupling Reaction of Aromatic Carbonyl Compounds***

In order to ascertain the potential of Sm/TMSCl reduction system accelerated by trace amounts of water, various carbonyl compounds were reacted and the results were shown in **Table 3**. **Table 3** indicates that aromatic aldehydes and ketones react easily with Sm/TMSCl/$H_2O$(trace) and give the corresponding 1,2-diols in good yields. The ratio of *dl/meso* is nearly 1/1 ($^1$H NMR). Aliphatic aldehydes and ketones fail in the reaction.

**Table 3.** Reductive Coupling Reaction of Aromatic Carbonyl Compounds

| Entry | Substrate | Yield(%) [a] | *dl*:*meso* [b] |
|---|---|---|---|
| 8 | $C_6H_5CHO$ | 82 | 55:45 |
| 9 | *p*-$ClC_6H_4CHO$ | 83 | 56:44 |
| 10 | *p*-$CH_3C_6H_4CHO$ | 78 | 54:46 |
| 11 | *p*-$BrC_6H_4CHO$ | 83 | 50:50 |
| 12 | *m*-$BrC_6H_4CHO$ | 80 | 52:48 |
| 13 | $C_6H_5COCH_3$ | 80 | 50:50 |
| 14 |  | -- | -- |
| 15 |  | -- | -- |

a. Isolated yields. b. Ratios determined by $^1$H NMR.

***Reductive Dimerization Cyclization of 1,1-Dicyanoalkenes: One-pot Syntheses of Functionalized Cyclopentenes***

The enamine is one of the important synthetic intermediate in organic synthesis.[15] It is not only an

intermediate for the indirectly selective alkylation or acylation of an aldehyde or ketone,[16] but it also can be converted into carbonyl compound, or into a carboxylic acid or its derivaties.[17] It is well known that the Thorpe-Ziegler method is an effective synthetic route to enamino-nitriles.[18] The base-catalyzed condensation of two molecules of nitriles, or cyclisation of a dinitrile yields imines which tautomerize to enamines, but usually a strong base such as sodium ethoxide or sodium methyl anilide is used in the reaction. It is desirable to develop milder methods for enamine preparation. In order to expand the scope of the Sm/TMSCl/$H_2O$(trace) reduction system, we have examined the reductive dimerization cyclization of 1,1-dicyanoalkenes. The results are listed in **Table 4**.

**Table 4.** Reductive Coupling Cyclization of 1,1-Dicyanoalkenes(**4**)

| Entry | Ar | R | Yield(%)[a] | **6/5** [b] |
|---|---|---|---|---|
| 16 | $C_6H_5$ | H | 85 | 85/15 |
| | | | 0[c] | -- |
| 17 | *p*-$CH_3C_6H_4$ | H | 82 | 90/10 |
| 18 | *p*-$CH_3OC_6H_4$ | H | 78 | 80/20 |
| 19 | *p*-$BrC_6H_4$ | H | 87 | 88/12 |
| 20 | *p*-$ClC_6H_4$ | H | 90 | 85/15 |
| 21 | *p*-$FC_6H_4$ | H | 86 | 80/20 |
| 22 | p-$CF_3C_6H_4$ | H | 90 | 90/10 |
| 23 | *m*-$BrC_6H_4$ | H | 83 | 80/20 |
| 24 | *o*-$BrC_6H_4$ | H | 80 | 75/25 |
| 25 | $C_6H_5$ | $CH_3$ | 70 | 60/40 |
| 26 | *p*-$BrC_6H_4$ | $CH_3$ | 72 | 60/40 |

a. Isolated yields. b. Ratios determined by $^1$H NMR. c. Without $Me_3SiCl$.

From **Table 4**, it is seen that substrates **4** derived from aromatic aldehydes give the products **5** and **6** in good to excellent yields at room temperature, with the *trans*-isomer **6** is in the majority. The ratio of *trans/cis* falls in the range of 75/25 to 90/10. Substrates **4** derived from aromatic ketones give **5** and **6** in moderate yields with *trans/cis* ratios 60/40. When **4** is derived from aliphatic aldehydes or ketones, no reductive coupling cyclization product was isolated.[19]

***Determination of Ratio and Configuration of the Product***

To the pinacolic coupling products of aromatic carbonyl compounds, the ratios of products were determined from the intensities of benzylic protons in $^1$H NMR spectra (entries 8-12), in which the protons of

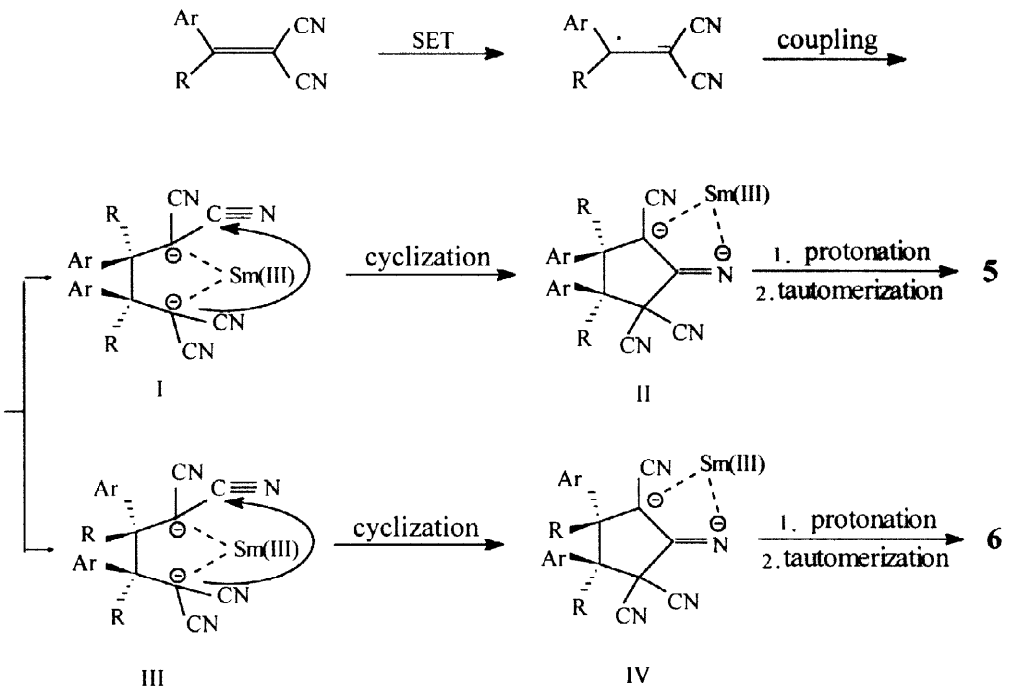
*dl* isomer appeared at a higher field, compared to that of the *meso* isomer, and from the intensities of methyl protons in $^1$H NMR spectra (entry 13), in which the methyl protons of *dl* isomer appeared at higher field of that of the *meso* isomer.[20]

The configuration of **5** and **6** was determined by $^1$H NMR and NOE spectra. In the $^1$H NMR spectra, the coupling constants of the two protons on the ring in substituted cyclopentene **5** and **6** were in the range of 7-8 Hz and 9-10 Hz respectively (entries 16-24). The two protons with J values of 7-8 Hz are oriented *cis* to each other, and there exists a strong NOE effect between the signal in the NOE spectra, while the two protons with J values of 9-10 Hz are oriented *trans* to each other, and no NOE effect was found between them.

The ratios of **6/5** were determined from the intensities of the methene protons (entries 16-24) or methyl protons (entries 25-26) in $^1$H NMR.

***Reaction Mechanism***

When chlorotrimethylsilane reacts with metallic samarium powder in THF under nitrogen atmosphere at room temperature, the samarium partly dissolved and the solution became light blue-green. As trace amounts of water were added to the mixture, the remaining samarium powder was gradually consumed. This result is similar to that of Sm/$Me_3SiCl$/NaI or Sm/$Me_3SiBr$.[14] In the pinacolic coupling reaction of aromatic aldehydes and ketones, the reaction mechanism with Sm/TMSCl/$H_2O$(trace) is the same as that with $SmI_2$.[21] A possible mechanism for the formation of **5** and **6** is depicted in **Scheme 1**. A radical anion of the electron-deficient




**Scheme 1.** A possible mechanism of the reductive coupling cyclization

olefin may be formed by a one-electron transfer process under the reaction conditions due to the electron withdrawing property of CN group, and this reacts with another to form a dianion (coupling process). Eventually, the dianion gives the functionlized cyclopentenes through cyclization, tautomerization and protonation. From **Scheme 1**, we assume that anions I and III are key intermediates in the course of the formation of **5** and **6** respectively. Considering the stability of anion I, III and products, it is obvious that **6** is easy to form. However, the reaction mechanism of trace amounts of water in the Sm/TMSCl reduction system is not fully clear and a more detailed study is in progress in our laboratory.

## CONCLUSION

We have demonstrated Sm/TMSCl/$H_2O$(trace) system can be used to mediate the reductive coupling of aromatic carbonyl compounds and the reductive dimerization cyclization of 1,1-dicyanoalkenes to form the corresponding 1,2-diols and the functionalized cyclopentenes respectively. The notable advantage of this method are mild reaction condition, simple operation, high yields.

## EXPERIMENTAL

$^1$H NMR spectra were recorded on a Brucker AC-80 instrument. All NMR samples were measured in $CDCl_3$ using TMS as internal standard. IR spectra were obtained on a Perkin-Elmer 683 infrared spectrophotometer as KBr discs. The IR peak intensities were recorded as w (weak), m (medium) and s (strong). Mass spectra were determined on a Finnigan MAT GC/MS spectrometer. Elemental analyses were carried out on a Carlo-Erba 1106 instrument.

Metallic samarium, aldehydes and ketones were purchased from commercial sources and used without purification. Chlorotrimethylsilane was redistilled prior to use and kept under inert atmosphere and molecular sieve. THF was freshly distilled from sodium/benzophenone ketyl prior to use. 1,1-Dicyanoalkenes were synthesized by the reaction of a carbonyl compound with a malononitrile following the usual procedure.

### *General Procedure for Pinacolic Coupling Reaction of Aromatic Carbonyl Compounds*

Under nitrogen atmosphere, metallic samarium powder (0.113g, 0.75 mmol) and aromatic carbonyl compound (1.0 mmol) were placed in a reaction flask and TMSCl (0.5 ml) and THF (5 ml) were added in one portion. Then $H_2O$ (18 μl) was added to the mixture and the resulting mixture was magnetically stirred for 3 h at room temperature until the powdered samarium was almost consumed. Water (2 ml) was added to quench the reaction and the mixture was extracted with ether (20 ml × 2). After the extracts were washed with brine, dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure, the residue was then

purified by preparative TLC on silica gel with petroleum ether/ether as the eluent.

***General Procedure for the Syntheses of Functionalized Cyclopentenes in One-pot***

Under nitrogen atmosphere, metallic samarium powder (0.113g, 0.75 mmol) and 1,1-dicyanoalkene (1.0 mmol) were placed in a reaction flask and TMSCl (0.5 ml) and THF (5 ml) were added .Then $H_2O$ (18 μl) was added to the mixture and the resulting mixture was stirred for 3 h at room temperature until the powdered samarium was almost consumed. Water (2 ml) was added to quench the reaction and the mixture was extracted with ether (20 ml × 2). After the extracts were washed with brine, dried over anhydrous $Na_2SO_4$ and the solvent was removed under reduced pressure, the residue was then purified by preparative TLC on silica gel with cyclohexane/ethyl acetate as the eluent.

**1,2-diphenyl-1,2-ethanediol(dl- and meso-):** $^1$H NMR δ 3.03(2H, s, OH, this signal disappeared by adding $D_2O$), 4.47(*dl*) and 4.63(*meso*)(2H, s, PhCH), 6.70 ~ 7.50(10H, m, Ar). IR υ/cm$^{-1}$ 3100 ~ 3600(s).

**1,2-di(4-chlorophenyl)-1,2-ethanediol(dl- and meso-):** $^1$H NMR δ 3.23(2H, s, OH, this signal disappeared by adding $D_2O$), 4.40(*dl*) and 4.63(*meso*)(2H, s, PhCH), 6.70 ~ 7.40(8H, m, Ar). IR υ/cm$^{-1}$ 3100 ~ 3600(s).

**1,2-di(4-methylphenyl)-1,2-ethanediol(dl- and meso-):** $^1$H NMR δ 2.14(6H, s $CH_3$), 3.13(2H, s, OH, this signal disappeared by adding $D_2O$), 4.48(*dl*) and 4.58(*meso*)(2H, s, PhCH), 6.70 ~ 7.30(8H, m, Ar). IR υ/cm$^{-1}$ 3100 ~ 3600(s).

**1,2-di(4-bromophenyl)-1,2-ethanediol(dl- and meso-):** $^1$H NMR δ 2.95(2H, s, OH, this signal disappeared by adding $D_2O$), 4.56(*dl*) and 4.70(*meso*)(2H, s, PhCH), 6.80 ~ 7.40(8H, m, Ar). IR υ/cm$^{-1}$ 3150 ~ 3650(s).

**1,2-di(3-bromophenyl)-1,2-ethanediol(dl- and meso-):** $^1$H NMR δ 3.25(2H, s, OH, this signal disappeared by adding $D_2O$), 4.50(*dl*) and 4.67(*meso*)(2H, s, PhCH), 6.60 ~ 7.50(8H, m, Ar). IR υ/cm$^{-1}$ 3100 ~ 3600(s).

**2,3-diphenyl-2,3-butanediol(dl- and meso-):** $^1$H NMR δ 1.40(*dl*) and 1.50(*meso*) (6H, s, $CH_3$), 2.40(2H, s, OH, this signal disappeared by adding $D_2O$), 6.90 ~ 7.30(10H, m, Ar). IR υ/cm$^{-1}$ 3100 ~ 3600(s).

**2-amino-1,3,3-tricyano-4,5-diphenylcyclopentene(*cis*- and *trans*-):** Anal. for $C_{20}H_{14}N_4$: Calc.(found) C 77.40(77.67), H 4.55(4.72), N 18.05(17.80)%. IR υ/cm$^{-1}$ 3378(br), 3217(br), 3052(m), 2940(m), 2212(s), 1678(s), 1670(s), 1660(s), 1630(m), 1503(m), 1460(s), 696(s). $^1$H NMR δ 3.75(d, J=9.4Hz, 0.85H, *trans*-CH), 4.59(d, J=9.4Hz, 0.85H, *trans*-CH), 3.22(d, J=7.2Hz, 0.15H, *cis*-CH), 4.31(d, J=7.2Hz, 0.15H, *cis*-CH), 5.31 br(s) and 5.45 br(s) (2H, $NH_2$), 7.35(m, 10H, Ph × 2). MS(EI) 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).

**2-amino-1,3,3-tricyano-4,5-di(4-methylphenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{22}H_{18}N_4$: Calc.(found) C 78.08(77.87), H 5.36(5.60), N 16.56(16.74)%. IR υ/cm$^{-1}$ 3380(br), 3223(br), 3048(m), 2950(m), 2220(s), 1680(s), 1665(s), 1645(s), 1620(m), 1500(m), 1460(s), 1380(s), 826(m). $^1$H NMR δ 2.16(s, 3H), 2.21(s, 3H), 3.84(d, J=9.4Hz, 0.90H, *trans*-CH), 4.60(d, J=9.4Hz, 0.90H, *trans*-CH), 3.20(d, J=7.2Hz, 0.10H, *cis*-CH), 4.30(d, J=7.2Hz, 0.10H, *cis*-CH), 5.30 br(s) and 5.40 br(s) (2H, $NH_2$), 7.17(m, 8H, Ar × 2). MS(EI) m/z 339($M^+$+1, 16), 338($M^+$, 100), 325(12), 324(25), 155(20), 115(14), 91(12), 65(15) 51(12).

**2-amino-1,3,3-tricyano-4,5-di(4-methoxyphenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{22}H_{18}N_4O_2$: Calc.(found) C 71.34(71.57), H 4.90(4.66), N 15.13(15.01)%. IR υ/cm$^{-1}$ 3370(br), 3220(br), 3050(m), 2945(m), 2221(s), 1683(s), 1666(s), 1648(m), 1618(m), 1500(m), 1460(s), 1385(s), 820(m). $^1$H NMR δ 3.66(s, 3H), 3.81(s, 3.80H, $CH_3O$- and *trans*-CH), 4.42(d, J=9.4Hz, 0.80H, *trans*-CH), 4.06(d, J=7.2Hz, 0.20H, *cis*-CH), 3.13(d, J=7.2Hz, 0.20H, *cis*-CH), 5.30 br(s) and 5.40 br(s) (2H, $NH_2$), 7.08(m, 8H, Ar × 2). MS(EI) 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).

**2-amino-1,3,3-tricyano-4,5-di(4-bromophenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{20}H_{12}Br_2N_4$: Calc.(found) C 51.31(51.59), H 2.58(2.62), N 11.97(11.75)%. IR υ/cm$^{-1}$ 3380(br), 3215(br), 3050(m), 2945(m), 2210(s), 1680(s), 1668(s), 1660(s), 1630(m), 1500(m), 1460(s), 830(m). $^1$H NMR δ 3.71(d, J=9.0Hz, 0.88H, *trans*-CH), 4.50(d, J=9.0Hz, 0.88H, *trans*-CH), 3.35(d, J=7.2Hz, 0.12H, *cis*-CH), 4.21(d, J=7.2Hz, 0.12H, *cis*-CH), 5.29 br(s) and 5.40 br(s) (2H, $NH_2$), 7.33(m, 8H, Ar × 2). MS(EI) m/z 470($M^+$+4, 46), 468($M^+$+2, 100), 466($M^+$, 50), 391(25), 390(33), 389(70), 388(35), 309(34), 308(47), 155(44), 77(24), 75(25), 51(27).

**2-amino-1,3,3-tricyano-4,5-di(4-chlorophenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{20}H_{12}Cl_2N_4$: Calc.(found) C 63.34(63.57), H 3.19(3.02), N 14.77(14.90)%. IR υ/cm$^{-1}$ 3375(br), 3200(br), 3070(m), 2950(m), 2220(s), 1685(s), 1660(s), 1630(m), 1500(m), 1460(s), 828(m). $^1$H NMR δ 3.75(d, J=9.1Hz, 0.85H, *trans*-CH), 4.53(d, J=9.1Hz, 0.85H, *trans*-CH), 3.44(d, J=7.0Hz, 0.15H, *cis*-CH), 4.28(d, J=7.0Hz, 0.15H, *cis*-CH), 5.30 br(s) and 5.42 br(s) (2H, $NH_2$), 7.30(m, 8H, Ar × 2). MS(EI) m/z 382($M^+$+4, 13), 380($M^+$+2, 58), 378($M^+$, 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).

**2-amino-1,3,3-tricyano-4,5-di(4-fluorophenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{20}H_{12}F_2N_4$: Calc.(found) C 69.36(69.67), H 3.49(3.62), N 16.18(16.00)%. IR υ/cm$^{-1}$ 3377(br), 3205(br), 3080(m), 2960(m), 2215(s), 1690(s), 1660(s), 1635(m), 1500(m), 1460(s), 820(m). $^1$H NMR δ 3.60(d, J=9.4Hz, 0.80H, *trans*-CH),

4.42(d, J=9.4Hz, 0.80H, *trans*-CH), 3.13(d, J=7.0Hz, 0.20H, *cis*-CH), 4.12(d, J=7.0Hz, 0.20H, *cis*-CH), 5.28 br(s) and 5.40 br(s) (2H, $NH_2$), 7.17(m, 8H, Ar × 2). MS(EI) m/z 347($M^+$+1, 14), 346($M^+$, 100), 319(5), 318(5), 252(6), 175(5), 174(8), 173(20), 170(5), 147(5), 146(6), 109(6), 76(5), 75(10), 57(5), 51(5).

**2-amino-1,3,3-tricyano-4,5-di(4-trifluoromethylphenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{22}H_{12}F_6N_4$: Calc.(found) C 59.20(59.57), H 2.71(2.62), N 12.55(12.70)%. IR υ/$cm^{-1}$ 3380(br), 3220(br), 3070(m), 2950(m), 2220(s), 1690(s), 1680(s), 1660(s), 1640(m), 1520(m), 1460(s), 832(m). $^1$H NMR δ 3.80(d, J=9.2Hz, 0.90H, *trans*-CH), 4.63(d, J=9.2Hz, 0.90H, *trans*-CH), 3.33(d, J=7.2Hz, 0.10H, *cis*-CH), 4.33(d, J=7.2Hz, 0.10H, *cis*-CH), 5.33 br(s) and 5.42 br(s) (2H, $NH_2$), 7.50(m, 8H, Ar × 2). MS(EI) m/z 447($M^+$+1, 16), 446($M^+$, 100), 428(17), 379(8), 378(13), 377(23), 156(10), 155(25), 153(8), 69(11), 51(8).

**2-amino-1,3,3-tricyano-4,5-di(3-bromophenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{20}H_{12}Br_2N_4$: Calc.(found) C 51.31(51.57), H 2.58(2.79), N 11.97(12.20)%. IR υ/$cm^{-1}$ 3375(br), 3210(br), 3080(m), 2960(m), 2222(s), 1685(s), 1665(s), 1640(s), 1500(m), 1460(s), 790(m), 700(m). $^1$H NMR δ 3.57(d, J=9.4Hz, 0.80H, *trans*-CH), 4.48(d, J=9.4Hz, 0.80H, *trans*-CH), 3.12(d, J=7.2Hz, 0.20H, *cis*-CH), 4.15(d, J=7.2Hz, 0.20H, *cis*-CH), 5.48 br(s) and 5.60 br(s) (2H, $NH_2$), 7.33(m, 8H, Ar × 2). MS(EI) m/z 470($M^+$+4, 44), 468($M^+$+2, 100), 466($M^+$, 48), 390(22), 389(48), 388(33), 308(28), 156(18), 155(42), 128(19), 127(23), 101(17), 77(23), 76(33), 75(35), 63(20), 51(32).

**2-amino-1,3,3-tricyano-4,5-di(2-bromophenyl)cyclopentene(*cis*- and *trans*-):** Anal. for $C_{20}H_{12}Br_2N_4$: Calc.(found) C 51.31(51.65), H 2.58(2.32), N 11.97(11.80)%. IR υ/$cm^{-1}$ 3380(br), 3220(br), 3075(m), 2950(m), 2210(s), 1690(s), 1660(s), 1630(m), 1500(m), 1460(s), 752(m). $^1$H NMR δ 3.62(d, J=9.0Hz, 0.75H, *trans*-CH), 4.53(d, J=9.0Hz, 0.75H, *trans*-CH), 3.20(d, J=7.0Hz, 0.25H, *cis*-CH), 4.20(d, J=7.0Hz, 0.25H, *cis*-CH), 5.53 br(s) and 5.66 br(s) (2H, $NH_2$), 7.19(m, 8H, Ar × 2). MS(EI) m/z 470($M^+$+4, 44), 468($M^+$+2, 100), 466($M^+$, 44), 391(22), 390(37), 389(79), 388(42), 309(25), 308(47), 155(37), 77(24), 76(24), 75(25), 51(23).

**2-amino-1,3,3-tricyano-4,5-dimethyl-4,5diphenylcyclopentene(*cis*- and *trans*-):** Anal. for $C_{22}H_{18}N_4$: Calc.(found) C 78.08(77.87), H 5.36(5.12), N 16.56(16.80)%. IR υ/$cm^{-1}$ 3380(br), 3225(br), 3050(m), 2950(m), 2225(s), 1685(s), 1660(s), 1600(m), 1500(m), 1460(s), 1380(s), 690(s). $^1$H NMR δ 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, 0.6 × 3H, *trans*-$CH_3$), 5.37(br, 2H, $NH_2$), 7.10(m, 10H, Ph × 2). MS(EI) m/z 339($M^+$+1, 73), 338($M^+$, 73), 323(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).

**2-amino-1,3,3-tricyano-4,5-dimethyl-4,5-di(4-bromophenyl)cyclopentene(*cis*- and *trans*-):** Anal. for

$C_{22}H_{16}Br_2N_4$: Calc.(found) C 53.25(53.57), H 3.25(3.52), N 11.29(11.07)%. IR υ/cm$^{-1}$ 3370(br), 3230(br), 3060(m), 2960(m), 2220(s), 1690(s), 1660(s), 1600(s), 1520(m), 1460(s), 1380(s), 825(m). $^1$H NMR δ 1.20(s, 0.40 × 3H, *cis*-$CH_3$), 1.47(s, 0.60 × 3H, *trans*-$CH_3$), 1.90(s, 0.40 × 3H, *cis*-$CH_3$), 2.01(s, 0.6 × 3H, *trans*-$CH_3$), 5.35(br, 2H, $NH_2$), 7.08(m, 8H, Ar × 2). MS(EI) m/z 498($M^+$+4, 40), 496($M^+$+2, 100), 494($M^+$, 49), 248(23), 247(20), 170(32), 169(76), 168(32), 140(26), 115(27), 102(26), 77(33), 76(25), 75(23), 51(29).

## ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China(No. 29672007) and the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences for financial supports.

## REFERENCES AND NOTES

1. Kagan, H. B.; Namy, J. L. *Tetrahedron* **1986**, *42*, 6573. Molander, G. A. *Chem. Rev.* **1992**, *92*, 29. Molander, G. A. *Organic Reactions*, **1994**, *46*, 211. Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307. Yacovan, A.; Hoz, S. *J. Am. Chem. Soc.* **1996**, *118*, 261. Kanemasa, S.; Yamamoto, H.; Kobayashi, S. *Tetrahedron Lett.* **1996**, *37*, 8505.
2. Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.
3. Harada, Y.; Inanaga, J.; Yamaguchi, M. *J. Chem. Soc., Chem. Commun.* **1989**, 276.
4. Molander, G. A.; LaBelle, B. E.; Hahn, G. *J. Org. Chem.* **1986**, *51*, 5259.
5. Wipf, P.; Venkatraman, S. *J. Org. Chem.* **1993**, *58*, 3455. Curran, D. P.; Totleben, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6050.
6. Collin, J.; Namy, J. L.; Dallemer, F.; Kagan, H. B. *J. Org. Chem.* **1991**, *56*, 3118. Kagan, H. B.; Souppe, J.; Namy, J. L. *Tetrahedron Lett.* **1982**, *23*, 3497.
7. Collin, J.; Dallemer, F.; Namy, J. L.; Kagan, H. B. *Tetrahedron Lett.* **1989**, *30*, 7407.
8. Molander, G. A.; Kenny, C. *J. Am. Chem. Soc.* **1989**, *111*, 8263. Molander, G. A.; Kenny, C. *J. Org. Chem.* **1988**, *53*, 2132.
9. Molander, G. A.; Mokie, J. A. *J. Org. Chem.* **1991**, *56*, 4112. Barner, B. A.; Liu, Y.; Rahman, M. A. *Tetrahedron Lett.* **1989**, *45*, 6101.
10. Moriya, T.; Harada, Y.; Inanaga, J.; Yamaguchi, M. *Tetrahedron Lett.* **1988**, *29*, 6947. Molander, G. A.; Etter, J. *J. Am. Chem. Soc.* **1987**, *109*, 6556.
11. Yanada, R.; Negoro, N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1997**, *38*, 3271. Yanada, R.; Negoro,

N.; Yanada, K.; Fujita, T. *Tetrahedron Lett.* **1996,** *37*, 9313. Lautens, M.; Delanghe, P. H. *J. Org. Chem.* **1995**, *60*, 2474. Taniguchi, Y.; Fujii, N.; Takaki, K.; Fujiwara, Y. *J. Organomet. Chem.* **1995**, *491*, 173. Yamazaki, T.; Lin, J. T.; Takeda, M.; Kitazume, T. *Tetrahedron; Asymmetry* **1990**, *1*, 351. Molander, G. A.; Etter, J. B. *J. Org. Chem.* **1988**, *53*, 6077.

12. Hasegawa, E.; Curran, D. P. *J. Org. Chem.* **1993**, *58*, 5008.
13. Kanagawa, Y.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1992**, *57*, 6988.
14. Akane, N.; Kanagawa, Y.; Nishiyama, Y.; Ishii, Y. *Chem. Lett.* **1992**, 2431. Akane, N.; Hatano, T.; Kusui, H.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1994**. *59*, 7902.
15. Cook, A. G. *Enamines: Their Synthesis, Structure and Reaction*, Marcel Dekker, New York, **1969**.
16. Stork, G.; Brizzolaro, A.; Landesman, H.; Szmuszkovicz, J.; Terrel, R. *J. Am. Chem. Soc.* **1963**, *85*, 207. House, H. O. *Modern Synthetic Reaction*, 2nd ed, (W, Benjamin, California, **1972**), p 742.
17. Schaefer, J. P.; Bloomfield, J. J. *Organic Reactions*, **1967**, *15*, 1. Seitz, G.; Monnighoff, H. *Tetrahedron Lett.* **1971**, 4889. Helmers, R.; Kaiser, W. *Tetrahedron Lett.* **1971,** 3853. Wawzonek, S.; Zigman, A. R.; Hansen, G. R. *J. Electrochem. Soc.* **1970,** *117*, 1351.
18. Baron, H.; Remfry, F. G. P.; Thorpe, J. F. *J. Chem. Soc.* **1904**, *85*, 1726. Ziegler, K.; Eberle, E.; Ohlinger, M. *Ann*, **1933**, *504*, 94.
19. Probably this result may be attributed to the difference in stability of the radical anion intermediate. A benzyl radical anion intermediate from 1,1-dicyanoalkene derived from aromatic aldehyde or ketone is stabilized by the neighboring aromatic ring, so that it is easy to form and has enough time to react with another one to form dianion and eventually to give product **5** and **6**. The less stable radical anion intermediate from **4** derived from an aliphatic aldehyde or ketone is difficult to form, so that the starting material was recovered.
20. Handa, Y.; Inanaga, J. *Tetrahedron Lett*, **1987**, *28*, 5717. Balsells, R. E.; Frasca, A. R. *Tetrahedron* **1982**, *38*, 2525.
21. Souppe, J.; Danon, L.; Namy, J. L.; Kagan, H. B. *J. Organometal. Chem.*. **1983**, *250*, 227.