A New Synthetic Method of Highly Substituted Cyclopentadienes from α,β-Unsaturated Alkynones

ZHENG, Xing-Liang[a] **(郑兴良)** **ZHANG, Yong-Min** [*,a,b] **(张永敏)**

[a] *Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou, Zhejiang 310028, China*

[b] *State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

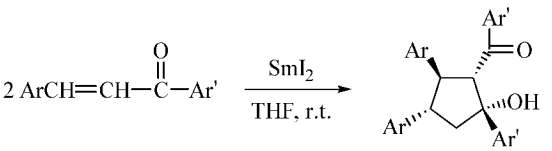
Promoted by samarium diiodide in THF, the α,β-unsaturated alkynones were reduced to afford intermolecular reductive coupling products. The multiply substituted cyclopentadienes were prepared conveniently in good yields.

Keywords samarium diiodide, α,β-unsaturated alkynone, multiply substituted cyclopentadiene

The cyclopentadiene and its derivatives are important organic compounds. Although some classical methods for the preparation of cyclopentadiene were reported,[1] there are only a few reports on the synthesis of highly crowded cyclopentadienes. The syntheses of multiphenyl and multi-*tert*-butyl-substituted cyclopentadienes are especially difficult.[2] For example, Touriya reported palladium-mediated cyclization of 1,5-hexadien-3-ols to 1-methyl-1,3-cyclopentadienes, but the reaction time was quite long and an expensive catalyst and substrates with complex structure were needed in their experiment.[3] Though the preparing method of 1,2,3-trisubstituted cyclopentadienes reported by Xi has some advantages, the low yield and using expensive zirconium complex are their drawbacks.[4,5] Phase transfer catalyzed *tert*-alkylations of cyclopentadiene reported by Dehmlow only low yields of products were obtained.[6] The crafty use of $TiCl_3$ is Russell's merit, but multiple steps are needed.[7] Using highly toxic organostannum to prepare highly crowded cyclopentadienes is a great disadvantage of the reaction reported by Rufanov[8] and Lenze.[9] In short, in these methods mentioned above, the use of complex substrates and expensive transition metals, multiple steps or low yields were inconsiderable. So exploring new synthetic method of highly substituted cyclopentadienes seems very desirable.

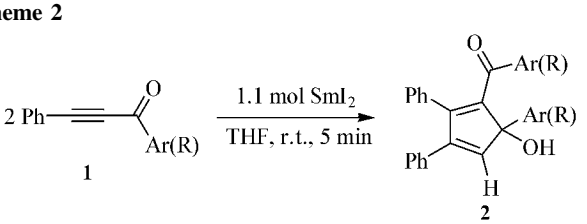
It is well known that the evolution of samarium diiodide for use in organic synthesis is one of the most important and exciting recent developments in organic chemistry.[10] It was reported that the cyclodimerization of arylmethylidene cyanoacetates,[11] arylmethylidene malononitriles[12] and α,β-unsaturated ketones[13] promoted by SmI_2 occurred easily (Scheme 1).

Scheme 1



Since electron deficient alkenes can be reduced by SmI_2 readily to afford coupling products, the electron deficient alkynes may be reduced by SmI_2 more easily. Therefore we studied the reduction of α, β-unsaturated alkynones mediated by SmI_2. Herein, we wish to report the results of our investigation to provide a simple and efficient method for the synthesis of multiply substituted cyclopentadienes (Scheme 2). When α,β-unsaturated alkynones were added to a THF solution of SmI_2 at room temperature, the reaction was completed within about 5 min and afforded the corresponding multiply substituted cyclopentadienes in good yields. The results are shown in Table 1. The reaction temperature and the amount of samarium diiodide used only slightly affect the yields of products.

Scheme 2



The detailed mechanism of the above reaction has not been clarified yet. According to previous reports,[13,14] it is probably a radical process. We propose a possible mechanism shown as follows (Scheme 3).

* E-mail: yminzhang@mail.hz.zj.cn

Received March 24, 2003; revised and accepted May 14, 2003.

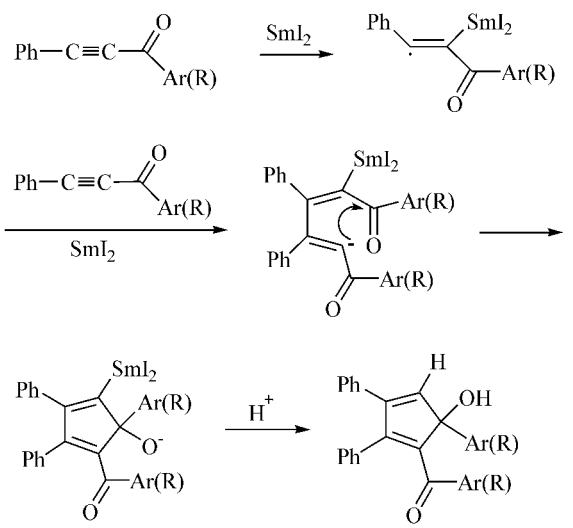
Project supported by the National Natural Science Foundation of China (No. 20072033) and the Specialized Research Fund for the Doctoral Program of Higher Education.

Table 1 Results of reduction reaction with different substituents

Entry	Ar (R)	T [a] (min)	Products	Yields[b] (%)
1	C_6H_5	5	**2a**	78
2	4-$CH_3C_6H_4$	5	**2b**	74
3	4-$CH_3OC_6H_4$	5	**2c**	72
4	4-ClC_6H_4	5	**2d**	83
5	2-ClC_6H_4	5	**2e**	85
6	2,6-$Cl_2C_6H_3$	5	**2f**	69
7	α-Furanyl	5	**2g**	88
8	3,4-$OCH_2OC_6H_3$	5	**2h**	81
9	$CH_3CH_2CH_2$	5	**2i**	79

[a] Reaction time; [b] isolated yields.

Scheme 3



In conclusion, the use of samarium diiodide is a convenient and efficient method to promote the cyclodimerization of α,β-unsaturated alkynones to highly substituted cyclopentadienes in good yields, which has not been achieved previously by any other methods.

Experimental

Melting points were uncorrected. IR spectra were recorded on a Bruker Vector-22 infrared spectrometer. ^{1}H NMR spectra were obtained with a Bruker AC-400 MHz spectrometer in $CDCl_3$ solution using TMS as the internal standard. Mass spectra were recorded on an HP 5989B mass spectrometer. The reactions were performed in a Schlenk-type glass apparatus under nitrogen atmosphere.

General procedure for the reduction reaction

A solution of α,β-unsaturated alkynone **1** (1 mmol) in THF (3 mL) was added to a solution of SmI_2 (1.1 mmol) in THF at room temperature under nitrogen atmosphere. The reaction was completed in 5 min and the color of the reaction mixture changed to brownish yellow. The reaction was quenched with diluted 0.1 mol/L HCl (2 mL) and extracted with ethyl ether. After usual work-up, the crude product was purified by preparative TLC or column chromatography (cyclohexane-ethyl acetate 12∶1 as eluent).

2a Light yellow solid. m.p. 171—172 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74—7.33 (m, 5H), 7.27—6.82 (m, 9H), 6.76—6.65 (m, 6H), 6.27 (s, 1H), 4.86 (s, 1H); IR (KBr) ν: 3444, 3058, 3028, 2925, 1623, 1597, 1574, 1490, 1447, 1332, 1177, 1046, 1008, 758, 695 cm^{-1}; MS (70 eV) *m/z* (%): 414 (M^+, 8.82), 415 (M^+ + 1, 2.98), 397 (M^+ − 17, 45.28), 309 (3.34), 291 (2.57), 208 (1.42), 207 (4.14), 206 (9.29), 179 (2.98), 178 (17.46), 176 (2.35), 129 (12.65), 106 (7.40), 105 (100), 77 (35.39), 51 (10.51). Anal. calcd for $C_{30}H_{22}O_2$: C 86.93, H 5.35; found C 86.90, H 5.32.

2b Light yellow solid. m.p. 93—94 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.71—7.26 (m, 8H), 7.10—6.63 (m, 10H), 6.26 (s, 1H), 4.85 (s, 1H), 2.21 (s, 3H), 2.35 (s, 3H); IR (KBr) ν: 3424, 3055, 3030, 2922, 2852, 1673, 1604, 1510, 1490, 1443, 1181, 1080, 1052, 815, 755, 691 cm^{-1}; MS (70 eV) *m/z* (%): 442 (M^+, 0.49), 425 (M^+ − 17, 0.75), 424 (1.66), 415 (0.21), 305 (4.85), 295 (1.10), 289 (2.90), 276 (1.29), 221 (2.93), 221 (10.49), 192 (6.46), 191 (6.16), 129 (29.51), 119 (100.00), 105 (9.21), 91 (45.20), 77 (7.21), 65 (13.00). Anal. calcd for $C_{32}H_{26}O_2$: C 86.84, H 5.92; found C 86.81, H 5.88.

2c Yellow solid. m.p. 123—125 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.83—7.15 (m, 8H), 7.14—6.61 (m, 10H), 6.24 (s, 1H), 4.88 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H); IR (KBr) ν: 3442, 2932, 2838, 1654, 1598, 1573, 1509, 1252, 1171, 1029, 833, 759, 698 cm^{-1}; MS (70 eV) *m/z* (%): 474 (M^+, 1.31), 458 (4.18), 355 (2.03), 339 (5.91), 326 (4.97), 324 (4.67), 237 (3.86), 178 (2.83), 165 (13.04), 135 (100.00), 105 (17.18), 107 (13.49), 92 (13.03), 77 (37.44). Anal. calcd for $C_{32}H_{26}O_4$: C 80.99, H 5.52; found C 80.96, H 5.50.

2d Yellow solid. m.p. 184—186 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.79—7.16 (m, 8H), 7.20—6.68 (m, 10H), 6.29 (s, 1H), 4.88 (s, 1H); IR (KBr) ν: 3442, 3058, 2925, 1661, 1590, 1489, 1443, 1400, 1092, 1014, 825, 756, 691 cm^{-1}; MS (70 eV) *m/z* (%): 466 (M^+ − 17, 2.26), 468 (2.29), 343 (9.15), 330 (5.97), 328 (4.70), 289 (5.01), 242 (11.65), 241 (25.81), 207 (19.14), 202 (5.24), 189 (6.69), 178 (9.10), 141 (35.21), 139 (100.00), 129 (26.99), 113 (22.16), 111 (65.10), 105 (16.86), 102 (15.08), 77 (28.63), 75 (38.59). Anal. calcd for $C_{30}H_{20}Cl_2O_2$: C 74.54, H 4.17, Cl 14.66; found C 74.52, H 4.16, Cl 14.63.

2e Yellow solid. m.p. 156—158 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.78—7.20 (m, 8H), 7.22—6.63 (m, 10H), 6.30 (s, 1H), 4.89 (s, 1H); IR (KBr) ν: 3423, 3059, 1662, 1559, 1489, 1444, 1381, 1272, 1204, 1104, 783, 760, 703 cm^{-1}; MS (70 eV)

m/z (%): 466 ($M^+ - 17$, 11.12), 381 (12.01), 380 (16.57), 379 (67.24), 378 (30.55), 377 (100.00), 279 (10.55), 278 (15.22), 277 (12.01), 276 (12.00), 202 (15.47), 200 (5.21), 177 (10.59), 176 (10.62), 175 (49.39), 173 (81.23), 147 (21.44), 145 (32.75), 139 (4.58), 111 (10.61), 109 (23.11), 105 (28.05), 102 (12.80), 77 (26.48), 75 (16.16). Anal. calcd for $C_{30}H_{20}Cl_2O_2$: C 74.54, H 4.17, Cl 14.66; found C 74.53, H 4.15, Cl 14.63.

2f Light yellow solid. m.p. 212—213 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.02—7.43 (m, 6H), 7.34—6.78 (m, 10H), 6.31 (s, 1H), 4.90 (s, 1H); IR (KBr) ν: 3442, 3059, 1654, 1590, 1567, 1489, 1468, 1433, 1384, 1266, 1072, 1032, 756, 696 cm^{-1}; MS (70 eV) *m/z* (%): 554 (0.49), 553 (0.26), 552 (0.44), 551 (0.68), 550 (M^+, 1.28), 533 ($M^+ - 17$, 0.33), 537 (0.10), 535 (0.11), 498 (0.25), 482 (9.52), 449 (6.60), 447 (18.22), 345 (19.43), 343 (53.13), 344 (14.19), 346 (5.57), 276 (7.09), 277 (6.48), 278 (7.58), 279 (8.13), 202 (12.39), 203 (6.47), 178 (7.74), 176 (7.52), 141 (31.32), 140 (8.85), 139 (100.00), 113 (15.49), 111 (41.48), 105 (36.26), 77 (32.32), 75 (27.36). Anal. calcd for $C_{30}H_{18}Cl_4O_2$: C 65.24, H 3.28, Cl 25.67; found C 65.23, H 3.26, Cl 25.64.

2g Brownish yellow solid. m.p. 88—90 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.77—7.24 (m, 6H), 7.12—6.37 (m, 10H), 6.22 (s, 1H), 4.81 (s, 1H); IR (KBr) ν: 3417, 1630, 1564, 1490, 1461, 1443, 1393, 1226, 1152, 1013, 757, 692 cm^{-1}; MS (70 eV) *m/z* (%): 394 (M^+, 5.28), 377 ($M^+ - 17$, 12.25), 326 (2.85), 299 (8.28), 252 (4.95), 207 (7.09), 198 (12.12), 197 (32.50), 196 (21.69), 168 (24.45), 140 (13.83), 139 (40.09), 129 (48.33), 115 (14.71), 101 (10.17), 95 (100.00), 91 (25.39), 77 (51.49), 75 (22.54). Anal. calcd for $C_{26}H_{18}O_4$: C 79.17, H 4.59; found C 79.13, H 4.57.

2h Light red solid. m.p. 77—79 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.69—6.57 (m, 16H), 6.25 (s, 1H), 5.88 (s, 2H), 5.97 (s, 2H), 4.76 (s, 1H); IR (KBr) ν: 3444, 2989, 2978, 1645, 1598, 1532, 1477, 1446, 1373, 1267, 1064, 1012, 756, 696 cm^{-1}; MS (70 eV) *m/z* (%): 502 (M^+, 0.31), 485 ($M^+ - 17$, 8.68), 447 (5.66), 431 (2.33), 403 (7.55), 397 (8.43), 360 (11.27), 359 (14.47), 356 (3.43), 331 (23.66), 274 (16.69), 232 (7.84), 177 (4.33), 163 (9.52), 149 (100.00), 121 (74.21), 105 (12.42), 77 (43.23). Anal. calcd for $C_{32}H_{22}O_6$: C 76.48, H 4.41; found C 76.47, H 4.39.

2i Light yellow solid. m.p. 61—63 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.62—7.13 (m, 10H), 5.96 (s, 1H), 4.48 (s, 1H), 2.23—2.31 (t, 2H, J = 7.2 Hz), 1.44—1.67 (m, 6H), 0.84—1.01 (m, 6H); IR (KBr) ν: 3446, 3056, 2988, 2858, 1635, 1596, 1567, 1486, 1438, 1414, 1362, 1277, 1109, 1047, 829, 761, 696 cm^{-1}; MS (70 eV) *m/z* (%): 346 (M^+, 1.42), 331 (2.23), 332 (2.12), 329 ($M^+ - 17$, 8.12), 318 (4.21), 303 (11.56), 286 (15.53), 275 (6.47), 269 (18.96), 215 (23.46), 192 (43.22), 77 (100.00), 75 (28.75), 71 (68.76). Anal. calcd for $C_{24}H_{26}O_2$: C 83.20, H 7.56; found C 83.21, H 7.54.

References

1 (a) Wilkinson, W. In *Organic Synthesis*, Coll. Vol. 4, Rabjohn, N., New York, **1963**, p. 476.
(b) Hiromi, K.; Yoshiaki, K.; Nariali, M. (Hitachi Chemical Co., Ltd.) *JP 7303802*, **1973** [*Chem. Abstr.* **1973**, *79*, 67609].
(c) Kenneth, F. J.; Frederic, H. H.; David, A. H. *Ger. Offen. 2126857*, **1971** [*Chem. Abstr.* **1972**, *76*, 72102].

2 (a) Thewalt, U.; Schmid, G. *J. Organomet. Chem.* **1991**, *412*, 343.
(b) Castellani, M. P.; Geib, S. J.; Rheingold, A. L.; Trogler, W. C. *Organometallics* **1987**, *6*, 345.
(c) Sitzmann, H. *Z. Naturforsch., B: Chem. Sci.* **1989**, *44*, 1293 and references cited therein.

3 Zair, T.; Santelli-Rouvier, C.; Santelli, M. *Tetrahedron* **1993**, *49*, 3313.

4 Takahashi, T.; Xi, Z.-F.; Kotora, M.; Xi, C.-J. *Tetrahedron Lett.* **1996**, *37*, 7521.

5 Xi, Z.-F.; Li, P.-X. *Angew. Chem., Int. Ed.* **2000**, *39*, 2950.

6 Dehmlow, E. V.; Bollmann, C. *Tetrahedron Lett.* **1991**, *32*, 5773.

7 Hughes, R. P.; Kowalski, A. S.; Lomprey, J. R. *J. Org. Chem.* **1996**, *61*, 401.

8 Rufanov, K. A.; Kazennova, N. B.; Churakov, A. V.; Lemenovskii, D. A.; Kuz'mina, L. G. *J. Organomet. Chem.* **1995**, *485*, 173.

9 Lenze, N.; Neumann, B.; Stammler, H. G.; Jutzi, P. *J. Organomet. Chem.* **2000**, *608*, 86.

10 Girard, P.; Namy, J. L.; Kagan, H. B. *J. Am. Chem. Soc.* **1980**, *102*, 2693.

11 Zhou, L.-F.; Zhang, Y.-M. *Tetrahedron Lett.* **1997**, *38*, 8063.

12 Zhou, L.-F.; Zhang, Y.-M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 2399.

13 Zhou, L.-F.; Zhang, Y.-M. *Synth. Commun.* **2000**, *30*, 597.

14 So, W. Y.; Heui, S. P.; Yong, H.-K. *Chem. Commun.* **2000**, 2005.

(E0303248 CHENG, B.; LU, Z. S.)