

Generation of Cyclopentadienyl Ligands via the Pauson–Khand and Retro-Diels–Alder Reactions

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Received December 6, 1993

The development of efficient approaches to the generation of highly substituted or functionalized cyclopentadienyl ligands is of continuing importance.¹ One of the strategies to synthesize cyclopentadienylmetal compounds is to use cyclopentenone as a starting material.² The Pauson–Khand reaction is one of the most effective methods in the syntheses of cyclopentenones.³ Herein we report a powerful new method for the preparation of 1,2-disubstituted or 1,2,3-trisubstituted cyclopentadienyl ligands via the retro-Diels–Alder reaction of the intermolecular Pauson–Khand reaction products. Stille reported⁴ the use of the retro-Diels–Alder reaction to generate cyclopentadienyl anions and to prepare a polymer containing cyclopentadiene units. However, to the best of our knowledge, this is the first example of the general method of preparation 1,2-disubstituted and 1,2,3-trisubstituted cyclopentadienyl ligands (Scheme 1).

The substrates **2** for the retro-Diels–Alder reaction could be efficiently prepared in two steps. The Pauson–Khand products **1**, obtained in high yields by using DMSO as a promoter,⁵ were transformed into compounds **2** in high yields (Table 1).

The retro-Diels–Alder reaction commonly requires high temperatures for convenient reaction.⁶ However, a number of retro-Diels–Alder reactions involving anionic intermediates take place at more moderate temperatures.⁷ Grutzner⁸ reported the retro-Diels–Alder reaction of 7-phenyl-7-methoxynorbornene at room temperature using excess sodium–potassium alloy. Karpf⁹ and Ichihara¹⁰ groups demonstrated the generation of multiply substituted cyclohexenes by treatment with potassium hydride at room temperature. Instead of using sodium–potassium alloy or potassium hydride, we used potassium and *n*-BuLi.¹¹ The retro-Diels–Alder reaction of **2** with potassium and *n*-BuLi was straightforward at room temperature within 2–3 h. The scope of the retro-Diels–Alder reaction was examined with a number of substrates (Table 1). We have observed an apparent require-

Scheme 1

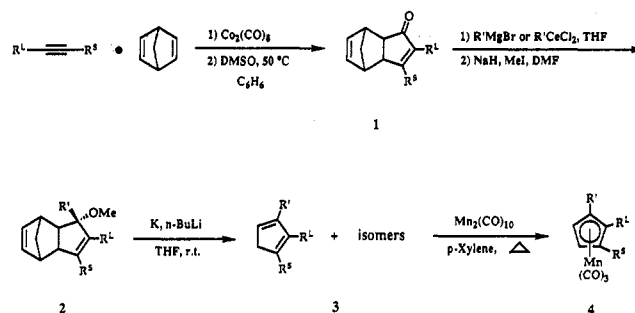


Table 1.

entry	R ^L	R ^S	R'	yield (%) ^a			
				1	2	3	4
1	Ph	Ph	Ph	84	78	90	80
2	Ph	Me	Me	97	87	63	54 ^b
3	Ph	Ph	Bu	84	79	86	58
4	Ph	Ph	Me	84	80	76	64
5	Bu	H	Ph	86	92	91	51 ^b
6	(CH ₂) ₃ OMe	H	Ph	90	90	68	75
7	(CH ₂) ₄ OMe	H	Ph	72	85	95	63
8	(CH ₂) ₂ CH=CH ₂	H	Ph	80	75	65	47
9		H	Ph	75	87	62	62

^a The reaction condition was not optimized. Isolated yields. ^b The monodealkylated product was obtained in ca. 10% yield.

ment for the presence of one phenyl group. Workup furnished an isomeric mixture of cyclopentadienes in 61–95%. Even with a methoxyalkyl substituent (entries 6 and 7), the reaction proceeded to give a high yield of cyclopentadienes. Furthermore, the reaction of substrates with an alkenyl substituent (entries 8 and 9) gave reasonable yields of cyclopentadienes. Compounds **3** are moderately air-stable and can be stored in hexane solution for 4–5 days. The isomeric mixture was reacted further.

Metalation of **3** was carried out by treatment with Mn₂(CO)₁₀ in refluxing xylene for 0.5–2 days. After reaction, compounds **4** were obtained in reasonable to high yields.¹² However, for entries 2 and 5, the reaction proceeded to give two kinds of products; one was **4** and the other was monodealkylated. Due to the dealkylation, the yields of **4** for entries 2 and 5 were rather low. Dealkylations via competitive activation of the carbon–carbon bond of the diene have been reported for other metal complexes.¹³

In summary, we have demonstrated that the retro-Diels–Alder reaction of the Pauson–Khand reaction product generates high

(1) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965. Okuda, J. *Top. Curr. Chem.* **1991**, *160*, 97. Janiak, C.; Schumann, H. *Adv. Organomet. Chem.* **1991**, *33*, 291. Siemeling, U. *J. Chem. Soc., Chem. Commun.* **1992**, 1335. Venier, C. G.; Casserly, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 2808.

(2) Halterman, R. L.; Vollhardt, K. P. C. *Organometallics* **1988**, *7*, 883. Halterman, R. L.; Vollhardt, K. P. C. *Tetrahedron Lett.* **1986**, *27*, 1461. Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707. Gibson, C. P.; Bem, D. S.; Falloon, S. B.; Hitchens, T. K.; Cortopassi, J. E. *Organometallics* **1992**, *11*, 1742. Bunel, E. E.; Valle, L.; Jones, N. L.; Carroll, P. J.; Gonzalez, M.; Munoz, N.; Manriquez, J. M. *Organometallics* **1988**, *7*, 789.

(3) Pauson, P. L.; Khand, I. U. *Ann. N. Y. Acad. Sci.* **1977**, *295*, 2. Pauson, P. L. *Tetrahedron* **1985**, *41*, 5855.

(4) Sekiya, A.; Stille, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 5096.

(5) Lee, B. Y.; Chung, Y. K.; Jeong, N.; Hudecek, M.; Pauson, P. L. *Organometallics* **1993**, *12*, 220.

(6) Ripoll, J.-L.; Rouessac, A.; Rouessac, F. *Tetrahedron* **1978**, *34*, 19. Lasne, M.-C.; Ripoll, J.-L. *Synthesis* **1985**, 121. Karpf, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 414. De Keyser, J.-L.; De Cock, C. J. C.; Poupaert, J. H.; Dumont, P. *J. Org. Chem.* **1988**, *53*, 4859.

(7) Rajanbaabu, T. V.; Eaton, D. F.; Fukunaga, T. *J. Org. Chem.* **1983**, *48*, 652. Bunnelli, W. H.; Shangraw, W. R. *Tetrahedron* **1987**, *43*, 2005.

(8) Bowman, E. S.; Hughes, G. B.; Grutzner, J. B. *J. Am. Chem. Soc.* **1976**, *98*, 8273.

(9) Karpf, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 414.

(10) Ichihara, A. *Synthesis* **1987**, 207.

(11) A typical procedure is as follows. A single piece of potassium (0.17 g, 4.4 mmol) and *n*-BuLi (1.3 mL, 2.0 mmol) were added to the THF solution (10 mL) of compound **2** (R^L = R^S = R' = Ph, 0.41 g, 1.04 mmol). After being stirred for 2–3 h, the reaction solution was transferred via syringe to a flask which contained 20 mL of aqueous, cold, saturated NaHCO₃ and 20 mL of hexane. The product was extracted with hexane. The product was purified by silica gel short-column chromatography eluting with hexane/ethyl acetate (v/v, 30:1). The yield was 90%. **3** (R = R = R = Ph): ¹H NMR (CDCl₃) δ 7.18–6.95 (m, Ph, 15 H), 6.46 (t, J = 1.7 Hz, CH=C, 1 H), 3.55 (d, J = 1.7 Hz, CH₂, 2 H).

(12) A typical procedure is as follows. Compound **3** (R = R = R = Ph), (0.15 g, 0.5 mmol), Mn₂(CO)₁₀ (0.214 g, 0.55 mmol), and xylene (25 mL) were placed in a Schlenk flask. After the mixture was refluxed for 2 days, the solvent was removed by rotary evaporation. The crude reaction product was purified by flash column chromatography eluting with hexane. The product was obtained as an oily compound, yield of 80%. **4** (R = R = R = Ph): IR (NaCl) ν_{CO} 2010, 1923 cm⁻¹; ¹H NMR (C₆D₆) δ 7.26–6.85 (m, Ph, 15 H), 4.51 (s, Cp, 2 H); ¹³C NMR (C₆D₆) δ 225.71 (CO), 133.08, 132.86, 132.59, 129.96, 129.46, 129.17, 128.72, 128.43 (Ph), 106.27, 103.94, 80.54 (Cp); HRMS M⁺ obsd 432.0560, calcd 432.0558.

(13) Hemond, R. C.; Hughes, R. P.; Locker, H. B. *Organometallics* **1986**, *5*, 2391. Filbracht, P.; Dahler, P. *Chem. Ber.* **1980**, *113*, 542. King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3773.

yields of cyclopentadienes which are used to prepare 1,2-disubstituted- and/or 1,2,3-trisubstituted cyclopentadienyl manganese compounds. The synthetic potential of this retro-Diels–Alder reaction is apparent from the generation of high yields of cyclopentadienyl precursors.

We expect that functionally substituted cyclopentadienyl transition-metal compounds produced by the above sequences can lead to a wide variety of new products of potential importance to organic, inorganic, and polymer chemistry. Further investigations along these lines are in progress in our laboratory.

Acknowledgment. We are grateful to the Korea Science and Engineering Foundation and the Ministry of Education, Republic of Korea (BSRI93-313).

Supplementary Material Available: ^1H NMR spectral data for 3 and complete characterization data for 4 (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.