ORGANIC LETTERS

2003
Vol. 5, No. 17
3151−3153

Facile Synthetic Access to Multisubstituted Benz[*f*]indenones and Their Application as Ligands to the First Synthesis of Group(IV) Metallocene Complexes

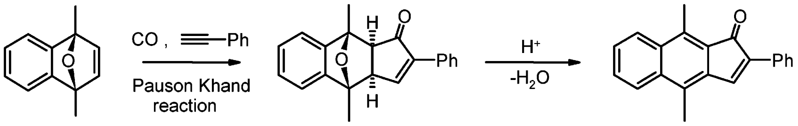
Do Han Kim, Seung Uk Son, and Young Keun Chung*

School of Chemistry and Center for Molecular Catalysis, Seoul National University,
Seoul 151-747, Korea

ykchung@plaza.snu.ac.kr

Received June 30, 2003

ABSTRACT



A very efficient method for the synthesis of benz[*f*]indenone derivatives was developed. This method allows the introduction of a variety of substituents to a molecule. The first zirconocene compound of benz[*f*]indene was synthesized.

Benz[*f*]indenones and benz[*f*]indenes are potentially useful building blocks in organic and organometallic synthesis. However, their chemistry has not been much explored. Recently, benz[*f*]indenones were used as important starting materials in the synthesis of kinamycin antibiotics, which showed excellent activity against gram-positive bacteria.[1] The use of benz[*f*]indene as a cyclopentadienyl ligand attracted much attention because an annulated benzo ring might increase both the stereocontrol and productivity of the catalytic system.[2] However, the use of benz[*f*]indene as a cyclopentadienyl ligand in the synthesis of group IV metal complexes was not successful. For example, attempts to use benz[*f*]indene and 2-methylbenz[*f*]indene in the synthesis of group IV metal complexes was unsuccessful, presumably due to the instability of the product.[3] Instead, a late transition metal complex, benz[*f*]indenyldicarbonylrhodium, was reported.[3a] We had envisioned that the substituents in benz[*f*]indenes might help to increase the stability of the product and that it would be possible to isolate the product. However, no general procedures to synthesize substituted benz[*f*]indenes are known.[4] We herein report a general methodology of the synthesis of multisubstituted benz[*f*]indenones and benz[*f*]indenes by combination of well-known reactions, Pauson−Khand and Diels−Alder reactions, and their use in the synthesis of zirconium complexes.

Transition metal-catalyzed cycloaddition reactions are very efficient and highly indispensable tools in organic synthesis.[5] In particular, a carbocyclization of alkene, alkyne, and carbonyl mediated by cobalt(0), known as the Pauson−Khand (P−K) reaction, has been recognized as one of the most powerful methods for the construction of five-membered rings.[6] Similarly, the Diels−Alder (D−A) reaction has been one of the most popular reactions for the construc-

---

[1] Kitani, Y.; Morita, A.; Kumamoto, T.; Ishikawa, T. *Helv. Chim. Acta* **2002**, *85*, 1186.

[2] (a) Spaleck, W.; Kueber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. F. *Organometallics* **1994**, *13*, 954. (b) Stehling, U.; Diebold, J.; Kristen, R.; Roell, W.; Brintzinger, H. H.; Juengling, S.; Muelhaupt, R. *Organometallics* **1994**, *13*, 964.

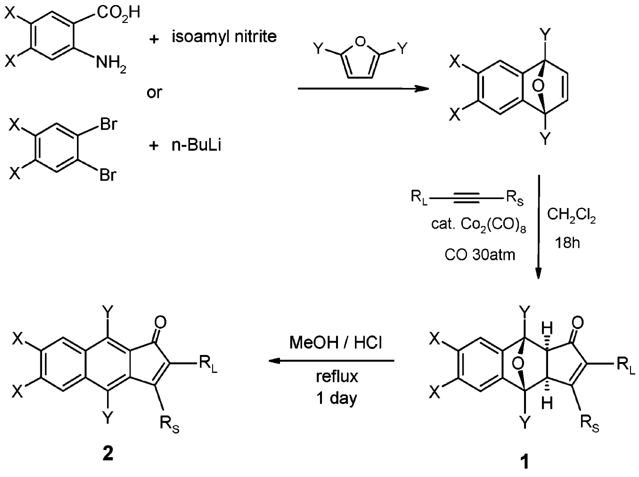
[3] (a) Foster, P.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **1998**, *569*, 121. (b) Foster, P.; Chien, J. C. W.; Rausch, M. D. *Organometallics* **1996**, *15*, 2404.

[4] For examples of the synthesis of benz[*f*]indenes, see: (a) Carpino, L. A.; Lin, Y.-Z. *J. Org. Chem.* **1990**, *55*, 247. (b) Carpino, L. A.; Cohen, B. J.; Lin, Y.-Z.; Stephens, K. E., Jr.; Triolo, S. A. *J. Org. Chem.* **1990**, *55*, 251. (c) Ghorai, S. K.; Hazra, N. K.; Mal, D. *Tetrahedron Lett.* **1998**, *39*, 689.

10.1021/ol0352106 CCC: $25.00

tion of six-membered rings.[7] Our strategy for the synthesis of benz[*f*]indenones is based on a combination of these two representative reactions: the D−A reaction and P−K reactions (Scheme 1).

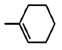
Scheme 1. Synthetic Strategy for Synthesis of Benz[*f*]indenones



Our novel method for the synthesis of benz[*f*]indenones consists of the D−A reaction, P−K reaction, and dehydration (Scheme 1 and Table 1). The D−A reactions were successfully carried out with good yields (see Supporting Information). The P−K reaction is well-known for its stereo- and regioselectivity: the P−K reaction products of alkyne, norbornene, and carbon monoxide have an exo conformation, and a bulky substituent of an alkyne is located at the α-position to the ketone of the reaction product. When oxabenzonorbornadienes were used as alkenes, the reaction products showed an excellent exo regioselectivity, which was confirmed by single-crystal X-ray analysis of **1b** (see Supporting Information).

Monosubstituted alkynes were excellent substrates (entries 1−4 and 6 in Table 1). However, an alkyne having a hydroxyl group showed a moderate yield, presumably due to the sensitivity of $Co_2(CO)_8$ to the hydroxyl group (entry 5 in Table 1). Disubstituted alkynes were anticipated to be poor substrates due to their bulkiness. Contrary to our expectation, they turned out to be good substrates and resulted in excellent yields (entries 7−10).

Table 1. Synthesis of Benz[*f*]indenones Using Various Substrates

entry	X	Y	R_s	R_L	yield^{a}(%)	
					PKR^{b}	dehydration^{c}
1	H	H	H	Ph	98(**1a**)^{d}	84(**2a**)^{d}
2	H	H	H	$Si(CH_3)_3$	95(**1b**)	71(**2b**)
3	H	H	H	$(CH_2)_3CH_3$	98(**1c**)	59(**2c**)
4	H	H	H	$(CH_2)_5CH_3$	97(**1d**)	63(**2d**)
5	H	H	H	$(CH_2)_3OH$	67(**1e**)	75(**2e**)
6	H	H	H		95(**1f**)	61(**2f**)
7	H	H	CH_3	CH_3	88(**1g**)	58(**2g**)
8	H	H	CH_2CH_3	CH_2CH_3	89(**1h**)	43(**2h**)
9	H	H	$(CH_2)_2CH_3$	$(CH_2)_2CH_3$	86(**1i**)	46(**2i**)
10	H	H	Ph	Ph	90(**1j**)	73(**2j**)
11	H	CH_3	H	Ph	92(**1k**)	90(**2k**)
12	H	CH_3	CH_3	CH_3	85(**1l**)	92(**2l**)
13	H	Ph	H	Ph	96(**1m**)	99(**2m**)
14	F	H	H	Ph	93(**1n**)	47(**2n**)
15	OCH_3	H	H	Ph	82(**1o**)	35(**2o**)

[a] Isolated yield. [b] Reaction conditions: 1.0 mmol of alkynes, 2.0 mmol of oxabenzonorbornadienes, 50 μmol of $Co_2(CO)_8$, 130 °C, dichloromethane, 30 atm of CO pressure. [c] Reaction conditions: MeOH/hydrochloric acid (15:1 v/v), reflux. [d] Compound synthesized is shown in parentheses.

Next we conducted dehydration of P−K reaction products to obtain benz[*f*]indenones. The dehydration yields were very dependent upon Y and Rs. When Y and Rs were H, the dehydration yields were good. However, when Y was H and Rs was not H, the products were isolated in moderate yields, presumably due to a steric effect. Surprisingly, the substituent Y dramatically improved the yield (entries 11−13), presumably by enhancing aromatization. One of the dehydration products was analyzed by a single-crystal X-ray diffraction study (see Supporting Information).

Thus, we can introduce a variety of substituents to a molecule in (a) specific position(s) through D−A and P−K reactions from available materials. The substituents X and Y can be introduced to benz[*f*]indenone in the D−A reaction step, and various Rs and R_L can be introduced in the P−K reaction step.

Benz[*f*]indenes were prepared from benz[*f*]indenones as shown in Scheme 2.

Recently, benz[*f*]indenones and benz[*f*]indenes were used as target molecules for computational chemistry.[8] We expect that our structural data may be useful to computational chemists.

Next we investigated the use of benz[*f*]indenes as ligands in the synthesis of organometallic compounds. Zirconocenes especially attracted our attention because of their latent use in olefin polymerization. As already mentioned, Rausch et

---

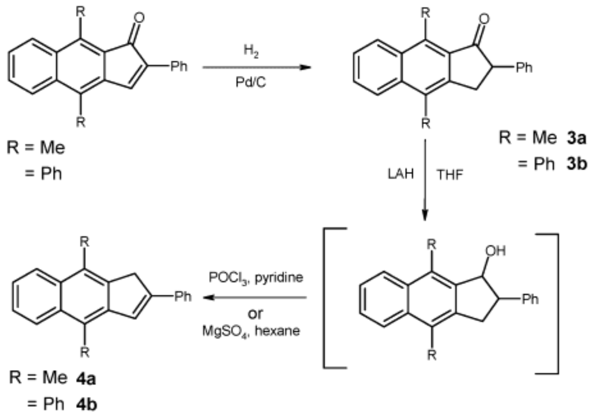
(5) (a) Ojima, I.; Tzamarioudaki, M.; Li, Z.; Donavan, R. J. *Chem. Rev.* **1996**, *96*, 635. (b) Rosenthal, U.; Pellny, P.-M.; Kirchbauwe, F. G.; Burlakov, V. V. *Acc. Chem. Res.* **2000**, *33*, 119. (c) Herndon, J. W. *Tetrahedron* **2000**, *56*, 1257. (d) Harvey, D. F.; Sigano, D. *Chem. Rev.* **1996**, *96*, 271. (e) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12. (f) Mongomery, J. *Acc. Chem. Res.* **2000**, *33*, 467. (g) Yet, L. *Chem. Rev.* **2000**, *100*, 2963. (h) Li, C.-L.; Liu, R.-S. *Chem. Rev.* **2000**, *100*, 3127. (i) Saito, S.; Yamamoto, Y. *Chem. Rev.* **2000**, *100*, 2901.

(6) For recent reviews, see: (a) Gibson, S. E.; Stevenazzi, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1800. (b) Hanson, B. E. *Comments Inorg. Chem.* **2002**, *23*, 289. (c) Brummond, K. M.; Kent, J. L. *Tetrahedron* **2000**, *56*, 3263. (d) Chung, Y. K. *Coord. Chem. Rev.* **1999**, *188*, 297.

(7) For recent papers, see: (a) Tsuda, A.; Fukumoto, C.; Oshima, T. *J. Am. Chem. Soc.* **2003**, *125*, 5811. (b) Heckrodt, T. J.; Mulzer, J. *J. Am. Chem. Soc.* **2003**, *125*, 4680. (c) Juhl, K.; Jorgensen, K. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 1498. (d) Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 2458. (e) Faller, J. W.; Grimmond, B. J.; D'Alliessi, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 2525.

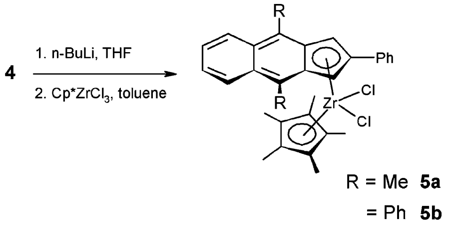
(8) Gonzales, J. M.; Barden, C. J.; Brown, S. T.; Schleyer, P. V. R.; Schaefer, H. F., III; Li, Q.-S. *J. Am. Chem. Soc.* **2003**, *125*, 1064.

Scheme 2. Synthesis of Benz[*f*]indenes from Benz[*f*]indenones



al. attempted to synthesize group IV metallocenes of benz[*f*]indenes.[3] They used 2-methylbenz[*f*]indene to synthesize a zirconocene derivative. However, none of their trials were successful because of the instability of the product. Instead of 2-methylbenz[*f*]indene, we used 2-phenylbenz[*f*]indene. Unfortunately, we obtained a result similar to that of Rausch. However, when we used benz[*f*]indene having a substituent R, we could obtain the first zirconocene compound of benz[*f*]indene (Scheme 3).

Scheme 3. Synthesis of Zirconocene Compounds



As with other methods, there could be a problem in the purification of the reaction product. When R was a phenyl group, we failed to obtain a purified product. However, when R was a methyl group, a purified product was obtained by recrystallization and its structure was confirmed by a single-crystal X-ray diffraction study (Figure 1).

Figure 1 shows an interesting bonding pattern between Zr and the Cp ring. The Zr is significantly closer to carbons C(1), C(2), and C(13) than carbons C(3) and C(12) [Zr−C(1) = 2.576 Å, Zr−C(2) = 2.572 Å, Zr−C(3) = 2.643 Å, Zr−C(12) = 2.592 Å, and Zr−C(13) = 2.465 Å], and the bond distance of C(3)−C(12) is shorter than other C−C bond distances of the Cp ring. This special pattern may originate from an enhanced aromaticity of naphthalene ring compared to other indenyl rings. Thus, the zirconium metal makes regular bonds with three carbon atoms as in an η^3-bonding mode and relatively weak bonds with the remaining two carbons as in an η^2-bonding mode. This bonding situation may explain the instability of zirconocene compounds of benz[*f*]indenes. From a catalytic point of view, this bonding situation may help an olefin to approach an active site and eventually to enhance catalytic activity in olefin polymerization. Catalytic activity in olefin polymerization will be discussed in due course.[9]

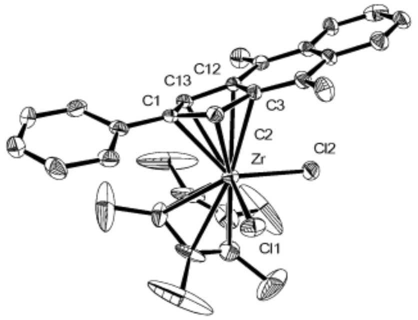


Figure 1. ORTEP drawing of **5a**.

In conclusion, we developed a very efficient method for the synthesis of benz[*f*]indenone derivatives by using Pauson−Khand and Diels−Alder reactions. Our method allows the introduction of a variety of substituents to a molecule. Using the prepared benz[*f*]indenes, we could synthesize the first zirconocene compound of benz[*f*]indenes and use them as catalysts in the ethylene polymerization. Further investigations involving broadening the scope of the synthesis of transition metal complexes of benz[*f*]indenes are currently in progress.

Acknowledgment. We thank the Ministry of Commerce, Industry, and Energy and the Korea Science and Engineering Foundation through Center Molecular Catalysis. D.H.K. and S.U.S. are grateful for a Brain Korea 21 fellowship.

Supporting Information Available: Synthetic procedures and spectral and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0352106

---

[9] Preliminary results show a high activity in ethylene polymerization. Kim, D. H.; Son, S. U.; Lee, B. Y.; Chung, Y. K. Manuscript in preparation.