

# Convenient Synthesis of Diene–Zirconocenes and Regioselective Partial Reduction of the More Highly Substituted Double Bonds of Conjugated Dienes via Complexation with Zirconocenes and Protonolysis

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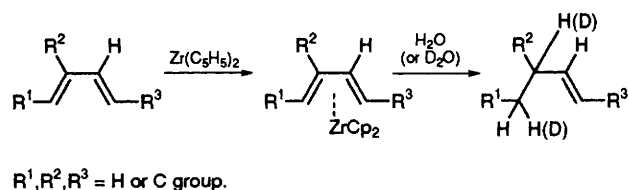
Conjugated dienes can be initially converted to their zirconocene complexes most conveniently by their reaction with  $(C_5H_5)_2ZrCl_2$  and freshly ground Mg; the resultant complexes can then be protonolysed with 3 mol  $dm^{-3}$  HCl to give regioselectively monoenes corresponding to partial hydrogenation of the more highly substituted double bond.

Partial catalytic hydrogenation of dienes preferentially reduces the less substituted double bond.<sup>1</sup> The reverse regioselectivity appears to be very rare. We now report that conversion of conjugated dienes to the corresponding diene– $Zr(C_5H_5)_2$  complexes followed by protonolysis (or deuterolysis) provides a regioselective method for this rare synthetic task (Scheme 1).

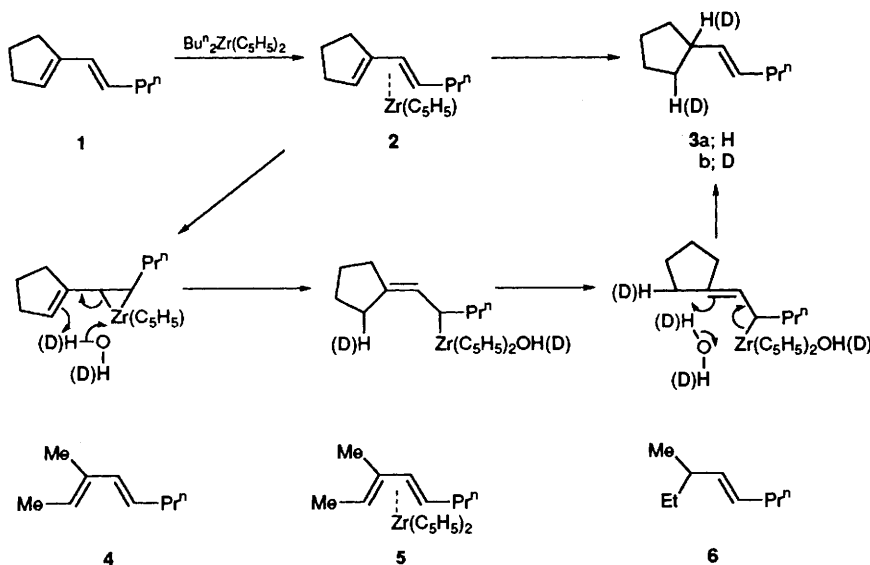
Typically, 1-[(*E*)-pent-1-enyl]-1-cyclopentene **1** was treated with 1 equiv. of  $Bu^n_2Zr(C_5H_5)_2$ <sup>2</sup> in tetrahydrofuran (THF) first at  $-78^\circ C$  for 1 h and then at  $20^\circ C$  for 20 h to give **2**.<sup>3</sup> Its treatment with 3 mol  $dm^{-3}$  HCl at  $0^\circ C$  cleanly produced (*E*)-1-cyclopentylpent-1-ene **3a** in 85% yield, which was  $\geq 95\%$  isomerically pure. The use of  $D_2O$  in place of  $H_2O$  gave the corresponding dideuterio derivative **3b** which was  $\geq 95\%$  deuteriated in the indicated positions. The formation of conjugated diene– $Zr(C_5H_5)_2$  complexes followed by hydrolysis to give monoenes is precedented.<sup>4</sup> However, all but one are derived from symmetrical dienes, and the regiochemical information has been very limited. The observed results appear to be best accommodated by the following tandem six-centred hydrolysis scheme involving preferential release of the sterically more demanding, more highly substituted double bond (Scheme 2). Similarly, (2*E*,4*E*)-3-methyloct-2,4-

diene **4** was converted to **5** in 88% NMR yield by treatment with  $Bu^n_2Zr(C_5H_5)_2$  and then to  $\geq 95\%$  isomerically pure **6** via protonolysis in 69% yield based on **4**, only traces of by-products were detected.

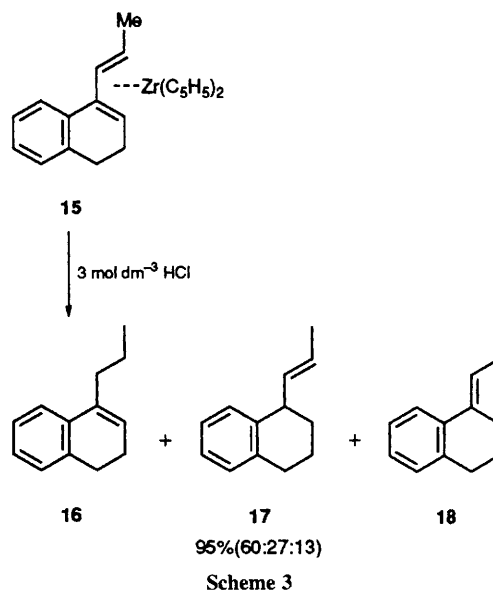
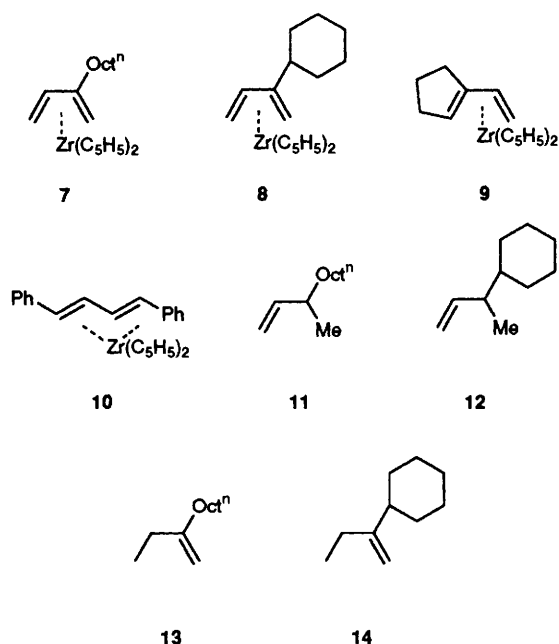
As reported previously, the  $Bu^n_2Zr(C_5H_5)_2$  procedure is not satisfactory as a method for converting sterically less demanding dienes into diene– $Zr(C_5H_5)_2$  complexes, because but-1-ene derived from  $Bu^n_2Zr(C_5H_5)_2$  gets incorporated into the products.<sup>5</sup> Although there are a few other procedures for the preparation of conjugated diene– $Zr(C_5H_5)_2$  complexes,<sup>4,6</sup> we sought a simpler and more convenient procedure and found that a reagent generated *in situ* by treatment of  $(C_5H_5)_2ZrCl_2$  with freshly ground Mg turnings without  $HgCl_2$ ,<sup>7</sup> an added reagent previously used for related but different purposes, was quite satisfactory for this purpose. Typically, Mg turnings (Fisher Scientific) were lightly ground by means of a mortar and a pestle so as to expose active Mg surfaces. 2-(*n*-Octyl)-but-1,3-diene,  $(C_5H_5)_2ZrCl_2$  (1 equiv.), and the freshly ground Mg turnings (10 equiv.) were placed in a flask under  $N_2$ . Addition of THF induced a smooth reaction within several minutes, and the reaction was over within 12 h at  $25^\circ C$ . Analysis by  $^1H$  NMR spectroscopy using *p*-xylene as an internal standard indicated the formation of **7** in 80–90% yield. One previously developed procedure<sup>4</sup> involves conversion of dienes to 2-ene-1,4-diylmagnesiums by their reaction for five days at  $10$ – $15^\circ C$  with Mg activated by treatment with iodine and conjugated diene for 30 h at  $70^\circ C$  prior to addition of  $(C_5H_5)_2ZrCl_2$ . In the present reaction, Mg probably reacts first with  $(C_5H_5)_2ZrCl_2$  to give ' $Zr(C_5H_5)_2$ ', which then reacts with dienes. This procedure appears to be generally applicable to the synthesis of diene– $Zr(C_5H_5)_2$  complexes. Thus, **8**–**10**, in addition to **2**, **5** and **7**, were also prepared from the corresponding conjugated dienes in  $\geq 80\%$  NMR yields and characterized by  $^1H$  and  $^{13}C$  NMR spectroscopy. The  $^1H$



Scheme 1



Scheme 2



NMR chemical shifts in  $\delta$  unit (THF, *p*-xylene,  $\text{SiMe}_4$ ) for the  $\text{C}_5\text{H}_5$  groups of these complexes are as follows; **2** (5.01 and 5.51), **5** (5.01 and 5.55), **7** (5.42), **8** (5.43), **9** (5.14 and 5.60), and **10**<sup>4</sup> (5.16). Those complexes derived from unsymmetrically substituted dienes having substituents on C-1 and/or C-4, e.g. **2**, **5** and **9** display two discrete  $\text{C}_5\text{H}_5$  signals, while those derived from 1,4-unsubstituted dienes (e.g. **7** and **8**) show only one  $\text{C}_5\text{H}_5$  signal due to rapid interconversion between the two non-equivalent  $\text{C}_5\text{H}_5$  groups. The complex **10** has been reported to be the *s-trans* isomer.<sup>4</sup>

Protonolysis of **7** and **8** with  $3 \text{ mol dm}^{-3}$  HCl gave the expected monoene products in 99 and 80% isolated yields based on the starting conjugated dienes. The ratio of the monosubstituted alkene (**11** or **12**) to the 1,1-disubstituted alkene (**13** or **14**, respectively) in each case was approximately 80:20. In any of the reactions discussed above, the amount of the double bond shifted monoalkene, i.e., 3-methylundec-2-ene or 1-methylprop-1-enylcyclohexane, respectively, was <5%, if any. On the other hand, protonolysis with  $3 \text{ mol dm}^{-3}$  HCl of **15** [<sup>1</sup>H NMR  $\text{C}_5\text{H}_5$  signals (THF, *p*-xylene,  $\text{SiMe}_4$ )  $\delta$  5.21 and 5.90], prepared in 86% NMR yield, gave a mixture of **16**–**18** in 95% combined isolated yield. Interestingly, the **16**:**17**:**18** ratio was 60:27:13. Both the predominance of the more highly substituted alkene **16** and the formation of a significant amount of the double bond shifted product **18** are attributable to the strong tendency of  $\text{Zr}(\text{C}_5\text{H}_5)_2$  to be in the benzylic position.<sup>8</sup> Even in the absence

of such electronic influences, regiochemical scrambling may occur in cases where presumed allylzirconium intermediates can undergo a facile allylic rearrangement, Scheme 3.

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