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Hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene and (*E*)-3-phenyl-2-propenol

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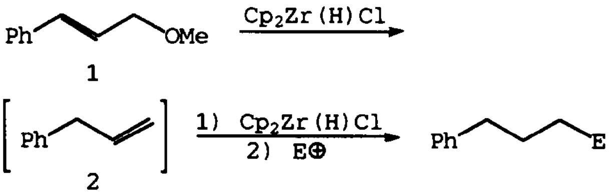
Abstract

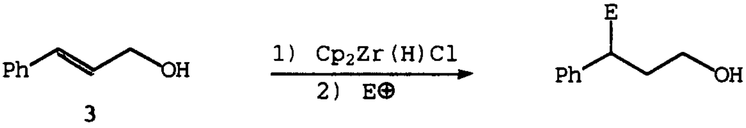
Hydrozirconation–deuterolysis of (*E*)-3-methoxy-1-phenyl-1-propene was found to give α- and ω-deuterated propylbenzenes after elimination of the ether function. An unforeseen high degree of benzylic substitution in the propylbenzenes was observed. In an effort to account for the regiochemical outcome of the reaction, hydrozirconation of propenylbenzenes with mixed reagents and deuterozirconation was investigated. Hydrozirconation of (*E*)-3-phenyl-2-propenol results in loss of the hydroxyl group to only a small extent, and after hydrozirconation and deuterolysis fair yields of benzenepropan-γ-*d*-ol are formed. Carbonyl insertion into 3-hydroxy-1-phenyl-1-zirconocene-propane gives low yields of the lactone dihydro-3-phenyl-2(3*H*)-furanone.

Introduction

Recently we have been investigating hydrozirconation–isomerisation [1] of oleyl alcohol [2] and the corresponding ethers [3], as part of a continuing study of the factors that govern the hydrozirconation of functionalised olefins. We found that the zirconium moiety can interact with the functional group in various ways. Thus, in the case of oleyl-alkyl ethers [3], migration towards the non-functionalised end yields the ω-deuterated ether after deuterolysis. Migration towards the functional group causes loss of the ether functionality, probably via a β-elimination process [4], resulting in an alkene, which is subsequently hydrozirconated by excess reagent, to provide the α-deuterated alkane after deuterolysis.



Scheme 1



Scheme 2

Thus we assumed that ω-functionalised α-arylpropanes would be obtained by hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene (**1**) (Scheme 1). The postulated intermediate 2-propenylbenzene (**2**), after a second hydrozirconation, preferentially yields the ω-zirconium isomer, as previously reported by Gibson [5].

When oleyl alcohol was subjected to hydrozirconation [2], only a minor amount of the functional group was eliminated, and instead the zirconium moiety was trapped at the 3-position relative to oxygen, thus yielding γ-deuterated stearyl alcohol, in addition to ω-deuterated stearyl alcohol. This selectivity towards γ-functionalisation could in turn lead to a specific transformation of phenyl-substituted allylic alcohols into γ-substituted γ-arylpropanols (Scheme 2). In the special case of hydrozirconation–carbonylation, lactones might be obtained [2,6].

We report here the results of a study of the hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene (**1**) and (*E*)-3-phenyl-2-propenol (**3**).

Results and discussion

*Hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene*

Hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene (**1**) with 3 equivalents of $Cp_2Zr(H)Cl$ (prepared *in situ*) in 1,4-dioxane for 24 h at the temperatures shown in Table 1, followed by deuterolysis gave the deuterated propylbenzenes (**4** and **5**), small amounts of non-deuterated propylbenzene (**6**), and (*E*)-1-propenylbenzene (**7**) (Scheme 3). Compound **2** was not detected.

At room temperature, the reaction was not complete in 24 h. At 30 ° C or more, essentially all starting material was consumed. At 30–36 ° C and 39–41 ° C, the α to ω ratio was approximately 40 : 60 and 25 : 75, respectively. Although use of elevated temperatures ($\geqslant$ 40 ° C) gives more ω-substitution [5], use of still higher temperatures generally results in some decomposition of the hydrozirconation reagent [7] and increased hydrogenation [8].

Hydrozirconation of 2-propenylbenzene (**2**) at approximately 30 ° C, with reagent prepared *in situ*, gave an isomer distribution $\alpha : \omega$ of 8 : 92 (Table 2, entry 1), in good accord with Gibson's results [5]. This result should be compared with the $\alpha : \omega$ ratio of 40 : 60 observed at the same temperature with **1** as starting material.

Isolated $Cp_2Zr(H)Cl$ was used in a control experiment to check whether the *in situ* generation of the reagent was the cause of the extensive α-substitution observed after hydrozirconation of **1**. Approximately the same isomer distribution as with the *in situ* generated reagent was obtained (Table 1, entry 5).

It was difficult to find an explanation of the high α-ratio obtained with **1**, and so we performed a few experiments intended to throw light on the origin of these unexpected results.

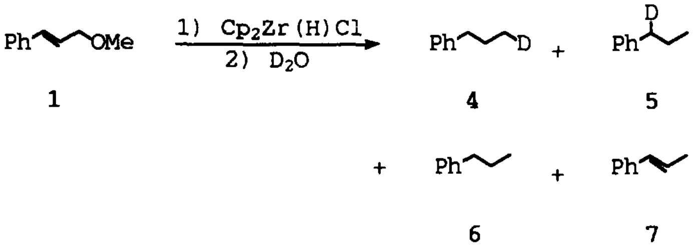
As stated in Scheme 3 and Table 1, a small amount of (*E*)-1-propenylbenzene (**7**) was formed in the hydrozirconation reaction of **1**. The formation of **7** could take

Table 1

Hydrozirconation of (*E*)-3-methoxy-1-phenyl-1-propene (**1**) in 1,4-dioxane for 24 h, followed by deuterolysis [a]

Entry	Temp. (°C)	Reagent [b]	Product distribution					Degree of Deuteration [c] (%)	Relative D-distribution	
			4	**5**	**6**	**7**	**1**		α	ω
1	r.t.	A	55 [d]		1	4	26	98	– [d]	– [d]
2	30–34	A	47–52	33	1	10–15	1–4	99	39–41	59–61
3	36	A	52	33	4	8	<1	96	39	61
4	39–41	A	62–69	20–24	6–7	5–7	<1	92–94	22–28	72–78
5	30–33	B	54	30	8	3	3	91	36	64

[a] Yields determined by combination of mass spectral-, ^{2}H NMR-, and GLC-analyses. [b] A = 3 equiv. of $Cp_2Zr(H)Cl$, prepared *in situ* B = 3 equiv. of isolated $Cp_2Zr(H)Cl$. [c] In the propylbenzenes. [d] The position of the deuterium was not determined in this experiment.

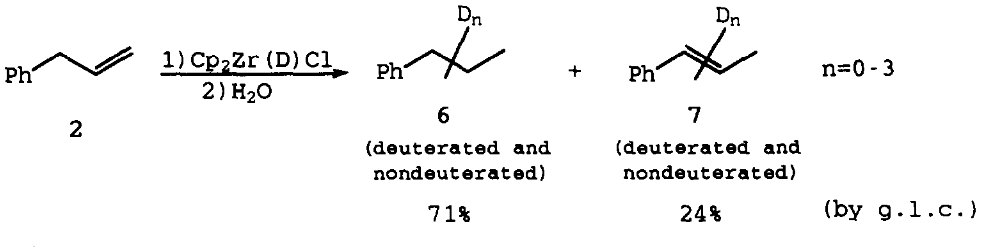


Scheme 3

place via a Markownikoff-type addition of the hydrozirconation reagent across the double bond of the intermediate **2**. This reaction path is supported by the fact that ω-deuterated propylbenzene was obtained after deuterozirconationhydrolysis of **2** (Scheme 4, Table 3). However, low deuterium-incorporation in the 1-propenylbenzenes **7** (70% contained no deuterium atom) was observed. These results suggest that the isomerisation may in fact occur by an alternative process, not involving deuterozirconation [9*]. A related deuterozirconation experiment with **1** also produced a complex mixture of products.

Although the mechanism of the formation of **7** was obscure, it seemed reasonable to assume that one reason for the high α content might be hydrozirconation of the internal olefin. A control experiment with **7** revealed that in fact an α : ω ratio of only 19 : 81 (Table 2, entry 2) was obtained with this starting material [5]. Thus it seems that the relatively high α : ω ratio can not be explained solely by assuming an initial double bond isomerisation.

At this stage we tended to believe that $Cp_2Zr(H)OMe$ (formed via β-elimination of the ether functionality and subsequent reduction of $Cp_2Zr(Cl)OMe$ with $Cp_2Zr(H)Cl$) was responsible for the high α : ω ratio. This hydrozirconating reagent might have different properties from $Cp_2Zr(H)Cl$ in respect of migration. We have previously experienced that the isomer distribution, and the overall outcome of the hydrozirconation reaction, can be influenced by small modifications in the protecting group (i.e. 4,4-dimethyl-2-oxazoline vs. 4,4,6-trimethyl-5,6-dihydro-1,3-oxazine [10]), as well as the nature of the hydrozirconating reagent (i.e. $(\eta^5\text{-}C_5H_5)_2Zr(H)Cl$ vs. $(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)Zr(H)Cl$ [11]). There are, to our knowledge, no reports of the use of alkoxy-zirconium-hydrides in hydrozirconation reactions. Thus the reactivity of $Cp_2Zr(Cl)OMe$ [12] was examined.



Scheme 4

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* Reference number with asterisk indicates a note in the list of references

Table 2

Hydrozirconation of 2-propenylbenzene (**2**) and (*E*)-1-propenylbenzene (**7**) in 1,4-dioxane for 24 h followed by deuterolysis [a]

Entry	Starting material	Temp. (°C)	Reagent [b]	Product distribution					Degree of Deuteration [c] (%)	Relative D-distribution	
				4	**5**	**6**	**7**	**2**		α	ω
1	**2**	30–35	A	80	7	9	3	<1	91	8	92
2	**7**	30–33	B	66	15	7	3	–	92	19	81
3	**2**	33	C	72	5	11	4	<1	88	6	94
4	**7**	30–33	C	25	40	15	20	–	81	38	62
5	**2**	29–30	D	61	6	28	5	<1	71	9	91

[a] Yields determined by combination of mass spectral-, ^{2}H NMR-, and GLC-analyses. [b] A = 2 equiv. of $Cp_2Zr(H)Cl$, prepared *in situ*, B = 2 equiv. of isolated $Cp_2Zr(H)Cl$, C = 1.2 equiv. of $Cp_2Zr(H)Cl$ (isolated) and 0.6 equiv. of $Cp_2Zr(OMe)Cl$, D = 1.2 equiv. of $Cp_2Zr(H)Cl$ (isolated) and 0.6 equiv. of Cp_2ZrH_2. [c] In the propylbenzenes.

Table 3

Analysis of products obtained after reaction of 2-propenylbenzene (**2**) with $Cp_2Zr(D)Cl$ in 1,4-dioxane for 24 h, followed by hydrolysis [a]

Product	Composition of product with respect to degree of deuteration [b]				Position of deuterium [c]		
	d_0	d_1	d_2	d_3	α	β	ω
6	18	76	5	1	2	85	13
7	70	25	4	1	3	26	71

[a] For experimental details, see experimental part. Yields of **6** and **7** are given in Scheme 4. [b] Determined by GLC-MS at 16 eV. (cf. Experimental part). [c] Determined by ^2H NMR spectroscopy.

2-Propenylbenzene (**2**) was treated with a mixture of 1.2 equivalents of isolated $Cp_2Zr(H)Cl$ and 0.6 equivalents of $Cp_2Zr(Cl)OMe$ at 33°C (Table 2, entry 3). An isomer distribuiton $\alpha : \omega$ of 6 : 94 was observed, i.e. approximately the same as that when $Cp_2Zr(H)Cl$ was used. However, when (*E*)-1-propenylbenzene (**7**) was treated with the same mixture of $Cp_2Zr(H)Cl$ and $Cp_2Zr(Cl)OMe$, an $\alpha : \omega$ ratio of 38 : 62 was observed (Table 2, entry 4). Although complete conversion of the starting material was not achieved, these results indicate that both (*E*)-1-propenylbenzene (**7**) and $Cp_2Zr(Cl)OMe$ (or possibly $Cp_2Zr(H)OMe$) in combination is required to get the $\alpha : \omega$ ratio observed in the experiments with (*E*)-3-methoxy-1-phenyl-1-propene (**1**).

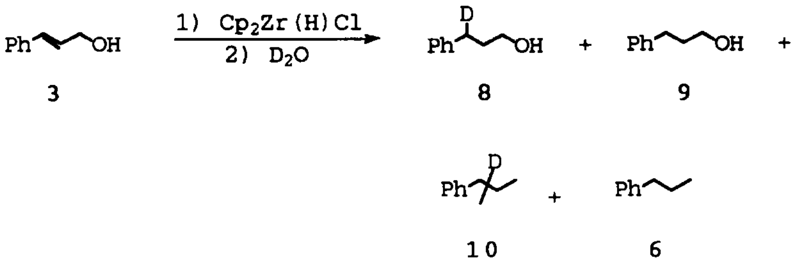
It is important to note that the degree of hydrogenation of the propylbenzenes, obtained after hydrozirconation and deuterolysis, in these cases was larger than usual (12–19% as compared with 1–9%). This might be due to the formation of Cp_2ZrH_2, by disproportionation of $Cp_2Zr(H)OMe$ [13]. A high degree of reduction was observed when **2** was subjected to reaction with a mixture of Cp_2ZrH_2 and $Cp_2Zr(H)Cl$ (Table 2, entry 5), but the $\alpha : \omega$ ratio was apparently not affected by the use of this reagent ($\alpha : \omega = 9 : 91$).

We conclude that an unexpected and low regioselectivity is obtained with **1**, and that selective ω-functionalisation, as depicted in Scheme 1, is not feasible with this substrate. A hydrozirconation–isomerisation process, possibly involving $Cp_2Zr(H)OMe$ or $Cp_2Zr(Cl)OMe$, seems to favour benzylic functionalisation.

*Hydrozirconation of (*E*)-3-phenyl-2-propenol*

Hydrozirconation of (*E*)-3-phenyl-2-propenol (**3**) with 4 equivalents of $Cp_2Zr(H)Cl$ (prepared *in situ*) in 1,4-dioxane for 24 h at the temperatures given in Table 4, gave, after deuterolysis, benzenepropan-γ-*d*-ol (**8**) and benzenepropanol (**9**), in addition to deuterated **10** and non-deuterated propylbenzene (**6**) (Scheme 5, Table 4). At 30°C the reaction was incomplete after 24 h (Table 4, entry 1). The reaction was, however, complete after 24 h at 42–45°C, giving 68% of **8**, according to combined GLC, mass spectral and ^2H NMR data (Table 4, entry 2).

Compound **8** is most likely derived from a zirconacycle (possibly partly dimeric, in analogy with **13**) [14,15]. Trapping of the reaction intermediate with carbon monoxide and iodine gave only 34% of the lactone **11** (Scheme 6), as indicated by GLC analysis, although 68% of **8** was formed after hydrozirconation–deuterolysis under similar conditions.



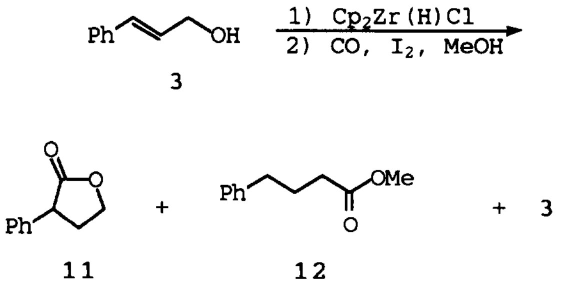
Scheme 5

Table 4

Hydrozirconation of (*E*)-3-phenyl-2-propenol (**3**), with 4 equivalents of $Cp_2Zr(H)Cl$ in 1,4-dioxane for 24 h, followed by deuterolysis [a]

Entry	Temp. (°C)	Product distribution				
		8	**9**	**10**	**6**	**3**
1	30	48	3	27	1	21
2	42–45	68	2	28	2	–

[a] Yields determined by combination of mass spectral-, ^2H NMR-, and GLC-analyses.



Scheme 6

The low yield of **11** might be the result of steric hindrance from the phenyl group, or possibly coordinative saturation, preventing the addition of carbon monoxide. Complex **13** (see Fig. 1) has been reported not to react with carbon monoxide, and this was rationalised in terms of coordinative saturation and low solubility of the

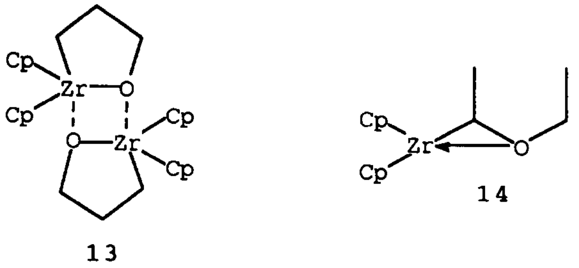


Fig. 1

complex in the solvent used (benzene) [15]. It is notable that the related complex **14** has been reported to react reversibly with carbon monoxide [4].

Methyl 4-phenylbutanoate (**12**) and (*E*)-3-phenyl-2-propenol (**3**) were also formed, in 15 and 20% yields, respectively, in addition to the lactone **11** (Scheme 6). According to GLC analysis, all starting material was consumed before carbonylation. Therefore, the (*E*)-3-phenyl-2-propenol in the product mixture is probably formed by elimination from the intermediate 3-iodo-3-phenylpropanol, which in turn originates from the organozirconium intermediate that does not react with carbon monoxide.

In conclusion we find that hydrozirconation of (*E*)-3-phenyl-2-propenol involves more elimination of the hydroxyl group than does that of oleyl alcohol. Propylbenzene is formed after hydrozirconation of an unsaturated intermediate. The reaction in Scheme 2 is not general with respect to the functionalisation of the organozirconium intermediate. Fair yields of α-functionalised product can be obtained when deuterium oxide is used as the electrophilic reagent, whereas carbonylation so far has been less satisfactory.

Experimental

Materials

Deuterium oxide (99.8% D; Norsk Hydro), bis(cyclopentadienyl)-zirconium dichloride (Aldrich), 2-propenyl-benzene (Janssen) and (*E*)-1-propenylbenzene (Aldrich) were used as received from commercial sources. (*E*)-3-Phenyl-2-propenol (> 98%; Merck) was recrystallised from pentane before use. $Cp_2Zr(H)Cl$ [16], $Cp_2Zr(D)Cl$ [16], $Cp_2Zr(Cl)OMe$ [12], and Cp_2ZrH_2 [17] were prepared by published procedures.

General

^1H NMR and ^2H NMR spectra were recorded on a Varian XL-300 MHz spectrometer at 299.943 and 46.004 MHz, respectively. The ^1H NMR shifts are given relative to TMS in $CDCl_3$, and ^2H NMR shifts relative to TMS-d_{12} in $CHCl_3$. Infrared spectra were recorded on a Perkin–Elmer 298 infrared spectrophotometer. Mass spectra were recorded on a Finnigan 4021 (Data System Incos 2100) spectrometer operating at 16 eV for determination of the deuterium content, otherwise at 60 or 70 eV. The degree of deuteration, after hydrozirconation and deuterolysis (alternatively deuterozirconation and hydrolysis) of the alkyl-zirconium intermediate, was calculated from mass spectra with non-deuterated compounds as references. The reference compound was either purchased or obtained by hydrolysis of samples withdrawn from the hydrozirconation mixtures. Gas chromatographic analyses were performed on a Varian 3300 gas chromatograph, equipped with a 2 m glass column containing 3% Carbowax 20M on Supelcoport 100/120. Pentadecane was used as internal standard for quantitative GLC analyses. Elution band areas were determined electronically with a Varian 4270 integrator.

General procedures

All the hydrozirconation reactions were carried out under dry nitrogen or argon. Solvents (toluene (Merck) and 1,4-dioxane (BDH)) were dried by refluxing over sodium wire, and distilled under nitrogen prior to use. Solid transfers to thoroughly dried glassware were performed under nitrogen in a dry-box. Liquid transfers were performed with a syringe or by the septum technique under nitrogen pressure. Red–Al ($NaAlH_2(OCH_2CH_2OCH_3)_2$; Aldrich) was diluted in anhydrous toluene, to give an 1.50 *M* solution.

*(*E*)-3-Methoxy-1-phenyl-1-propene (1)*

The general procedure of Johnstone and Rose was used [18]. Powdered potassium hydroxide (59.6 mmol) was added to Me_2SO (30 mL). After 5 min stirring, (*E*)-3-phenyl-2-propenol (14.9 mmol) was added, followed immediately by methyl iodide (29.8 mmol). The mixture was stirred for 30 min, added to water, and extracted three times with dichloromethane. The combined organic extracts were washed with water, dried over $MgSO_4$, and concentrated *in vacuo*. Flash chromatography [19] on Silica gel 60 (0.040–0.063 mm (Merck)), with a mixture of pentane and ethyl acetate (7 : 3) as eluent, gave 1.99 g (90%) of the title compound.

Analysis. MS (60 eV): *m/e* 148 (63); 147 (30); 117 (74); 116 (60); 115 (100); 105 (50); 103 (25); 91 (45); 79 (22); 77 (53); 65 (20%). ^1H NMR: δ 3.41 (s, 3H, O–*Me*); 4.11 (dd, 2H, CH_2–O, $J = 1.4$ Hz, 6.0 Hz); 6.30 (dt, 1H, C*H*–CH_2), $J = 6.0$, 16.0 Hz); 6.63 (dt, 1H, C*H*–Ph, $J = 1.4$, 16.0 Hz); 7.22–7.44 (m, 5H, Ph). The ^1H NMR spectrum was consistent with those reported in the literature [20].

Hydrozirconation of 1, 2, or 7 with $Cp_2Zr(H)Cl$

Either *in situ* generated (Table 1, entries 1–4; Table 2, entry 1) or isolated (Table 1, entry 5; Table 2; entry 2) reagent was used. The *in situ* generated reagent was prepared from Cp_2ZrCl_2 (9.00 mmol for hydrozirconation of **1**, 6.00 mmol for hydrozirconation of **2**) and Red–Al (4.2 mmol and 2.8 mmol, respectively, 1.5 *M* solution) in 35.0 mL of dry 1,4-dioxane. The *in situ* generated reagent was stirred for 2–3 h before the addition of the substrate. The isolated $Cp_2Zr(H)Cl$ (9.00 mmol for hydrozirconation of **1**, 6.00 mmol for hydrozirconation of **7**) was dissolved in the same amount of solvent as the *in situ* generated reagent. Substrate (**1**, **2**, or **7**, respectively; 3.00 mmol) and internal standard (see General), dissolved in 5 mL of 1,4-dioxane, were added. The mixture was stirred at the temperature indicated in Tables 1 and 2. After 24 h the reaction was quenched with 5 mL of deuterium oxide, and the mixture was stirred for 2 h, whereupon a GLC sample was withdrawn. The remaining mixture was filtered through a 3–4 cm column of neutral alumina, with 300 mL of ether as eluent. The solution was concentrated *in vacuo* and a sample of the concentrate was analysed by ^2H NMR spectroscopy. On several occasions the concentrate was chromatographed on TLC-plates (Silica gel 60 F_{254}, 20 × 20 cm, layer thickness 2 mm (Merck)) with pentane as eluent. The ^2H NMR spectrum of the deuterated propylbenzene obtained after chromatography was in these instances always, within experimental error, indentical with that obtained after concentration.

Analysis. MS (**4**, **5** and **6**) (16 eV): *m/e* 122 ($d_2 - M^+$); 121 ($d_1 - M^+$); 120 $d_0 - M^+$). ^2H NMR (mixture of **4** and **5**): δ 0.90–1.01 (br s, CH_2D); 2.53–2.64 (br s, Ph–CH*D*). The values varied slightly depending on the amount of residual 1,4-dioxane. The difference between α and ω deuterium signals was, however, always 1.63 ppm.

Hydrozirconation of 2 or 7 with mixed reagents

With $Cp_2Zr(H)Cl$–$Cp_2Zr(Cl)OMe$ mixture. A solution of substrate (**2** or **7**) (1.00 mmol) and internal standard (see General) in 1,4-dioxane (12 mL), was added to a mixture of $Cp_2Zr(H)Cl$ (1.20 mmol) and $Cp_2Zr(Cl)OMe$ (0.60 mmol). The mixture was stirred for 24 h and then treated with 3 mL of deuterium oxide, and stirred for a further 2 h, and a GLC sample was then withdrawn. The remaining mixture was filtered through a 3–4 cm column of neutral alumina with 125 mL of ether as eluent. The ether and 1,4-dioxane were removed by distillation and a sample of the remaining substance was analysed by ^2H NMR spectroscopy.

Analysis. See above (hydrozirconation of **1**, **2** or **7** with $Cp_2Zr(H)Cl$).

With $Cp_2Zr(H)Cl$–Cp_2ZrH_2 mixture. A solution of 2-propenylbenzene (**2**) (1.00 mmol) and internal standard (see General) in 1,4-dioxane (12 mL), was added to a mixture of $Cp_2Zr(H)Cl$ (1.20 mmol) and Cp_2ZrH_2 (0.60 mmol). The procedure was then as described for the reaction with the $Cp_2Zr(H)Cl$–$Cp_2Zr(Cl)OMe$ mixture.

Analysis. See above (hydrozirconation of **1**, **2** or **7** with $Cp_2Zr(H)Cl$).

Deuterozirconation of 2

A solution of 2-propenylbenzene (**2**) (3.00 mmol) and internal standard (see General) in 1,4-dioxane (5 mL), was added to a suspension of $Cp_2Zr(D)Cl$ (3.00 mmol) in 1,4-dioxane (35 mL). The mixture was stirred for 24 h and was then treated with 5 mL of water, and stirred for a further 2 h, and a GLC sample then withdrawn. The remaining mixture was filtered through a 3–4 cm column of neutral alumina with 300 mL of ether as eluent. The solution was concentrated *in vacuo* and a sample of the concentrate was analysed by ^2H NMR spectroscopy.

Analysis. MS (deuterated and non-deuterated **6**) (16 eV): m/e 123 ($d_3 - M^+$, 2); 122 ($d_2 - M^+$, 17); 121 ($d_1 - M^+$, 100); 120 ($d_0 - M^+$, 23%). MS (deuterated and non-deuterated **7**) (16 ev): m/e 121 ($d_3 - M^+$, 2); 120 ($d_2 - M^+$, 10); 119 ($d_1 - M^+$, 46); 118 ($d_0 - M^+$, 100%). ^2H NMR (deuterated **6**): δ 1.01 (br s, CH_2D); 1.72 (br s, CHD–CH_3); 2.64 (br s, Ph–CHD). ^2H NMR (deuterated **7**): δ 1.93 (br s, CH_2D); 6.31 (br s, CD–CH_3); 6.47 (br s, Ph–CD).

Hydrozirconation of 3

The hydrozirconation reagent was generated in 90 mL of dry 1,4-dioxane, from Cp_2ZrCl_2 (29.8 mmol) and Red–Al (14 mmol, 1.5 *M* solution in toluene). After 2–3 h stirring a solution of (E)-3-phenyl-2-propen-1-ol (**3**) (7.45 mmol) and the internal standard (see General) in 15 mL of 1,4-dioxane, was added. The mixture was stirred at the temperature indicated in Table 4 and after 24 h treated with 10 mL of D_2O. The mixture was stirred for a further 2 h and a GLC sample then withdrawn. (The organic layer of the GLC sample was washed with water before mass spectral analysis to replace the deuterium atoms in the hydroxyl group by protons.) The remaining mixture was filtered through a 3–4 cm column of neutral alumina with 600 mL of ether as eluent. The solution was concentrated *in vacuo* and subjected to flash chromatography [19] with ether before ^2H NMR spectroscopic analysis.

Analysis. MS (**6** and **10**) (16 eV): see above (Hydrozirconation of **1**, **2** or **7** with $Cp_2Zr(H)Cl$). MS (**8**) (16 ev): m/e 138 ($d_2 - M^+$); 137 ($d_1 - M^+$); 136 ($d_0 - M^+$); 120 (($d_2 - M^+$) – H_2O); 119 (($d_1 - M^+$) – H_2O); 118 (($d_0 - M^+$) – H_2O). ^1H NMR (mixture of **3**, **8**, and **9**): δ 1.42–1.52 (br s, OH, **8** and **9**); 1.62–1.75 (br s, OH, **3**); 1.85–1.95 (m, CH_2–CH_2OH, **8** and **9**); 2.66–2.74 (m, Ph–C(H)D and Ph–CH_2, **8** and **9**); 3.68 (t, CH_2–OH, $J = 6.5$ Hz, **8** and **9**); 4.30–4.37 (br d, CH_2–OH, **3**); 6.38 (dt, CH–CH_2OH, $J = 15.9$, 5.7 Hz, **3**); 6.63 (br d, Ph–CH, $J = 15.9$ Hz, **3**); 7.17–7.42 (m, Ph, **3**, **8**, and **9**). The ^1H NMR assignments for **8** and **9** were consistent with those reported in the literature [21]. ^{2}H NMR (benzene-γ-*d*-ol (**8**)) δ: 2.71 (br s, Ph–CH*D*).

Hydrozirconation–carbonylation of 3

A solution of (*E*)-3-phenyl-2-propen-1-ol (**3**) (3.73 mmol) and internal standard in 1,4-dioxane (15 mL), was added to a suspension of $Cp_2Zr(H)Cl$ (14.9 mmol) [22 *] in 1,4-dioxane (35 mL). The mixture was stirred for 24 h at 40 °C and the suspension then transferred to a dry centrifuge tube (sealed with a septum) and centrifuged. The supernatant liquid was transferred to a dry Parr flask. The flask was placed in a Parr apparatus, a 4 atm pressure of carbon monoxide was applied and the flask shaken overnight. The flask was removed from the Parr apparatus and a solution of iodine (3.73 mmol) in toluene (50 mL) was added. The mixture was stirred for 2 h and methanol (2 mL) was then added and the mixture stirred for an additional 2 h. A GLC sample was withdrawn from the reaction mixture. The remaining mixture was concentrated *in vacuo*. The lactone **11** was separated from the other components in the product by flash chromatography [19] with a mixture of pentane and ether (1 : 2) as eluent. The ester **12** was isolated by means of HPLC separation of the remainder after flash chromatography. The HPLC separation was performed on a 25 × 0.5 cm (i.d.) Nucleosil-OH column with a mixture of heptane and ethyl acetate (97.5 : 2.5) as eluent.

Analysis. MS (**11**) (70 eV): *m/e* 162 (22); 118 (62); 117 (100); 103 (19); 91 (36); 78 (20); 77 (26%). IR (**11**) (neat): 1765 cm^{-1} (C=O). ^{1}H NMR (**11**): δ 2.45 (m, 1H, CH_2–C(*H*)H–C(H)Ph, $J = 12.7$, 9.5, 9.2, 8.4 Hz); 2.73 (m, 1H, CH_2–C(H)*H*–C(H)Ph, $J = 12.7$, 9.5, 6.7, 3.5 Hz); 3.82 (br t, 1H, C(*H*)–Ph, $J = 9.5$ Hz); 4.36 (slightly distorted dt, 1H, O–C*H*(H)–CH_2, $J = 9.2$, 6.7 Hz, a $J \approx 9$ Hz coincides with the other couplings, resulting in slight broadening of the signals); 4.49 (slightly distorted dt, 1H, O–CH(*H*)–CH_2, $J = 8.4$, 3.5 Hz, $J \approx 9$ Hz (see comments above)); 7.27–7.44 (m, 5H, Ph). The ^{1}H NMR spectrum was consistent with that previously reported [23]. MS (**12**) (70 eV): *m/e* 178 (18); 147 (19); 146 (20); 105 (27); 104 (64); 91 (100); 74 (94); 65 (42%). IR (**12**) (neat): 1735 cm^{-1} (C=O). ^{1}H NMR (12): δ 1.96 (distorted quin., 2 H, CH_2–CH_2–C(O)); 2.34 (t, 2H, CH_2–C(O), $J = 7.5$ Hz); 2.65 (t, 2H, CH_2–Ph, $J = 7.6$ Hz); 3.67 (s, 3H, O–CH_3); 7.16–7.32 (m, 5H, Ph). The ^{1}H NMR [24a,b] and MS [24b,c] data for **12** were consistent with those reported in the literature.

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