enough for oxygenation of polychlorocatechols. However, the present result suggests that oxygenation of polyhalocatechols will be possible by the development of ligands in the future.

Experimental Section

The oxygenations were performed in a 20-mL cylindrical flask at 25 °C and under 1 atm of O_2. MeCN (5 mL) was added to $FeCl_3$ (0.01 mmol), **1** (0.30 mmol), and tpa (0.1 mmol), and the solution stirred. Aliquots of the reaction solution (0.5 mL) were diluted with CH_2Cl_2, washed with 2 N HCl to remove iron complexes, and quantitatively analyzed by ^{1}H NMR spectroscopy by monitoring specific ^{1}H NMR peaks (naphthalene as internal reference) and using the gravimetric method.[14] The products were separated by preparative HPLC and identified by ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectrometry. Two types of esters were detected for **3** and **4**, whose ratios were estimated to be about 2:1 for **3** and 1.4:1 for **4** based on the relative intensities of characteristic ^{13}C NMR signals for the products.

The 3- and 4-chlorocatecholatoiron complexes [Fe(tpa)(Cl-cat)]BPh_4 (**5** and **6**) were prepared by a modification of the reported methods.[19, 22] **5**: Elemental analysis calcd for $FeC_{48}H_{41}N_4O_2BCl$: C 71.34, H 5.11, N 6.93, Cl 4.39; found: C 71.05, H 5.25, N 6.88, Cl 4.40; FAB-MS: *m/z*: 488 ($M^+ - BPh_4$). **6**: Elemental analysis calcd for $FeC_{48}H_{41}N_4O_2BCl$: C 71.34, H 5.11, N 6.93, Cl 4.39; found: C 70.58, H 5.03, N 6.99, Cl 4.42.

The reaction of **5** or **6** with O_2 was started by adding MeCN (80 mL) to **5** or **6** (0.2 mmol) at 25 °C and under 1 atm of O_2. The oxygenations were also performed in the presence of **1** (5.8 mmol) and 2,6-lutidine (66.7 mmol).

2: HR-MS: *m/z* (E/I): 140.0113 (M^+); ^{1}H NMR ($CDCl_3$): $\delta = 5.96$ (d), 6.52 (dd), 8.37 (d); ^{13}C NMR ($CDCl_3$): 101.5, 125.1, 141.8, 161.9, 167.3, 169.6.

3 (mixture of two esters): HR-MS: *m/z* (E/I): 265.9980 (M^+); ^{1}H NMR ($CDCl_3$): $\delta = 6.17$ (d), 6.57 (dd), 8.40 (d), 6.92 – 7.19 (4-Cl-catH); ^{13}C NMR ($CDCl_3$): 100.3 (s), 100.4 (s), 125.5 (2s), 141.7 (2s), 162.5(2s), 163.1(s), 167.1 (2s), 118.2 – 147.7 (4-Cl-catH).

4 (mixture of two esters): HR-MS: *m/z* (E/I): 301.9750 (M^+); ^{1}H NMR ($CDCl_3$): $\delta = 2.91 - 3.45$ (m), 5.45 (dd), 6.27 (s), 6.77 – 7.13 (4-Cl-catH); ^{13}C NMR ($CDCl_3$): 36.6 (s), 36.7 (s), 79.5 (s), 79.6 (s), 118.4 (s), 159.1 (2s), 166.3 (s), 166.5 (s), 169.0 (2s), 117.8-148.4 (4-Cl-catH).

7: MS *m/z* (E/I): 176; ^{1}H NMR ($CDCl_3$): $\delta = 2.75$ (dd), 2.98 (dd), 5.38 (ddd), 7.48 (d); ^{13}C NMR ($CDCl_3$): 37.3, 76.2, 128.8, 146.4, 166.8, 172.1.

Received: August 22, 1997 [Z 10845 IE]
German version: *Angew. Chem.* **1998**, *110*, 527 – 530

Keywords: chlorocatechols · dioxygenases · enzyme mimetics · iron · non-heme iron complexes · oxygenations

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The Asymmetric Horner – Wadsworth – Emmons Reaction Mediated by An External Chiral Ligand**

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The past decade has witnessed considerable activity in the area of asymmetric Horner – Wadsworth – Emmons (HWE) reactions of prochiral ketones for the synthesis of olefins with a chiral axis.[1] Asymmetric HWE reactions of anions derived from chiral phosphoranes,[2] phosphane oxides,[3] phosphonamides,[4] phosphonamidates,[5] and phosphonates[6] to produce chiral olefins have been well documented. Carboxylic acid derivatives with chiral alcohol[7] or amine[8] moieties also lead to chiral carbonyl olefination products. In spite of impressive progress with asymmetric reactions based on internal chiral auxiliaries, comparatively little effort has been

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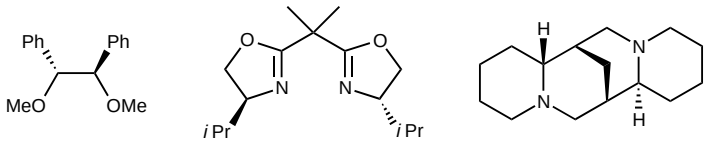
[**] We gratefully acknowledge financial support from the Japan Society for Promotion of Science (JSPS; RFTF-96P00302), the Japanese Ministry of Education, Science, Sports and Culture, and the Japanese Science and Technology Agency.

  1433-7851/98/3704-0515 $ 17.50+.50/0

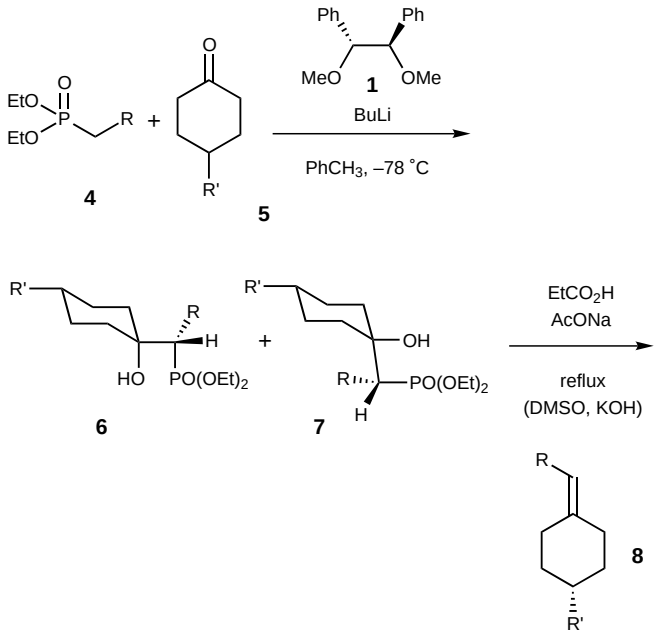
devoted to HWE or Wittig reactions controlled by external chiral ligands.[9, 10] We present here our approach to this problem, in which an achiral lithium phosphonate, controlled by an external chiral ligand, adds to a ketone, and the resulting chiral alcohol undergoes stereoselective olefination.[11]

Based on our previous studies on asymmetric reactions of lithiated carbonucleophiles,[12] chiral compounds **1**–**3** and



1 **2** **3**

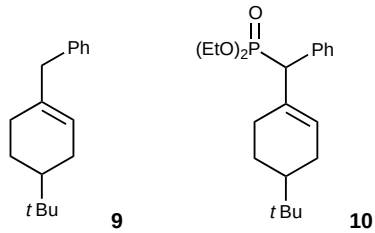
diethyl benzylphosphonate (**4**)[13] were chosen to be representative chiral ligands and the test nucleophile, respectively. Reaction of lithiated diethyl benzylphosphonate (**4**; R = Ph, 1.2 equiv) with 4-*tert*-butylcyclohexanone (**5**; R′ = *t*Bu) in the presence of **1** (1.4 equiv) in toluene at −78 °C for 0.5 h gave a separable diastereomeric mixture of (*S*)-*cis*-alcohol **6** and (*R*)-*trans*-alcohol **7** (R = Ph, R′ = *t*Bu)[14] in 82 and 12% *ee* and 89



4 **5** **6** **7** **8**

and 5% yield, respectively (Table 1, entry 1).[15] The chiral ligand **1** was recovered quantitatively.

Attempts to olefinate **6** (R = Ph, R′ = *t*Bu) by heating at 100 °C for 20 h in acetic acid[4, 16] gave an inseparable mixture of olefin **8** (R = Ph, R′ = *t*Bu) and isomerized olefin **9** in a ratio of 92:8 (73% yield) together with recovered **6** (9%). To minimize the production of **9** and to increase the conversion of **6**, compound **6** was heated in acetic acid at reflux in the presence of four equivalents of NaOAc for 2.5 h, which produced **8** in 79% yield and the dehydrated form of **10** in



9 **10**

14% yield. Compound **9** was not detected. Use of the less acidic propionic acid in place of acetic acid in the presence of NaOAc under reflux for 0.5 h gave **8** as the sole isolable product (85% yield). In the case of acid-sensitive compounds **6** or **8** (for example, allylidenecyclohexane), basic conditions were employed (KOH in DMSO, 50 °C, 0.5 h) to afford **8** in comparable yield.[3]

Heating **6** (82% *ee*, R = Ph, R′ = *t*Bu) with propionic acid/NaOAc it was readily provided (+)-(*S*)-benzylidene-4-*tert*-butylcyclohexane (**8**; R = Ph, R′ = *t*Bu) with 84% *ee* and no decrease in the enantiomeric purity of **6** (Table 1, entry 1). Heating **7** (12% *ee*, R = Ph, R′ = *t*Bu) also gave (+)-(*S*)-**8** with 12% *ee* in 76% yield, again without loss of enantiomeric purity in **7**. The absolute configuration of **8** (R = Ph, R′ = *t*Bu) was determined to be *S* by comparison of the specific rotation.[4b] Since the olefination is known to proceed in a *syn* fashion,[1] the absolute configurations of **6** and **7** (R = Ph, R′ = *t*Bu) are *S* and *R*, as indicated above. However, under the same addition reaction conditions, ligands **2**[17] and **3**[18] gave (*R*)- and (*S*)-**6** (R = Ph, R′ = *t*Bu) with only 15 and 17% *ee*, respectively.

Formation of a chelated complex with high enantioselectivity from the lithiated phosphonate and **1** requires warming the reaction mixture to 0 °C before adding **5**. In the absence of

Table 1. Asymmetric addition of phosphonates to 4-substituted cyclohexanones.

Entry	R	R′	**6**[a]		**7**[a]		**8**[b]		
			Yield [%]	*ee* [%]	Yield [%]	*ee* [%]	Yield [%]	*ee* [%]	Config.
1	Ph	*t*Bu	89	82	5	12	85	84	*S*
2	Ph	Me	92	71	7	0	84	70	*S*
3	Ph	Ph	94	64	4	51	80		
4	vinyl	*t*Bu	91	54	trace	–	83[c]	51	*S*
5	4-ClC_6H_4	*t*Bu	94	64	2	n.d.	84[c]		
6	1-naphthyl	*t*Bu	74	64	2	18	82[c]		
7	2-naphthyl	*t*Bu	99	90[d]	trace	–	84[c]		

[a] The *ee* values were determined by HPLC with a chiral stationary phase (Daicel Chiracel OD-H); n.d. = not determined. [b] The principal diastereomer **6** was transformed into **8**. The absolute configuration and *ee* value were established from the specific rotation of **8** (R = Ph, R′ = Me),[4b] (R = Ph, R′ = *t*Bu),[4b] and (R = vinyl, R′ = *t*Bu)[20]. The configuration was assigned by analogy to other olefins. [c] Olefination with DMSO/KOH at 50 °C. [d] The addition was carried out at −100 °C.

  1433-7851/98/3704-0516 $ 17.50+.50/0

warming this reaction gave **6** (R = Ph, R′ = *t*Bu) with 79% *ee*.[19] Other 4-substituted cyclohexanones **5** were converted into the corresponding *cis*-alcohols **6** (R = Ph) and benzylidenecyclohexanes **8** (R = Ph) in 64-84% *ee* (Table 1, entries 1–3). Other diethyl phosphonates **4** (R = 4-ClPh, 1- and 2-naphthyl, vinyl) gave the corresponding alcohol **6** and olefins **8** in 51–90% *ee* (entries 4–7).

The reaction described, which is controlled by external chiral ligands, has the advantage that tedious steps in the synthesis of chiral phosphonate derivatives can be omitted. Furthermore, it may open the way to a catalytic asymmetric HWE reaction.

Experimental Section

A solution of BuLi in hexane (0.81 mL, 1.48 M, 1.2 mmol) was added to a solution of **1** (338 mg, 1.4 mmol) in toluene (6.5 mL) at −78 °C. After the mixtures was stirred for 0.5 h a solution of **4** (274 mg, 1.2 mmol) in toluene (2.0 mL) was added dropwise over 5 min. The solution was stirred for 0.5 h at −78 °C and then for 0.5 h at 0 °C. A solution of **5** (R′ = *t*Bu; 154 mg, 1.0 mmol) in toluene (2.0 mL) was added dropwise over 5 min at −78 °C, and the reaction mixture was stirred for 0.5 h at −78 °C before it was quenched with a saturated solution of aqueous NaCl (10 mL). The aqueous layer was extracted with ethyl acetate (3 × 10 mL) and the combined organic layers were washed with a saturated solution of aqueous NaCl (20 mL) and dried over sodium sulfate. Concentration followed by column chromatography (silica gel, hexane/ethyl acetate 5/1 then 1/1) gave (*S*)-**6** (R = Ph, R′ = *t*Bu; 340 mg, 89% yield, 82% *ee*) and (*R*)-**7** (R = Ph, R′ = *t*Bu; 18 mg, 5% yield, 12% *ee*) together with recovered **1** (337 mg, 90%).

A mixture of (*S*)-**6** (R = Ph, R′ = *t*Bu; 82% *ee*, 203 mg, 0.67 mmol) and sodium acetate (220 mg, 2.5 mmol) in propionic acid (1.0 mL) was stirred under reflux for 0.5 h. The mixture was allowed to cool to room temperature and then diluted with ethyl acetate (10 mL). The organic layer was washed successively with saturated solutions of sodium hydrogencarbonate (10 mL) and aqueous NaCl (10 mL), and then dried over sodium sulfate. Concentration and purification by column chromatography (silica gel, hexane) gave olefin (*S*)-**8** (R = Ph, R′ = *t*Bu; 156 mg, 85%) with 84% *ee*.

Received: September 23, 1997 [Z 10962 IE]
German version: *Angew. Chem.* **1998**, *110*, 525–527

Keywords: asymmetric synthesis · carbanions · lithium · olefinations

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Methylalumoxane MCM-41 as Support in the Co-Oligomerization of Ethene and Propene with $[\{C_2H_4(1\text{-indenyl})_2\}Zr(CH_3)_2]$**

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With the advent of single-site metallocene catalysts, the field of polymerization of α-olefins has been drastically changed.[1] Next to geometric manipulation of the metallocene structure to induce stereoregular polymerization, substitution or reduction of the excessive amounts of methylalumoxane (MAO) is an important challenge. MAO acts as a weakly coordinating anion and activates the metallocene structure. Heterogenization of the alumoxane structure on support materials like silica and alumina may be a solution to minimize the amounts of MAO. However, after impregnation of MAO or trimethylaluminum (TMA), addition of supple-

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[**] This work was supported by an IUAP-PAI grant of the Belgian government. L.K.V.L. thanks IWT for a research grant. P.J.G. acknowledges the FWO for a research position. The constructive comments of D. De Vos are appreciated as well.

  1433-7851/98/3704-0517 $ 17.50+.50/0