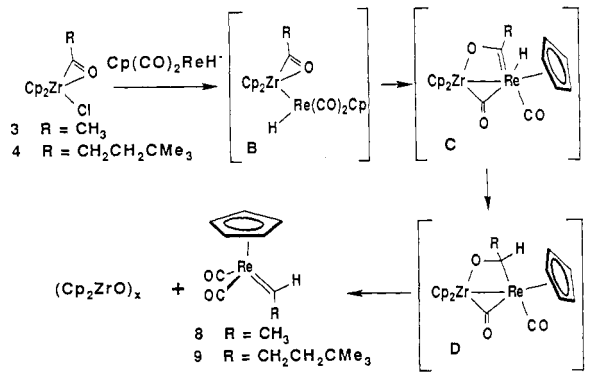
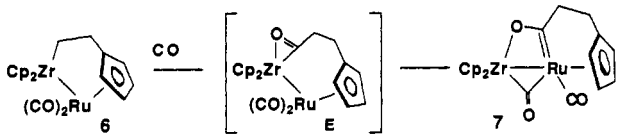
Scheme I



ensue to produce intermediate C which possesses the desired zirconoxycarbene and hydride ligands on rhenium (Scheme I). A similar migration of an η^2-acyl ligand from zirconium to ruthenium was proposed earlier to explain the carbonylation of the alkyl zirconium-ruthenium compound **6** to the zirconoxycarbeneruthenium compound **7** via intermediate E.[1] Here we report that reaction of η^2-acylzirconium compounds **3** and **4** with $K^+Cp(CO)_2ReH^-$ **5** leads not only to the reduction of the acyl ligand but also to formation of mononuclear rhenium-carbene complexes $Cp(CO)_2Re{=}CHR$ (**8**, R = CH_3; **9**, R = $CH_2CH_2CMe_3$).



The reaction of $Cp_2Zr(\eta^2\text{-}COCH_3)Cl$[3] and $K^+Cp(CO)_2ReH^-$[4] in THF-d_8 was followed by ^1H NMR at room temperature. New resonances were assigned to the mononuclear rhenium-carbene complex $Cp(CO)_2Re{=}CHCH_3$ (**8**) and to $(Cp_2ZrO)_x$[5] (major resonance at δ 6.31 and several minor resonances nearby). In a preparative reaction, a suspension of $K^+Cp(CO)_2ReH^-$ **5** (68 mg, 0.20 mmol) in 10 mL of THF was slowly added to a solution of $Cp_2Zr(\eta^2\text{-}COCH_3)Cl$ (**3**) (83 mg, 0.27 mmol) in 10 mL of THF at -40 °C. The resulting red solution was evaporated under vacuum at 10 °C, and the residue was dissolved in 4 mL of CH_2Cl_2 and chromatographed (silica gel, 10% CH_2Cl_2-hexane) to give an orange solid which was sublimed at 40 °C (0.05 mmHg) to give **8**[6] (35 mg, 52% yield), mp 68-69 °C. The key spectral features that establish the structure of **8** include characteristically far downfield chemical shifts of the carbene carbon at δ 292.3 (d, J_{CH} = 134 Hz) and of the proton on the carbene carbon at δ 16.11 (q, J = 7.3 Hz).

Similarly, the reaction of $Cp_2Zr(\eta^2\text{-}COCH_2CH_2CMe_3)Cl$[7] (92 mg, 0.25 mmol) with $K^+Cp(CO)_2ReH^-$ **5** (67 mg, 0.20 mmol) in THF followed by chromatography and sublimation at 50-60 °C under high vacuum led to the isolation of rhenium-carbene complex **9**[8] (47 mg, 58%) as an orange solid, mp 118-119 °C.

The formation of rhenium-carbene complexes **8** and **9** is necessarily a complex process since it must involve, at some stage, hydride addition to the acyl carbon, migration of carbon from zirconium to rhenium, and cleavage of the carbon-oxygen bond of the acyl unit. While we have no direct evidence favoring the mechanistic hypothesis shown in Scheme I, there are good analogies for the individual steps in the mechanism as pointed out earlier. The final step involving cleavage of the carbon-oxygen bond and breakup of the heterobimetallic complex is driven by formation of a zirconium oxo species which then oligomerizes.

The closest analogy to the formation of rhenium-carbene complexes **8** and **9** is the reaction of $Cp_2Zr(\eta^2\text{-}COC_6H_5)C_6H_5$ with Cp_2WH_2 which leads to the formation of $Cp_2W{=}CHC_6H_5$.[5]

The reactions reported here provide a very convenient, if nonobvious, synthesis of the previously unknown alkyl-substituted rhenium-carbene complexes. Earlier syntheses of $Cp(CO)_2Re$ carbene complexes include the reaction of $CpRe(CO)_3$ with RLi followed by O-alkylation which yields $Cp(CO)_2Re{=}C(OR')R$[9] and the reaction of cationic rhenium-carbyne complexes with nucleophiles which yields complexes such as $Cp(CO)_2Re{=}CHC_6H_5$.[10] These earlier routes are unsuitable for synthesis of **8** or **9** because cationic alkyl-carbyne complexes are unstable. In addition, any synthesis of **8** or **9** must avoid acidic workup since these rhenium-carbene complexes are rapidly decomposed by acid.

Acknowledgment. Support from the Department of Energy, Division of Basic Energy Sciences, is gratefully acknowledged.

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(4) Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500.
(5) Marsella, J. A.; Folting, K.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 5596.
(6) For **8**: ^1H NMR (270 MHz, benzene-d_6) δ 16.11 (q, J = 7.3 Hz, Re=CH), 4.88 (s, C_5H_5), 2.00 (d, J = 7.3 Hz, CH_3); ^{13}C NMR (126 MHz, benzene-d_6) δ 292.3 (d, J = 134 Hz, Re=C), 204.5 (s, CO), 91.4 (d, J = 178 Hz, C_5H_5), 50.4 (q, J = 124 Hz, CH_3); IR (THF) 1980, 1900 cm^{-1}. HRMS calcd for $C_9H_9O_2{}^{187}Re$ 336.0158, found 336.0161. Anal. Calcd for $C_9H_9O_2Re$: C, 33.23; H, 2.71. Found: C, 33.25; H, 2.76.
(7) Carr, D. B.; Schwartz, J. *J. Am. Chem. Soc.* **1979**, *101*, 3521.
(8) For **9**: ^1H NMR (270 MHz, benzene-d_6) δ 16.07 (t, J = 7.6 Hz, Re=CH), 4.94 (s, C_5H_5), 2.49 (m, Re=CHCH_2), 1.43 (m, CH_2CMe$_3$), 0.91 (s, C(CH_3)$_3$); ^{13}C NMR (126 MHz, benzene-d_6, couplings from INEPT) δ 298.1 (d, J = 129 Hz, Re=CH), 204.2 (s, CO), 91.5 (d, J = 179 Hz, C_5H_5), 59.4 (t, J = 126 Hz, Re=CHCH_2), 40.5 (t, J = 126 Hz, CH_2CMe$_3$), 29.9 (s, CMe_3), 29.3 (q, J = 124 Hz, C(CH_3)$_3$); IR (THF) 1980, 1900 cm^{-1}; HRMS calcd for $C_{14}H_{19}O_2{}^{187}Re$, 406.0943, found 406.0965. Anal. Calcd for $C_{14}H_{19}O_2Re$: C, 41.47; H, 4.72. Found: C, 41.34; H, 4.91.
(9) Fischer, E. O.; Riedel, A. *Chem. Ber.* **1968**, *101*, 156.
(10) (a) Fischer, E. O.; Clough, R. L.; Stückler, P. *J. Organomet. Chem.* **1976**, *120*, C6. (b) Fischer, E. O.; Frank, A. *Chem. Ber.* **1978**, *111*, 3740.

The Stereoselective Synthesis of α-Amino Acids by Phase-Transfer Catalysis

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New syntheses of α-amino acids are important because of the widespread use of these compounds in the physical and life sciences.[1] During the past 20 years major advances have been realized in the asymmetric synthesis[2] of amino acids, especially those which use stoichiometric amounts of chiral auxiliaries.[3-5]

(1) (a) *α-Amino Acid Synthesis*; O'Donnell, M. J., Ed. Tetrahedron Symposium-in-Print, Pergamon: London, 1988; Vol. 44, Issue 17. (b) Barrett, G. C. *Chemistry and Biochemistry of the Amino Acids*; Chapman and Hall: London, 1985. (c) *Amino Acids, Peptides and Proteins*; Specialist Periodical Reports, The Royal Society of Chemistry: London, 1969-1985; Vol. 1-16. (d) *Amino Acids and Peptides*; Specialist Periodical Reports, The Royal Society of Chemistry: London, 1986-1987; Vol. 17-18.
(2) Evans, D. A. *Science* **1988**, *240*, 420-426, and cited references.
(3) Recent lead references involving stoichiometric auxiliaries in the asymmetric synthesis of α-amino acids by C_α-C_β bond formation with anionic or cationic amino acid precursors: (a) Owa, T.; Otsuka, M.; Ohno, M. *Chem. Lett.* **1988**, 83-86. (b) Belokon', Y. N.; Bakhmutov, V. I.; Chernoglazova, N. I.; Kochetkov, K. A.; Vitt, S. V.; Garbalinskaya, N. S.; Belikov V. M. *J. Chem. Soc., Perkin Trans. 1* **1988**, 305-312. (c) McIntosh, J. M.; Leavitt, R. K.; Mishra, P.; Cassidy, K. C.; Drake, J. E.; Chadha, R. *J. Org. Chem.* **1988**, *53*, 1947-1952. (d) Harding, K. E.; Davis, C. S. *Tetrahedron Lett.* **1988**, *29*, 1891-1894. (e) Fitzi, R.; Seebach, D. *Tetrahedron* **1988**, *44*, 5277-5292. (f) Schöllkopf, U.; Tiller, T.; Bardenhagen, J. *Tetrahedron* **1988**, *44*, 5293-5305. (g) Ojima, I.; Chen, H.-J. C.; Qiu, X. *Tetrahedron* **1988**, *44*, 5307-5318. (h) El Achqar, A.; Boumzebra, M.; Roumestant, M.-L.; Viallefont, P. *Tetrahedron* **1988**, *44*, 5319-5332. (i) Ikegami, S.; Uchiyama, H.; Hayama, T.; Katsuki, T.; Yamaguchi, M. *Tetrahedron* **1988**, *44*, 5333-5342. (j) Bretschneider, T.; Miltz, W.; Münster, P.; Steglich, W. *Tetrahedron* **1988**, *44*, 5403-5414. (k) Yamamoto, Y.; Ito, W. *Tetrahedron* **1988**, *44*, 5415-5423. (l) Williams, R. M.; Zhai, W. *Tetrahedron* **1988**, *44*, 5425-5430, and cited references.

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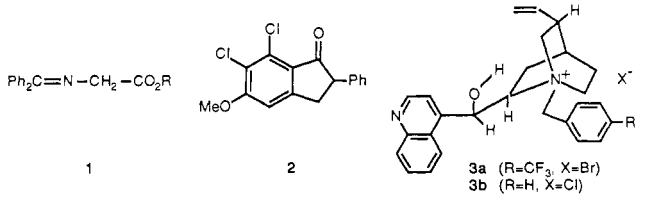
Table I. Effect of Ester Group R on Asymmetric PTC Alkylation of **1**[10]

1	ester group R	% ee of (*R*)-**4**	1	ester group R	% ee of (*R*)-**4**
1a	$PhCH_2$-	28	**1g**	Et-	36
1b	4-NO_2-C_6H_4-CH_2-	22	**1h**	Me_2CH-	42
1c	4-MeO-C_6H_4-CH_2-	30	**1i**	Me_3C-	56
1d	Ph_2CH-	14	**1j**	Me_3CCH_2-	44
1e	1-naphthyl-CH_2-	28	**1k**	Et_3C-	40
1f	Me-	30			

However, methods utilizing *catalytic* quantities of the enantiocontrol element are far fewer in number.[6]

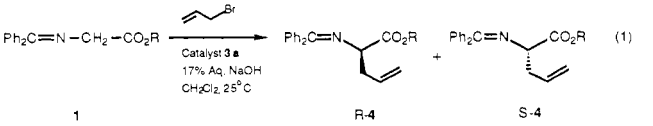
Asymmetric synthesis of α-amino acids by phase transfer catalytic (PTC) alkylation using a chiral catalyst and a prochiral protected glycine derivative **1**[7,8] would provide a particularly attractive method for the preparation of optically active α-amino acids. Our attention was drawn to similarities between the benzyl ester of protected glycine derivative **1** and indanone **2**, which has been alkylated with high induction by using PTC with a catalyst **3a** derivated from the cinchona alkaloids.[9] Two potentially



1 2 3a (R=CF_3, X=Br) 3b (R=H, X=Cl)

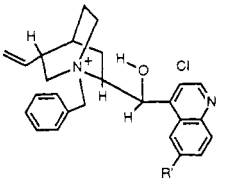
complicating factors are that **1** is acyclic and, additionally, that it will be necessary to *selectively monoalkylate*[7g] **1** to yield an active methine product which should not be racemized subsequent to alkylation. Despite these possible difficulties, we have pursued the alkylation of derivatives of **1** with catalysts **3** and describe herein our preliminary results which have led to *the first practical asymmetric synthesis of α-amino acids using phase-transfer catalysis*.

The first experiment,[10] using conditions similar to those described for alkylation of indanone **2**,[9] with substrate **1a** (R = CH_2Ph), allyl bromide, catalyst **3a**,[12] and 17% aqueous NaOH/toluene resulted in a disappointingly small induction (5% ee, 52.5% R, 47.5% S) with a chemical yield of 75% and reaction time of 24 h. Changing the solvent to CH_2Cl_2 increased the optical yield (28% ee). The induction was improved further by systematically varying the ester group on the protected glycine substrate. Best results (56% ee) were obtained (eq 1) by using the *tert*-butyl ester Schiff base **1i**;[13] a variety of benzylic-type esters as well as alkyl esters which were either less or more sterically demanding than *tert*-butyl gave poorer inductions.



1 R-4 S-4 (1)

The potential for preparing *either enantiomer of 4* by simply changing the catalyst from the cinchonine (**3**) to the cinchonidine (**5**)[14] series was explored next. Catalyst **5a** (R′ = H)[12] gave 56% ee of the *S* enantiomer ((*S*)-**4**), while the quinine-derived catalyst **5b** (R′ = OMe) gave only 20% ee of (*S*)-**4**. These results prompted use of the less expensive cinchonine catalyst **3b** (R = H, X = Cl),[12] which gave inductions (56% ee, (*R*)-**4**) equivalent to those using catalyst **3a**.



5a (R′=H)
5b (R′=OMe)

Several other variables were studied by alkylation of substrate **1i** using catalyst **3b** in CH_2Cl_2.[10] (a) Increasing the concentration of aqueous base resulted in both an increase in optical yield and a decrease in reaction time, % aqueous NaOH (% ee (*R*)-**4**, time): 17% (56% ee, 16+ h), 33% (59% ee, 8 h), 50% (65% ee, 4 h). (b) Using 50% aqueous NaOH as base the best leaving group is bromide, allyl-X (% ee (*R*)-**4**, time): allyl-Cl (34% ee, 12 h), allyl-Br (65% ee, 4 h), allyl-I (44% ee, 5 h). (c) Changing the concentration of **1i** in CH_2Cl_2 from 0.04 to 0.64 molar shortened the reaction time (24 to 1 h, respectively). (d) The amount of catalyst can be reduced to 10% (0.1 equivalent), and (e) it is best to use 20 equiv of base.

Finally a variety of alkyl halide types can be used: allylic, benzylic, methyl, and primary alkyl halides (eq 2). The resulting

(4) Recent lead reference involving stoichiometric auxiliaries in the asymmetric synthesis of α-amino acids by C_α–H bond formation ("deracemization"): Duhamel, L.; Duhamel, P.; Fouquay, S.; Eddine, J. J.; Peschard, O.; Plaquevant, J.-C.; Ravard, A.; Solliard, R.; Valnot, J.-Y.; Vincens, H. *Tetrahedron* **1988**, *44*, 5495–5506, and cited references.

(5) Recent lead references involving stoichiometric auxiliaries in the asymmetric synthesis of α-amino acids by C_α–N bond formation: (a) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F., Jr. *Tetrahedron* **1988**, *44*, 5525–5540. (b) Oppolzer, W.; Moretti, R. *Tetrahedron* **1988**, *44*, 5541–5552. (c) Guanti, G.; Banfi, L.; Narisano, E. *Tetrahedron* **1988**, *44*, 5553–5562. (d) Cardani, S.; Bernardi, A.; Colombo, L.; Gennari, C.; Scolastico, C.; Venturini, I. *Tetrahedron* **1988**, *44*, 5563–5572, and cited references.

(6) (a) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106–112. (b) Ito, Y.; Sawamura, M.; Shirakawa, E.; Hayashizaki, K.; Hayashi, T. *Tetrahedron* **1988**, *44*, 5253–5262. (c) Genêt, J.-P.; Jugé, S.; Achi, S.; Mallart, S.; Montès, J. R.; Levif, G. *Tetrahedron* **1988**, *44*, 5263–5275.

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(8) Other syntheses of amino acid derivatives involving phase-transfer reactions: (a) Schöllkopf, U.; Hoppe, D.; Jentsch, R. *Chem. Ber.* **1975**, *108*, 1580–1592. (b) Beck, W.; Girnth, M. *Chem. Ber.* **1976**, *109*, 965–969. (c) Schöllkopf, U.; Hausberg, H. H.; Hoppe, I.; Segal, M.; Reiter, U. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 117–119. (d) Juliá, S.; Ginebreda, A.; Guixer, J. *Chem. Commun.* **1978**, 742–743. (e) Landini, D.; Montanari, F.; Rolla, F. *Synthesis* **1979**, 26–27. (f) Kolodziejczyk, A. M.; Arendt, A. *Polish J. Chem.* **1980**, *54*, 1327–1329. (g) Gelmi, M. L.; Pocar, D.; Rossi, L. M. *Synthesis* **1984**, 763–765. (h) Belokon', Y. N.; Chernoglazova, N. I.; Kochetkov, C. A.; Garbalinskaya, N. S.; Belikov, V. M. *Chem. Commun.* **1985**, 171–172. (i) Bram, G.; Galons, H.; Farnoux, C. C.; Miocque, M. *Pharmazie* **1987**, *42*, 199; *Chem. Abstr.* **1988**, 108:112906e. (j) Yu, L.; Wang, F. *Gaodeng Xuexiao Huaxue Xuebao* **1987**, *8*, 336–340; *Chem. Abstr.* **1988**, 108:112909h. (k) Jiang, Y.; Zhou, C.; Wu, S.; Chen, D.; Ma, Y.; Liu, G. *Tetrahedron* **1988**, *44*, 5343–5353, and cited references.

(9) (a) Dolling, U.-H.; Davis, P.; Grabowski, E. J. J. *J. Am. Chem. Soc.* **1984**, *106*, 446–447. (b) Hughes, D. L.; Dolling, U.-H.; Ryan, K. M.; Schoenewaldt, E. F.; Grabowski, E. J. J. *J. Org. Chem.* **1987**, *52*, 4745–4752, and cited references.

(10) Typical experimental conditions for exploratory studies: **1** (1 mmol), RX (1.2–5 equiv), catalyst (0.2 equiv), aqueous NaOH (20 equiv), solvent (10 mL). Asymmetric inductions were determined directly by using chiral HPLC with a Pirkle column. Products were then worked up (chemical yield 60–90%). Absolute configuration of products were determined by correlation with commercial or authentic samples.[11]

(11) Samples of both enantiomers of 4-chlorophenylalanine and 2-naphthylalanine were kindly provided by Dr. M. Karten of the National Institutes of Health and Dr. P. N. Rao of the Southwest Foundation for Biomedical Research.

(12) The following cinchona derived catalysts are available commercially (Fluka): **3a**, **3b** and **5a**.

(13) Starting substrate **1i** is readily prepared[7d] from benzophenone imine (Aldrich or Pickard, P. L.; Tolbert, T. L. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, pp 520–522) and glycine *tert*-butyl ester hydrochloride (Sigma or Moore, A. T.; Rydon, H. N. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, pp 586–589).

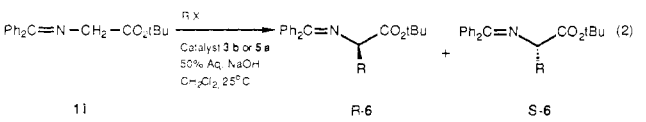
(14) (a) Wynberg, H. *Recl. Trav. Chim.* **1981**, *100*, 393–399. (b) Wynberg, H. CHEMTECH **1982**, 116–121.

Table II. Asymmetric PTC Alkylation of **1i** with Various Alkyl Halides[a]

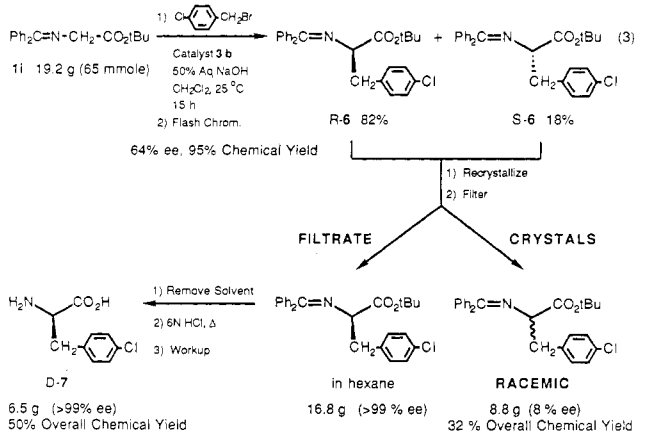
RX	equiv	6	major enantiomer	% ee (% R, % S)	chemical yield (%)	time (h)
CH_2=$CHCH_2Br$	5	**6a**	R	66 (83, 17)	75	5
CH_2=$CHCH_2Br$[b]	5	**6b**	S	62 (19, 81)	78	5
$PhCH_2Br$	1.2	**6c**	R	66 (83, 17)	75	9
$PhCH_2Br$[b]	1.2	**6d**	S	64 (18, 82)	85	9
MeBr	5	**6e**	R	42 (71, 29)	60[c]	24
n-BuBr	5	**6f**	R	52 (76, 24)	61	14
4-Cl-$C_6H_4CH_2Br$	1.2	**6g**	R	66 (83, 17)	81	12
4-Cl-$C_6H_4CH_2Br$[b]	1.2	**6h**	S	62 (19, 81)	82	12
2-naphthylCH_2Br[d]	1.2	**6i**	R	54 (77, 23)	82	18
2-naphthylCH_2Br[b,d]	1.2	**6j**	S	48 (26, 74)	81	18

[a] Unless otherwise noted, all reactions were conducted using catalyst **3b** (0.1 equiv).[10] [b] Reactions using catalyst **5a** (0.1 equiv). [c] Quantitative yield of a 60:40 mixture (TLC) of product **6** and starting material **1i**. [d] Product hydrolyzed to amino acid and induction determined by HPLC of GITC derivative.[15]

products are formed in up to 66% ee and either enantiomer is available by simply changing the PTC catalyst.



Methods for the separation of product enantiomers are important in any asymmetric synthesis which is less than 100% stereoselective. Known methods of resolution, either enzymatic[16] or classical,[17] could be employed on derivatives of a particular α-amino acid. We are, however, interested in a *general* method by which one or the other enantiomer of a product such as **6** could be purified directly following asymmetric alkylation. A single example illustrates the potential of such methodology. Stereoselective alkylation of **1i** (19.2 g) with 4-chlorobenzyl bromide and catalyst **3b**, followed by removal of racemic product [(±)-**6**] by a single recrystallization,[18] and then deprotection gave 4-chloro-D-phenylalanine (D-**7**, 6.5 g) in >99% ee![19]



In summary, a systematic study of substrate, catalyst, reagents, and reaction conditions has led to a simple, stereoselective synthesis of α-amino acid derivatives using chiral phase-transfer catalysis. Research continues toward increasing optical yields and understanding the origin of the optical induction in this important reaction.

Acknowledgment. We gratefully acknowledge the National Institutes of Health (GM 28193) for support of this research. Support for our ongoing collaboration with the laboratory of Prof. L. Ghosez in Belgium by the North Atlantic Treaty Organization is acknowledged. We also thank Dr. W. L. Scott and Prof. P. L. Fuchs for helpful discussions.

Supplementary Material Available: Full experimental details and HPLC spectra for the conversion of **1i** to 4-chloro-D-phenylalanine (D-**7**) in >99% ee (5 pages). Ordering information is given on any current masthead page.

(15) Nimura, N.; Ogura, H.; Kinoshita, T. *J. Chromatogr.* **1980**, *202*, 375-379.

(16) Yamada, H.; Shimizu, S. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 622-642.

(17) Jacques, J.; Collet, A.; Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley-Interscience: New York, 1981.

(18) (a) "...racemic compound crystals are generally more stable than enantiomer crystals." Reference 17, p 28. (b) For a recent example, see: Bhattacharya, A.; Dolling, U.-H.; Grabowski, E. J. J.; Karady, S.; Ryan, K. M.; Weinstock, L. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 476-477.

(19) Products **6h**, **6i**, and **6j** can also be prepared in high % ee using this technique.

Phenyl- and Mesitylynol: The First Generation and Direct Observation of Hydroxyacetylenes in Solution

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Hydroxyacetylenes or ynols, **1**, are the triple bond analogues of enols, **2**, and, like enols, are tautomers of carbonyl compounds, in this case ketenes, **3**. Unlike enols, however, whose chemistry

RC≡COH RCH=CHOH RCH=C=O
1 **2** **3**

is currently undergoing vigorous exploration,[1] very little is known about ynols. The first direct observation of an ynol was in fact made only 3 years ago: the parent substance, hydroxyacetylene was generated in the gas phase and was characterized by its mass spectrum.[2,3] Very recently, it was prepared again, in an argon matrix, by photodecarbonylation of hydroxycyclopropenone, and was identified there by its infrared spectrum.[4] We now report that this reaction may also be employed to generate ynols in

(1) See, e.g.: (a) Kresge, A. J. *L' Actualitē Chim.* **1988**, 233-240. CHEMTECH **1986**, *16*, 250-254. (b) Capon, B.; Guo, B.; Kwok, F. C.; Siddhanta, A.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 137-140. Rappoport, Z.; Biali, S. E. *Acc. Chem. Res.* **1988**, *21*, 442-449. Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1-77.

(2) von Baar, B.; Weiske, T.; Terlouw, J. K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 282-284.

(3) Hydroxyacetylene has also been characterized by high level ab initio MO calculations, see: Bouma, W. J.; Nobes, R. H.; Radom, L.; Woodward, C. E. *J. Org. Chem.* **1982**, *47*, 1869-1875, and references cited therein.

(4) Hochstrasser, R.; Wirz, J. *Angew. Chem.* **1989**, *101*, 183-185.

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