actions or redox processes should be possible. The properties of the metal complex, quencher, and substrate should be widely tunable to achieve reagents of varying strength, solubility, and selectivity; the possibilities here are indicated by the rather pronounced differences in redox potential, solubility, and reactivity observed between **1** and **2** by a rather small modification of the ligand. Experiments are underway to determine the scope and products formed with other substrates and solvents.

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Patricia J. DeLaive, Charles Giannotti,* David G. Whitten*
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514, and
Institut de Chimie des Substances Naturelles, C.N.R.S.
91190 Gif-sur-Yvette, France

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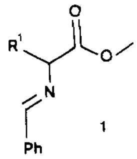
Deracemization by Enantioselective Protonation. A New Method for the Enantiomeric Enrichment of α-Amino Acids

Sir:

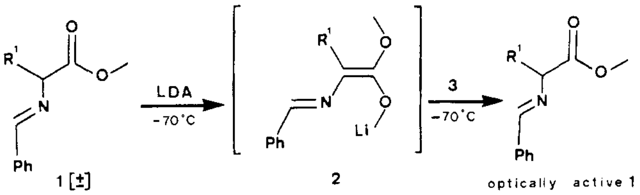
Optically active α-amino acids are generally obtained by separation of peptide hydrolysates, resolution of synthetic racemates, asymmetric synthesis,[1] or, less frequently, by spontaneous crystallization of one chiral form with an optically active acid.[2] We report a new method for the enantiomeric enrichment of α-amino acids, based on the principle of deracemization by enantioselective protonation, a technique essentially applied to carbonyl compounds.[3] The protonation of enolates **2** of racemic Schiff base esters **1** by an optically active acid **3** gives the optically active Schiff base **1** with enantiomeric ratio as high as 81:19 (62% ee).

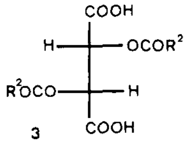


1

1a, R^1 = Ph
b, R^1 = $PhCH_2$
c, R^1 = 3-indolylmethyl
d, R^1 = *i*-Pr

The Schiff base methyl esters **1** are readily available in two steps from the corresponding α-amino acids in almost quantitative yields.[4] They are converted by lithium diisopropylamide to the corresponding anions **2**, according to reported procedure.[5] We have treated anions **2** by various (2*R*,3*R*)-diacyltartaric acids **3**;[6] the products of the reaction are optically active Schiff base esters **1** (Table I). Hydrolysis of the Schiff base esters **1** to the corresponding amino ester or amino acid can easily be effected without racemization and with good yields.[5] The acids **3** can easily be retrieved after protonation with an excellent yield and with conservation of enantiomeric purity.





3

3a, R^2 = *t*-Bu
b, R^2 = *t*-$BuCH_2$
c, R^2 = *t*-$Bu(CH_2)_2$
d, R^2 = Ph
e, R^2 = $PhCH_2$
3f, R^2 = $Ph(CH_2)_2$
g, R^2 = $(CH_3)_2CBr$
h, R^2 = cyclohexyl
i, R^2 = β-styryl
j, R^2 = 1-adamantyl

In a typical experiment, 0.885 g of (±)-methyl *N*-benzylidenephenylglycinate (**1a**, 3.5 mmol) in 6 mL of dry tetrahydrofuran was added under nitrogen at −70 °C to lithium diisopropylamide (5 mmol) prepared from 3.12 mL of a solution of *n*-butyllithium (1.6 M in hexane (5 mmol)) and 0.5 g of diisopropylamine (5 mmol) in 15 mL of dry tetrahydrofuran. After 5 min, protonation was carried out at −70 °C by addition of a solution of 3.18 g of dipivaloyltartaric acid (**3a**, 10 mmol) ($[\alpha]^{25}_D$ −24.1° (*c* 2, dioxane)) in 10 mL of dry tetrahydrofuran. The reaction was continued at −70 °C during a period of 15 min. The homogeneous reaction mixture was allowed to warm to room temperature; the solution was washed once with 10% aqueous sodium bicarbonate and with water. A usual workup gave the crude product, which was recrystallized in hexane (85% yield, $[\alpha]^{25}_D$ −41.9° ($CHCl_3$), *S* configuration). The diacyltartaric acid **3a** was obtained from the aqueous layer

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Table I. Enantioselective Protonation of Enolates **2** of Schiff Base Methyl Esters **1** by Diacyltartaric Acids **3**

racemic Schiff base	acid	active Schiff base: obsd $[\alpha]^{25}_D$,[a] deg, in $CHCl_3$ (c)	enantiomeric ratio S:R	chemical yield,[e] %
1a	**3a**	−41.9 (3.3)	79:21[b,c]	85
	3b	−13.6 (3.4)	59:41	84
	3c	−28.2 (3.3)	70:30	82
	3d	−10.3 (3)	57:43	80
	3e	−6.95 (2.4)	55:45	81
	3f	−5.36 (3)	54:46	83
	3g	−28.96 (3.3)	70:30	85
	3h	−30.1 (2)	71:29	85
	3i	−21.1 (3.3)	65:35	86
	3j	−44.7 (1.5)	81:19	79
1b	**3a**	−66.15 (2.4)	63:37	65
	3b	−19.6 (3.1)	54:46	64
	3c	−43.36 (4)	59:41	65
	3d	−82.06 (4)	67:33	60
	3e	−36.75 (3.3)	57:43	61
	3f	−7.35 (2.5)	51:49	64
1c[d]	**3a**	−88.45 (2.5)	65:35	95
	3b	−31.03 (2)	55:45	93
	3c	−42.34 (2.4)	57:43	92
	3d	−36.54 (2.8)	56:44	90
	3e	−11 (2.2)	52:48	95
	3f	−20.3 (2)	53:47	95
1d	**3a**	−43.55 (4.5)	67:33[c]	82
	3d	−50.05 (2.6)	69:31[c]	76
	3h	−45.5 (4.5)	67:33	80

[a] References ($CHCl_3$) (this work): **1a,** *R*, $[\alpha]^{25}_D$ +71.5° (c 3); **1b,** *S*, $[\alpha]^{25}_D$ −245° (c 4) **1c,** *S*, $[\alpha]^{25}_D$ −290° (c 3); **1d,** *S*, $[\alpha]^{25}_D$ −130° (c 4). All rotations were measured in a 1-mL cell (10 cm) on a Perkin-Elmer Model 241 polarimeter. [b] This corresponds to an enantiomeric excess (% ee) of 58%. [c] These results were confirmed by NMR analysis in the presence of tris(3-heptafluoropropylhydroxymethylene)-D-camphoratoeuropium. The signals followed were PhC*H* for **1a** and $COOCH_3$ for **1d.** The corresponding racemic products gave two equal signals in the same conditions, while the optically pure products gave a single one. [d] One equivalent of *N*-benzylidenetryptophan methyl ester is treated by 2.5 equiv of LDA, and then by 3.5 equiv of diacyltartaric acid. [e] The chemical yields correspond to recrystallized product for **1a, 1b,** and **1c,** and to crude product for **1d.**

after acidification (95% yield, $[\alpha]^{25}_D$ −24.1° (c 2, dioxane)).

Our results show that the enantiomeric ratios of Schiff base esters **1** are largely affected by the structure of the acid **3** used for the protonation. The asymmetry of the reaction seems to be favored by the proximity of the hindering group contained in R^2 and the carboxyl group. On the other hand, enantiomeric enrichment does not decrease gradually when the distance between the hindering group and the carboxyl group increases.

The present method is simple and versatile. It has the advantages of giving Schiff base esters **1** in good enantiomeric purity in the best cases from their racemic mixture in a one-pot reaction, which would allow easy preparation of optically active α-amino acids, as well as easy recovery of the chiral reagent **3** for reuse without any racemization. Further studies are in progress.

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Lucette Duhamel,* Jean-Christophe Plaquevent
Laboratoire de Chimie Organique de la Faculté
des Sciences et des Techniques de Rouen
76130 Mont Saint Aignan, France

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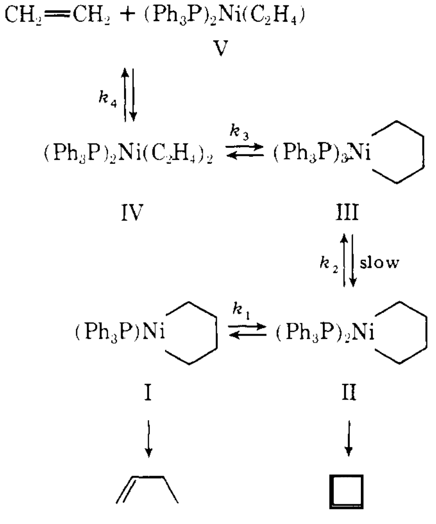
Metallacyclopentanes as Catalysts for the Linear and Cyclodimerization of Olefins

Sir:

Transition metals can catalyze the dimerization of olefins to either cyclo-[1] or linear[2] dimers. Linear dimers are produced by a large number of catalytic systems while only very specific catalysts have been observed to cyclodimerize strained olefins.[3] Cyclodimers have not been observed from simple, unstrained unsaturated hydrocarbons. In most cases, the linear dimers are the result of metal hydride catalysts,[2,4,5] while cyclodimerization appears to proceed through metallacyclopentane intermediates.[6]

We recently reported that phosphine nickelacyclopentanes decomposed to produce cyclobutane, ethylene, or 1-butene depending on the coordination number of the complex[7] and that a bisethylene complex was in equilibrium with the metallacycle.[8]



These observations suggested that the nickelacyclopentane III might be a catalyst for the formation of dimers from ethylene.

Consequently, when tris(triphenylphosphene)tetramethylenenickel(II) (III) was dissolved in toluene and treated with ethylene (80 psi), cyclobutane[9] and butenes were formed. As can be seen in Table I, the products were produced catalytically. Since the production of the proposed reaction interme-

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