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Convenient Synthesis of Chiral *trans*-2-Phenylcyclopropanecarboxylic Acid

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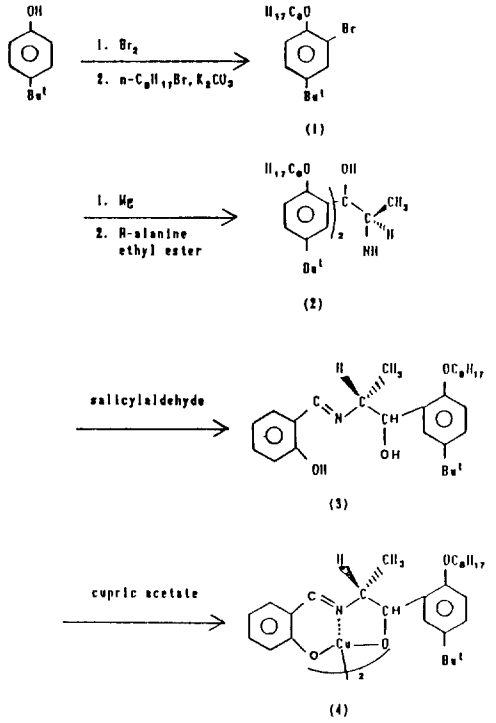
(−)-(1R, 2R) and (+)-(1S, 2S)-menthyl-*trans*-2-phenylcyclopropanecarboxylate have been synthesized with the aid of chiral Cu(II) complex catalyst by the addition reaction of *l*-menthyldiazoacetate to styrene. The yield was 75%, with the purity of trans isomer over 95% and the optical purity of 95%.

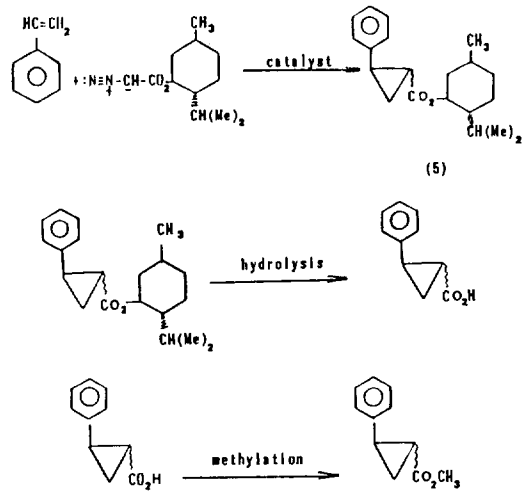
Introduction

For the syntheses of chiral cyclopropane derivatives have been utilized the reactions[1,2] of olefine with stoichiometric amounts of chiral sulfonium yildes, the Simmons-Smith reaction[3-5] (CH_2X_2/Zn) employing chiral substrates, or catalytic olefin cyclopropanation[6-11] with diazoalkanes under the influence of chiral metal complexes. The most desirable enantioselectivity has been achieved through asymmetric carbenoid reactions of diazo compounds catalyzed by bis(α-camphorquinonedioximato)cobalt (II) complex. Despite the high enantioselectivity, the cobalt catalyst system produced two geometrical isomers, *cis* and *trans*-2-phenylcyclopropanecarboxylate, in roughly comparable amounts. Chiral copper catalyst[8] was reported to show less enantioselectivity comparing with the cobalt catalyst, but it mainly produced trans isomer.

Thus, we decided to synthesize *trans*-2-phenylcyclopropanecarboxylic acid utilizing the copper catalyst. The synthesis of an optically active copper catalyst was patterned after the work of Aratani, Yoneyshi and Nagase on asymmetric synthesis of chrysanthemic acid. 2-Bromo-4-*tert*-butylphenyl *n*-octyl ether (**1**) was given by monobromination[12] of 4-*tert*-butylphenol followed by alkylation[13] with *n*-octyl bromide using potassium carbonate in acetone. The corresponding Grignard reagent was allowed to react[14] with (R)-alanine ethyl ester in tetrahydrofuran to give (2R)-1,1-diaryl-2-amino-1-propanol (**2**). This primary amine was condensed with salicylaldehyde (benzene, *p*-toluenesulfonic acid) to afford a salicylaldimine (**3**) as a bright yellow oil. When this imine was treated with cupric acetate and aqueous sodium hydroxide in ethanol, there was obtained copper complex (**4**) as a viscous, dark green oil.

In the presence of this chiral copper catalyst, the addition reaction of *l*-menthyl diazoacetate to styrene produced a mixture of *cis* and *trans* ester (**5**). To measure the ratio of *trans* to *cis* isomer and the optical purity, NMR spectroscopy was employed after conversion to the methyl esters. The sequence of steps[15] used to convert menthyl esters to the corresponding methyl esters is outlined in Scheme 1. The ratio





(5)

Scheme 1

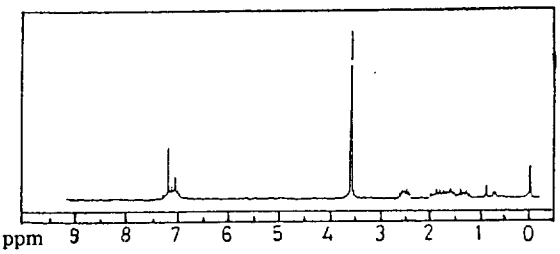


Figure 1. Proton Magnetic Resonance of Methyl *cis* and *trans*-2-Phenylcyclopropanecarboxylate Obtained *via* the Addition Reaction of *l*-Menthyldiazoacetate to Styrene Catalyzed by Cupric Sulfate as an Achiral Copper Catalyst.

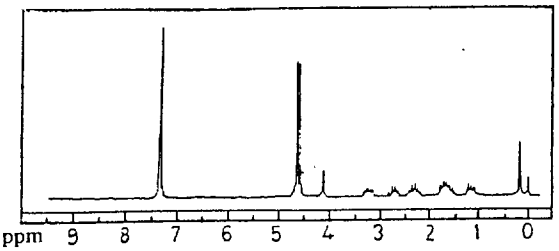


Figure 2. Proton Magnetic Resonance Taken in the Presence of Eu(hfc)$_3$, of Methyl *trans*-2-Phenylcyclopropanecarboxylate Racemate Obtained *via* the Addition Reaction of *l*-Menthyldiazoacetate to Styrene Catalyzed by Cupric Sulfate as an Achiral Copper Catalyst.

of *trans* to *cis* isomer was determined by the integrations of methyl groups on the mixtures of *cis* and *trans* methyl esters. The optical purity also was evaluated by means of the integrations of methyl groups in the presence of optically active chemical shift reagent Eu(hfc)$_3$.[16]

To test the asymmetric induction via the *l*-menthyl diazoacetate we tried the addtion reaction in the presence of copper(II) sulfate as an achiral catalyst. The methyl *trans*-2-phenylcyclopropanecarboxylate was formed in purities as high as 98%, but it was recemic mixture. The chemical shift of 3.7ppm[15,17] in Figure 1 presents the methyl group of methyl *trans*-2-phenylcyclopropanecarboxylate. Figure 2 shows proton magnetic resonance of methyl group in methyl *trans*-2-phenylcyclopropanecarboxylate equally separated in-

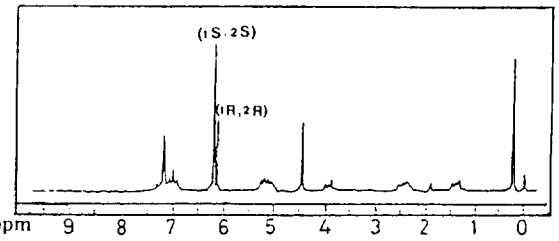


Figure 3. Proton Magnetic Resonance Taken in the Presence of Eu(hfc)$_3$, of Methyl *cis* and *trans*-2-Phenylcyclopropanecarboxylate Obtained *via* the Addition Reaction of *l*-Menthyldiazoacetate to Styrene Catalyzed by (R)-Copper Catalyst.

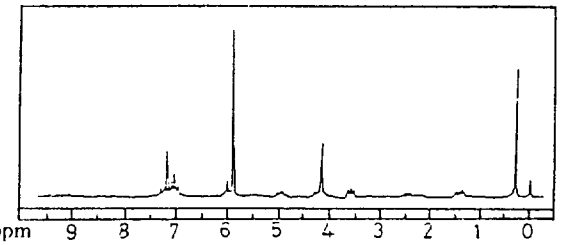


Figure 4. Proton Magnetic Resonance Taken in the Presence of Eu(hfc)$_3$, of Methyl *cis* and *trans*-2-Phenylcyclopropanecarboxylate Obtained *via* the Addition Reaction of *l*-Menthyldiazoacetate to Styrene Catalyzed by Optically Active (S)-Copper Catalyst.

to two different methyl chemical shifts in the presence of Eu(hfc)$_3$. Similar asymmetric induction[15] was reported in the addition of *l*-menthyl diazoacetate to styrene catalyzed by copper(I) chloride (homogeneous solution).

The chirality of copper catalyst is derived from the stereochemistry of alanine ethyl ester. The chiral copper catalyst ((R)-copper catalyst), started from (R)-alanine ethyl ester, induced mainly to produce the (+)-antipode, (1S, 2S)-*trans*-2-phenylcyclopropanecarboxylate as shown in Figure 3. Figure 3 represents the proton magnetic resonance of methyl *cis* and *trans*-2-phenylcyclopropanecarboxylate in the presence of (hfc)$_3$, which was made via the catalytic addition of *l*-menthyl diazoacetate to styrene utilizing the optically active (R)-copper catalyst. The more downfield chemical shift of methyl group represents methyl group in (1S, 2S)-methyl-*trans*-2-phenylcyclopropanecarboxylate. This assignment of the absolute configurations has been established by comparison with the optical rotation[18] of (+) and (–)-methyl-*trans*-2-phenylcyclopropanecarboxylate. Similarly, the same catalyst of the opposite configuration (S)-copper catalyst) attained from (S)-alanine ethyl ester, aided predominantly to produce the (–)-antipode, (1R, 2R)-*trans*-2-phenylcyclopropanecarboxylate as shown in Figure 4.

The direction of asymmetric induction was found to depend upon only the absolute configuration of the chiral ligand in copper(II) catalyst. However, the optically active copper catalysts do not have much influence on the ratio of *trans* to *cis* isomer as shown in Table 1. The optical purity is dependent on the concentration of the chiral copper catalyst as shown in Table 1. The chemical yield, however, remains about the same at the various concentrations of the catalyst.

(+)-(1S, 2S) and (–)-(1R, 2R)-2-*trans*-phenylcyclopropanecarboxylate can be synthesized utilizing the chiral copper catalyst according to configuration of the chiral ligand in

Table 1. Effect of the Concentration of the Chiral Copper Catalyst on the Ratios of Trans to Cis Isomer and Optical Purities of Trans Isomer

Configuration of Chiral Copper Catalyst	Concentrations of Copper Catalyst (%)	Yield of Menthyl Ester (%)	Trans Isomer (%)	Configuration and Optical Purities (%) of Trans Isomer
$CuSO_4$	4.90	70	98	recemic mixture
R	0.65	71	90	80(1S, 2S)
S	1.30	76	98	95(1R, 2R)
R	1.30	72	95	98(1S, 2S)
R	3.50	69	98	95(1S, 2S)

[a] *l*-Menthyl diazoacetate was 1.6 equivalent excess to styrene. The concentration of copper catalyst is the percent to the moles of *l*-menthyl diazoacetate. [b] The percents of trans isomers were measured by pmr integrations of methyl groups of methyl *cis* and *trans*-2-phenylcyclopropanecarboxylate. [c] The percents of optical purity were measured by pmr integrations of methyl groups of methyl *cis* and *trans*-2-phenylcyclopropanecarboxylate in the presence of $Eu(hfc)_3$.

purities as high as 98%. The concentration of copper catalyst is required more than 1.3%. This novel pattern of selectivity may be interpreted in terms of carbomenthoxy carbene-copper complex intermediate,[19] in which a chiral ligand controls the orientation of an approaching styrene. Menthyl diazoacetate attacks the vacant site of chiral copper catalyst from the less hindered side to give a carbomenthoxy carbene-copper complex while evolving the nitrogen gas.

Experimental

^1H NMR spectra were taken on a Varian EM-360 instrument using $CDCl_3$ solutions. The chemical shifts were reported in ppm downfield from tetramethylsilane. Optical rotations were recorded on Jasco DIF 140 polarimeter.

2-Bromo-4-*tert*-butylphenol. Bromination[12] of 4-*tert*-butylphenol (15g, 0.1mole) with bromine (16g, 0.1mole) in chloroform and carbontetrachloride (25m*l*+25m*l*) gave 22.4g (98%) of product (95°C/2mmHg).

2-Bromeo-4-*tert*-butylphenyl *n*-Octyl Ether (1). The phenol (9.16g, 0.04mole) was alkylated[13] with *n*-octyl bromide (8.49g, 0.044mole) using potassium carbonate (5.66g 0.04mole) in acetone (30m*l*). Kugelrohr distillation at 165-170°C/2mmHg gave 10.9g (80%) of ether.

(2R)-2-Amino-1,1-bis(4-*tert*-butyl-2-*n*-octyloxyphenyl)-1-propanol(2). (R)-Alanine ethyl ester hydrochloride (2.32g, 15.1 mmole) was allowed to react[14] with the Grignard reagent derived from 2-bromo-4-*tert*-butylphenyl *n*-octyl ether (25.8g, 75.6 mmole) in refluxing tetrahydrofuran. Normal work-up was followed. Most of the unreacted starting material and side products of 4-*tert*-butylphenyl octyl ether were removed by distillation at reduced pressure. The residue was column-chromatographed with benzene on 70-230 mesh silica gel to give 2.6g (39%) of amino alcohol as a clear viscous oil.

Salicylaldimine (3). Amino alcohol (2) (1.8 mmole, 1.1g) and salicylaldehyde (2 mmole, 0.24g) were refluxed for 4 hrs in benzene with a catalytic amount of *p*-toluenesulfonic acid monohydrate while water was removed azeotropically. Concentration of the benzene solution and column chromatography (70-230 mesh silica gel, ether: benzene = 2:1) gave 0.84g (65%) of salicylaldimine as a bright yellow oil.

(+)-(R)-Copper(II) Complex[8] of Aldimine (4). Salicylaldimin (3) (0.3 mmole, 0.2g) and cupric acetate monohydrate (0.3 mmole, 0.06g) were dissolved in 70m*l* ethanol. Aqueous sodium hydroxide (10%, 5m*l*) was added and the mixture was stirred for 1hr. The solution was diluted with water and extracted three times with benzene. The benzene extracts were dried (K_2CO_3), filtered, and concentrated to produce a dark-green oil. Column chromatographicseparation (silica gel 70-230 mesh, $CHCl_3$) gave 0.2g (98%) of copper complex.

1-Menthyl Glycinate[20]. Glycine (13g, 0.17mole), *l*-menthol (0.2 mole, 31.2 g) and *p*-toluenesulfonic acid monohydrate were refluxed in benzene until the theoretical amount of water was collected in Dean-Stark trap. The reaction mixture was cooled, filtered, and washed with aqueous saturated sodium bicarbonate to remove acidic material. The reaction mixture was washed again with water and brine, dried ($MgSO_4$), and filtered. Kugelrohr distillation at 90°C (50 mmHg) gave 10g (49%) of *l*-menthyl glicynate.

1-Menthyl diazoacetate[21]. A benzene solution of menthyl glycinate (42 mmole, 5.9 g), acetic acid (12 mmole, 0.73 g) and isoamyl nitrite (46 mmole, 5.6 g) were heated to reflux for 6 hrs, until a positive ninhydrin test was no longer obtained. The reaction mixture was cooled and washed in sequence with cold 10% sulfuric acid, ice water, cold saturated sodium bicarbonate, again with ice water, and finally with cold brine. It was then dried (Na_2SO_4), filtered, and concentrated. The column chromatographic separation (70-230 mesh silica gel, benzene) gave 7.0 g (75%) of *l*-menthyl diazoacetate.

(−)-(1S, 2S)-Menthyl-*trans*-2-phenylcyclopropanecarboxylate. The copper catalyst (**4**) (0.2 g, 0.27 mmole) was added to styrene (1.25 g, 12 mmole) in 10 m*l* of cyclohexane. Under nitrogen atmosphere the solution was heated to reflux as *l*-menthyl diazoacetate (4.5 g, 20 mmole) in 8 m*l* of cyclohexane was added dropwise over a period of 8 hrs.[8] The reaction mixture was cooled and concentrated. The residue was subjected to Kugelrohr distillation (150°C, 0.1 mmHg) to afford 2 g (72%) of ester.

(+)-(1S, 2S)-*trans*-2-Phenylcyclopropanecarboxylic acid[15]. The ester prepared above (5.0 g, 17 mmole) was heated to reflux overnight with 30 m*l* ethanol and 35 m*l* of 50% aqueous sodium hydroxide. When the solution was cooled, it was extracted with ether to remove menthol. The aqueous phase was acidified with concentrated hydrochloric acid and extracted with ether. This ether extract was washed with brine, dried ($MgSO_4$), filtered, and concentrated. This residue was 2.4 g (90%) of (+)-(1S, 2S)-*trans*-2-phenylcyclopropanecarboxylic acid. This was methylated with diazomethane. The ratio of *trans* to *cis* isomer was 98: 2 determined by integrations of the methyl groups in proton magnetic resonance. This sample was shown to have an optical purity of 98% with the aid of the optically active shift reagent $Eu(hfc)_3$ in chloroform. And the optical rotation of 95% ethanolic solution was dextrorotatory.

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Syntheses and Spectroscopic Properties of Palladium(II) Complexes with Bidentate Aminophosphine of N,N-Dialkyl-N′-diphenylphosphinodiaminoethane

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Several new palladium(II) complexes of aminophosphines, ($Pd(L)X_2$), ($L = Ph_2PNH \sim NR_2$; R = CH_3 (L_1), C_2H_5(L_2): X = Cl, Br, I, and NCS) that contain two different donor atoms of nitrogen and phosphorus as π-electron acceptor, were synthesized and characterized by conductivity measurement, ir, and UV/Vis-spectra. For the dithiocyanatopalladium(II) complexes with aminophosphines, it was confirmed that the thiocyanate group trans to phosphorus is coordinated as Pd-NCS mode and the one trans to nitrogen as Pd-SCN mode, and the aminophosphines form six-membered chelate ring. The spectra of dihalogenopalldium(II) complexes with aminophosphines show that the band maxima are shifted to the short wavelengths as the concentration is decreased.

Introduction

(N,N-dialkyl-N'-diphenylphosphino)diaminoethane can act as bidentate ligand with phosphorus and nitrogen donor atoms.

Bidentate ligands with two types of donor sites are well known and have been the subject of many reports. These ligands are of interest, because they can bridge dissimilar metals or, if one donor is easily replaced, yield complexes that readily provide a coordination site for incoming substrates.[1] For example, there are phosphines that contain a nitrogen or oxygen donor atom.[2-9]

Of the nitrogen containing phosphines, 2-(diphenylphosphino)pyridine,[2] 2-aminoalkylphosphine,[3] 3-(diphenylphosphino)-N,N-dimethylpropylamine,[4-6] 3-(diphenylphosphino)-propionitrile,[7] and o-(diphenylphosphino)benzonitrile[8] are the ligands that collectively function as chelate ligands.

In our previous work, the palladium(II) complexes, {Pd $(L)X_2$}; {L = 1,2-bis((diphenylphosphino)amino)alkane; X = Cl,Br,I, and NCS} have been synthesized and characterized, and we concluded that these complexes formed the seven-membered chelate ring.[10]

We have new synthesized several dihalogenopalladium (II) complexes with (N,N-dimethyl-N'-diphenylphosphino)di-