from oxidation of the alkyl chain by the nitric acid.[4] In the *N*-octyl system this side reaction is especially critical and when the reaction is carried out at room temperature, an extremely rapid and dangerous exothermic reaction takes place.

In summary, high yields of pure 4-nitro-*N*-methylphthalimide can be obtained from the nitration of *N*-methylphthalimide. Although the nitration of **1a** at 15–25 °C gives excellent yields of pure **2a**, we feel that it is much safer to carry out these reactions under conditions which provide for a controlled exotherm. The small amount of 3-nitro isomer which is isolated in the product under these conditions can easily be separated by methanol treatment to give pure **2a**. The nitration of *N*-ethyl- and *N*-butylphthalimide gives reaction mixtures containing primarily the corresponding 4-nitro compounds which can also be isolated by a methanol treatment although the yields of the recovered products **2** are lower than for the *N*-methyl system. The nitro group of these compounds is extremely labile to nucleophilic displacement which makes these nitro imides useful starting materials for the synthesis of a variety of new phthalimide derivatives.[5]

Experimental Section

All ^1H spectra were recorded with a Varian Associates T-60 NMR spectrometer using tetramethylsilane as an internal standard and deuteriochloroform or Me_2SO-d_6 as a solvent. All ^{13}C NMR spectra were recorded with a Varian Associates CFT-20 NMR spectrometer using complete ^1H decoupling at 79.5 MHz with simultaneous ^{13}C observation at 20.0 MHz. Chemical shifts were measured from internal tetramethylsilane or calibrated to this standard using known chemical shifts of solvent peaks. Mass spectra were determined on a CEC 21-104 analytical mass spectrometer at 70 eV. Vapor phase chromatography (VPC) was carried out on a Hewlett Packard 5750 instrument using a 6 ft 10% UC-W98 on 80/100 Chromosorb W column with temperature programming between 150 and 300 °C at 8 °C/min. Melting points were determined on a Thomas-Hoover instrument and are uncorrected.

All N-substituted phthalimides were prepared by reacting the appropriate alkylamine with either phthalic anhydride, 3-nitrophthalic anhydride, or 4-nitrophthalic anhydride in refluxing acetic acid. The structures of these imides were confirmed by ^{13}C NMR (see Supplemental Material Available paragraph), mass spectral analysis, and by a comparison of the melting points with literature values. The nitric and sulfuric acid solutions were purchased commercially and were used as received.

Analysis of the *N*-methyl system was done by both ^{13}C NMR and VPC. All other systems were analyzed only by VPC. VPC yields were obtained using an internal standard and correcting for detector response differences. Integrations were done on a Spectra Physics SP4000. The ^{13}C NMR analyses were done in Me_2SO-d_6 with the ratios of the products being determined from the average relative peak heights of the carbons for the 4 isomer at 129.4, 124.5, and 117.6 and for the 3 isomer at 136.1, 128.0, and 126.6 ppm.

Typical Nitration Procedure. The Nitration of *N*-methylphthalimide (1a). A. At Lower Temperature. A mixture of 30.8 mL of 96% sulfuric acid and 5.13 mL of 90% nitric acid was cooled to 15 °C. To this well-stirred solution was added 5.00 g of **1a** at such a rate to maintain the reaction temperature between 15 and 20 °C. When addition was complete, a clear bright yellow-orange solution was obtained. The mixture was allowed to slowly warm to room temperature and then to stand overnight at room temperature. The reaction mixture was then poured into ca. 600 mL of ice and the resulting precipitate was filtered, washed with cold water, and dried to give 5.80 g (90%) of **2a** which was pure by VPC analysis.

This reaction was repeated using 50 g of **1a** to give a crude product containing 98.5% of **2a** and 1.5% of **3a**. This material was stirred with 250 mL of methanol and filtered to give 56.53 g (88%) of pure **2a**, mp 175–176 °C (lit.[1] 177–178 °C).

B. At Elevated Temperature. A mixture of 5.0 g of **1a** and 5.28 mL of 96% sulfuric acid was heated at 70 °C with an oil bath. The bath was removed and 2.93 mL of 90% nitric acid was added at such a rate as to maintain the internal temperature at 70 °C (ca. 20 to 30 min). The reaction mixture was then heated at 70 °C for an additional 1.5 h, cooled to room temperature, and added to 200 mL of ice. The resulting precipitate was collected by filtration and dried to give 5.39 g of material. Analysis of this material by VPC showed it to consist of 92% of **2a** and 8% of **3a** for an isolated yield of 77% **2a** and 7% **3a**.

The reaction was repeated using 50 g of **1a**. The nitric acid was added over a period of ca. 100 min. Workup gave a crude product which contained 1% of **1a**, 88% of **2a**, and 11% of **3a**. This crude product was stirred with 250 mL of methanol to give 51.5 g (80.5%) of **2a** which was pure by VPC analysis, mp 175–177 °C (lit.[1] 177–178 °C).

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Registry No.—**1a**, 550-44-7; **1b**, 5022-29-7; **1c**, 1515-72-6; **1d**, 20320-48-3; **1e**, 59333-62-9; **2a**, 41663-84-7; **2b**, 55080-56-3; **2c**, 54395-37-8; **2d**, 65311-53-7; **2e**, 65311-54-8; **3a**, 2593-81-9; **3b**, 2778-84-9; **3c**, 54395-36-7; **3d**, 2593-84-2; **3e**, 2593-54-6.

Supplementary Material Available: Tabulated ^{13}C NMR chemical shifts for all the *N*-alkylphthalimides studied (1 page). Ordering information is given on any current masthead page.

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(2) Both 3- and 4-nitro-substituted phthalimides can easily be prepared from the reaction of the appropriate alkyl amine with either 3- or 4-nitrophthalic anhydride. Unfortunately, the nitration of phthalic anhydride results in an ca. 50/50 mixture of 3- and 4-nitro isomers which are very difficult to separate.
(3) E. H. Huntress and R. L. Shriner report that the nitration of phthalimide at 10–25 °C gives a 52% yield of the pure 4-nitro isomer ("Organic Syntheses", Collect. Vol. 2, John Wiley, New York, N.Y., 1943, p 459). L. F. Levy and H. Stephen (*J. Chem. Soc.*, 79 (1931)) report that if the nitration mixture is allowed to warm to 80 °C for 30 min, 78% of the pure 4-nitro isomer could be obtained.
(4) N. C. Cook and G. C. Davis have shown that some oxidation of the alkyl group takes place even when R = CH_3 (private communication, General Electric Co., Corporate Research and Development).
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Convenient Synthesis of a Highly Efficient and Recyclable Chiral Director for Asymmetric Induction

Harry E. Ensley,* [1a] Carol A. Parnell, and Elias J. Corey* [1b]

Departments of Chemistry, Tulane University, New Orleans, Louisiana 70118, and Harvard University, Cambridge, Massachusetts 02138

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Asymmetric syntheses utilizing the menthyloxy group as a chirality director have been reported frequently; however, optical yields are generally too low to be really useful.[2] Although Lewis-acid catalyzed Diels–Alder reactions of menthyl acrylate are unusually efficient (optical yields approach 80%[3]), the menthyloxy group is still far from ideal.

As a result of a study directed toward the enantioselective synthesis of intermediates useful for the preparation of naturally occurring prostaglandins we introduced the use of (1*S*,2*R*,5*S*)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexanol, (+)-**1**, which proved to be an exceptionally efficient chirality director.[4]

The reaction of the acrylate ester of (−)-**1** with cyclopentadiene afforded the *endo*-norbornenecarboxylic ester **2** in 82% yield with 99% enantiselectivity.[5] Similarly, the acrylate ester of (+)-**1**, on reaction with 5-benzyloxymethylcyclopentadiene, resulted in the formation of **3** in 89% yield and 97% enantioselectivity.[4]

The preparation of (−)-**1** in 71% yield from (*R*)-(+)-pule-

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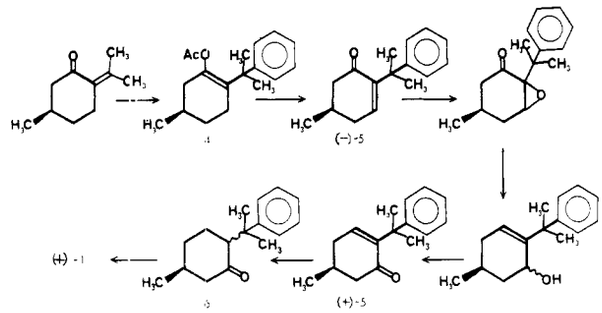
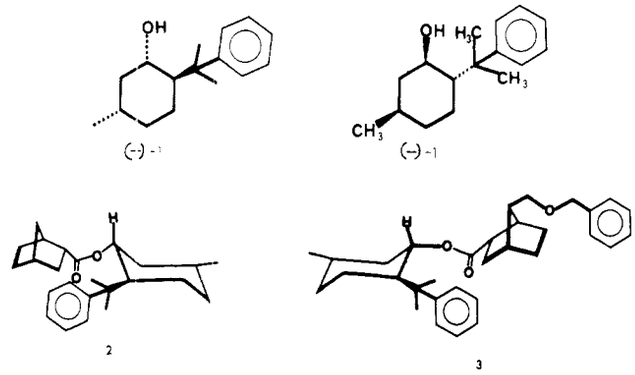
Scheme I



gone provides a convenient route to this enantiomer. Previously, (+)-1 has been prepared in an identical fashion from (*S*)-(−)-pulegone.[5] However, due to the lesser availability of (*S*)-(−)-pulegone,[6] a more convenient preparation of (+)-1 was desirable.



We report herein a convenient procedure (which is amenable to large scale reactions) for the preparation of (+)-1 directly from (*R*)-(+)-pulegone (Scheme I).

Cuprous iodide catalyzed conjugate addition of phenylmagnesium bromide to (*R*)-(+)-pulegone followed by trapping the resulting enolate with excess acetyl chloride affords a 91% yield of the enolacetate **4**.[7] Conversion of **4** to the desired α-bromo ketone (as an epimeric mixture) could be accomplished by regiospecific generation of the lithium enolate followed by addition of bromine[8] (88% yield) or more conveniently by direct bromination of **4** in methylene chloride at −78 °C (89% yield).[9] Treatment of the α-bromo ketone with a slurry of lithium bromide and sodium carbonate in refluxing dimethylformamide[10] gave an 89% yield (from **4**) of the α,β-unsaturated ketone (−)-**5**. Conversion of (−)-**5** to its enantiomer was accomplished in 78% yield by base-catalyzed epoxidation with hydrogen peroxide,[11] treatment with hydrazine in the presence of a catalytic amount of acetic acid,[12] and in situ Collins' oxidation[13] of the allylic alcohol. Birch reduction of (+)-**5** followed by Jones oxidation affords **6** as a 1:1 mixture of cis and trans isomers in 85% yield. Base treatment of the ketones gives an equilibrium mixture comprised of 85% trans and 15% cis forms. Reduction of this mixture with sodium in isopropyl alcohol produces (+)-1 in 91% yield.

Experimental Section

(5R)-1-Acetoxy-2-(1-methyl-1-phenylethyl)-5-methylcyclohexene (4). A slurry of 5.8 g (0.03 mol) of purified cuprous iodide in 70 mL of ether was cooled to −20 °C and treated with 300 mL (0.45 mol) of 1.5 M phenylmagnesium bromide. The resulting solution was stirred at −20 °C for 15 min and a solution of 40 g (0.263 mol) of (*R*)-(+)-pulegone, $[\alpha]^{23}D$ +24° (*c* 2, EtOH), in 100 mL of ether was added dropwise at −20 °C. After the addition, the reaction mixture was stirred for 3 h at 25 °C. The reaction mixture was cooled to −20 °C and a solution of 100 g (1.27 mol) of acetyl chloride in 250 mL of ether was added dropwise. The solution was stirred for 1 h at 0 °C and overnight at 25 °C and then poured into 2 L of ice-cold, saturated ammonium chloride. The mixture was filtered, the organic layer was separated, and the aqueous layer was extracted with 300 mL of ether. The combined organic layers were dried (Na_2SO_4) and evaporated and the residue was distilled at reduced pressure to give 64.8 g (0.238 mol, 90%) of **4**: bp 106–110 °C (0.3 mm); $[\alpha]^{22}D$ +46.18° (*c* 2.39, EtOH); IR 1750 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.2–7.0 (m, 5 H, aromatic), 2.3–0.9 (m, 7 H), 1.52 (s, 3 H, O_2CCH_3), 1.37 (s, 6 H, CH_3CPh), 0.96 (d, J = 6.5 Hz, 3 H, $CHCH_3$). Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.14; H, 8.62.

(5*R*)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohex-2-enone [(−)-5]. To a solution of 25.0 g (91.0 mmol) of **4** in 250 mL of methylene chloride at −78 °C was added dropwise a solution of 14.8 g (92.5 mmol) of bromine in 100 mL of methylene chloride. The reaction mixture was quenched 5 min after completion of the addition with 50 mL of saturated sodium bicarbonate at −78 °C. The organic layer was separated and the aqueous layer was extracted with 100 mL of methylene chloride. The combined organic layers were dried (Na_2SO_4) and the solvent was evaporated at 40 °C (20 mm) to give 28.6 g (101%) of crude α-bromo ketone which was dehydrobrominated without further purification. The crude α-bromo ketone was dissolved in 50 mL of dry dimethylformamide and added dropwise to a heated (150 °C) slurry of 20 g (230 mmol) of lithium bromide and 20 g (241 mmol) of sodium carbonate in 200 mL of dry dimethylformamide. The solution was heated at 150 °C for 2 h, cooled, filtered, diluted with 500 mL of water, and extracted twice with 200 mL of benzene. The combined benzene extracts were evaporated and the residue was distilled at reduced pressure to afford 18.6 g (81.6 mmol, 89%) of (−)-**5**: bp 110–111 °C (0.2 mm); $[\alpha]^{22}D$ −57.35° (*c* 1.36, EtOH); IR 1680 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.4–6.9 (m, 5 H, aromatic), 6.83–6.70 (m, 1 H, vinyl), 2.56–0.9 (m, 8 H), 1.44 (s, 6 H, CH_3CPh). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.82. Found: C, 84.21; H, 8.61.

(5*S*)-2-(1-Methyl-1-phenylethyl)-5-methylcyclohex-2-enone [(+)-5]. To a cooled (0 °C) solution of 18 g (78.9 mmol) of (−)-**5** in 250 mL of ethanol was added a solution of 1.6 g (40 mmol) of sodium hydroxide in 6 mL of water and 50 mL (580 mmol) of 30% hydrogen peroxide. The solution was stirred at 25 °C for 24 h and an additional 1.0 g (25 mmol) of sodium hydroxide in 5 mL of water and 25 mL (290 mmol) of 30% hydrogen peroxide was added. The solution was stirred for 24 h at 25 °C and then concentrated to 150 mL at reduced pressure. The residue was diluted with 200 mL of water and extracted twice with 200 mL of benzene. The combined layers were dried (Na_2SO_4), evaporated, and distilled to give 18.5 g (75.8 mmol, 96%) of epoxy ketone: bp 110–113 °C (0.3 mm); $[\alpha]^{22}D$ + 20.74° (*c* 3.76, EtOH); IR 1710 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 7.22–6.95 (m, 5 H, aromatic), 3.54 (bs, 1 H, oxirane), 2.5–1.08 (m, 5 H), 1.50 (s, 3 H, CH_3CPh), 1.12 (s, 3H, CH_3CPh), 0.86 (d, J = 6.5 Hz, 3 H, $CHCH_3$). Anal. Calcd for $C_{16}H_{20}O_2$; C, 78.65; H, 8.25. Found: C, 78.52; H, 7.98.

A solution of 15.7 g (64.3 mmol) of epoxy ketone in 250 mL of methanol was cooled to 0 °C and 60 mL (1.70 mol) of 95% hydrazine was added. The solution was warmed to 25 °C and 0.5 g (8.3 mmol) of acetic acid was added. Additional 0.5-g portions of acetic acid were added at 12-h intervals (2.0-g total, 30 mmol) and after 2 days at 25 °C the reaction mixture was warmed to 50 °C for 12 h. The solvent and excess hydrazine were evaporated at reduced pressure and the residue was taken up in 150 mL of benzene. The benzene solution was washed twice with 100 mL of water and twice with 50 mL of 10% sodium dihydrogen phosphate. The benzene solution was dried (Na_2SO_4) and evaporated to give 13.3 g (57.9 mmol, 90%) of the allylic alcohol as a mixture of epimers.

To a solution of 58 g (720 mmol) of pyridine in 600 mL of methylene chloride at 0 °C was added 36 g (360 mmol) of chromium trioxide. The solution was stirred for 15 min at 20 °C and then treated with 14.0 g (60 mmol) of the mixture of epimeric allylic alcohols in 50 mL of methylene chloride. After stirring 45 min at 20 °C, the solution was filtered and the residue was washed several times with ether. The combined filtrate and washings were washed twice with 100 mL of 10% sodium hydroxide, dried (Na_2SO_4), concentrated, and distilled to give 12.6 g (55 mmol, 92%) of (+)-**5**: bp 110–112 °C (0.2 mm); $[\alpha]^{22}D$ +56.31° (*c* 1.15, EtOH); IR and NMR identical to authentic (−)-**5**. Anal. Calcd for $C_{16}H_{20}O$; C, 84.16; H, 8.82. Found: C, 84.24; H, 8.91.

(1*S*,2*R*,5*S*)-2-(1-methyl-1-phenylethyl)-5-methylcyclohexanol [(+)-1]. To 100 mL of liquid ammonia at −78 °C was added 0.56 g (0.08 g-atom) of lithium wire. Then a solution of 4.56 g (20 mmol) of (+)-**5** and 3.00 g (40.5 mmol) of *tert*-butyl alcohol in 20 mL of tetrahydrofuran was added. The solution was stirred at −78 °C for 30 min and then quenched by addition of solid ammonium chloride. The excess ammonia was evaporated and the semisolid residue was washed twice with 50 mL of benzene. Filtration and evaporation of the solvent gave 4.52 g of an oil consisting of saturated ketone and

alcohol. The residue was dissolved in 50 mL of acetone and excess 8 N chromic acid was added at 0 °C. The oxidation mixture was diluted with 100 mL of water and extracted twice with 100 mL of benzene. The combined organic extracts were dried (Na_2SO_4) and evaporated to afford 3.91 g (17 mmol, 85%) of **6** as a 1:1 mixture of cis and trans isomers. Equilibration of the mixture by heating at 70 °C in 100 mL of ethanol containing 1 equiv of 3 N sodium hydroxide gave 3.90 g (17 mmol, 100%) of **6** as an 85:15 mixture of trans to cis ketone.

To 2.30 g (0.100 g-atom) of sodium in 75 mL of refluxing toluene was added 3.80 g (16.5 mmol) of the 85:15 mixture of trans- and cis-**6** in 8.4 g (140 mmol) of isopropyl alcohol. After 2 h at reflux the sodium had dissolved. After another 15 min the solution was cooled and quenched with 50 mL of saturated sodium dihydrogen phosphate. The layers were separated and the aqueous layer was extracted with 50 mL of toluene. The combined organic layers were dried (Na_2SO_4) and concentrated and the residue was chromatographed on silica gel (5% ether/petroleum ether) to afford 3.37 g (14.5 mmol, 88%) of (+)-**1** as an oil: $[\alpha]^{22}D$ +26.3° (*c* 2.30, EtOH); IR 3420 (OH) cm^{-1}; NMR ($CDCl_3$) δ 7.33–7.08 (m, 5 H, aromatic), 3.50 (d of t, J = 3.5 Hz, J = 10.5 Hz, 1 H, HCO), 2.00–1.02 (m, 9 H), 1.40 (s, 3 H, CH_3CPh), 1.27 (s, 3 H, CH_3CPh), 0.85 (d, J = 5 Hz, 3 H, $CHCH_3$).

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Registry No.—(+)-**1**, 57707-91-2; **4**, 65253-05-6; (−)-**5**, 65253-06-7; (+)-**5**, 65253-07-8; **5** epoxy ketone, 65253-08-9; **5** alcohol isomer I, 65253-09-0; **5** alcohol isomer II, 65337-05-5; **6** isomer I, 65337-06-6; **6** isomer II, 57707-92-3; phenyl bromide, 108-86-1; (*R*)-(+)-pulegone, 89-82-7; acetyl chloride, 75-36-5.

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Synthesis of Heavily Substituted Cyclopropylethylenes by Titanium(0) Catalyzed Cross-Coupling of Ketones. Restricted Rotation in 1,1-Dicyclopropyl-2,2-di(2-propyl)ethylene

Shinya Nishida* and Fumio Kataoka

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, Hokkaido, 060, Japan

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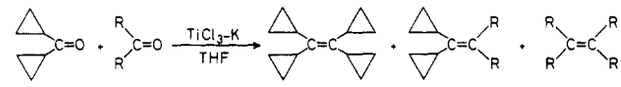
Carbonyl coupling reaction employing low-valent titanium[1] is a valuable method for preparing sterically hindered olefins.[2–4] Recently, McMurry and Krepski[5] have demonstrated further that the method is equally effective for cross-couplings between aryl ketones and aliphatic carbonyl compounds. We investigated the cross-couplings between dicyclopropyl ketone and aliphatic ketones in the hope that heavily substituted cyclopropylethylenes could be prepared. Although we were not without doubts regarding the survival of the cyclopropane ring under the reaction conditions, cross-coupled cyclopropylethylenes as well as tetracyclopropylethylene[6,7] were obtained in satisfactory yields.

The cross-coupling was performed by refluxing a 1:1 mixture of dicyclopropyl ketone and 2,4-dimethyl-3-pentanone with the titanium(0) reagent[1] in tetrahydrofuran under a nitrogen atmosphere for 12 h. As a result, an olefinic fraction composed of three components was obtained in a 29% yield. The major component (ca. 60%) was characterized as a cross-coupled olefin, 3-dicyclopropylmethylene-2,4-dimethylpentane (1,1-dicyclopropyl-2,2-di(2-propyl)ethylene, **2a**). The other two were homocoupled products, namely tetracyclopropylethylene (**1**) and 2,5-dimethyl-3,4-di(2-propyl)hex-3-ene (**3a**). Similarly, the reaction of dicyclopropyl ketone with 3-pentanone produced cross-coupled 3-dicyclopropylmethylenepentane (**2b**) as the major olefinic product. All olefins produced were separated and purified by column chromatography and GLC. The amounts of the crossed olefins were somewhat greater than the statistical value.[8]



		1	2	3	
a	R = $CH(CH_3)_2$	29% (2.5	6	1.5)	[9]
b	R = CH_2CH_3	31% (1	6.5	2.5)	[10]

An application of the titanium(0) coupling procedure for the reaction of cyclopropyl phenyl ketone was fruitless. However, *trans*- and *cis*-1,2-dicyclopropylstilbenes (**4a** and **4b**) were satisfactorily prepared by the coupling of the ketone with $TiCl_4$–Zn reagent[11] in dioxane.

Olefin **3a** has been reported to exhibit temperature-dependent NMR[2,3] and a suggestion has been made that olefin **1** should behave similarly.[2] However, in our observations, we noted that olefin **1** showed practically no change in its NMR down to −160 °C. We in fact noted that olefin **2a** lies between **1** and **3a**. It was found that the methyl signal in the 2-propyl group coalesced at −105 °C (168 K) in Freon 12. At −140 °C or below, it split into a pair of doublets at δ 0.94 and 1.22.[12] From these results, $\Delta G_c^{\ddagger}$ at 168 K is calculted to be 8.3 kcal/mol.[13] Further, signals due to the cyclopropyl ring protons in **2a** also appeared to coalesce,[14] suggesting that the cogwheel effect[15] including all four substituents was in operation.

The present results clearly demonstrated that the size of the cyclopropyl group is significantly smaller than that of the 2-propyl. It is natural, therefore, that the coalescence temperature for **1** should be lower than −160 °C.

Experimental Section

IR spectra were recorded on a Hitachi 215 grating infrared spectrophotometer, UV were recorded on a Cary Model 17 spectrometer, and NMR were recorded on a JEOL PS-100 high-resolution spectrometer. Both preparative and analytical GLC were carried out on a Hitachi 063 gas chromatograph. All boiling and melting points are uncorrected.

Cross-Coupling between Dicyclopropyl Ketone and Aliphatic Ketone with Titanium(0) Reagent. Under a nitrogen atmosphere, the titanium(0) reagent[1] was prepared from 19.5 g (126 mmol) of titanium trichloride and 14.0 g (358 mg-atom) of potassium in 350 mL of dry tetrahydrofuran. Under ice-cooling, a solution of 1.65 g (15 mmol) of dicyclopropyl ketone, 1.71 g (15 mmol) of 2,4-dimethyl-3-pentanone, and 255 mg of dodecane (internal standard for GLC analysis) in 70 mL of dry tetrahydrofuran was added slowly to the reagent, and the resulting mixture was stirred at room temperature for 1 h and then at reflux for 12 h. The cooled reaction mixture was treated with a small amount of ethanol and then poured onto a mixture of 300 mL of water and 500 mL of hexane. After filtration to remove resinous precipitates, the hexane layer was separated. The water layer was extracted with two portions of hexane. The combined hexane solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed and the resulting oily product was analyzed by GLC (Apiezon L 20%

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