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

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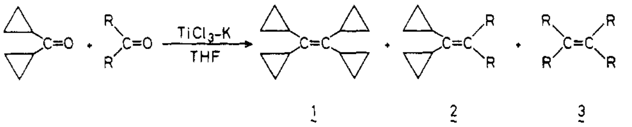
Carbonyl coupling reaction employing low-valent titanium[1] is a valuable method for preparing sterically hindered olefins.[2-4] Recently, McMurry and Krepski[5] have demonstrated further that the method is equally effective for cross-couplings between aryl ketones and aliphatic carbonyl compounds. We 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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on Chromosorb with temperature programming from 80 to 250 °C). The yields of **1**, **2a**, and **3a**, determined by GLC with respect to the internal standard, were 8, 16, and 5%, respectively. In a separate experiment, the product mixture was separated briefly by column chromatography (silica gel with low boiling petroleum ether as eluant). Each component was purified by GLC. Olefin **1** was characterized by comparison against authentic specimen.[6] Olefin **3a** melted at 119.5–121 °C (lit. 116–117 °C,[2] 125–125.5 °C[3]) and gave the same NMR as that reported.[2]GLC purified **2a** gave the following spectral and analytical data: IR (liquid film) 3090, 3020, 1630 (broad and weak), 1035 cm^{-1}; NMR ($CDCl_3$) δ 0.4–0.7 (m, 8), 1.07 (d, 12, $J = 7$ Hz), 1.1–1.5 (m, 2), 3.05 (heptet, 2, $J = 7$ Hz). Anal. Calcd for $C_{14}H_{24}$: C, 87.4; H, 12.6. Found: C, 87.5; H, 12.3.

Similar treatment of dicyclopropyl ketone (2.09 g, 19 mmol) and 3-pentanone (1.64 g, 19 mmol) with the titanium(0) reagent gave 1.30 g of an olefinic fraction, bp 40–82 °C at 4 mmHg. GLC analysis of the fraction showed the existence of three major components (74% of the total peak area) and many minor components. The three components were characterized as **1** (3%), **2b** (21%), and **3b** (7%). GLC purified **2b** gave the following data: IR (liquid film) 3080, 3020, 1635, 1010 cm^{-1}; NMR (CCl_4) δ 0.3–0.8 (m, 8), 0.95 (t, 6, $J = 7.5$ Hz), 1.0–1.4 (m, 2), 2.23 (quartet, 4, $J = 7.5$ Hz). Anal. Calcd for $C_{12}H_{20}$: C, 87.7; H, 12.3. Found: C, 87.7; H, 12.2.

In both coupling reactions, the ratio of **1**:**2**:**3** given in the text is an average of two to four runs.

1,2-Dicyclopropylstilbene. To 26.6 g (140 mmol) of titanium tetrachloride in 300 mL of dry dioxane 10.2 g (70 mmol) of cyclopropyl phenyl ketone was added. Under a nitrogen atmosphere, 18.3 g (280 mg atom) of zinc powder was then added in one portion and the resulting mixture was refluxed for 8 h.[11] After cooling down the mixture, 400 mL of water was added and organic material was extracted with three portions of benzene. The combined benzene solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a solid residue which was recrystallized from ether to give 2.09 g (23%) of crystalline product **4a**, mp 147.5–148.5 °C. The mother liquid of the recrystallization was concentrated and the residue was placed on top of a silica gel column (50 g), and elutions were carried out with hexane. From relatively later fractions, the second product **4b**, mp 78–79 °C (from ethanol), 1.85 g (20%), was obtained. Olefins **4a** and **4b** were characterized as isomeric 1,2-dicyclopropylstilbene from the following data. Olefin **4a:** NMR ($CDCl_3$) δ 0.0–0.6 (m, 8), 1.2–1.6 (m, 2), 7.0–7.5 (m, 10); mass *m/e* 260 (M^+); UV_{max} (hexane) 242 nm (ϵ 6400). Anal. Calcd for $C_{20}H_{20}$: C, 92.3; H, 7.7. Found: C, 92.2; H, 7.8. Olefin **4b:** NMR (CCl_4) δ 0.1–0.4 (m, 4), 0.5–0.8 (m, 4), 2.0–2.3 (m, 2), 6.6–7.0 (m, 10); mass *m/e* 260 (M^+); UV_{max} (hexane) 254 nm (ϵ 8400). Anal. Calcd for $C_{20}H_{20}$: C, 92.3; H, 7.7. Found: C, 92.5; H, 7.9. Olefin **4a**, which may be the same substance as that described by Bennett and Bunce (mp 139.8–140.2 °C),[16] is assigned as a trans isomer. Heating of either **4a** or **4b** in 1,2-dichloroethane[17] at 100 °C for 44 h resulted in the formation of a mixture with the same composition (**4a**/**4b** = 75:25). Regarding the UV data, it is reported that the trans isomer of 1,2-dialkylstilbenes exhibits the maximum at wavelengths shorter than that for the cis isomer.[18]

NMR Examination of 2a and 1. Forty-six milligrams of **2a** was placed in an NMR tube and ca. 0.8 mL of Freon 12 was condensed in the tube. The tube was sealed and NMR measurements were performed at several temperatures (down to −160 °C). The methyl signal coalesced at −105 °C as described in the text. The signals due to the methine protons coalesced at −95 °C and they appeared at δ 2.44 and 3.57 at −140 °C or below. Thus, $\Delta G_c^{\ddagger}$ at 178 K is calculated to be 8.5 kcal/mol.[13] The signals due to the cyclopropyl groups also changed their shapes and split at least into four signals at ca. δ 0.3, 0.6, 0.9, and 1.7 at −140 °C or below.

On the other hand, NMR signals of **1** remained practically unchanged down to −160 °C. Slight line broadenings observed may be due to the viscosity increase.

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Registry No.—**1**, 23534-93-2; **2a**, 65045-41-2; **2b**, 65045-42-3; **3a**, 7090-88-2; **3b**, 868-46-2; **4a**, 65045-43-4; **4b**, 65045-44-5; titanium trichloride, 7705-07-09; potassium, 7440-09-7; dicyclopropyl ketone, 1121-37-5; 2,4-dimethyl-3-pentanone, 565-80-0; 3-pentanone, 96-22-0; titanium tetrachloride, 7550-45-0; cyclopropylphenyl ketone, 3481-02-5.

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(10) Average of four runs.

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Sesquiterpenoids from the Hawaiian Marine Alga *Laurencia nidifica*. 7. (+)-Selin-4,7(11)-diene

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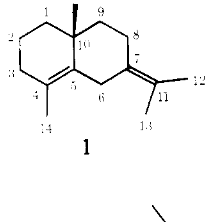
The selinane skeleton is one of the most common in sesquiterpenoids of terrestrial origin. Its presence in marine organisms has also been noted in a gorgonian,[1] a sponge,[2] and a brown alga.[3] Very recently the prolific *Laurencia* genus has been found to produce (−)-selin-7-ene derivatives.[4] We report here the isolation of (+)-selin-4,7(11)-diene (**1**) from the green variety of the Hawaiian marine alga *Laurencia nidifica.* To our knowledge this material has not been previously recorded as naturally occurring.

(+)-Selin-4,7(11)-diene (**1**) was isolated as an unstable



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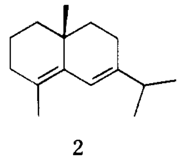

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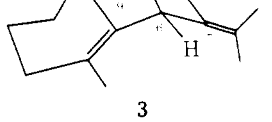

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colorless oil in 0.08% yield from the dry alga. High resolution mass spectroscopy established its molecular formula as $C_{15}H_{24}$. Its infrared spectrum showed only carbon–hydrogen absorptions. ^{13}C NMR indicated the presence of four quaternary olefinic carbons (119.8, 123.7, 131.7, 135.2) and a fifth quaternary center at 34.8. ^1H NMR confirmed the absence of