solid BCl_3·EE in the reaction flask. The BCl_3·EE in the reaction flask was washed twice with pentane at 0 °C, and the washings were added to the main solution in the second flask. Pentane was then removed using a water aspirator and the product was distilled at 66–68 °C at 18 mm over an 8 in. Vigreaux column (to prevent frothing over). The *trans*-1-hexenyldichloroborane was obtained in 69% yield, which was identified by ^1H NMR. The *cis*-3-hexenyldichloroborane was synthesized (83% yield, bp 56–58 °C at 17 mm) and identified in exactly the same way starting with 3-hexyne.

The corresponding *B*-dimethoxy derivatives were prepared by adding a drop of methanol to a drop of the alkenyldichloroborane in CCl_4, taken in an NMR tube (5 mm o.d.). The *B*-dimethoxy derivatives were identified by ^1H NMR of the sample [$B(OCH_3)_2$ proton resonance at δ 3.58].

Dihydroboration of Alkynes with $BHCl_2$·EE in the Presence of BCl_3 in Pentane. The experiment using 1-hexyne is described as the typical example. A 100-ml reaction flask was set up as described in the previous experiment. Pentane (2.825 ml), 5 mmol of 1-hexyne (0.575 ml), and 10 mmol of BCl_3 in pentane (5 ml) were introduced into the flask. While stirring vigorously at 0 °C, 10 mmol of $BHCl_2$·EE (1.6 ml) was slowly added. Within 5 min after the addition of $BHCl_2$, a small aliquot was withdrawn and analyzed for any residual 1-hexyne by GC after destroying the chloroboranes using aqueous NaOH at 0 °C. Aliquots (2 ml) were withdrawn at 15 min and 1 h at 0 °C and analyzed for residual hydride by hydrolyzing and measuring the hydrogen evolved. Afterwards, the reaction mixture was brought to 25 °C and stirred vigorously for 1 h. A 2-ml aliquot was withdrawn at this time and analyzed for residual hydride. The experiment was repeated using 3-hexyne in place of 1-hexyne.

At the end of 1 h at 25 °C, 5 ml of methanol was added to the 1-hexyne reaction mixture and stirred for 15 min. The pentane and other volatile materials were removed using a water aspirator, and the ^1H NMR spectrum of the crude product was examined. The spectrum displayed a singlet at δ 3.55 (12 H) due to $B(OCH_3)_2$ protons and a broad multiplet between δ 0.7 and 1.8 (12 H) due to alkyl protons.

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The Palladium(II) Catalyzed Olefin Carbonylation Reaction. The Stereochemistry of Methoxypalladation[1]

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Abstract: The reaction of carbon monoxide with *cis*- and *trans*-2-butene at 2–3 atm in methanol in the presence of a catalytic amount of palladium(II) chloride and copper(II) chloride as reoxidant yielded, in the initial stages of the reactions, methyl *threo*- and *erythro*-3-methoxy-2-methylbutanoate, respectively. These results demonstrated that stereospecific trans methoxypalladation is the exclusive reaction pathway. Addition of equimolar amounts of sodium acetate to the reaction mixture completely changed the course of the reaction. Carbonylation of *trans*-2-butene gave exclusively *dl*-dimethyl 2,3-dimethylsuccinate while *cis*-2-butene afforded only the meso diastereomer. Stereospecific cis carbomethoxypalladation was therefore the exclusive reaction pathway.

The addition of nucleophiles to monoolefin–transition metal complexes is an important type of synthetic reaction.[3-6] Whereas the nucleophilic addition to a diolefin complex produces a stable σ-bonded enyl complex, the analogous σ-bonded complex from reaction of a monoolefin is generally unstable and decomposes because of the absence of chelation. In the case of the diolefins, the stereochemistry of the addition with a variety of nucleophiles is trans.[7-10] It has been argued,[11-13] however, that the chelating diolefins are atypical, and the stereochemical results cannot be extended to monoolefins since approach of an external nucleophile from the cis side presents steric problems. The trans stereochemistry has also been attributed to the inability of the chelating diolefins to rotate 90° from the position perpendicular to the square plane of the metal complex to a position which would favor cis addition of the metal and a ligand attached to it.[14] In the Wacker process, the kinetics of oxidation of olefins suggest, but do not require, the cis hydroxypalladation of olefins.[11,15]

The addition–elimination reaction of olefins presents a dichotomy of mechanistic results in that many of the reactions are consistent with either a cis addition, cis elimina-

Table I. Catalytic Carbonylation of *cis*- and *trans*-2-Butene[a]

Olefin	Time, h	Products[b] Methyl 3-methoxy-2-methyl butanoate, % Yield	Threo	Erythro	Dimethyl 2,3-butanedicarboxylate, % Yield	*dl*	Meso	Olefin isomerization % cis	% trans
cis-2-Butene	2	1.4	100	0				100	0
	8	6.7	100	0				85	15
	100	33	87	13	1	60	40	23	77
trans-2-Butene	2	0.7	0	100				0	100
	8	1.9	0	100				5	100
	100	19	40	60	1	100	0	20	95
cis-2-Butene[c]	100	0			3	0	100	100	0
trans-2-Butene[c]	100	0			20	100	0	0	100

[a] Reaction conditions; 50 mmol of olefin, 2.8 mmol of $PdCl_2$, 100 mmol of $CuCl_2$, 75 ml of methanol, and 3 atm of CO at 28 °C. [b] Yield ± 0.5%, determined by VPC and based on olefin. Isomer distribution ±0.5%, determined by VPC. [c] 100 mmol of sodium acetate added to the reaction mixture.

tion or a trans addition, trans elimination and, in others, either a cis addition followed by a trans elimination or vice versa. Furthermore, in more cases predominantly Markownikoff addition is observed, and in others it is anti-Markownikoff.

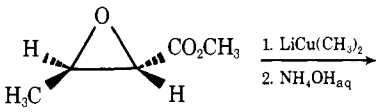
Most of these mechanistic differences with simple olefins can be rationalized by considering two types of addends or nucleophiles: those which are coordinated to palladium transferring directly from palladium to an olefin carbon, and those which are solvated but not coordinated, forming a bond with carbon by external nucleophilic attack. An inspection of the literature reveals that those addition-elimination reactions in which the addend or nucleophile can be considered to be coordinated to palladium just prior to reaction proceed by cis addition, anti-Markownikoff, and cis elimination. Those addition-elimination reactions in which the nucleophile can be considered to be solvated and uncoordinated proceed by trans addition, Markownikoff, and trans elimination.

One approach to the problem of determining the stereochemistry of the unstable palladium-carbon σ-bonded intermediate is its trapping by replacement of the palladium with some other group by a reaction that takes place at least competitively with elimination. The carbonylation of such intermediates is known to occur more rapidly than the elimination and proceeds with *100% retention of configuration* at the carbon bearing the palladium.[9,16]

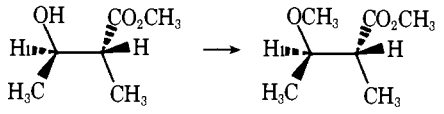
Results and Discussion

The reaction of carbon monoxide with *cis*- and *trans*-2-butene at 2–3 atm in methanol in the presence of a catalytic amount of palladium(II) chloride and a stoichiometric quantity of copper(II) chloride as reoxidant demonstrated the stereochemistry of the oxymetalation of simple olefins. In the initial stages of the reaction, stereospecific trans methoxypalladation was observed, yielding exclusively the *threo*- and *erythro*-β-methoxy esters, respectively (Table I). In the latter stages of the reaction, as the reaction mixture became increasingly acidic, cis-trans isomerization of the 2-butenes occurred to such an extent that trans methoxypalladation of the cis-trans mixture yielded both erythro and threo products. After the reaction was 20–30% complete, for example, methoxy ester product ratios of 87% threo/13% erythro from *cis*-2-butene and 40% threo/60% erythro from *trans*-2-butene were obtained.

The erythro and threo isomers were identified by the independent synthesis of methyl *threo*-3-methoxy-2-methylbutanoate. Reaction of the epoxide of methyl crotonate (**1**) with lithium dimethylcuprate followed by acid hydrolysis afforded exclusively hydroxy ester **2** via a trans ring-opening process.[17] Methylation of **2** yielded the authentic threo diastereomer.



1



2

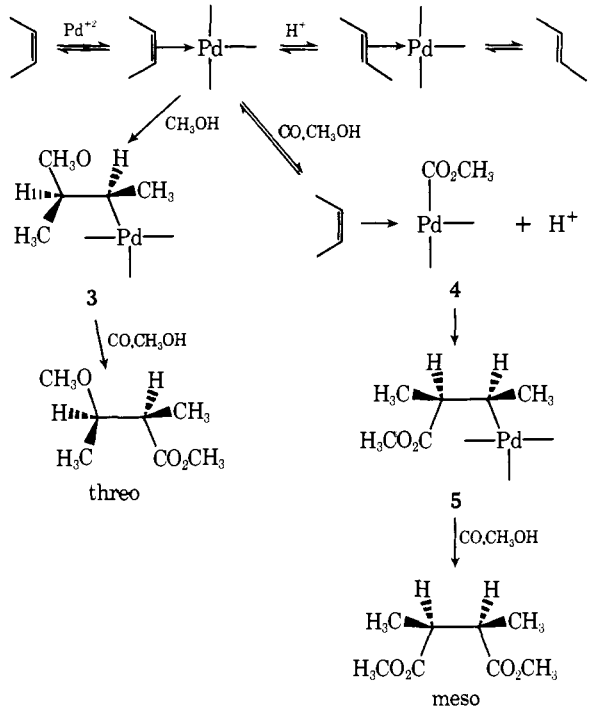
Formed coincidentally with the methoxy esters, although in relatively smaller amounts, were substituted succinic esters. *cis*-2-Butene gave a mixture of meso and *dl* diesters, while *trans*-2-butene yielded only the *dl* enantiomers. Interestingly, the course of the reaction was completely changed by the addition of sodium acetate. Equimolar amounts (based on copper(II)) of the carboxylate base effectively eliminated methoxy ester production as well as trans isomerization and the dimethylsuccinates were the exclusive products. The carbonylation of *trans*-2-butene gave exclusively the *dl*-succinic ester while *cis*-2-butene afforded only the meso diastereomer.

These results are consistent with the mechanism as shown in Scheme I for *cis*-2-butene.

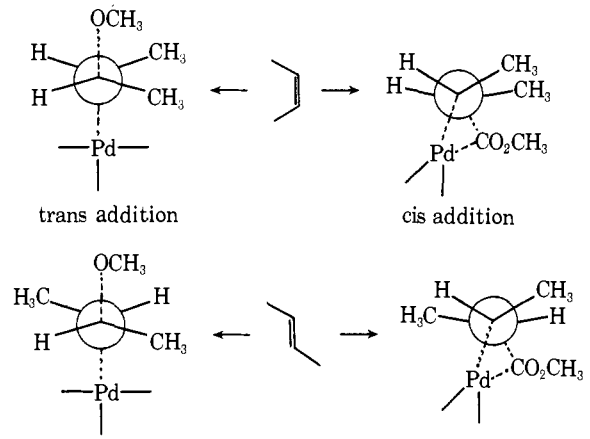
Several aspects of this mechanism deserve comment. The cis-trans isomerization reaction is acid catalyzed as isomerization does not occur in the early stages of the reaction or under basic conditions. The isomerization reaches equilibrium at approximately 80% trans–20% cis in each case. The *threo*-β-methoxy ester is obtained from carbonylation of intermediate **3**, which is formed from trans methoxypalladation of *cis*-2-butene. The olefin-carbomethoxypalladium complex **4**[18] is the most probable intermediate in the pathway to the diester products and is formed in significant amounts in the presence of the sodium acetate base. Cis addition of palladium and coordinated carbomethoxy ligand yields σ-bonded complex **5**, carbonylation of which gives the observed meso diester.

The relative rate data, which demonstrate that the overall rate of formation of the trans methoxypalladation product is greater for the cis isomer, is consistent with this mechanism and is evidence of the importance of the complexation and metalation steps. A faster rate of conversion of *cis*-2-butene to β-methoxy ester relative to *trans*-2-butene is in accordance with a stereospecific trans methoxypalladation mechanism which requires formation of a more stable π complex for the cis isomer[19-21] and greater relief of steric repulsion in the transition state for the trans addition

Scheme I



Scheme II. Structures of Methoxy- and Carbomethoxypalladation Transition States for *cis*- and *trans*-2-Butene



to the cis olefin (Scheme II). In this reaction, the transition states resemble the products.[20] The relative rates of diester formation are reversed, however. The overall rate of the carbomethoxypalladation reaction is slower for *cis*-2-butene because cis addition of coordinated carbomethoxy ligand and palladium requires greater steric crowding than that observed for the trans isomer in transition states which more closely resemble the reactants (Scheme II). These data strongly suggest that **5** is not an intermediate in the formation of *both* β-methoxy ester and diester products. Although SN2 displacement of palladium by nucleophile has been demonstrated in acetic acid systems[22] and postulated for alcoholic systems,[23] it is clear that β-methoxy ester and diester products are best explained by two distinctly different intermediates arising from the rate-determining step (formation of the palladium-carbon σ-bonded complex).

Experimental Section

Carbonylation Apparatus. All low-pressure carbonylation reactions were carried out using a modified Paar series 3910 hydrogenation apparatus in 250-ml or 500-ml heavy-walled Pyrex bottles, and the mixture was stirred with a magnetic stirrer rather than shaken.

Alternatively, a 200-ml heavy-walled Pyrex serum bottle containing the reaction mixture and fitted with a neoprene septum was used. The carbon monoxide was introduced through a needle clamped securely into the pressure tubing leading from the ballast tank. In this configuration, the atmosphere above the reaction and/or the reaction mixture could be sampled with the appropriate capacity gas-tight syringe fitted with a Hamilton inert No. 1FM1 two-way valve and a needle.

General Procedure for the Determination of Percent Yield. Unless otherwise specified, the percent yields based on olefin were obtained by VPC analysis. Prior to reaction, a readily available and inert compound (usually a diester which eluted after the product) was chosen as an internal standard. A solution of known composition (usually a 1:1 mole ratio) was prepared and analyzed by VPC in order to determine the response factor relationship between the product(s) and the standard. The response factor was calculated from relative peak areas and was the average of at least five injections. Upon completion of the reaction studied, a given amount (based on an anticipated yield approximated from a previous reaction so as to be near to a 1:1 molar relationship) of internal standard was added to the reaction mixture. The usual work-up procedure was followed and the product with standard was analyzed by VPC. The percent yield was calculated using the previously obtained response factor and the peak areas of the product and internal standard from the reaction. The reported yields are the average of at least three injections from two separate runs. Standard deviations of 0.5% were attained. Alternatively, the internal standard could be added prior to carbonylation.

Catalytic Carbonylation of *cis*-2-Butene. Formation of Methyl *threo*- (6) and *erythro*-3-Methoxy-2-methylbutanoate (7) and Dimethyl *meso*- (8) and *dl*-2,3-Dimethylbutanedioate (9). To 35 ml of methanol in a 250-ml pressure bottle was added in succession with stirring, 13.44 g (100.0 mmol) of cupric chloride, 10 ml of methanol, 2.81 g (50.0 mmol) of *cis*-2-butene in 10 ml of methanol, 0.50 g (2.8 mmol) of palladium(II) chloride, and 20 ml of methanol (total methanol, 75 ml). The reaction vessel was then placed on the carbonylation apparatus and was pressurized with 3 atm of carbon monoxide. The reaction was allowed to proceed at room temperature until palladium(0) had precipitated from solution (24–100 h). Upon completion, the solvent was removed under reduced pressure and the residue was stirred with several portions of pentane. The pentane extracts were combined, filtered, and then concentrated under diminished pressure until all of the solvent was removed. The work-up provided 2.4 g of product. VPC analysis on the 10 ft × ⅜ in. 30% DEGS column showed the presence of four components. The two major components, β-methoxy esters, were formed in a 33% yield based on olefin and in a ratio of 13 to 87. The predominant product was identified as **6** by VPC and NMR comparison with an authentic sample (vide infra): ^{1}H NMR ($CDCl_3$) δ 1.09 (d, 3 H, J = 8 Hz, C-1′ methyl), 1.11 (d, 3 H, J = 6 Hz, C-4 methyl), 2.60 (m, 1 H, C-2 methyne), 3.30 (s, 3 H, methoxyl), 3.5 (m, 1 H, C-3 methyne), and 3.67 ppm (s, 3 H, carboxylate methyl); ^{13}C NMR (neat) δ 12.08 (C-1′ methyl), 15.70 (C-1″ methyl), 45.36 (C-2 methyne), 51.30 (carboxylate methyl), 56.48 (methoxyl), 78.43 (C-3 methyne), and 175.20 ppm (carbonyl); mass spectrum (70 eV) *m/e* (relative intensity) 131 ($M^+ - CH_3$, 3), 116 ($M^+ - CH_2O$, 4), 115 ($M^+ - CH_3O$, 11), 75 ($C_3H_7O_2$, 13), 60 (HCO_2CH_3, 6), and 59 (CO_2CH_3, B).

Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.62; H, 9.72.

The lesser methoxy ester component was therefore assigned the structure **7**: ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 3 H, J = 6 Hz, C-1′ methyl), 1.18 (d, 3 H, J = 7 Hz, C-4 methyl), 2.54 (m, 1 H, C-3 methyne), 3.33 (s, 3 H, methoxyl), 3.6 (m, 1 H, C-2 methyne), and 3.68 ppm (carboxylate methyl); ^{13}C NMR (neat) δ 12.46 (C-1′ methyl), 16.94 (C-1″ methyl), 45.80 (C-2 methyne), 51.30 (carboxylate methyl), 56.49 (methoxyl), 78.21 (C-3 methyne), and 175.10 ppm (carbonyl); mass spectrum (70 eV) *m/e* (rel intensity) 131 ($M^+ - CH_3$, 3), 116 ($M^+ - CH_2O$, 4), 115 ($M^+ - CH_3O$, 11), 75 ($C_3H_7O_2$, 13), 60 (HCO_2CH_3, 6), and 59 (CO_2CH_3, B).

Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.62; H, 9.72.

The two minor components were formed in a 1% yield and a ratio of 40 to 60. These were identified as the diesters **8** and **9**, respectively (vide infra).

Catalytic Carbonylation of *trans*-2-Butene. Formation of 6, 7,

and **9.** A stirred solution of 2.81 g (50.0 mmol) of *trans*-2-butene, 0.50 g (2.8 mmol) of palladium(II) chloride, and 13.44 g (100.0 mmol) of cupric chloride in 75 ml of methanol was allowed to react with carbon monoxide (3 atm) for 100 h at room temperature. The usual work-up afforded 1.4 g of product. VPC analysis of the product using the 10 ft × ⅜ in. 30% DEGS column showed the presence of three components. The two major components, formed in a 19% yield based on olefin and in a ratio of 60 to 40, were **7** and **6,** respectively. The minor product (1% yield based on olefin) was the diester **9.**

Relative Rates of the Catalytic Carbonylation and Isomerization of *cis*- and *trans*-2-Butene. Simultaneously, two reaction mixtures, one containing 2.81 g (50.0 mmol) of *cis*-2-butene, the other containing 2.81 g (50.0 mmol) of *trans*-2-butene, and both containing 0.50 g (2.8 mmol) of palladium(II) chloride, 13.44 g (100.0 mmol) of cupric chloride, and 5 mmol of an internal standard in 75 ml of methanol, were pressurized to 3 atm with carbon monoxide and stirred at room temperature for 100 h. Periodically, 400 μl of the atmosphere above the reaction mixture was withdrawn and analyzed by VPC using a 20 ft × ⅛ in. 35% propylene carbonate/Chromosorb W column.[24] At the same time three 1-ml samples were withdrawn from the liquid reaction mixture. The usual work-up of the individual aliquots afforded small amounts of product which were separately analyzed on the 10 ft × ⅜ in. 30% DEGS column. The results of these reactions are summarized in Table I.

Catalytic Carbonylation of *cis*-2-Butene in the Presence of Sodium Acetate. Formation of 8. To 35 ml of methanol in a 250-ml pressure bottle were added in succession, with stirring, 13.44 g (100 mmol) of cupric chloride, 10 ml of methanol, 8.20 g (100 mmol) of sodium acetate, 10 ml of methanol, 2.81 g (50.0 mmol) of *cis*-2-butene in 10 ml of methanol, 0.50 g (2.8 mmol) of palladium(II) chloride, and 10 ml of methanol (total methanol, 75 ml). The reaction vessel was then placed on the carbonylation apparatus and was pressurized with 3 atm of carbon monoxide. The reaction was allowed to proceed at room temperature until palladium(0) had precipitated from the mixture (100 h). After reaction, the precipitate was removed by gravity filtration and was washed with methanol. The combined methanol filtrates were concentrated under reduced pressure on a rotary evaporator and the residue was extracted with several portions of pentane. The pentane extracts were filtered, combined, and then concentrated under diminished pressure until all of the solvent was removed. The work-up afforded 0.32 g of a single compound identified as the meso diester **8** (3% yield based on olefin) by VPC and NMR analysis: ^{1}H NMR ($CDCl_3$) δ 1.16 (m, 6 H, C-2 and C-3 methyl), 2.76 (m, 2 H, C-2 and C-3 methynes), and 3.70 ppm (s, 6 H, carboxylate methyl); ^{13}C NMR (neat) δ 14.94 (C-2 and C-3 methyl), 42.61 (C-2 and C-3 methyne), 51.73 (carboxylate methyl), and 175.04 ppm (carbonyl); mass spectrum (70 eV) *m/e* (rel intensity) 143 ($M^+ - CH_2{=}\dot{C}HCO_2CH_3$, 73), 87 (16), 83 (22), and 59 (B).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.02; H, 8.31.

VPC analysis of the atmosphere above the reaction mixture demonstrated that olefin isomerization had not occurred. A sample of **8** was hydrolyzed to the meso diacid, mp 210° (lit.[25] 209°).

Catalytic Carbonylation of *trans*-2-Butene in the Presence of Sodium Acetate. Formation of 9. A bright green slurry of 2.81 g (50.0 mmol) of *trans*-2-butene, 0.50 g (2.8 mmol) of palladium(II) chloride, 13.44 g (100.0 mmol) of cupric chloride, and 8.20 g (100 mmol) of sodium acetate in 75 ml of methanol was allowed to react with carbon monoxide (3 atm) for 100 h at room temperature. The usual work-up provided 1.8 g of product. VPC analysis showed the presence of one component in a 20% yield (based on olefin) which was identified as the *dl* diester by VPC and NMR analysis: ^{1}H NMR ($CDCl_3$) δ 1.16 (m, 6 H, C-2 and C-3 methyl), 2.82 (m, 2 H, C-2 and C-3 methyne), and 3.69 ppm (s, 6 H, carboxylate methyl); ^{13}C NMR (neat) δ 13.57 (C-2 and C-3 methyls), 41.70 (C-2 and C-3 methynes), 51.57 (carboxylate methyls), and 175.47 ppm (carbonyl); mass spectrum (70 eV) *m/e* (rel intensity) 143 ($M^+ - CH_3O$, 51), 142 (10), 115 ($M^+ - CO_2CH_3$, 50), 114 (28), 88 ($M^+ - CH_2{=}CHCO_2CH_3$, 73), 87 (16), 83 (22), and 59 (B).

Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 55.02; H, 8.31. VPC analysis of the atmosphere above the reaction mixture demonstrated that olefin isomerization had not occurred. A sample of **9** was hydrolyzed to the *d,l*-succinic acid, mp 127° (lit.[25] 127°).

Preparation of an Authentic Sample of Methyl *threo*-3-Methoxy-2-methylbutanoate (6).[17] To 43 g (0.25 mol) of *m*-chloroperbenzoic acid in dichloromethane was added, with stirring, 20 g (0.20 mol) of methyl crotonate, and the reaction was heated at the reflux temperature for 3 h. After reaction, excess peracid was destroyed by addition of a 10% solution of sodium sulfite. The organic layer was washed with a 5% bicarbonate solution, then water, and finally a saturated sodium chloride solution. The solution was then dried over anhydrous magnesium sulfate, the solvent was removed in vacuo, and the product was distilled to give 10.5 g of methyl 2,3-epoxybutanoate (**1**), bp 85–86° (48 mm). To a slurry of 3.81 g (20.0 mmol) of cuprous iodide in 60 ml of anhydrous ether at 0° was added slowly 27 ml of a 1.5 M solution of methyllithium. To the resulting tan solution was added 1.16 g (10.0 mmol) of **1** in 80 ml of ether over 30 min. The reaction was then stirred for 3 h at 0°. The mixture was hydrolyzed by the addition 80 ml of a saturated ammonium chloride solution. The mixture was stirred for 3 h at room temperature; then the aqueous layer was separated and extracted with two 40 ml portions of ether. The combined ether extracts were washed with 40 ml of a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The ether was removed by distillation and the product, methyl 3-hydroxy-2-methyl-butanoate (**2**), was purified by preparative VPC using the 10 ft × ⅜ in. DEGS column: ^{1}H NMR ($CDCl_3$) δ 1.14 (d, 3 H, J = 7 Hz, C-1′ methyl), 1.20 (d, 3 H, J = 7 Hz, C-4 methyl), 2.51 (m, 1 H, C-2 methyne), 3.56 (s, 1 H, hydroxyl), 3.73 (s, 3 H, carboxylate methyl), and 3.89 ppm (m, 1 H, C-3 methyne). To 11.0 g (77.0 mmol) of methyl iodide was added 0.21 g (1.6 mmol) of **2,** 0.51 g (3.7 mmol) of anhydrous calcium sulfate, and 0.37 g (1.6 mmol) of silver(I) oxide. The stirred mixture was heated in the absence of light in a 60° oil bath for 27 h. Upon completion, 20 ml of chloroform was added, the mixture was filtered by suction using a sintered glass funnel, and the solid residue was washed with two 20-ml portions of chloroform. The chloroform was removed by distillation and purification of the product was obtained by preparative VPC. The NMR spectrum of the product and VPC retention times on three columns were identical with the *threo*-β-methoxy ester **6.**

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References and Notes

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