crude acid chloride was dissolved in carbon disulfide (30 ml). To this solution was added stannic chloride (7.9 g, 0.03 mol) in carbon disulfide (30 ml) at 0°. This mixture was stirred for 0.5 hr at 0°, and then 4 hr at room temperature. After cooling to 0°, water (20 ml) was added, the layers were separated, and the aqueous phase was washed with ether. The combined organic phases were washed with 10% Na_2CO_3 solution, dried ($MgSO_4$), and evaporated to give 3.2 g (61%) of crude keto chlorides. Vpc analysis showed two components. Using the procedure described for **9**, the crude keto chlorides (1.7 g, 9.5 mmol) and DBN (3.7 g, 30 mmol) yielded 1.1 g (82%) of **15** which was purified by chromatography on silica gel or by evaporative distillation: bp 160° (bath temp) (19 mm); ir ($CHCl_3$) 1740 cm^{-1}; nmr ($CDCl_3$) δ 5.4 (broad s, 1), 1.73 (broadened s, 3), and 2.8–1.6 ppm (m, 8).

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.24; H, 8.96.

Registry No.—**1**, 7086-71-7; **3a**, 2716-23-6; **3b**, 53216-65-2; **4a**, 6553-12-4; **4b**, 53216-66-3; **5**, 18240-10-3; **9**, 31444-32-3; **15**, 53216-75-4; DBN, 3001-72-7; 4-methyl-3-cyclohexen-1-ylmethanol, 39155-38-9; ethyl 4-methyl-3-cyclohexene-1-carboxylate, 20292-15-3; 4-methyl-3-cyclohexene-1-acetonitrile, 53216-76-5; 4-methyl-3-cyclohexene-1-acetic acid, 7086-66-0; 4-methyl-3-cyclohexene-1-acetic acid sodium salt, 53216-77-6.

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Stereochemistry of the Thermal Addition of β-Pinene to Methyl Pyruvate[1]

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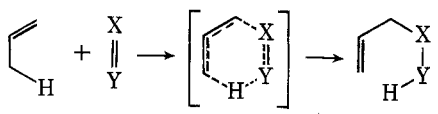
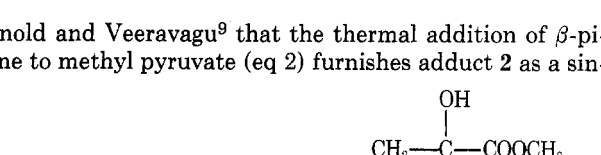
An nmr investigation of the adduct **2** formed in the ene reaction between β-pinene and methyl pyruvate has shown it to be a 1:1 mixture of diastereomers, not a single stereoisomer as originally believed. The pure adducts have been separated and their absolute configurations determined by degradation to citramalic acid. It is concluded that steric and stereoelectronic factors play little part in creating the new asymmetric center.

Many olefins react thermally with compounds containing reactive double bonds (C=C, C=O, N=N, etc.) to form 1:1 adducts in a process believed usually to involve a cyclic transition state[2] and broadly classified as the "ene" reaction[3] (eq 1). Consistent with its description as a concerted


(1)

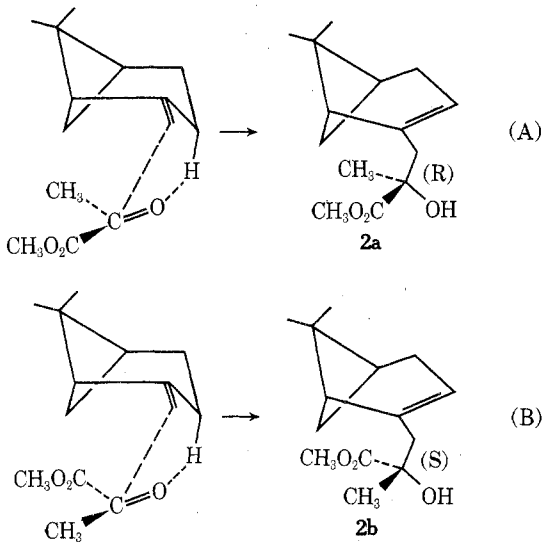
1,5-sigmatropic hydrogen transfer, the ene reaction exhibits several facets of stereospecificity. (1) The new C–C and C–H bonds are generated cis to each other.[4] (2) Asymmetric induction may be observed when the α carbon of the olefin is chiral, transferring chirality to the new asymmetric center in the enophile.[5] (3) In an olefin with multiple asymmetric centers, one of the diastereotopic allylic hydrogens is selectively transferred; in β-pinene (**1**), *e.g.*, only the endo hydrogen is involved in ene reactions.[6,7] It is not yet clear whether this is due to simple steric factors or to a stereoelectronic preference for breaking that C–H bond parallel to the π orbitals of the double bond. (4) In the cases so far investigated, endo orientation of the addends predominates over exo.[7,8]

During the course of our studies[5,7] on the stereospecificity of the ene reaction, we were attracted by the report of Arnold and Veeravagu[9] that the thermal addition of β-pinene to methyl pyruvate (eq 2) furnishes adduct **2** as a single stereoisomer. Most ene adducts of β-pinene, such as those with maleic anhydride, methyl maleate, and methyl fumarate,[10] as well as the maleic anhydride adducts of cyclopentene and *cis*- and *trans*-2-butene,[8] are mixtures of stereoisomers resulting from competing endo and exo addition, and it is surprising that this simple keto ester should exhibit such pronounced stereospecificity.[11] Arnold and Veeravagu suggested that the favored transition state should be that with minimum nonbonded repulsions, in which the pyruvate approaches the olefin from the methylene bridge side with the carbomethoxyl group oriented away from the hydrocarbon moiety.[9] As depicted in Chart IA, this would result in an *R* configuration at the new asymmetric center. On the other hand, were stereoelectronic considerations to favor endo orientation (Chart IB) as is the case with other ene additions of β-pinene,[7] then the


(2)

1 **2**

Chart I
Possible Stereochemical Courses of Addition of β-Pinene to Methyl Pyruvate



other diastereoisomer with the *S* configuration at the new asymmetric center would predominate.

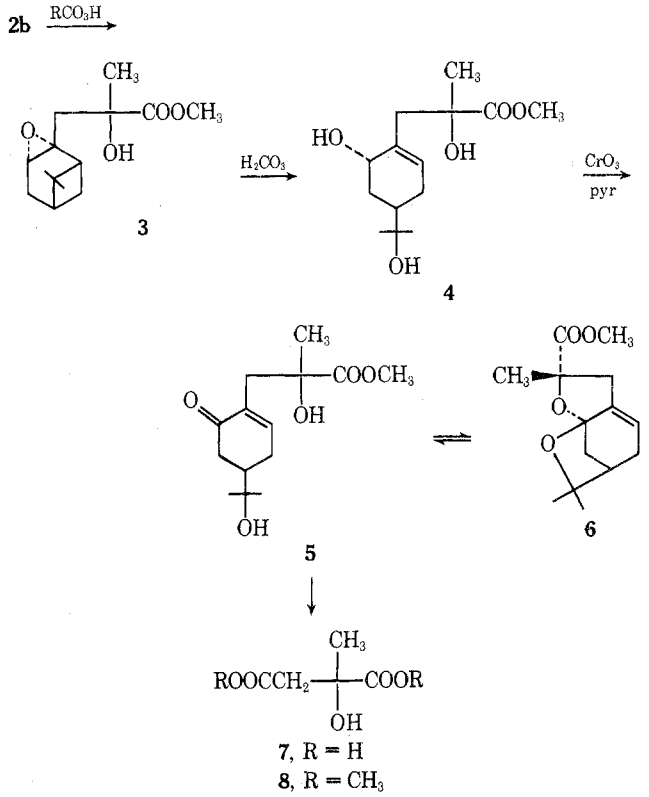
These considerations made clear the importance of determining the absolute configuration at the new asymmetric center in adduct **2**, for the identification of which diastereomer is formed would reveal whether simple steric or stereoelectronic factors were responsible for the unexpected stereospecificity. We undertook a study of this adduct with this aim in mind, but soon found that adduct **2** is not a single stereoisomer but rather a 1:1 mixture of the two possible diastereomers.

Demonstration of Adduct Inhomogeneity. Adduct **2** was prepared from methyl pyruvate and (−)-β-pinene as described and had properties similar to those reported. Arnold and Veeravagu reported that glc analysis on a polyester column showed a single peak, and we obtained a single peak on a Carbowax column as well. Moreover, nmr spectra in chloroform, benzene, carbon tetrachloride, or pyridine showed no doubling of peaks indicative of a mixture. Addition of the nmr shift reagent Eu(fod)$_3$ to a carbon tetrachloride solution of **2**, however, caused the methoxyl singlet at δ 3.66 to split into two singlets of equal intensity at 3.80 and 3.85, and the side-chain methyl signal at δ 1.29 also to split into two signals of equal intensity at 1.57 and 1.68. None of the other peaks, though shifted, showed any doubling. The shift reagent undoubtedly complexes with the ester and/or hydroxyl oxygens and affects only those substituents in the immediate vicinity.

Confirming evidence was obtained from the proton-decoupled ^{13}C nmr spectrum of adduct **2**. The signals due to the carbinol carbon, the three carbons attached to it (carbonyl, methyl, and methylene), and the two olefinic carbons all appeared as doublets of comparable intensity, again showing the presence of diastereomers.[12]

With this evidence that adduct **2** is a mixture of diastereomers, efforts were made to separate them. Arnold and Veeravagu had found that saponification of the adduct and recrystallization of the potassium salt gave a pure isomer, and we were able to confirm this, obtaining a less soluble salt as shiny platelets, mp 105–107°, by recrystallization from ethyl acetate. From the mother liquors, in addition, we could isolate a more soluble salt which crystallized as prisms, mp 204–206°, from ethyl acetate. Each of the potassium salts was converted into a pure diastereomer of **2** by acidification and esterification with diazomethane. Isomer **2a**, from the high-melting salt, had $[\alpha]_D$ −33.4°, while isomer **2b**, from the low-melting salt, had $[\alpha]_D$ −12.5°. The homogeneity of each was confirmed in two ways. The methoxyl and side-chain methyl singlets in the nmr spectra of both remained as singlets upon the addition of Eu(fod)$_3$, and the proton-decoupled ^{13}C nmr spectra of both showed each carbon signal as a sharp singlet.

Scheme I
Degradation of Adduct 2b to Methyl Citramalate



These results demonstrate that the β-pinene–methyl pyruvate adduct is not a single stereoisomer, but that diastereomers **2a** and **2b** are formed in approximately equal amounts. Several control experiments were run to see whether this 1:1 ratio is kinetically or thermodynamically controlled.

(1) Each of the pure diastereomers **2a** and **2b** was heated separately with β-pinene for 89–96 hr, under the conditions of the original ene reaction. Reisolation of the adduct and nmr analysis with added Eu(fod)$_3$ showed that the starting material in each case was recovered stereochemically pure and with unchanged optical rotation. Thus the adducts do not equilibrate under the conditions of their formation.

(2) The reaction between β-pinene and methyl pyruvate was interrupted after various periods. After 6, 24, 48, and 96 hr the yields of adduct were 9, 19, 34, and 57%, respectively. The adduct isolated in each case had the same optical rotation, however, and nmr analysis with added Eu(fod)$_3$ showed the same 1:1 ratio of diastereomers in each run. The product ratio does not change with time and appears to be kinetically controlled, *i.e.*, **2a** and **2b** are formed at about equal rates. This of course means that the transition states leading to **2a** and **2b** are of approximately equal energy; neither steric nor stereoelectronic factors play a decisive role in orienting the pyruvate in the transition state.

Determination of Absolute Configuration. It was still of interest to determine which adduct corresponds to **2a** and which to **2b**, *i.e.*, to assign absolute configurations at the new asymmetric center. An efficient degradative se-

quence was devised to destroy the chiral pinene moiety and relate the remaining asymmetric center to that of citramalic acid (Scheme I). Isomer **2b** was oxidized with peroxytrifluoroacetic acid to give epoxide **3**; the oxide is assigned the α configuration by analogy with the epoxidation of α-pinene.[13] Following the procedure used to convert α-pinene oxide into *trans*-sobrerol,[14] the oxide was treated with a mixture of Dry Ice and water to afford triol **4**. Collins oxidation led to ketone **5**; however, if the crude oxidation product was distilled, a different substance, lacking hydroxyl and ketone absorption in the infrared, was isolated. Infrared and nmr spectra were consistent with the ketal structure **6**. Aqueous acid hydrolysis gave **5**, which could be distilled unchanged after washing with dilute alkali. Finally, ruthenium tetroxide oxidation of **5** destroyed the cyclohexenone ring; esterification of the acidic products with diazomethane, distillation, and purification by glc afforded (*S*)-(+)-methyl citramalate (**8**), $[\alpha]D$ +26.4°, identical with a sample prepared from (*S*)-(+)-citramalic acid (**7**).

This correlation establishes that adduct **2b** has the *S* configuration at the new asymmetric center, and isomer **2a** accordingly has the *R* configuration at this site.

Experimental Section

Melting points were determined in a Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on Varian HA-100, Hitachi R-20, and Varian T-60 instruments. Chemical shifts are reported as δ units, with tetramethylsilane as an internal standard. Carbon-13 nuclear magnetic resonance spectra were recorded on a JEOL PFT-100 instrument. Infrared spectra were recorded on a Perkin-Elmer Model 257 infrared spectrophotometer. Ultraviolet spectra were recorded on a Perkin-Elmer Model 202 spectrophotometer. A 1-dm cell was used to determine optical rotations in a Perkin-Elmer Model 141 polarimeter; *c* is expressed as grams per 100 milliliter solution. Elemental analyses of liquid samples were performed at Galbraith Laboratories in Knoxville, Tenn., and elemental analyses of solid samples were performed at the University of Georgia.

Methyl 2′-Hydroxy-2′-methyl-3′-(6,6-dimethyl)bicyclo[3.1.1]hept-2-en-2-yl propionate (2). (1*S*,5*S*)-(−)-β-Pinene (Aldrich Chemical Co.) was purified by fractional distillation at reduced pressure; bp 66° (28 mm), $[\alpha]^{25}D$ −22.1° (neat).

Following the procedure of Arnold and Veeravagu,[9] a solution of methyl pyruvate (30.6 g), hydroquinone (0.1 g), and β-pinene (408 g) was refluxed gently for 96 hr. The excess reagents were removed by distillation up to 60° (8 mm). The resulting viscous liquid was fractionated, collecting the adduct at 79–89° (0.2 mm): 40.82 g, 57.1%; ir (neat) 3550, 2950, 1740, and 1210 cm^{-1}; nmr (CCl_4) 5.20 (m, 1 H), 3.66 (s, 3 H), 2.91 (s, hydroxyl, 1 H), 2.19 (m, 8 H), 1.29 (s, 3 H), 1.21 (s, 3 H), and 0.79 (s, 3 H); mass spectrum M^+ 238; R_f 29 on 12 ft 10% Carbowax column, 150°, as single peak; d_{25} 1.0119. Several runs gave $[\alpha]^{26}D$ −21.0° (neat), $[\alpha]^{30}D$ −22.6° (neat), $[\alpha]^{28}D$ −20.4° (ethanol, *c* 16.3); reported[9] bp 88–89° (0.5 mm), $[\alpha]^{26}D$ −30.2°.

Addition of the nmr shift reagent Eu(fod)$_3$ to a carbon tetrachloride solution of the adduct caused the methoxyl singlet at δ 3.66 to split into two singlets of equal intensity at 3.80 and 3.85, and the methyl singlet at δ 1.29 to split into two signals of equal intensity at 1.57 and 1.68.

Saponification of 2 and Separation of Potassium Salts. A mixture of adduct **2** (17.71 g, 74.3 mmol) and 4.17 g (74.3 mmol) of potassium hydroxide in 60 ml of water and 20 ml of ethanol was refluxed for 2 hr and stirred overnight. After extracting with ether, the aqueous solution was reduced to dryness. The dark residue was taken up in 150 ml of hot ethyl acetate and on cooling, scratching induced crystallization. Recrystallization twice from ethyl acetate gave 6.30 g of one pure potassium salt: mp 105–107°; ir (KBr) 3450, 2920, 1590, and 1120 cm^{-1}; $[\alpha]^{25.5}D$ −18.4° (abs EtOH, *c* 1.67).

The washings and mother liquors were combined and concentrated to a volume of 150 ml. Crystallization occurred on standing. Recrystallization from ethyl acetate–ethanol gave 5.49 g of the diastereomeric potassium salt, mp 204–209°; $[\alpha]^{25.5}D$ −12.1° (abs EtOH, *c* 1.70). A mixture of the two salts melted at 105–210°.

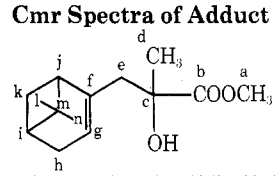
Diastereomeric Adducts 2a and 2b. A solution of 15.75 g of the potassium salt of mp 105–106° was neutralized with 6.50 g of 36% hydrochloric acid. The acidic solution was extracted with three 200-ml portions of chloroform. The extracts were combined, dried, and concentrated to give 13.5 g of crude acid. The acid was treated with excess ethereal diazomethane and the solvents were removed *in vacuo*. Ester **2b** was isolated by distillation as a low-melting solid: bp 72–80° (0.20 mm); 13.90 g, 96.5%; ir (neat) 3510, 2950, 1740, and 1201 cm^{-1}; nmr (CCl_4) 5.29 (m, 1 H), 3.71 (s, 3 H), 2.89 (s, hydroxyl, 1 H), 2.26 (m, 8 H), 1.35 (s, 3 H), 1.29 (s, 3 H), and 0.82 (s, 3 H); mass spectrum M^+ 238; $[\alpha]^{25}D$ −12.5° (abs EtOH, *c* 4.93); lit.[9] $[\alpha]^{26}D$ −29.42°.

The potassium salt of mp 204–207°, 9.49 g, was converted into the ester in the same manner to give 9.56 g, 95%, of the low-melting methyl ester **2a**: bp 74–80° (0.15 mm); ir (neat) 3540, 2940, 1739, and 1199 cm^{-1}; nmr (CCl_4) 5.10 (m, 1 H), 3.64 (s, 3 H), 2.85 (s, hydroxyl, 1 H), 2.15 (m, 8 H), 1.31 (s, 3 H), 1.25 (s, 3 H), and 0.81 (s, 3 H); $[\alpha]^{23}D$ −33.4° (abs EtOH, *c* 1.95).

Addition of Eu(fod)$_3$ to each diastereomer **2a** and **2b** caused no detectable splitting of the methoxyl or methyl singlets in the nmr, demonstrating that each was a pure isomer.

The natural abundance cmr spectra of the adduct mixture and the pure diastereomer **2a** are tabulated in Table I. Assignment of signals was based on coupling and on the published assignment to the spectrum of α-pinene.[15]

Table I
Cmr Spectra of Adduct



Adduct mixture **2**	Isomer **2a**	Carbon	Coupling
177.177, 177.016	176.922	b	s
144.888, 144.399	144.694	f	s
121.924, 121.392	121.198	g	d
75.768, 75.088	75.574	c	s
52.177	52.080	a	q
48.391, 48.197	48.003	e	t
47.566	47.323	j	d
41.110	40.916	i	d
33.198	37.955	m	s
32.180	31.986	h	t
32.034	31.986	k	t
26.646, 26.404	26.549	d	q
26.161	26.307	l	q
21.453	21.307	n	q
0	0	TMS	

Control Experiments. A. A solution of adduct **2a** (500 mg, $[\alpha]^{22}D$ −33.4°) and 5 mg of hydroquinone in 12 ml of β-pinene was refluxed for 96 hr. Removal of solvent gave a residue which was distilled in a Kugelrohr apparatus to give the unchanged adduct (331 mg), $[\alpha]^{25*}D$ −33.1° (abs EtOH, *c* 2.12). The ir and nmr spectra were identical with starting material, and addition of Eu(fod)$_3$ caused no splitting of nmr signals.

B. A solution of adduct **2b** (700 mg, $[\alpha]^{25}D$ −12.5°) and 7 mg of hydroquinone in 12 ml of β-pinene was refluxed for 89 hr. Removal of solvent gave a residue which was distilled in a Kugelrohr apparatus to give unchanged **2b** (484 mg), bp 56–60° (0.18 mm), $[\alpha]^{24}D$ −12.9° (abs EtOH, *c* 4.60). The ir and nmr spectra were unchanged, and addition of Eu(fod)$_3$ caused no splitting of the nmr signals.

C. In three separate experiments, a solution of 68.0 g of β-pinene, 0.0166 g of hydroquinone, and 5.1 g of methyl pyruvate was gently refluxed for 6, 24, and 48 hr, respectively. Excess β-pinene and methyl pyruvate were removed at reduced pressure. The residue was distilled in a Kugelrohr apparatus to afford adduct, **2**, bp 60–70° (0.19 mm), in 8.9, 19.1, and 34.4% yields, respectively. The respective optical rotations were −18.9, −18.1, and −18.6° (abs EtOH, *c* 5.3–5.9). Examination of the nmr spectrum of each product with added Eu(fod)$_3$ showed that an approximately 1:1 mixture of diastereomers was formed in each case.

Preparation of Epoxide 3. To a solution of 4.737 g of acetic anhydride (46.4 mmol), 30 ml of ethylene chloride, and 1.338 g of 80% hydrogen peroxide (31.5 mmol) was added 0.15 g of trifluoroacetic acid. After stirring for 2 hr, the peracid solution was added dropwise to a mixture of 4.8710 g of diastereomer **2b** (20.4 mmol), 9.9652 g of anhydrous sodium carbonate (94.1 mmol), and 0.2 g of anhydrous sodium acetate in 120 ml of dry methylene chloride. After stirring 12 hr, the salts were filtered and the solution concentrated to an oil. The epoxide was purified by distillation at 96–102° (0.15 mm) to give a colorless liquid: 4.53 g, 87.5%; ir (neat) 3510, 2960, 1745, and 1225 cm^{-1}; nmr (CCl_4) 3.70 (s, 3 H), 3.40 (s, hydroxyl, 1 H), 3.29 (m, 1 H), 1.95 (m, 8 H), 1.29 (s, 3 H), 1.25 (s, 3 H) and 0.95 (s, 3 H); R_f 0.72, hexane–ethyl acetate (9:1) on silica gel: mass spectrum M^+ 254; $[\alpha]^{24}D$ −69.9° (abs EtOH, *c* 3.63). *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.12; H, 8.72. Found: C, 66.36; H, 8.82.

Preparation of Triol 4. Dry Ice, 0.5 g, was added to 20 ml of water at 0°. Rapidly, 750 mg of epoxide **3** was added, the flask stoppered, and the solution mixed. After stirring 30 min, the solution was extracted with chloroform. The extracts were combined, dried, and concentrated to afford an oil. The triol was chromatographed on 15 g of 60–200 mesh silica gel, the product appearing in the 1800–1900 ml volume of eluent using hexane–ethyl acete (9:1), and characterized as an oil: 0.486 g, 60.5%; ir (neat) 3350, 2940, 1739, and 1208 cm^{-1}; nmr (acetone-d_6) 5.62 (m, 1 H), 4.4 (br s, hydroxyl, 3 H), 4.15 (br s, 1 H), 3.80 (s, 3 H), 2.25 (m, 7 H), 1.40 (s, 3 H), and 1.19 (s, 6 H); mass spectrum M^+ 254; R_f 0.1 using hexane–ethyl acetate (9:1) on silica gel; $[\alpha]^{23}D$ −94.0° (abs EtOH, *c* 15.8).

The same procedure, beginning with the adduct mixture **2**, gave an oil, which was crystallized from benzene–hexane to a white solid (40%): mp 133–135°; ir (KBr) 3350, 2960, 1730, and 1199 cm^{-1}; nmr (acetone-d_6) 5.65 (m, 1 H), 4.4 (br s, hydroxyl, 3 H), 4.10 (br s, 1 H) 3.70 (s, 3 H), 2.0 (m, 7 H), 1.38 (s, 3 H), and 1.10 (s, 6 H); nmr ($CDCl_3$) 5.68 (m, 1 H), 4.60 (br s, hydroxyl, 3 H), 4.18 (m, 1 H), 3.80 (s, 3 H), 2.20 (m, 7 H), 1.40 (s, 3 H), 1.22 (s, 3 H), and 1.19 (s, 3 H); $[\alpha]^{25}D$ −91.0° (abs EtOH, *c* 0.95). *Anal.* Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.98; H, 8.97.

Preparation of Ketone 5. To a solution of 125 ml of methylene chloride and 15.70 g of pyridine (198.3 mmol) was added 9.92 g of chromium trioxide (99.2 mmol) in the usual manner. The triol **4** (4.4519 g) in 20 ml of methylene chloride was added and stirring continued for 30 min. Ether was added and the mixture filtered. The ethereal solution was washed with dilute acid, base, and saturated salt solution and dried. Removal of the solvent gave crude ketone which was purified by distillation: 3.15 g, 73.6%; bp 145–150° (0.1 mm); ir (neat) 3465, 2980, 1740, 1670, and 1110 cm^{-1}; nmr (acetone-d_6) 7.0 (m, 1 H), 3.70 (s, 3 H), 3.35 (s, hydroxyl, 2 H), 2.4 (m, 7 H), 1.39 (s, 3 H), and 1.35 (s, 6 H); λ_{max} (EtOH) 239 nm (ϵ 9500); mass spectrum M^+ 252; $[\alpha]^{23}D$ −17.4° (abs EtOH, *c* 2.5).

Preparation of Ketal 6. The crude enone **5** from the Collins oxidation above was freed of inorganic salts by filtration, concentrated, and distilled to give the ketal **6** as a colorless liquid: 3.39 g, 82.5%; bp 110–120° (0.1 mm); ir (neat) 2980, 1741, 1050, and 1010 cm^{-1}; nmr ($CDCl_3$) 5.1 (m, 1 H) 3.58 (s, 3 H), 2.3 (m, 7 H), 1.49 (s, 3 H), 1.20 (s, 3 H), and 1.15 (s, 3 H); mass spectrum M^+ 234; R_f 0.82 using hexane–ethyl acetate (9:1) on silica gel; $[\alpha]^{23}D$ −1.31° (abs EtOH, *c* 2.82). *Anal.* Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.55; H, 7.87. A solution of the ketal (1.50 g) in 10 ml of dioxane and 110 ml of water was treated with 6 drops of concentrated hydrochloric acid. After stirring at 40° for 3 hr, the solution was extracted with chloroform. The extracts were combined, washed with bicarbonate, and dried. Concentration of the chloroform solution gave an oil which was distilled in a Kugelrohr apparatus, yielding the ketone **5**, bp 160–170° (0.1 mm). The ir and nmr spectra, as well as the optical rotation, were identical with those of the ketone described above.

Ruthenium Tetroxide Oxidation. A solution of ketone **5** (1.55 g, 5.75 mmol) in 50 ml of acetone was added to a solution of ruthenium tetroxide. The tetroxide was freshly prepared by adding 1.00 g of sodium periodate (4.67 mmol) in 20 ml of water to 173.7 mg of 52.7% ruthenium dioxide (0.69 mmol) in 50 ml of acetone. As the reaction progressed, 5.0 g of sodium periodate (23.4 mmol) in a solution of 50 ml of water–20 ml of acetone was added portionwise.

After stirring the mixture 5 hr at room temperature, 20 ml of 2-propanol was added and the mixture was filtered. The solvents were removed *in vacuo*, and the residue was esterified with excess diazomethane. The ether was removed and the product distilled in a Kugelrohr apparatus to give 0.865 g (85.6%) of ester: bp 80–110° (2.0 mm), $[\alpha]^{21}D$ +15.5° (chloroform, *c* 9.42). The sample was further purified by glc to give (*S*)-(+)-dimethyl citramalate,[16,17] purity 95% by glc; ir (neat) 3510, 2960, 1740, and 1195 cm^{-1}; nmr ($CDCl_3$) 3.80 (s, hydroxyl, 1 H), 3.71 (s, 3 H), 3.61 (s, 3 H), 2.90 and 2.60 (AB quartet, 2 H, $J \approx 15$ Hz), and 1.40 (s, 3 H); $[\alpha]^{21}D$ +26.4° (chloroform, *c* 4.22) [lit.[17] $[\alpha]^{20}D$ +30.6° (chloroform, *c* 3.24)]. The mass spectrum and glc retention time were identical with those of a sample of dimethyl citramalate prepared from racemic citramalic acid.[18]

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Registry No.—**1**, 18172-67-3; **2a**, 53216-67-4; **2a** K salt, 53216-68-5; **2b**, 53216-69-6; **2b** K salt, 53216-70-9; **3**, 53216-71-0; **4**, 53216-72-1; **5**, 53216-73-2; **6**, 53216-74-3; **8**, 38574-61-7; methyl pyruvate, 600-22-6.

References and Notes

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