dryness. Chromatography (Whatman No. 3MM, solvent A) gave the product **14**, R_f 0.84, 21 mg (34%).

5'-(*p*-Bromophenacyloxytrityl)uridylyl-(3'–5')-uridylyl-(3'–5')-uridine (5'-BPTr-UpUpU, 18).—The preceding trinucleoside diphosphate **14** (7 mg) was treated with concentrated ammonia (5 ml) for 15 hr. Preparative paper chromatography on Whatman No. 3MM paper (solvent A) gave **18** (5'-BPTr-UpUpU), R_f 0.63, 4.5 mg (83%).

Detritylation of 14, 5'-BPTr-U(OAc)pU(OAc)pU(OBz)$_2$, and 18, 5'-BPTr-UpUpU.—Portions (0.5 mg) of the trinucleoside diphosphates **14** and **18** were treated with 10, 20, and 40% acetic acid (0.2 ml) and zinc dust (2 mg) and the reactions followed by tlc (cellulose, solvent A).

The detritylation of **18**, R_f 0.63, was complete in 1 hr with 20 and 40% acetic acid and zinc to give UpUpU, R_f 0.27. In the case of **14**, R_f 0.84, the detritylation was also complete in under 1 hr with 20 and 40% acid to give **17**, U(OAc)pU(OAc)pU(OBz)$_2$, R_f 0.43, but again side products were formed, R_f 0.49 and 0.53.

Treatment of **14**, 5'-BPTr-U(OAc)pU(OAc)pU(OBz)$_2$ (30 OD_{260} units), with 90% formic acid (1 ml) at room temperature for 10 min, followed by evaporation and chromatography (Whatman No. 3MM, solvent A), gave **17**, U(OAc)pU(OAc)pU(OBz)$_2$, 21 OD_{260} units, R_f 0.43. Treatment with concentrated ammonia for 16 hr gave UpUpU.

Registry No.—**2f**, 33608-41-2; **3f**, 33608-42-3; **4a**, 33531-85-0; **4b**, 33608-43-4; **4c**, 33531-86-1; **4d**, 33531-87-2; **4e**, 33531-88-3; **4f**, 33531-89-4; **5a**, 33531-90-7; **5b**, 33531-91-8; **5c**, 33531-92-9; **5d**, 33531-93-0; **6a**, 33531-94-1; **6b**, 33531-95-2; **6c**, 33531-96-3; **6d**, 33531-97-4; **7a**, 33531-98-5; **7b**, 33531-99-6; **8a**, 1969-54-6; **8b**, 10300-41-1; **9b**, 33532-02-4; **10a**, 33532-03-5; **10b**, 33532-04-6; **11**, 33532-05-7; **12**, 33532-06-8; **14**, 33545-29-8; **15**, 33608-44-5; **18**, 33608-45-6; 5'-(*p*-bromophenacyloxytrityl)uridine 2',3'-cyclic phosphate, 33532-07-9; 5'-(*p*-bromophenacyloxytrityl)uridine 3'-phospate, 33532-08-0.

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Partial Asymmetric Induction in the Ene Reaction

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Asymmetric induction in the ene reaction of (−)-menthyl glyoxylate with pent-1-ene has been studied. Optical yields were found to depend on temperature, solvent, and catalyst. The configuration of the new dissymmetric center in the obtained adducts changed with catalyst. In the presence of $SnCl_4$, BF_3, and $TiCl_4$ configuration *S* was induced, whereas with $AlCl_3$ center with configuration *R* was obtained. Postulation of an equilibrium between transition states derived from single- (s-) cisoid and transoid conformations of carbonyl groups of (−)-menthyl glyoxylate accounts for the results of asymmetric induction in the examined ene reaction.

Studies of partial asymmetric synthesis are of theoretical and preparative interest. On one hand they may be used as a tool to establish or relate configuration,[1] or, when configuration of the substrate and product is known, asymmetric induction may serve as a criterion of the assumed geometry of a transition state. On the other hand, high (70–100%) optical yields achieved for several reactions[2] open the possibility of applying asymmetric synthesis as a method for the preparation of optically active compounds with the desired absolute configuration. Though the area has been studied extensively with respect to both of these possibilities, little is known about asymmetric induction in the ene[3] reaction, for which so far only two examples have been examined.[4] In this paper we describe the results of the asymmetric induction in the ene condensation of pent-1-ene with (−)-menthyl glyoxylate in the presence of Lewis acid type catalyst.

Results

Data reported by Klimova, *et al.*,[5] indicate that butyl glyoxylate is an enophile of low reactivity. The thermal reaction (150°) with olefins gives poor yields; however, when catalyzed by Lewis acids it takes place readily at room temperature. Accordingly, we found that (−)-menthyl glyoxylate in the presence of 1 equiv of tin tetrachloride at room temperature reacted with pent-1-ene to afford in 87% yield the expected adduct, (−)-menthyl 2-hydroxy-4-heptenoate (**1**). Likewise high yields of adduct **1** were obtained with other Lewis acids ($AlCl_3$, BF_3, $TiCl_4$). The structure of **1** was confirmed by analysis, spectral data (ir, nmr), and chemical transformations shown in Scheme I.

Adduct **1** was comprised of two components[6] (vpc) which we assumed to be cis and trans isomers, since catalytic hydrogenation of the double bond of adduct **1** yielded dihydro derivative **2**, giving only one peak in vpc, whereas methanolysis of **1** gave methyl ester **3** as a two-component mixture (vpc).

The optical yield of the ene reaction and the absolute configuration of the new dissymmetric center predominantly formed in adduct **1** were established by correlation of the latter with a compound of known specific rotation and absolute configuration, *i.e.*, methyl (−)-malate. To this end adduct **1** was subjected to ozonolysis, oxidative decomposition of the ozonide, and subsequent hydrolysis and methylation of malic acid with diazomethane (Scheme I). The methyl malate

(1) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 72.

(2) T. D. Inch, *Synthesis*, 466 (1970), and references cited therein.

(3) For the review, see H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).

(4) R. K. Hill and M. Rabinowitz, *J. Amer. Chem. Soc.*, **86**, 965 (1964).

(5) (a) E. I. Klimova and Y. A. Arbuzow, *Dokl. Akad. Nauk SSSR*, **167**, 1060 (1966); *Chem. Abstr.*, **65**, 3736h (1966); (b) E. I. Klimova, E. G. Treshchova, and Y. A. Arbuzow, *Dokl. Akad. Nauk SSSR*, **180**, 865 (1968); *Chem. Abstr.*, **69**, 67173b (1968); (c) E. I. Klimova and Y. A. Arbuzow, *Dokl. Akad. Nauk SSSR*, **173**, 1332 (1967); *Chem. Abstr.*, **67**, 108156c (1967).

(6) In principle, adduct **1** is a four-component mixture: geometric isomers of two diastereoisomers. However, separation by vpc of isomers other than cis and trans in this case is rather unlikely, as follows from the vpc examination of the hydrogenation and methanolysis products.

TABLE I

EFFECT OF SOLVENT AND QUANTITY OF CATALYST ON OPTICAL YIELD

No.	Catalyst (equiv)	Solvent	Temp, °C	Specific rotation of methyl malate[a] c	$[\alpha]_{578}$	$[\alpha]_{546}$	$[\alpha]_{436}$	Optical yield, %	Configuration
1	$SnCl_4$ (0.12)	CH_2Cl_2	20	11.04	−1.18	−1.30	−1.90	13.3	*S*
2	$SnCl_4$ (0.25)	CH_2Cl_2	20	10.47	−1.32	−1.46	−2.07	14.7	*S*
3	$SnCl_4$ (0.50)	CH_2Cl_2	20	10.75	−1.38	−1.52	−2.16	15.4	*S*
4	$SnCl_4$ (1.00)	CH_2Cl_2	20	11.60	−1.28	−1.42	−2.01	14.3	*S*
5	$SnCl_4$ (1.00)	$C_6H_5CH_3$	20	7.57	−1.70	−1.93	−2.77	19.4	*S*
6	$SnCl_4$ (1.00)	CH_3NO_2	20	8.18	−1.97	−2.21	−3.24	22.5	*S*
7	$SnCl_4$ (1.00)	CH_3CN	20	4.65	−1.94	−2.11	−3.14	21.8	*S*

[a] Obtained from adducts **1**.

TABLE II

EFFECT OF LEWIS ACID AND TEMPERATURE ON OPTICAL YIELD

No.	Catalyst (1 equiv)	Solvent	Temp, °C	Specific rotation of methyl malate[a] c	$[\alpha]_{578}$	$[\alpha]_{546}$	$[\alpha]_{436}$	Optical yield, %	Configuration
1	$SnCl_4$	CH_2Cl_2	20	11.60	−1.28	−1.42	−2.01	14.3	*S*
2	$SnCl_4$	CH_2Cl_2	−70	10.08	−2.01	−2.25	−3.15	22.2	*S*
3	$TiCl_4$	CH_2Cl_2	20	9.17	−1.09	−1.24	−1.79	12.5	*S*
4	$TiCl_4$	CH_2Cl_2	0	9.72	−1.23	−1.38	−1.96	13.9	*S*
5	$TiCl_4$	CH_2Cl_2	−20	8.59	−2.31	−2.55	−3.59	25.7	*S*
6	BF_3	CH_2Cl_2	10	6.27	−0.48	−0.56	−0.89	5.8	*S*
7	BF_3	CH_2Cl_2	−25	10.13	−0.69	−0.82	−1.24	8.3	*S*
8	$AlCl_3$	CH_2Cl_2	20	9.42	+0.70	+0.77	+0.98	7.5	*R*
9	$AlCl_3$	CH_2Cl_2	0	5.35	+0.93	+1.07	+1.42	10.4	*R*
10	$AlCl_3$	CH_2Cl_2	−15	11.17	+0.98	+1.10	+1.47	10.8	*R*
11	$AlCl_3$	CH_2Cl_2	−22	4.32	+0.58	+0.63	+0.72	6.0	*R*
12	$SnCl_4$	CH_3NO_2	0	8.06	−2.81	−3.10	−4.33	31.2	*S*
13	$SnCl_4$	CH_3CN	0	4.98	−2.01	−2.23	−3.17	22.5	*S*
14	None	None	160	10.05	+0.16	+0.18	+0.30	1.8	*R*

[a] Obtained from adducts **1**.

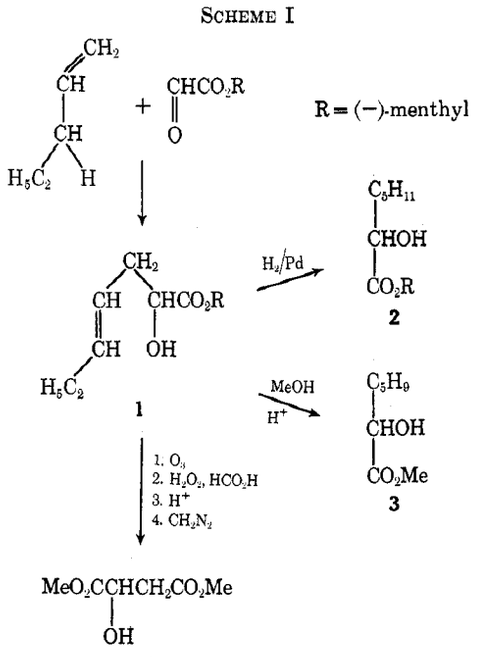
thus obtained was purified by column chromatography on silica gel, and its purity was checked by tlc and vpc.

The ene reaction of (−)-menthyl glyoxylate with pent-1-ene was run at several temperatures with different catalysts and solvents. Optical yields and absolute configurations of adducts **1** are collected in Tables I and II.

Optical yields of examined ene reaction carried out with various amounts of $SnCl_4$ as catalyst (0.12–1.00 equiv) remained unchanged (Table I, entries 1–4). Therefore in the subsequent experiments equivalent amounts of catalyst were used. The solvent effected the optical yield of the reaction (Table I, entries 4–7). Replacement of dichloromethane by nitromethane, methyl cyanide, or toluene caused an increase in optical yields. This may be related to the higher dielectric constant and/or the ability of these solvents to form complexes with Lewis acids. However, the decisive influence on the asymmetric induction was the presence and nature of the catalyst. Lewis acids used ($SnCl_4$, BF_3, $AlCl_3$, $TiCl_4$) caused an increase in optical yields as compared with thermal condensation; moreover, the absolute configuration of the induced dissymmetric center depended on the nature of the catalyst (Table II). Optical yields increased[7] at lower temperatures. However in neither case did optical yields reach values which permit use of this ene reaction as a method for the synthesis of optically active α-hydroxy acids (after hydrolysis and hydrogenation of the double bond).

We have shown that adducts **1** could not be equilibrated under the conditions of ene reaction. The action of $AlCl_3$ or BF_3 on adduct **1** obtained with $SnCl_4$ as well as treatment with $SnCl_4$ of adduct **1** prepared in the presence of $AlCl_3$ failed to bring about any changes, either in the optical purity or ratio of cis–trans isomers.

SCHEME I

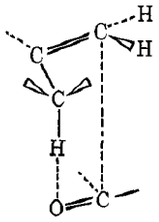


Discussion

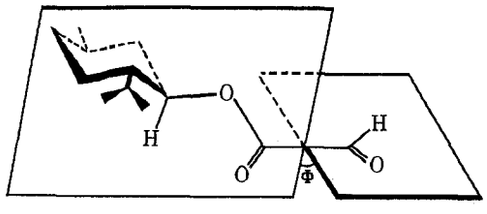
We assume that in the synchronous ene reaction the olefin approaches the aldehydic carbonyl group preferentially from the less shielded side and attains a transitional state geometry which maximizes the allylic

(7) With the exception of the reaction run in the presence of $AlCl_3$ (Table II, entries 8–11). In this case there appeared a maximum between 0 and −15°, optical yields being smaller at higher and lower temperatures.

resonance;[8] *i.e.*, the ruptured C–H bond takes position parallel to the π orbital of the double bond.[9]

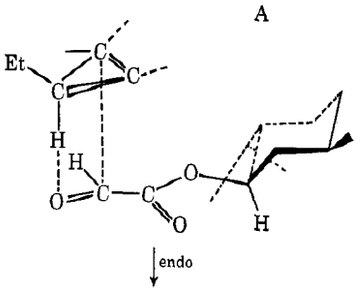


To choose the less hindered side of the aldehydic group it is necessary to consider the preferred conformation of (−)-menthyl glyoxylate, particularly the relative position of both carbonyl groups and the orientation of the (−)-menthyl residue relative to the ester group. According to previous studies[10] the alkyl α hydrogen of an ester is coplanar with the carboxyl group and faces the carbonyl oxygen. This was found for simple esters[10] and esters of α-keto acids[11] in the solid state and in solution alike. On the other hand, the angle between the carbonyl groups found for two keto esters amounted to 75° for ethyl *p*-bromophenylglyoxylate[11a] at 104° for (−)-menthyl *p*-bromophenylglyoxylate.[11b] Per analogy we ascribe to (−)-menthyl glyoxylate the conformation depicted below, where Φ is an dihedral angle approaching 90°.



It has been noticed before[11b] that for such conformations steric hindrance of both sides of the aldehydic carbonyl group should be independent of the substituents of the alkoxyl residue; consequently, the asymmetric induction of the ene reaction would be negligible. On the other hand, to interpret the results of an asymmetric induction in the diene reaction of (−)-menthyl glyoxylate with 1-methoxybuta-1,3-diene, transition states based on conformations of (−)-menthyl glyoxylate with parallel and antiparallel orientation of carbonyl groups were postulated.[12] Analogously, to accommodate our results we assume that under the conditions of catalytic ene reaction, depending on the Lewis acid used, either antiparallel (s-transoid) or parallel (s-cisoid) conformation of the carbonyl groups of (−)-menthyl glyoxylate is induced.[13] From these conformations four transition states, A, B, C, and D, are derived which determine the direction of asymmetric induction. Transition states A and B, with s-cisoid orientation of the carbonyl groups correspond to endo and exo addition, respectively.

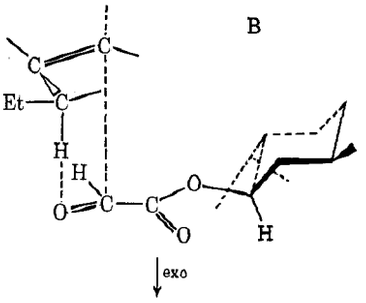
A



endo

(−)-menthyl *cis*-2-(*S*)-hydroxy-4-heptenoate

B



exo

(−)-menthyl *trans*-2-(*S*)-hydroxy-4-heptenoate

Both yield adduct **1** with configuration *S* of the newly formed dissymmetric center; *i.e.*, they predominate in the ene reaction catalyzed by $SnCl_4$, BF_3, and $TiCl_4$. The difference between endo and exo addition is reflected[14] in the formation of cis and trans iomers of **1**. According to Berson, *et al.*,[15] endo addition predominates in ene reaction, though not so decidedly as in diene synthesis.[16] Our results also indicate lack of positive preference of one mode of addition over another;[17] the proportion of the geometric isomers of adduct **1** varied in the range of 3:7 to 4:6, depending on both catalyst and temperature.

Likewise, transition states C and D derived from the s-transoid conformation of (−)-menthyl glyoxylate correspond to endo and exo addition, respectively, leading to geometric isomers of adduct **1**, with *R* configuration at the newly created dissymmetric center. Thus, they are favored in the ene reaction catalyzed by $AlCl_3$ (Table II, entries 8–11).

According to the postulated mechanism of the asymmetric ene synthesis the configuration and optical yield of the product depend on the equilibrium between four different transition states with s-cisoid (A and B) and s-transoid (C and D) conformations of the carbonyl groups. Factors which affect the relative rates of formation of products include solvent, temperature, and, most importantly, catalyst. We think that Lewis acids influence the equilibria between transition states

(8) Reference 3, p 575.

(9) Postulation of such a transition state well accommodated the results of the ene reaction between (*S*)- or (*R*)-3-phenylbut-1-ene and maleic anhydride.[4]

(10) (a) A. McL. Mathieson, *Tetrahedron Lett.*, 4137 (1965); (b) J. P. Jennings, W. Klyne, W. P. Mose, and P. M. Scopes, *Chem. Commun.*, 553 (1966); (c) J. P. Jennings, W. P. Mose, and P. M. Scopes, *J. Chem. Soc.*, 1273 (1967).

(11) (a) G. Oehme and A. Schellenberger, *Chem. Ber.*, **101**, 1499 (1968); (b) R. Parthasarathy, J. Ohrt, A. Horeau, J. P. Vigneron, and H. B. Kagan, *Tetrahedron*, **26**, 4705 (1970).

(12) (a) J. Jurczak, Ph.D. Dissertation, Institute of Organic Chemistry, Polish Academy of Sciences, 1970; (b) J. Jurczak and A. Zamojski, *Tetrahedron*, in press.

(13) s-Cisoid and s-transoid conformations are extreme cases used for the sake of simplicity. In fact, for our argument it is sufficient to postulate conformations with the dihedral angle between carbonyl groups much smaller and larger than 90°.

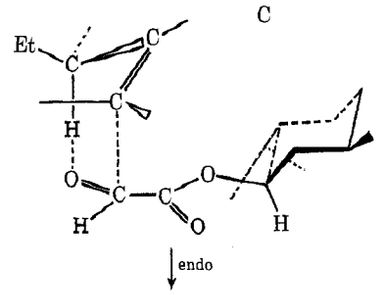
(14) We assume that owing to the steric hindrance pent-1-ene reacts in a conformation with the ethyl residue located outside the transition complex.

(15) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *J. Amer. Chem. Soc.*, **88**, 187 (1966).

(16) For review see (a) J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961); (b) J. Sauer, *Angew. Chem.*, **79**, 76 (1967).

(17) This conclusion can be drawn without assignment of cis and trans configuration.

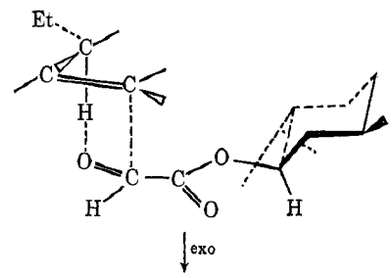
C



endo

(−)-menthyl *cis*-2-(*R*)-hydroxy-4-heptenoate

D



exo

(−)-menthyl *trans*-2-(*R*)-hydroxy-4-heptenoate

owing to their ability to form complexes with carbonyl groups.[18] On the other hand, the difference in steric shielding as related to the bulkiness of the substituents in the alkoxy residue is not decisive[19] for the direction of asymmetric induction.

Experimental Section

Boiling points refer to the air bath temperature and are uncorrected. Ir spectra were taken as liquid films using a Perkin-Elmer Model 137 spectrophotometer. Pmr spectra were obtained from a Varian HA-60/IL instrument in CCl_4 using TMS as internal standard. Optical rotations (°) were measured on a Perkin-Elmer 141 photopolarimeter at three wavelengths (436, 546, 578 nm) on *ca.* 10% methanolic solutions. Vapor phase chromatographic analyses were performed on a Willy Giede gas chromatograph 18.3.

Pent-1-ene[20] and (−)-menthyl glyoxylate hydrate[21] were prepared by known methods. The latter was dehydrated by distillation before use. A reference sample of methyl malate, $[\alpha]_{436}^{20}$ −13.88, $[\alpha]_{546}^{20}$ −9.94, $[\alpha]_{578}^{20}$ −9.00 (*c* 10.2, MeOH), was obtained by esterification with diazomethane of commercial malic acid. All condensations of (−)-menthyl glyoxylate with pent-1-ene and equilibrations of adduct **1** were carried out in an analogous manner.

(−)-Menthyl 2-Hydroxy-4-heptenoate (1). A. Catalytic Condensation.—To a stirred solution of 1.965 g (9.28 mmol) of (−)-menthyl glyoxylate in 10 ml of methylene chloride at 0° were added in succession solutions of 2.41 g (9.28 mmol) of tin tetrachloride and of 1.30 g (18.56 mmol) of pent-1-ene, each in 5 ml of methylene chloride. The reaction was stirred for 24 hr at 0°, and then 0.94 g (9.28 mmol) of triethylamine was added to neutralize the solution. The mixture was diluted with 100 ml of ether, washed with water, dried ($MgSO_4$), concentrated, and distilled, giving 2.26 g (87%) of **1**, which solidified on standing, bp 110–115° (10^{-1} mm). Vpc analysis of **1** showed it to be 4:6 mixture: ir 3500 (OH), 1730 cm^{-1} (C=O); pmr δ 5.80–5.05 (m, 2, CH=CH), 4.72 (broad t, 1, J = 9.0 Hz, $-CO_2CH<$), 4.16 (t, 1, J = 5.5 Hz, CHOH), 2.83 (s, 1, OH), 2.42 (t, 2, J = 5.8 Hz, CH_2CHOH), 2.30–1.00 (m, 11), 0.97 (t, 3, J = 7.0 Hz, CH_2CH_3), 0.88 [d, 6, J = 7.0 Hz, $-CH(CH_3)_2$], 0.75 (d, 3, J = 7.0 Hz, $>CHCH_3$).

Anal. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71. Found: C, 72.03; H, 10.59.

B. Thermal Condensation.—A mixture of 2.12 g (10.0 mmol) of (−)-menthyl glyoxylate and 1.40 g (20.0 mmol) of pent-1-ene was heated in a sealed tube for 24 hr at 160°, then was chromatographed over 60 g of silica gel (mesh 200–300). Elution with benzene–ethyl acetate (9:1), evaporation of appropriate (tlc) fractions, and distillation afforded 0.65 g (23%) of product identical (tlc, ir, pmr) with the specimen obtained according to procedure A.

Attempted Equilibration of Adduct 1.—To a stirred solution of 1.41 g (10.0 mmol) of **1** (prepared using $SnCl_4$ as catalyst) in 10 ml of methylene chloride at −10° a solution of 1.33 g (10.0 mmol) of aluminum chloride in 10 ml of methylene chloride was added and the mixture was left for 48 hr at −10°; then 1.01 g (10.0 mmol) of triethylamine was added, and the reaction mixture was diluted with 100 ml of ether, washed with water, dried ($MgSO_4$), and evaporated to dryness. The optical purity and cis:trans ratio of the product was the same, within experimental error, as that of the starting material.

(−)-Menthyl 2-Hydroxyheptanoate (2).—A solution of 523 mg of adduct **1**, $[\alpha]_{436}^{20}$ −107.16, $[\alpha]_{546}^{20}$ −64.85, $[\alpha]_{578}^{20}$ −57.29, $[\alpha]_{589}^{20}$ −55.09 (*c* 10.13, MeOH), in 10 ml of acetic acid was hydrogenated in the presence of 57 mg of platinum oxide. Removal of catalyst and solvent (at reduced pressure) afforded 505 mg of **2**: bp 105–110° (10^{-4} mm); $[\alpha]_{436}^{20}$ −122.71, $[\alpha]_{546}^{20}$ −74.03, $[\alpha]_{578}^{20}$ −65.25, $[\alpha]_{589}^{20}$ −62.82 (*c* 10.38, MeOH); ir 3500 (OH), 1735 cm^{-1} (C=O); pmr δ 4.75 (broad t, 1, J = 9.0 Hz, $-CO_2CH<$), 4.05 (t, 1, J = 5.0 Hz, $>CHOH$), 3.35 (s, 1, OH), 2.20–0.70 (m, 29).

Anal. Calcd for $C_{17}H_{32}O_3$: C, 71.78; H, 11.34. Found: C, 71.70; H, 11.10.

Methyl 2-Hydroxy-4-heptenoate (3).—A solution of 665 mg (2.36 mmol) of adduct **1**, $[\alpha]_{436}^{20}$ −107.16, $[\alpha]_{546}^{20}$ −64.85, $[\alpha]_{578}^{20}$ −57.29, $[\alpha]_{589}^{20}$ −55.09 (*c* 10.13, MeOH), and 54 mg (10.0 mmol) of sodium methoxide in 10 ml of anhydrous methanol was left overnight at room temperature; then the reaction mixture was brought to pH 2 with diluted hydrochloric acid and evaporated to dryness, the residue was dissolved in benzene, and inorganic salt was filtered off. The solvent was removed to give 650 mg of crude product, which was chromatographed over 20 g of silica gel (mesh 200–300). Elution with benzene–ethyl acetate (95:5) and evaporation of appropriate fractions (tlc) afforded 202 mg of (−)-menthol and 147 mg of ester **3**: bp 65–70° (16 mm); $[\alpha]_{436}^{20}$ +5.32, $[\alpha]_{546}^{20}$ +2.84, $[\alpha]_{578}^{20}$ +2.48, $[\alpha]_{589}^{20}$ +2.45 (*c* 8.69, MeOH); ir 3500 (OH), 1735 cm^{-1} (C=O); pmr δ 5.80–5.05 (m, 2, CH=CH), 4.09 (t, 1, J = 5.5 Hz, $>CHOH$), 3.21 (s, 3, CO_2CH_3), 3.28 (s, 1, OH), 2.32 (t, 2, J = 5.5 Hz, CH_2CHOH), 2.20–1.80 (m, 2, CH_2CH_3), 0.95 (t, 3, J = 7.0 Hz, CH_2CH_3).

Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.54; H, 8.68.

Ozonolysis of Adduct 1.—A solution of 1.87 g (6.63 mmol) of **1**, $[\alpha]_{436}^{20}$ −107.16, $[\alpha]_{546}^{20}$ −64.85, $[\alpha]_{578}^{20}$ −57.29, $[\alpha]_{589}^{20}$ −55.09 (*c* 10.13, MeOH), in 40 ml of methylene chloride was cooled in a Dry Ice–acetone bath and saturated with ozone until the blue color persisted; then the solvent was removed, 10 ml of formic acid and 10 ml of 30% hydrogen peroxide were added, the reaction mixture was heated on the steam bath for 40 min, and the solvents were evaporated under reduced pressure. To the amorphous residue 60 ml of 5% hydrochloric acid was added, and the mixture was heated on the steam bath for 60 min and then steam distilled until no more menthol passed over. The solution was taken to dryness *in vacuo*, and the residue was dissolved in 2 ml of methanol, treated with an excess of diazomethane in ether, and evaporated again. Chromatography over 20 g of silica gel (mesh 200–300) in benzene–ethyl acetate (9:1) afforded, after concentration and distillation, 650 mg (60%) of methyl malate: bp 83–85° (0.8 mm); $[\alpha]_{436}^{20}$ −2.01, $[\alpha]_{546}^{20}$ −1.42, $[\alpha]_{578}^{20}$ −1.28 (*c* 11.60, MeOH); identical with an authentic sample (tlc, vpc, ir, pmr).

Registry No.—*cis*-(*R*)-**1**, 33537-19-8; *trans*-(*R*)-**1**, 33495-66-8; *cis*-(*S*)-**1**, 33495-67-9; *trans*-(*S*)-**1**, 33495-68-0; (*R*)-**2**, 33537-20-1; (*S*)-**2**, 33495-69-1; *cis*-**3**, 33495-70-4; *trans*-**3**, 33537-21-2.

(18) H. F. Lappert, *J. Chem. Soc.*, 542 (1962).

(19) The presently postulated mechanism of asymmetric induction is substantially different from that adopted by Prelog[1] for addition of Grignard reagent to α-keto esters in which the direction and optical yield depended solely on the relative size of the substituents of the optically active ester group. It should be mentioned that Prelog's results can be interpreted in terms of our model of asymmetric induction providing one assumes prevalence of the s-cisoid orientation of carbonyl groups.

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