nated during the Morgan–Elson reaction, and any mechanism proposed for this reaction should take this into account. Because the colored products of the Morgan–Elson reaction are unstable and disappear in a few hours, I have not attempted to identify the colored compounds bound to solid supports. These experiments represent one example of an approach to elucidating reaction mechanisms. In cases where the product may be removed from the solid support and its structure identified, this method will lead to useful models of reaction mechanisms.

Acknowledgment. This work was supported by USPHS Grant AI-10360 and by the Washington State University College of Agriculture Research Center, Project 0056, Scientific Paper No. 4341.

Registry No.—**7** (minus support group), 54814-95-8; **8** (minus support group), 54814-96-9.

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(5) The purpose of synthesizing these compounds is for affinity chromatography of glucosamine phosphate isomerase (E.C. 5.3.1.10) which is activated allosterically by 2-acetamido-2-deoxy-D-glucose 6-phosphate. The 2-succinamido-2-deoxy-D-glucose-6-P moiety mimics the physiological activator, binding the enzyme to the immobile Sepharose phase via the allosteric site. Subsequently, the enzyme can be eluted with a basic gradient: R. L. Benson, *Fed. Proc., Fdd. Am. Soc. Exp. Biol.*, **33**, 1477 (1974).
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Asymmetric Decarboxylation of Ethylphenylmalonic Acid in a Cholesteric Liquid Crystal Solvent

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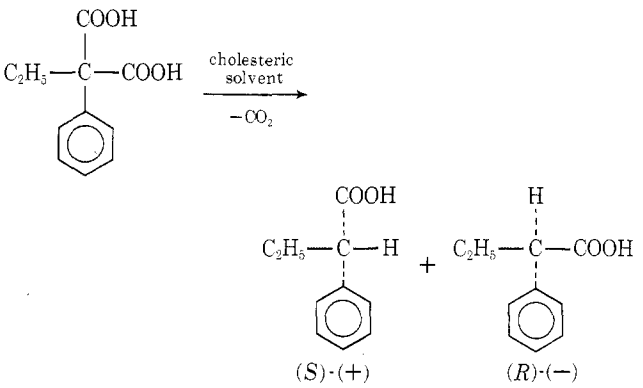
In connection with our interest in liquid crystals,[1] we have been investigating the use of cholesteric liquid crystals as chiral media for asymmetric reactions. Cholesteric or twisted-nematic phases occur in many derivatives of steroids, most commonly cholesterol, as well as in some nonsteroidal compounds. Common features of molecules which exhibit cholesteric mesomorphism are that they are relatively rigid, have a molecular length considerably greater than their breadth, and are, without exception, chiral. The model of the cholesteric phase is that of a layered nematic liquid twisted about an axis at right angles to the molecular layers. Along the direction of the twist axis a gradual change in molecular orientation within the layers occurs, imparting a helical macrostructure to the liquid. Thus, in contrast to the more usual optically active solvents, cholesteric liquid crystals appear particularly attractive as solvents for asymmetric reactions, since they possess not only molecular chirality but also an overall macrochirality owing to the helical arrangement of the mesophase.

Previous asymmetric reactions in isotropic chiral media have been reviewed by Morrison and Mosher.[2] Generally, stereoselectivities are in the range of 5–10%. The only report pertinent to the present work is a recent communication of the use of a cholesteric liquid crystal solvent for the Claisen rearrangement of methylallyl *p*-tolyl ether.[3] The methylallylphenol rearrangement product exhibited optical activity but the absolute configuration and optical purity of the phenol are unknown.

In this report we describe the results of the asymmetric decarboxylation of ethylphenylmalonic acid in the liquid crystal phase of cholesteryl benzoate (Chart I) and in the isotropic chiral solvent, bornyl acetate.

Chart I



Ethylphenylmalonic acid is an achiral molecule but contains two prochiral ligands. The carboxyl group at the top of the structure in Chart I is the pro-*R* ligand, since preferential loss of this group would yield the (*R*)-(−) enantiomer of 2-phenylbutanoic acid. The other carboxyl group is then the pro-*S* one.

A solution containing 10 mol % of the malonic acid in cholesteryl benzoate (2 g in 50 g) was smoothly decarboxylated by heating at 160° for 2 hr.[4] Vacuum distillation of the reaction mixture afforded 1.6 g of 2-phenylbutyric acid (80% yield), which was shown by a combination of TLC and VPC to be free of contaminants. Determination of the rotation utilizing a photoelectric polarimeter gave $[\alpha]^{27}D$ −14.2° (*c* 1.3, absolute EtOH). Based on the highest reported rotation for 2-phenylbutanoic acid of $[\alpha]^{25}D$ 78.5° (absolute EtOH),[5] the phenylbutanoic acid formed in this asymmetric decarboxylation has a minimum optical purity of 18%. This value is based on the assumption that the 20% of unrecovered acid has the same enantiomeric composition as the distilled material. If it does not, the stereoselectivity would be different from the observed 59:41 ratio. However, stability experiments involving the distillation of optically active and racemic 2-phenylbutanoic acid gave material having unchanged rotation in the former case and zero rotation in the latter case.

In contrast to the 18% enantiomeric excess found in the ordered cholesteric solvent, decarboxylation of ethylphenylmalonic acid in bornyl acetate, an isotropic chiral solvent, yielded 2-phenylbutanoic acid which was essentially racemic.

The stereoselectivity in the present asymmetric decarboxylation is relatively high compared to typical asymmet-

ric reactions in isotropic chiral media.[2] Our results indicate that for the system studied, a chiral environment due only to molecular chirality is not sufficient for a significant asymmetric bias to occur. One predicts that a preponderance of (*S*)-(+)-2-phenylbutanoic acid would result by use of a cholesteric mesophase having chirality opposite to that used here and that a shorter helical pitch of the mesophase would result in increased optical purity. While the nature of the diastereomeric solute–solvent interaction is not known, we note a certain parallel to the induced circular dichroism phenomenon[6] in which achiral molecules become optically active when dissolved in a cholesteric mesophase. The induced circular dichroism presumably results in part from a particularly strong interaction between the solute and solvent molecules. Work on other asymmetric reactions in chiral liquid crystal solvents is in progress.

Experimental Section

NMR spectra were measured on a Varian A-60 instrument with internal Me_4Si as standard. The vapor phase chromatograph was a Hewlett-Packard Model 5750 with FID, modified for on-column injection. Optical rotations were measured on a Jasco photoelectric spectropolarimeter. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Temperatures are corrected.

Ethylphenylmalonic acid. Freshly distilled (152–155°, 1 Torr) diethyl ethylphenylmalonate (Eastman, 44.0 g, 0.166 mol) was dissolved in 100 ml of 95% ethanol and a solution of KOH (19.0 g, 0.34 mol) in 20 ml of water was added. The reaction mixture was stirred vigorously at 28° for 20 hr. The solvent was then removed by vacuum distillation and the remaining solid was dried in a vacuum desiccator. The solid was washed well with ether (150 ml). The remaining solid (33.5 g) was placed in 150 ml of ether and acidified with 6 *M* hydrochloric acid (ice bath) to the Congo Red point. Water (55 ml) was added and the mixture was stirred vigorously until all the solid had dissolved. The ether layer was separated, dried (anhydrous sodium sulfate), and filtered, and the ether was removed on a rotary evaporator. The remaining material was recrystallized from pentane followed by a second recrystallization from ether–ligroin (bp 30–60°) to afford ethylphenylmalonic acid (21.7 g, 63%): mp 158–161° dec; NMR (methyl ethyl ketone) δ 6.5–7.0 (aryl H's), 10.45 (singlet, carboxyl protons).

Anal. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.15; H, 5.70.

Asymmetric Synthesis of 2-Phenylbutanoic Acid. Cholesteryl benzoate (50 g), prepared as described in ref 1 [crystal-cholesteric point 150.2°, cholesteric–isotropic point 178.0°, $[\alpha]^{27}D$ −20.8° (*c* 1.72, heptane)], was intimately mixed with 2.0 g of ethylphenylmalonic acid and the mixture was heated for 2 hr at 160° under a nitrogen atmosphere. The reaction flask was then attached to an 18-in. Teflon spinning band column and 1.6 g of 2-phenylbutanoic acid was collected at 95–97° (0.1 mm). The sample was examined for the presence of steroidal and other impurities by TLC on silica gel GF 254 [developing solvent ethyl acetate–heptane (1.6:1)] and by VPC on 1 m × 4 mm stainless steel columns packed with OV-1, 3% on 100/120 Gas Chrom Q and on 2 m × 4 mm copper columns packed with 10% Carbowax 20M on 100/120 Chromosorb W. No contaminants were observed under these conditions. Elemental analysis of 2-phenylbutanoic acid gave the following results.

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.40; H, 7.68.

Measurement of the optical rotation yielded $[\alpha]^{27}D$ −14.2° (*c* 1.3, absolute ethanol) [lit.[5] $[\alpha]^{25}D$ 78.5° (absolute ethanol)].

Decarboxylation of ethylphenylmalonic acid in bornyl acetate [Aldrich Chemical Co., $[\alpha]^{27}D$ −38.0° (neat)] under the conditions described above led to 2-phenylbutanoic acid which exhibited no optical rotation.

Registry No.—Ethylphenylmalonic acid, 1636-25-5; diethylethylphenyl malonate, 76-67-5; 2-phenylbutanoic acid, 938-79-4; cholesteryl benzoate, 604-32-0.

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Electronic Structure of β-Vinyl Substituted Phosphonium Salts by Carbon-13 Nuclear Magnetic Resonance

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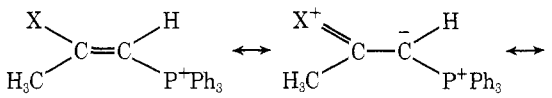
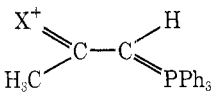
We have previously examined the ^{13}C NMR for a large variety of triphenylphosphonium salts and ylides.[1] The focus of the current work is directed toward β-vinyl substituted phosphonium salts having the general structure shown below, where X = Me, NHR, OEt, and the counter-



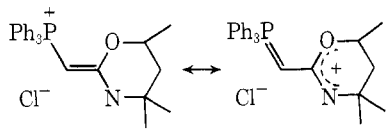
1a **1b**



1c

anion Br^- or Cl^-. One would expect that when X possesses unshared pairs of electrons, the resonance form **1b** should be a large contributor to the total electronic structure. In addition, there is also the possibility of the transfer of excess charge from the π system into empty d orbitals[2] on phosphorus. This latter interaction is illustrated by resonance form **1c**. It is expected that when X = CH_3 charge polarization via hyperconjugation[3] may contribute to **1b**. However, this effect should be of smaller magnitude than that previously described for X = –N̈– or –Ö–.

Support for the contribution of resonance forms **1b** and **1c** has been recently published by Trefonas.[4] In this study the X-ray structure of a related phosphonium salt, **2**, was examined. The shortened P–C, C–O, and C–N bond lengths and a long C=C bond compared to model compounds was claimed to be a result of the intervention of resonance structure **2b**.



2a **2b**

Results and Discussion

The ^{13}C chemical shifts and ^{31}P–^{13}C nuclear spin couplings of vinyltriphenylphosphonium salts and related compounds are reported in Tables I and II, respectively. The assignments of the carbons were made by the use of single frequency off-resonance decoupling and comparisons to model analogs. The assignments of the cis and trans methyl carbons in 2-methylpropenyltriphenylphosphonium chloride (**3**) were discussed previously.[1] The stereochemistry about the carbon–carbon double bond was