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Asymmetric Decarboxylation of 2-Ethyl-2-(4-Methylphenyl)-Propane-1,3-Dioic Acid in Cholesteric Liquid Crystals†

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Asymmetric decarboxylation of 2-ethyl-2-(4-methylphenyl)-propane-1,3-dioic acid was studied in some cholesteric liquid crystalline media such as 2,4-hexadienoic, benzoic, 2,4-dichlorobenzoic, and trans-cinnamic acids at 158–163°C, and compared with the solution reaction in bornyl acetate. Several experiments were conducted as described by Verbit, *et al.*, or with various changes in the procedures, but all invariably afforded low optical active 2-(4-methylphenyl)butanoic acid in high chemical yields. This is also confirmed by chiral recognition through diastereomeric complex formation with optical active shift reagent in ^{1}H NMR spectroscopy. This decarboxylation, thus, should not clearly demonstrate the ability of the chiral mesophase to induce appreciable asymmetric reaction: The solvent order or macroscopic helical structure formed by cholesteric liquid crystals appears to play little role in determining the stereochemical course of this decarboxylation.

INTRODUCTION

Cholesteric liquid crystals possess not only molecular chirality but also an overall macrochirality owing to the helical structure formed by the chiral organization of nematic-like layers with uniaxial molecular arrangement within the layers.[1] This type of ordering within the cholesteric meso-

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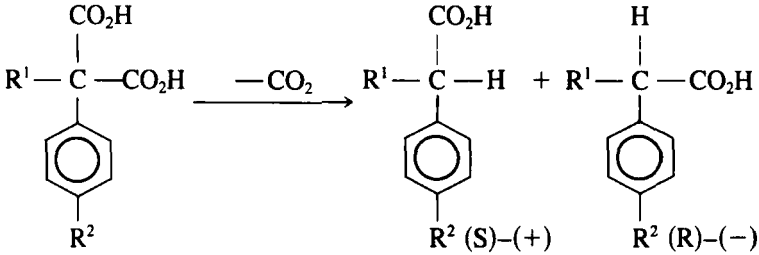
phases would affect chemical reactivity in many specific ways. Thus, cholesteric mesogens appear particularly attractive as solvents for asymmetric reactions, in contrast to the more usual optically active solvents. Several asymmetric reactions, indeed, have been carried out into the chiral mesophases.[2–7]

Such information, as far as the decarboxylation of dibasic acids is concerned, has been reported by Verbit, *et al.*,[3] who studied the formation of optical active 2-phenylbutanoic acid (IIb) by decarboxylation of 2-ethyl-2-phenylpropane-1,3-dioic acid (Ib) in cholesteryl benzoate and claimed an 18% enantiomeric excess to the butanoic acid. Recently, Eskenazi, *et al.*,[7] have reinvestigated this asymmetric decarboxylation using 2-methyl-2-phenylpropane-1,3-dioic (Ia) and 2-ethyl-2-phenylpropane-1,3-dioic (Ib) acids and obtained only the corresponding racemic butanoic acids (IIa and IIb).



Ia: $R^1=CH_3$ $R^2=H$ IIa: $R^1=CH_3$ $R^2=H$ (1)
Ib: $R^1=C_2H_5$ $R^2=H$ IIb: $R^1=C_2H_5$ $R^2=H$
Ic: $R^1=C_2H_5$ $R^2=CH_3$ IIc: $R^1=C_2H_5$ $R^2=CH_3$

In connection with our interest in liquid crystals, the use of cholesteric mesogens has been investigated as chiral media for asymmetric reactions, and those studies mentioned above prompt us to report our investigation of the contributions of the cholesteric mesophases to this decarboxylation. Previously,[8] we have reported a preliminary study on the decarboxylation of 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid in some cholesteric liquid crystalline media and the present paper gives details of the reaction. The purpose of this work is to compare the influence of the helical ordered cholesteric state with that of the random order of the isotropic liquid on the asymmetric reaction.

EXPERIMENTAL

Materials

2-Ethyl-2-(4-methylphenyl)propane-1,3-dioic acid (Ic) was prepared by hydrolysis of the corresponding diethyl ester with potassium hydroxide in

ethanol/water at 50°C for 24 hr, using the similar method of Verbit, *et al.*[3] Repeated crystallization of the hydrolyzate from diethyl ether and hexane yielded a pure product proved by ^{1}H NMR spectroscopy: mp 161–163°C with decomposition (See Figure 1, mp 146°C in Ref. 9); NMR ($CDCl_3$) δ 0.8 (m, CH_3 in C_2H_5), 1.8–2.2 (m, CH_2 in C_2H_5), 2.5 (m, CH_3 in $CH_3C_6H_4$), 7.7 (m, C_6H_4 in $CH_3C_6H_4$). Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.78; H, 6.44. Diethyl 2-ethyl-2-(4-methylphenyl) propane-1,3-dioate was reagent grade (Aldrich) and used after distillation.

The cholesteryl esters of 2,4-hexadienoic, benzoic, 2,4-dichlorobenzoic, and trans-cinnamic acids were all reagent grade (Eastman) and recrystallized repeatedly with methyl ethyl ketone or benzene as the solvent

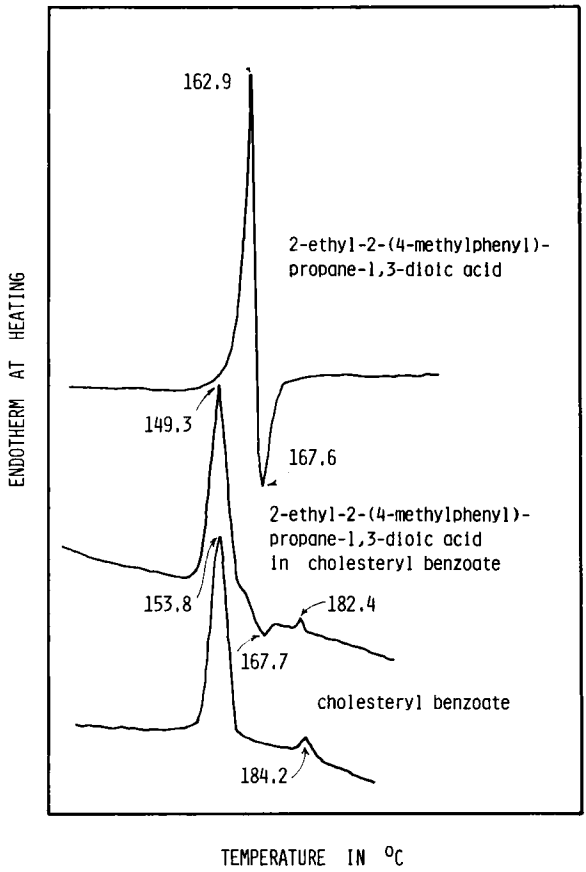


FIGURE 1 DTA curves of 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid, cholesteryl benzoate, and their mixture (2.6 mg of Ic/9.7 mg of benzoate).

and methanol as the precipitant. Purified samples showed a single spot in the thin layer chromatogram using a mixed solvent or cyclohexane/ethyl acetate (99.5/0.5, v/v) or petroleum ether/diethyl ether/acetic acid (90/10/1, v/v/v) for development at 25°C. The mesomorphic phases between 128–169 (127–168),[10] 154–184 (150.5–182.6),[10] 131–204 (129.5–202),[10] and 163-216 (162.6–215.2)[10] for 2,4-hexadienoic, benzoic, 2,4-dichlorobenzoic, and trans-cinnamic acids, respectively, were observed in heating curves of DTA.

Reagent grade organic solvents were purified and dried by standard methods.[11] All other chemicals were of reagent grade and were used without further purification.

DECARBOXYLATION PROCEDURE

2-Ethyl-2-(4-methylphenyl)propane-1,3-dioic acid (Ic: 3×10^{-4} mol; 70 mg or 7×10^{-4} mol; 160 mg) was intimately mixed with 4 or 8 g of a cholesteric mesogen. The mixture was heated for 2 or 3 hr at 158–163°C under a nitrogen atmosphere, in a thermostated silicon oil bath. At the end of the reaction, the reaction flask was attached to a distilation apparatus, and the reaction products (48 or 120 mg) were collected under 0.1 or 1 mm at 160–170°C. The sample was examined for the presence of steroidal impurities by the thin layer chromatogram on silica gel using a mixed solvent of ethyl acetate/heptane (19/10, v/v)[3] or petroleum either/diethyl ether/acetic acid (90/10/1, v/v/v) for development at 25°C. No contaminants were observed under these conditions, while Eskenazi, *et al.*,[7] obtained 5% of benzoic acid as a by-product in the case of decarboxylation of 2-ethyl-2-phenylpropane-1,3-dioic acid (Ib) in cholesteryl benzoate. A second distillation gave 77–85% of pure 2-(4-methylphenyl)-butanoic acid (IIc) having a low but significant optical rotation, as mentioned in Table I.

Distillation of mixtures of optically active and racemic 2-(4-methylphenyl)butanoic acid (IIc) in cholesteryl benzoate under the conditions described above afforded materials with unchanged specific rotations.

In order to study the influence of the experimental conditions, several ways were tested to prepare the reaction mixtures of the propane-1,3-dioic acid (Ic) in cholesteryl benzoate: Crystallized mesogen and the acid (Ic) were intimately mixed. The dibasic acid (Ic) was progressively introduced into the mesophase preheated at 160°C. A sample of the acid (Ic) and the liquid crystalline solvent were dissolved in diethyl ether/dichloromethane to give a homogeneous solution, and introduced into a reaction flask. By evaporating the mixture of diethyl ether and dichloromethane, the sample was allowed to spread over the inner wall of the flask in layer. Then the

TABLE I

Decarboxylation of 2-Ethyl-2-(4-methylphenyl) propane-1,3-dioic acid in cholesteric phase[a]

	2-(4-Methylphenyl) butanoic acid					
		$[\alpha]^{23}$ [b]				
Decarboxylation solvent	Chemical yield (%)	at 589 nm	at 578 nm	at 546 nm	at 436 nm	at 365 nm
Cholesteryl benzoate	86(76[c])	−0.13	−0.25	−0.36	−1.08	−0.84
2,4-dichlorobenzoate	92(80[c])	+0.15	+0.18	+0.24	+0.26	+0.26
2,4-hezadienoate	98(83[c])	−0.18	−0.15	−0.33	−0.40	−0.40
trans-cinnamate	90(73[c])	+0.11	+0.11	+0.10	+0.00	+0.00
Bornyl acetate	87(80[c])	+0.00	+0.00	+0.00	−0.00	−0.00

[a]Average value of duplicate experiments.
[b]The concentrations at which the rotations were measured were between 0.83 and 2.75 g/100 ml in absolute ethanol.
[c]Yields in the 2nd distillation.

flask was placed in a constant temperature bath, kept at an angle, and rotated occasionally for varying periods of time to prevent the sample layer attached to the inner wall from flowing down to the bottom of the flask. In all cases, no significant difference could be found among the values of optical rotation obtained for the resultant butanoic acid (IIc).

TEST METHOD

The thermal behavior of the specimens was observed with an HP-DT-1500M differential thermal analyzer (Ulvac Corporation).[12] The thermal analyzer has been previously calibrated with standard substances. DTA thermograms were obtained at a fixed heating rate of 5°C/min. The mesomorphic phase of the sample was also observed through a hot stage microscope with crossed nicols.

Optical rotations were measured on a Perkin-Elmer 241 photoelectric spectropolarimeter at 365, 436, 546, 578, and 589 nm. The infrared (IR) absorption spectra in the region of 650 to 4000 cm^{-1} were measured for a sample on a Hitachi Model 215 IR spectrophotometer. The sample was prepared by the neat technique on KBr plate or by the KBr pellet technique.

The proton nuclear magnetic resonance (NMR) spectra were obtained at 360 MHz with a Nicolet NT-360 spectrometer equipped with NIC 1180 Computer Data System. Deuterobenzene and deuterochloroform were used as solvents. Chemical shifts are given in ppm relative to the internal reference standard, tetramethylsilane (TMS).

RESULTS AND DISCUSSION

A curve obtained with a differential thermal analyzer of 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid (Ic) exhibited a sharp endothermic peak which was followed by a sharp exothermic peak as shown in Figure 1. The endo- and exothermic peaks correspond to melting and decomposition, respectively. The curve for a mesogen or cholesteryl benzoate showed two sharp endothermic peaks which correlate to crystalline-cholesteric and cholesteric-isotropic liquid transitions. The DTA curve of the mixture of the dibasic acid (Ic) and the mesogen presented a larger endothermic peak, corresponding to crystalline-cholesteric transition of the benzoate and melting of the dibasic acid, and smaller exo- and endothermic peaks which correspond to decomposition of the dibasic acid and cholesteric-isotropic liquid transition of the reaction system, respectively. Thus, this shows that the binary mixture was cholesteric between 149 and 182°C at this concentration (2.6 mg of the dibasic acid in 9.7 mg of the benzoate), and that the dibasic acid (Ic) decomposed smoothly in the cholesteric phase.

Vacuum distillation of the reaction mixture afforded 90–96% of a decarboxylation product, which was suggested to be free of contaminants by a thin layer chromatogram on silica gel using a mixed solvent of ethyl acetate/heptane or petroleum ether/diethyl ether/acetic acid for development. Eskenazi, *et al.*,[7] reported that 5% of benzoic acid was obtained as a by-product in the case of decarboxylation of 2-ethyl-2-phenylpropane-1,3-dioic acid (Ib) in cholesteryl benzoate. A second distillation gave 77–85% of pure 2-(4-methylphenyl)butanoic acid (IIc), as mentioned in Table I.

In Figure 2, are shown the infrared absorption spectra of diethyl 2-ethyl-2-(4-methylphenyl)propane-1,3-dioate at liquid film, and of 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid (Ic) and its decarboxylation product (IIc) in KBr matrix. The dibasic acid (Ic) and the decomposition product (IIc) have very broad and intense OH stretching absorptions in the region of 3300 to 2500 cm^{-1}, which are not observed in the spectrum of the diester. The characteristic bands assigned to the stretching modes of the carbon-oxygen single and double bonds for the dimeric acid appear at 1270, and 1680 and 1700 cm^{-1} in the spectra of the dibasic acid and the product, respectively. The bands arising from the out-of-plane and the in-plane bendings of the bonded OH of the dimeric carboxylic groups are also observed at 920 and 940, and 1400 and 1410 cm^{-1}, respectively in these spectra. The band at 810 cm^{-1} of these spectra can be assigned to the out-of-plane hydrogen deformation mode of a 1,4-di-substituted benzene. These suggest the carboxylic acid of the structure IIc for the decomposition product.

The ^{1}H NMR spectrum was measured in deuterochloroform on the decarboxylation product and is shown in Figure 3. Assignments of the resonance signals were carried out by the conventional spin-decoupling method and through comparison of the peaks of the diester and the dibasic acid (Ic). Six groups of peaks are observed in the following position with the following integrated intensities (the multiplicity, position in ppm, and relative in-

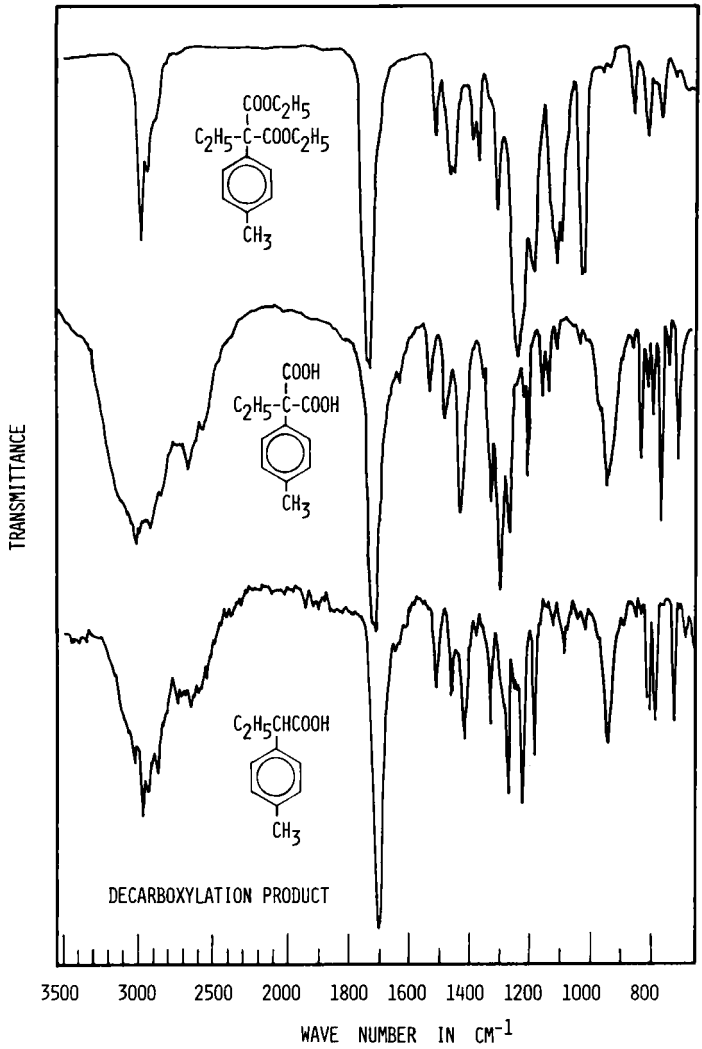


FIGURE 2 The infrared absorption spectra of diethyl 2-ethyl-2-(4-methylphenyl)propane-1,3-dioate, 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid, and 2-(4-methylphenyl)butanoic acid obtained from decarboxylation of the propane-1,3-dioic acid.

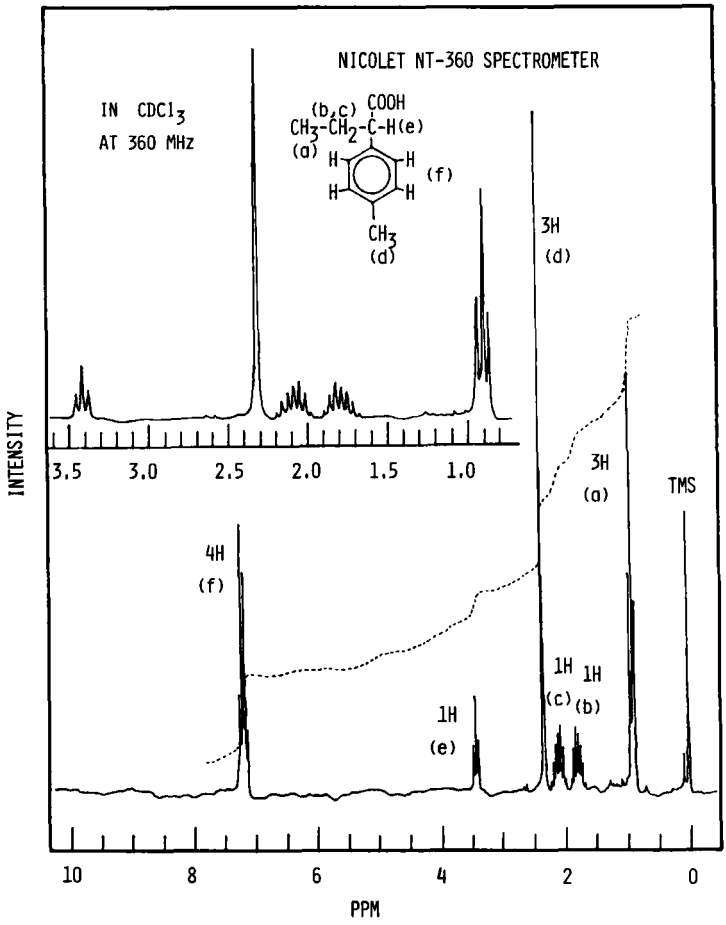


FIGURE 3 The proton nuclear magnetic resonance spectra in $CDCl_3$ of the decarboxylation product.

tensity are given): 3, 0.9, 3; m, 1.8, 1; m, 2.1, 1; 1, 2.3, 3; 3, 3.4, 1; and m, 7.2, 4. The 4 protons at 7.2 are the 4 benzene ring protons. The triplet of one proton at 3.4 represents the CH group substituted by 4-methylphenyl, carboxyl and ethyl groups. The singlet at 2.3 and the triplet at 0.9 of 3 protons are due to the CH_3 in 4-methyl-phenyl and in ethyl groups, respectively. The multiplet peaks of one proton at 1.8 and 2.1 ppm represent the methylene in ethyl group. Thus, the ^1H NMR spectrum of the product provides almost conclusive confirmation for the above mentioned structure of 2-(4-methylphenyl)butanoic acid (IIc).

In chiral solvents[13] or upon addition of chiral additives in achiral solvents,[14] two enantiomers reside in diastereomeric environments and, hence, are distinguishable by the splitting of the peaks in their NMR spectra. Recently, these phenomena were applied to the determination of optical purity[15] and to the assignment of absolute configuration.[16] Thus, we tried to determine the optical purity of enantiomeric complexes of the carboxylic acid (IIc) with an optical active amine such as (R)-(+)-1-phenylethylamine or a chiral shift reagent like tris[3-(2,2,2-trifluoro-1-hydroxylethylidene)-d-camphorate]-europium by NMR spectroscopy. A solution of the acid (IIc) in C_6D_6 or $(CD_3)_2SO$ was titrated with the chiral reagent, while the ^1H NMR spectra were examined. Addition of the chiral amine resulted in no splitting of the proton resonances of the acid. On the other hand, the stepwise addition of the d-camphorato-europium up to large excess amount (ca. 10 eq.) induces the splittings and the low-field shifts of the CH_3 proton signals in ethyl and in 4-methylphenyl groups and of the benzene ring proton signals with slightly broadening, as shown in Figure 4. This finding corresponds to the enantiotopic recognition of the chiral shift reagent between the enantiomers of the carboxylic acid (IIc). When the concentration of the chiral shift reagent increases, however, the relative integrated intensities of the enantiotopic proton resonances are not truly constant but depend on the amounts of the chiral additive. Therefore, the enantiomeric composition of the decarboxylation product (IIc) could not be determined under this condition.

Determination of the optical rotation utilizing a photoelectric polarimeter gave small but reproducible amounts of asymmetric induction and Table I shows the results. Since the chiroptical property of 2-(4-methylphenyl) butanoic acid has not yet been reported nor determined in this experiment, the optical purity cannot be calculated accurately but estimated with the reported values of various substituted acetic acids, 4-R′-$C_6H_4CRHCO_2H$ (R, R′, and $[\alpha]_D$ in ethanol are given):[17] CH_3, H, 81.1; C_2H_5, H, 78.5; $CH_3CH_2CH_2$, H, 63.4; $(CH_3)_2CH$, H, 58.6; $(CH_3)_3C$, H, 47.7; CF_3, H, 65.8; C_2H_5, CH_3O, 64.5. If the highest value of rotation for 2-(4-methylphenyl)butanoic acid is similar to those for the acetic acids mentioned above as 60 to 80 degrees, the butanoic acids formed in this decarboxylation seem to have minimum optical purities of 0.2 to 0.3%. These values are based on the assumption that unrecovered acid has the same enantiomeric composition as the distilled material: Stability experiments involving the distillation of optical active and racemic 2-(4-methylphenyl)butanoic acid gave material having unchanged and zero rotations in the former and the latter cases, respectively.

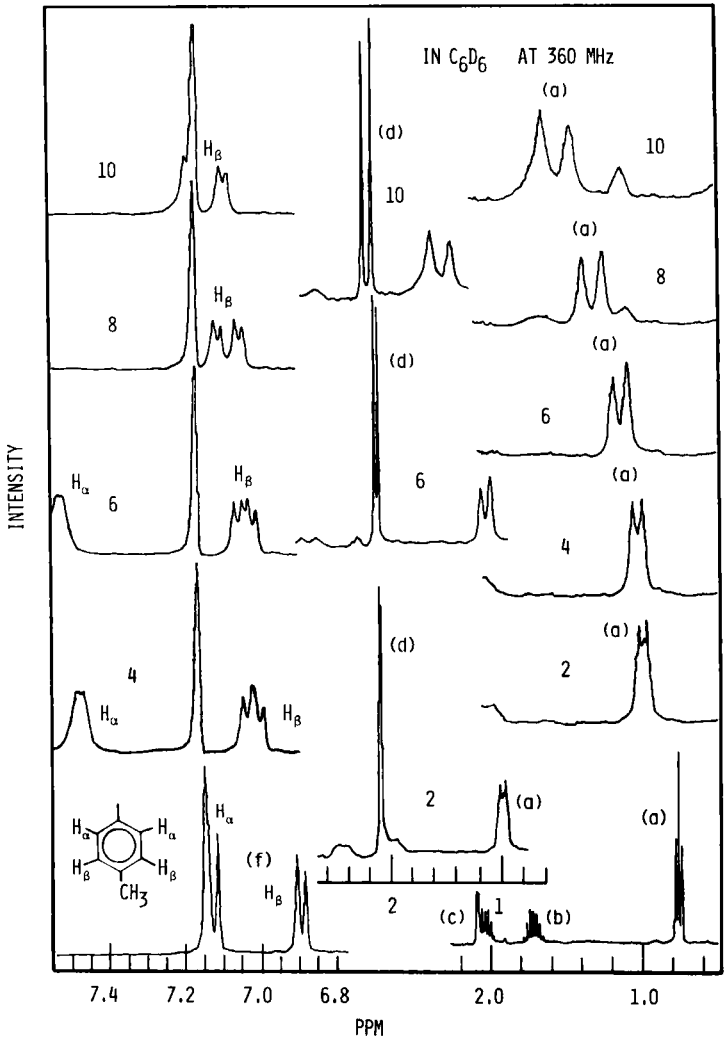


FIGURE 4 The proton nuclear magnetic resonance spectra in C_6D_6 of the decarboxylation product or 2-(4-methylphenyl)butanoic acid in the presence of various concentrations of tris[3-(2,2,2-tri-fluoro-1-hydroxylethylidene)-d-camphorato]europium or $Eu(TFC)_3$. The numbers of 2, 4, 6, 8, and 10 show the molar ratios of $Eu(TFC)_3$ to the butanoic acid (IIc). (a), (b), (c), (d), (e), (f), H_α, and H_β show positions of the protons of the butanoic acid (IIc) shown in Figure 3.

In contrast to the small but significant enantiomeric excess found in the ordered cholesteric solvents, decarboxylation of 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid in bornyl acetate, an isotropic chiral solvent, yielded 2-(4-methylphenyl)butanoic acid which was essentially racemic.

These results indicate that a chiral environment due only to molecular chirality is not sufficient for a significant asymmetric bias to occur for the system studied. The stereoselectivity in the present asymmetric decarboxylation, however, is relatively low compared to the result of Verbit, *et al.*,[3] and inconsistent with that of Eskenazi, *et al.*[7]

All of the cholesteric esters used are considered to form a right-handed helix in the cholesteric mesophase with the data of Baessler and Labes,[18] Leder,[19] Saeva,[20] and Sackmann and Möhwald.[21] A helix having a right-handed screw direction transmits right circularly polarized light and reflects left circularly polarized light. Here, these liquid crystals are called right handed in contrast to Leder.[19] Table I shows that decarboxylation of 2-ethyl-2-(4-methylphenyl)propane-1,3-dioic acid (Ic) affords small but significant enrichment in the (S)–(+) enantiomer in cholesteryl trans-cinnamate and 2,4-dichlorobenzoate, and in the (R)–(−) enantiomer in cholesteryl benzoate and sorbate. This observation demonstrates that the sense of helical macrostructure alone does not control the stereochemical sense of enrichment.

The asymmetric transformation effects of a chiral mesophase could be described by the specific solute-solvent interactions which play a role in locating the solute molecules in the helical ordered mesophase. The solubility process in the cholesteric phase is found[22,23] to be complex. The positive heats and entropies of solution are unusual for nonelectrolytic solutions and described by a possible interpretation that the solute molecules may be dissolving in between the layers, to a small extent in the smectic phase and to a much larger extent in the cholesteric phase. No sharp NMR lines have been observed[24] for molecules dissolved in a pure cholesteric mesophase, whereas the NMR spectra of solute molecules dissolved in a nematic phase show a detailed and highly resolved structure. Furthermore, achiral molecules are known[25] to become optically active when dissolved in a cholesteric phase. This induced circular dichroism should result in part from a particularly strong interaction between the solute and solvent molecules.

In conclusion, the mesomorphic anisotropic ordering or the specific interactions between the solute and solvent molecules in the cholesteric mesophase should not play so important a role that this system clearly demonstrates the ability of the chiral mesophase to induce the appreciable asymmetric reaction shown in Equation (1).

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