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(47) Sodium hydride is generally supplied as a suspension in oil. The oil can be removed by washing with dry petroleum ether.
(48) Cf. R. Srinivasan and S. Boué, *J. Am. Chem. Soc.*, **93,** 5606 (1971), footnote 30.
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(53) A 10 ft × 1/4 in. glass column packed with 20% Carbowax 20M on Chromosorb P with a carrier gas flow rate of 80 mL/min.
(54) A similar chromatogram was obtained when the photooxidation was carried out in CH_3CN.
(55) M. Santelli and M. Bertrand, *Tetrahedron*, **30,** 227, 232 (1974), compound **24.**
(56) Reference 28, compound **18A.** Note, however, that there is a typographical error in the NMR data, which should read δ 1.18 instead of δ 1.68. The NMR data cited in ref 24 (compound **2**) are incorrect.
(57) Nakanishi[58] lists 1690 and 1720 cm^{-1} as the carbonyl absorption for α,β-unsaturated acid (group 3a, page 43) and 1785 and 1725 cm^{-1} for acrylic acid anhydrides.
(58) K. Nakanishi, "Practical Infrared Absorption Spectroscopy", Holden-Day, San Francisco, Calif, 1962, Table VIII.
(59) For an explanation of proton designations, see the diagram in the Experimental Section on **9A.**
(60) When the reaction was carried out in CD_3OD, this absorption was absent.

Asymmetric Induction in Cholesteric Media Revisited

C. Eskenazi, J. F. Nicoud, and H. B. Kagan*

Laboratoire de Synthèse Asymétrique associé au CNRS (LA No. 040255-02), Université de Paris-Sud, Centre d'Orsay, 91405-Orsay, France

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The photocyclization of α-(*N*-methylanilino)styrene (**1**) to indoline **2** proceeded in a cholesteric liquid crystal medium with no detectable asymmetric induction. Similarly, the photochemical interconversion of methyl α-naphthyl sulfoxide (**11**) in a cholesteric phase afforded a negligible (<1–2%) enantiomeric excess. On the basis of these results and after reinvestigating several of the reported cases of asymmetric inductions in cholesteric media, we conclude that asymmetric transformation in cholesteric phases, as in ordinary chiral solvents, can generally result in only low optical yields although exceptions may be found in special cases where strong and specific interactions between solute and solvent exist.

There is a great current interest[1-11a] in the possibility of influencing or controlling chemical reactivity by an organized medium such as a liquid crystal. Part of this interest is due to the analogies between liquid crystal and some biological media.

Nematic mesophases were used as reaction solvent in xanthogenate pyrolysis[2] and Claisen rearrangements of *O*-allyl aryl ethers.[3] Although initial kinetic measurements indicated a definite effect when compared to isotropic solvents, further work[4,5] failed to substantiate any specific effect of the nematic solvent on Claisen rearrangement. Dewar[5] hypothesized that bimolecular reactions would be more sensitive to the nematic environment, but for several years there was no evidence for any positive result in this area.[6] One of the few chemical reactions strongly influenced by the organization of a liquid crystal was the polymerization of nematic or cholesteric phases which retains in the solid polymer the features of the liquid crystal structure.[7] It is only recently that a large rate enhancement was described in the photodimerization of acenaphthylene to *syn*- and *anti*-cyclobutane dimers;[8] it was concluded that solvent order exerts a dramatic influence on the efficiency of dimerization but plays little role in determining the stereochemical course of the reaction.

In contrast to the lack of evidence for control over reactivity of nonphotochemical reactions in nematic solvents, asymmetric inductions were recently reported to occur in cholesteric media.[9-11a] In view of the successful asymmetric photocyclizations of various substrates with circularly polarized light,[12] we repeated these reactions with natural light in various cholesteric systems[13] in an attempt to observe asymmetric synthesis. However, photocyclization of α-(*N*-methylanilino)styrene (**1**) into *N*-methyl-2-phenylindoline (**2**) gave a racemic material.

We turned then to another simple cyclization reaction, the transformation **3** → **4.** We were encouraged to investigate this photosynthesis of chiral oxaziridines because photocyclization of nitrones to optically active oxaziridines in a chiral solvent has been described.[14] We indeed obtained good chemical yields (75%) but the irradiation in the cholesteric J mixture[13] at 28–30 °C gave **4** having a very low specific rotation ($(\alpha)_D$ = +0.18 ± 0.04°). When cholesteryl 2-(2-ethoxyethoxy)ethylcarbonate (ChEC) was used as a cholesteric phase (mesomorphic range, −5 to +32 °C) we obtained a completely racemic oxaziridine **4** after photocyclization at 0 °C.

Due to the negative results in asymmetric photocyclization of **3,** even at low temperature, we decided to reinvestigate some of the asymmetric reactions previously described.[9-11] First we reproduced the Claisen rearrangement of **5** to **6** in cholesteryl *p*-nitrobenzoate (ChNB) at 200 °C (in the mesomorphic region) as indicated in ref 9. Phenol **6** was isolated by two different procedures and had no significant specific rotation. The CD curve of **6** showed a very weak positive Cotton effect ($\Delta\epsilon/\epsilon$ 4 ± 2 × 10^{-5} at 275 nm). Since the chiroptical properties of **6** are not known the optical purity of **6**[9a] cannot be calculated

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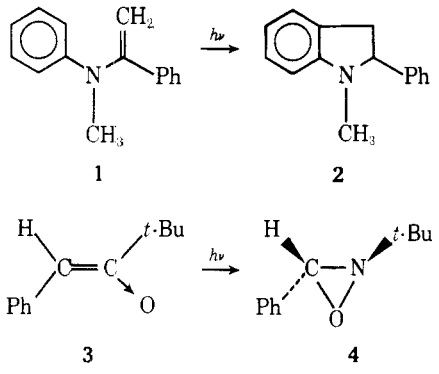
Scheme I



and the system does not clearly demonstrate the ability of the chiral mesophase to induce appreciable asymmetric reaction.

Reinvestigation of the reported asymmetric decarboxylation of **7a** into **8a** was of special interest because an 18% ee to **8a** was claimed[10] when the medium was cholesteryl benzoate (ChB) (mesomorphic range, 149–166 °C). Several experiments were conducted as described in ref 10 or with various changes in the procedures but all invariably afforded in our hands racemic α-phenylbutyric acid **8a** (70% yield of pure material). Similar results were obtained in the preparation of hydratropic acid **8b** through decarboxylation of **7b**.

We then turned to the most recent report in this field, dealing with equilibration between diastereomers or enantiomers.[11a] The equilibrium **9** ⇄ **10** was studied in several cholesteric or isotropic phases and it was concluded that the equilibrium was dependent on the anisotropic nature of the cholesteric phase but not on its helicity. Cholesteryl methanesulfinate was prepared by treatment of cholesterol with methanesulfinyl chloride and pyridine and was obtained as a mixture of **9** and **10** after crystallization from hexane. From the specific rotations given for **9** and **10**[11a] the composition was determinated as 59:41 (18% ee in *S* configuration at the sulfur atom). By heating the mixture of **9** and **10** in various solvents or liquid crystals we obtained the results of Table I. An important difference with ref 11a is entry 2; in our hands there was no reversal of configuration at the sulfur atom when working in toluene instead of a cholesteric mesophase.

The thermal interconversion of enantiomeric sulfoxides in a cholesteric liquid crystalline reaction medium has also been reported to lead to a nonracemic composition.[11a] We reinvestigated the specific case of methyl α-naphthyl sulfoxide (**11**) which was dissolved (4% by weight) in ChNB and heated at 190 °C in a sealed, degassed ampule. At this temperature the cholesteric mesophase is retained. The sulfoxide **11** was

Scheme II

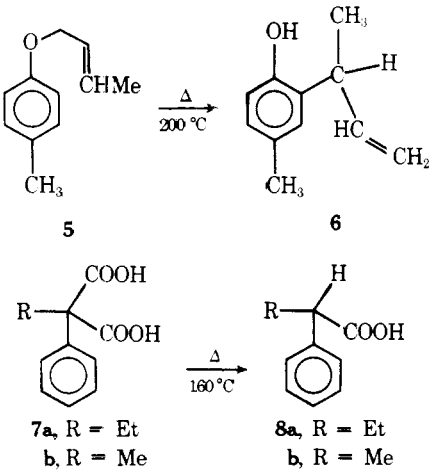


Table I. Equilibration between Diastereomers 9 and 10 of Cholesteryl Methanesulfinate by Heating in Various Solvents[a]

no.	solvent	time, h	temp, °C	ee, %[b]	config at S atom	ref
1	toluene	3	85	28 ± 3	*R*	
2	toluene	3	110	18 ± 2	*R*	
		3	110	20	*S*	11a
3	xylene	3	145	10 ± 3	*R*	
4	ethyl propionate	3	85	11 ± 2	*R*	
5	isopropyl aclohol	3	83	3 ± 1	*R*	
6	cholesteryl benzoate	0.5	145	16.9	*R*	
		0.5	145 mesomorphic	16 ± 2	*R*	
		0.5	175 isotropic	14 ± 2	*R*	

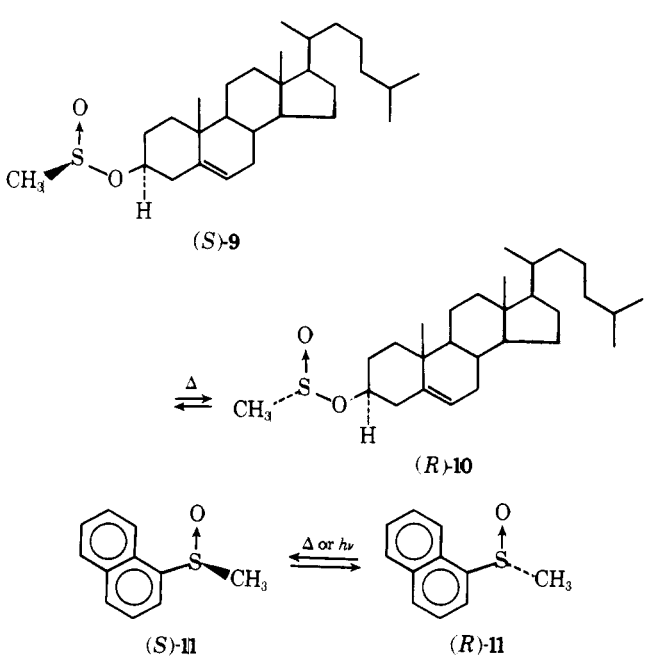
[a] Concentration of solute is between 2 and 3% in all experiments. [b] Calculated for sulfur atom from the diastereomeric composition.

then recovered by chromatography over silica gel followed by sublimation at 80 °C and found to be essentially a racemic mixture (as determined by polarimetry), in contradiction with the reported result (9.2% e.e. in *R* configuration).[11a] It is interesting to point out that this reported result was the basis of the argument of independence of stereochemistry of asymmetric synthesis on the handedness of the cholesteric liquid crystal. A racemic mixture was likewise obtained from this sulfoxide heated at 145 °C in ChB.

Discussion

One of the major difficulties in performing asymmetric reactions in cholesteric mesophases is the isolation and purification of final products, since the solute concentration has to remain less than 5% in order not to disturb the anisotropic arrangement. We took great cautions for the workup, which is detailed in the Experimental Section. Volatile chiral products (**2**, **4**, **6**, and **8**) were isolated by vacuum sublimation

Scheme III



(0.01–0.05 mm). No volatility of cholesteric compounds was detected under these conditions. It is important to be certain that the products are totally uncontaminated by the chiral phase for a correct interpretation of results and therefore, for the separation of **9** and **10** from the cholesteryl benzoate, careful chromatography was performed. One source of experimental error could be a change of enantiomeric composition during the vacuum distillation of product from mesophases. We therefore checked that *dl*-**2**, *dl*-**4**, *dl*-**6**, *dl*-**8**, and *dl*-**11** were recovered devoid of optical activity. We checked, too, that partially resolved **8** (18% ee) or **11** (13% ee) was recovered with the initial enantiomeric excess.

With regard to the decarboxylation of **7** to chiral **8**[10] we hypothesized that some transesterification with cholesteryl benzoate could obscure the interpretation of the reaction. Indeed, we always detected some benzoic acid, but its origin could arise from thermal elimination from ChB.[15] Since **8** was obtained as a racemic mixture the origin of benzoic acid was not established. Another difficulty in asymmetric synthesis of **8** lies in the fact that decarboxylation of the malonic acid starts at 140–145 °C, below the cholesteric region of ChB. In order to avoid synthesis of **8** in a noncholesteric phase we prepared the mixture of **7** and ChB in three different ways: (i) As in ref 10, **7** was intimately mixed with ChB. (ii) The solute and mesophase were dissolved in ether which was then evaporated. In both cases the mixture obtained was rapidly heated to 160 °C and then kept at this temperature. (iii) Another procedure was to progressively introduce **7** into ChB preheated at 160 °C. In all of our experimental procedures we never succeeded in observing optical activity for **8**.

In the Claisen reaction leading to **6** we were able to detect a very weak CD; obviously the optical yield should be extremely small. In addition treatment of *dl*-**6** in ChNB with the same procedure as for Claisen reaction led to the recovery of **6** with essentially the same positive weak CD.

The thermal equilibration of diastereomeric sulfinates **9** and **10** is, as has been pointed out in ref 11a, a good case where stereochemical control might be attained because the solute is structurally "mimicking" the mesophase.

From our results, Table I, it is clear that the *R* configuration is always preferred whatever the solvent or the temperature. In an aromatic solvent (toluene, xylene) the enantiomeric excess decreases with increasing temperature (entries 1, 2, and 3). The strong changes with temperature preclude any comparison between cholestric mesophase and isotropic chiral phases which would not be made at the same temperature. Such a temperature effect in ChB working in the cholesteric mesophase or in the isotropic liquid chiral phase (entry 6) indicates a negligible, small effect of the mesophase. The nature of the solvent is important in determining the position of the equilibrium or the rate of interconversion between diastereomers (compare, for example, entries 1, 4, and 5). This solvent effect is an additional difficulty for discussing here the role of a cholesteric mesophase. In conclusion, there remains no proof that the **9** ⇄ **10** equilibrium or the (*R*)-**11** ⇄ (*S*)-**11** equilibrium is significantly affected by the cholesteric mesophase. Finally, as part of our interest in performing asymmetric photochemical syntheses, we investigate the photointerconversion between enantiomers of methyl α-naphthyl sulfoxide (**11**) in a low-temperature cholesteric phase. The reaction is possible because the naphthyl chromophore acts as a photosensitizer.[16] Racemic **11** was irradiated in ChEC at 8 °C and in J mixture at 30 °C, in the cholesteric mesophase range. The sulfoxide **11** was recovered by vacuum distillation at 80 °C as a racemic mixture. Irradiation of optically active **11** in J mixture under the same conditions gave recovered material with substantial racemization. In summary, and contrary to recent work in the field,[9-11a] it has not yet been demonstrated that a cholesteric mesophase has special advantages over chiral solvents of similar structure, as far as asymmetric induction is concerned. Optical yield remains very small in the Claisen reaction leading to **6**; **8** is obtained as a racemic mixture in the decarboxylation of **7** and the **9** ⇄ **10** equilibrium is not strongly affected by the nature of cholesteric mesophase (vide supra). The equilibrium between enantiomers of methyl α-naphthyl sulfoxide (**11**) may be slightly displaced toward the *R* or *S* enantiomer in some cholesteric liquid crystals but the enantiomeric excess is less than 2%.[11a] It is clear from the large amount of reinvestigated or new experimental data that, in general, cholesteric liquid crystals are very inefficient for stereochemical control dealing especially with asymmetric induction.[17] We would agree with the proposal in ref 11a that it is reasonable, even if it has not yet been demonstrated, that the macrostructural handedness of the mesophase cannot control the stereochemistry of an asymmetric transformation. It must be recalled that cholesteric helices have currently pitches of more than 3000 Å (which is much larger than the solute size). One might ask, what can be expected from a chiral mesophase? For example, induced CD on achiral ketones dissolved in cholesteric solvents was established in some cases[18] but the induced CD is always very weak and its relevance to asymmetric reaction is not obvious. A chiral solvent effect can always be expected.[19] Although the local ordering which is imposed by the mesophase may have some additional importance, this is compensated by the great ease of structural rearrangement.[20]

Table II

solvent	transition temp, °C: solid–chol.	transition temp, °C: chol.–isotropic	$(\alpha)^{25}_D$
ChB	148	176	−15 ° (*c* 6, $CHCl_3$)
ChNB	190	265 dec	−6° (*c* 1.5, $CHCl_3$)
ChEC	<0	32	−29° (*c* 1.5, $CHCl_3$)
ChOC	18[a]	31	−24° (*c* 2, $CHCl_3$)
J mixture	room temp[b]	78	

[a] Smectic–cholesteric transition. [b] Cholesteric at room temperature during several days but crystallizes slowly on standing.

It should be pointed out that nematic and cholesteric phases are thermodynamically much closer to isotropic liquids than they are to crystalline solids (where the high degree of order may exert considerable stereochemical control and afford appreciable asymmetric induction).[21] Thus, typical heat of phase transitions for nematic and cholesteric phases, to isotropic liquids, are only 0.2–0.4 kcal/mol whereas the values for crystal to nematic or cholesteric phase transitions are 3–4 kcal/mol.[22] These considerations suggest the use of chiral smectic C phases[23] which, by contrast, are much closer to crystalline phases: $\Delta H_{\text{smectic}\rightarrow\text{liquid}}$ = 3–4 kcal/mol.[22] Special effect of the mesophase might be to force solute molecules to autoassociate in some regions. This effect may have importance for reactions such as photodimerization[8] but is, probably, disfavorable for good control over asymmetric induction. A way to best use the local order effect of a chiral solvent or the very similar cholesteric mesophase could be to use solute molecules of the same shape and size as the mesophase molecules or to choose a solute giving rise to strong specific interactions with the mesophase.

In conclusion, the effect of mesomorphic anisotropic ordering on asymmetric induction remains to be clearly established.[24]

Experimental Section

Instrumentation. ^{1}H-NMR spectra were measured on a Perkin-Elmer R 32 instrument, with internal Me_4Si as standard. The vapor-phase chromatography was a Carlo Erba Model GI with N_2 as

carrier gas. Melting points and temperature transitions of the mesophases were determined with a Reichert polarizing microscope equipped with a suitable heating stage. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Optical rotations were measured on a Perkin-Elmer Model 141 polarimeter. CD measurements were made on a Roussel-Jouan apparatus.

Preparation of Cholesteric Liquid Crystal Solvents. Cholesteryl benzoate (ChB), cholesteryl oleyl carbonate (ChOC), cholesteryl nonanoate (ChN), cholesteryl oleate (ChO), and cholesteryl propionate (ChP) were supplied by Aldrich. Cholesteryl 2-(2-ethoxyethoxy)ethyl carbonate (ChEC) was supplied by Eastman.

ChB was recrystallized from hexane before use. ChEC and ChOC were purified by chromatography over silica gel. ChNB was prepared by treatment of cholesterol with p-nitrobenzoyl chloride in toluene in the presence of pyridine. Pyridine hydrochloride was removed by filtration and the brown solution was filtered over silica gel to give a light yellow solution. Recrystallization from hexane–ethyl acetate 60:40 afforded ChNB as yellow granules.

J mixture[6b] was prepared by mixing 50 wt % ChN, 37.5 wt % ChO, and 12.5 wt % ChP, after purification of each component by chromatography over silica gel.

The physical properties of the cholesteryl liquid crystal solvents used are summarized in Table II.

Photochemical Experiments. For all the experiments, the substrate was dissolved in the cholesteric solvent slightly above the cholesteric–isotropic transition temperature. When a clear homogeneous solution was obtained, the cholesteric mixture was cooled to the desired temperature so as to have a cholesteric mesophase. Cholesteric solutions were put in a flat Pyrex cell immersed in a thermostated water bath and irradiated with a Hanovia 450-W high-pressure mercury lamp through a Pyrex filter. The cholesteric layer in the cell did not exceed a few millimeters. At the end of the experiment the irradiated solutions were collected and submitted to vacuum molecular distillation in a sublimation apparatus, when the product was sufficiently volatile, or chromatographed over silica gel two or more times in order to ensure a pure product for measuring optical rotations. In all cases the products were checked to be free of contaminants by GLC or NMR spectroscopy.

***N*-Methyl-2-phenylindoline (2).** A solution of 200 mg (0.9×10^{-3} mol) of α-(*N*-methylanilino)styrene, **1**, in 4 g of ChOC was irradiated during 3 h at 20 °C under the above described conditions. The progress of the photocyclization was monitored by GLC. The indoline **2** was isolated by chromatography over silica gel (eluent, hexane–CH_2Cl_2, 70:30); a pure sample (33 mg) did not show any significant optical rotatory power, $(\alpha)^{25}_D$ 0.00 ± 0.05°.

Oxaziridine (4). A solution of 400 mg (2.26×10^{-3} mol) of nitrone (**3**) in 9.5 g of J mixture was irradiated at 28 °C for 4.5 h. Oxaziridine (**4**) (298 mg) was isolated by vacuum molecular distillation followed by chromatography over silica gel (eluent hexane–CH_2Cl_2 70:30) (75% yield). The product showed a weak optical activity, $(\alpha)^{25}_D$ + 0.18 ± 0.04° (*c* 11.0, $CHCl_3$) and $(\alpha)^{25}_{436}$ +0.35 ± 0.09°.

In order to check that optical enrichment did not occur by preferential photodestruction of one enantiomer, 300 mg of racemic oxaziridine (**4**) in 7 g of J mixture were irradiated under the same conditions as the previous experiment. The recovered oxaziridine (70%) did not show any significant optical rotation, $(\alpha)^{25}_D$ 0.00 ± 0.05°. To study a possible temperature effect on the optical yield during the photocyclization **3** → **4**, a solution of 300 mg of nitrone (**3**) in 8 g of ChEC was irradiated between −4 and 0 ° C for 4 h. Oxaziridine (**4**) was isolated (231.8 mg, 77.5%) without significant optical rotation, $(\alpha)^{25}_D$ 0.00 ± 0.05°.

Sulfoxide 11. A solution of 110 mg (0.58×10^{-3} mol) of racemic α-naphthyl methyl sulfoxide in 5 g of J mixture was irradiated during 2.5 h at 30 °C. The reaction mixture was submitted to molecular distillation at 80 °C under vacuum (0.01 mm); 78.5 mg of sulfoxide were recovered (71%). It was shown that no thermal racemization occurs under such conditions. No optical rotation could be detected on the recovered irradiated sulfoxide. The same reaction was performed in ChEC at 8 °C with 200 mg of sulfoxide **11**. Sulfoxide (146 mg) was recovered (73%) without significant optical rotation, $(\alpha)^{25}_D$ 0.00 ± 0.05°. In order to check that a photochemical interconversion of sulfoxide **11** did occur in the mesophase, 60 mg (0.32×10^{-3} mol) of optically active sulfoxide **11**, $(\alpha)_D$ −83.5°, EtOH (21% ee), dissolved in 5 g of J mixture were irradiated at 29 °C during 2.5 h. Pure sulfoxide (46.0 mg) was recovered (77%) having $(\alpha)_D$ −40.5°, EtOH (51% racemization).

Thermal Experiments. (1) Decarboxylation of Ethylphenylmalonic Acid (7a). Ethylphenylmalonic acid (**7a**) (0.96×10^{-3} mol; 200 mg) was intimately mixed with 5 g of ChB. The mixture was heated for 2 h at 160 °C, under a nitrogen atmosphere, in a thermostated silicone oil bath. The reaction products (170 mg) were collected by molecular distillation under vacuum (0.05 mm) at 160 °C and consisted of a mixture of 95% 2-phenylbutanoic acid (**8a**) and 5% benzoic acid. A second distillation gave 160 mg (80%) of pure **8a** having no significant optical rotation, $(\alpha)^{25}_D$ 0.00 ± 0.07°.

Molecular distillation of mixtures of optically active and racemic 2-phenylbutanoic acid (**8a**) in ChB under the conditions described above afforded materials with unchanged specific rotations. The same experiments were made with phenylmethylmalonic acid (**7b**) which led to the recovery of racemic hydratropic acid **8b**. In order to study the influence of the experimental conditions during the decarboxylation experiments of **7a**, several ways were tested to prepare the reaction mixtures of **7a** in ChB. (a) Crystallized ChB and **7a** were intimately mixed. (b) ChB and **7a** were dissolved in ether to give a homogeneous solution, and the solvent was removed under vacuum. (c) Ethylphenylmalonic acid (**7a**) was progressively introduced into the mesophase (ChB preheated at 160 °C). In all cases, no optical rotation could be detected for **8a**.

(2) Claisen Rearrangement of γ-Methylallyl *p*-Tolyl Ether (5). γ-Methylallyl *p*-tolyl ether (**5**) (650 mg; 4×10^{-3} mol) was dissolved in 13 g of ChNB (5 wt %). The solution was heated in a sealed degassed ampule at 200 ± 4 °C in an oil bath during 5 h. The product of the rearrangement was isolated by vacuum distillation at 100 °C (0.1 mm). The collected product was then purified over silica gel [eluent: hexane–CH_2Cl_2 50:50 to give 338 mg of 2-(α-methylallyl)-4-methylphenol (**6**) (52%)]. Measurement of optical rotation of this sample in absolute ethanol did not show an appreciable value of rotatory power: $(\alpha)^{25}_D$ 0.00 ± 0.05°C.

CD measurements were made at 22 °C in cyclohexane. A very weak positive circular dichroism was detected for **6** between 260 and 290 nm ($\Delta\epsilon/\epsilon(4 \pm 2 \times 10^{-5})$, λ 275 mm). In order to find the actual origin of this very weak optical activity, 400 mg of racemic phenol **6** was dissolved in 8.6 g of ChNB and heated under the same conditions as those described above. No optical rotation could be detected for the recovered phenol **6** but a positive circular dichroism of the same order of magnitude ($\Delta\epsilon/\epsilon(3 \pm 2 \times 10^{-5})$, λ 275 nm) observed in the previous experiment was measured. This fact led us to consider that partial thermal asymmetric destruction of the phenol **6** could occur during the heating at 200 °C. In addition we always detected *p*-nitrobenzoic acid in the reaction mixture.

(3) Thermal Equilibration of Cholesteryl Methanesulfinates, Epimers 9 and 10. (a) In Achiral Solvent. Preparation of Cholesteryl Methane sulfinates 9 and 10. Sulfinyl chloride[25] (2.18 g; 0.022 mol) in toluene (25 mL) was added to a mixture of cholesterol (8.15 g; 0.022 mol), pyridine (1.76 g, 0.0226 mol), and toluene (25 mL). After 24 h of stirring the pyridinium chloride was filtered off and the solvent was evaporated. Two recrystallizations of the crude product from hexane gave 5.56 g (56%) of cholesteryl methanesulfinates **9** and **10** (mp 118 °C), $(\alpha)^{25}_D$ −42.5 ± 1.5° (*c* 3.3, $CHCl_3$) (18% diastereomeric excess of the epimer with the *S* configuration at sulfur).[11]

Thermal Equilibration of Cholesteryl Methanesulfinates. In a typical experiment, 90 mg (0.2×10^{-3} mol) of cholesteryl methanesulfinates **9** and **10** with 18% diastereomeric excess of the epimer with the *S* configuration at sulfur was dissolved in 3 g of toluene and the solution was heated at 85 °C during 3 h. The solvent was rapidly removed at the same temperature under vacuum. The mixture of the two sulfinates was recovered after purification of the crude reaction mixture on a short silica gel column (eluent hexane–ether 1:1) to avoid any enrichment in one epimer. **9** and **10** (75.1 mg) were recovered (83%) and the diastereomeric composition was evaluated from the optical rotation of the mixture: $(\alpha)^{25}_D$ −18.5 ± 1.5° (*c* 2, $CHCl_3$). From the published data concerning the optical rotations of the pure diastereomers[11] [(*R*)-**10**, $(\alpha)^{24}_D$ 19.2°; (*S*)-**9**, $(\alpha)^{24}_D$ −85.3° (*c* 1–2, $CHCl_3$)] we concluded that the sulfinate epimerization in toluene at 85 °C afforded a 28 ± 3% enrichment in the *R* epimer.

(b) In Cholesteryl Benzoate (Cholesteric Mesophase). Cholesteryl methane sulfinate (250 mg) (with 18% diastereomeric excess of the epimer with the *S* configuration at sulfur) was intimately mixed with 3 g of ChB. The mixture was heated at 145 °C for 30 min (cholesteric mesophase). The reaction mixture was then rapidly cooled and chromatographed over silica gel. ChB was first eluted by hexane–CH_2Cl_2, 70:30. The sulfinate was then eluted by ether; 206 mg (82.5%) was recovered. A new purification over silica gel gave 180 mg of sulfinate having $(\alpha)^{25}_D$ −24.5° which corresponded to a 16 ± 2% enrichment in the *R* epimer.

(c) In Cholesteryl Benzoate (Isotropic Phase). The same reaction as described above was repeated in ChB in the isotropic phase. The mixture was kept at 175 °C for 30 min. Two chromatographic purifications over silica gel afforded 175 mg of sulfinate having $(\alpha)^{25}_D$ −25.7° which corresponded to a 14 % ± 2% enrichment in the *R* ep-

imer.

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Registry No.—**1**, 32897-40-8; **2**, 68875-92-3; **3**, 52392-70-8; **4**, 68907-09-5; **5**, 29654-59-9; **6**, 68875-93-4; **7a**, 1636-25-5; **7b**, 4371-02-2; **8a**, 7782-29-8; **8b**, 2328-24-7; **9**, 63520-69-4; **10**, 63520-66-1; **11**, 68907-10-8; ChNB, 23838-12-2; cholesterol, 57-88-5.

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Notes

X-ray Crystal and Molecular Structure of a Bridgehead Diene

William H. Rastetter* and Thomas J. Richard

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Jon Bordner and Glenn L. A. Hennessee

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650

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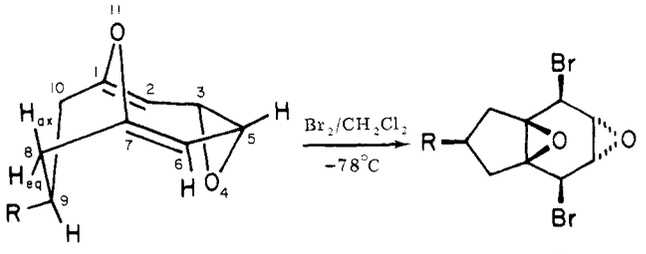
Recently we reported[1] the synthesis of the strained bridgehead diene **1a** (Scheme I) and the characterization of its transannular bromination product **2a** by X-ray crystal analysis. Examination of a molecular model of the oxepin oxide **1a** reveals considerable distortion of the bridgehead double bonds, but disappointingly the crystals of **1a** are not suitable for X-ray crystal analysis. Herein we report the synthesis, characterization, and X-ray crystal structure of derivative **1b** ((*ps*,3*R*,5*S*,9*s*)-9-methoxy-4,11-dioxatricyclo-[5.3.1.$0^{3,5}$]undeca-1,6-diene) and its transannular bromination to **2b**.

The synthesis of oxepin oxide **1b** from *syn*-2-hydroxyindane 3a,7a-oxide[2] follows the route previously reported[1] for the unsubstituted diene **1a**. The chemical consequences of locking

Scheme I



1a, R = H
1b, R = OCH_3

2a, R = H
2b, R = OCH_3

the oxepin oxides **1a** and **1b** into the pictured transoid[3] conformations have been discussed.[1]

Results and Discussion

An X-ray crystal analysis of oxepin oxide **1b** yields the perspective view of the molecule shown in Figure 1. In the crystal, the six-membered ring (C_1, C_{7-10}, and O_{11}) adopts a distorted chair conformation in which the bridgehead atoms C_1 and C_7 are held close together (distance C_1–C_7 = 2.176 (0.004)[4] Å; compare C_8–C_{10} = 2.564 (0.004)[4] Å). The methyl ether oxygen (O_{12}) assumes an equatorial position and the methyl group (C_{13}) takes a noneclipsed position between C_{10} and H_9 (dihedral angle C_{10}–C_9–O_{12}–C_{13} = 67.2° (0.3°)[4]).

The bridgehead double bonds display virtually identical

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