Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Finzi, L. , Maccagnani, G. , Masiero, S. , Samorí, B. and Zani, P.(1989) 'Searching for asymmetric inductions in chiral smectic mesophases', Liquid Crystals, 6: 2, 199 — 210
To link to this Article: DOI: 10.1080/02678298908033214
URL: http://dx.doi.org/10.1080/02678298908033214

LIQUID CRYSTALS, 1989, VOL. 6, NO. 2, 199–210

Searching for asymmetric inductions in chiral smectic mesophases

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(*Received 27 July 1989; accepted 7 February 1989*)

Searching for asymmetric synthesis in smectic phases is, to our knowledge, reported for the first time in this paper. Two different reactions able to lead to optical enrichment were carried out in smectic phases (S) composed of chiral molecules. The first was a thermally promoted 1,3 dipolar cycloaddition of a diazo compound to a prochiral thiocarbonyl derivative run in a chiral smectic C mesophase (S_C^*). The second was a monomolecular process, the photochemical inversion of chiral sulphoxides in a smectic A mesophase. In both cases the asymmetric induction was zero or, in the best run, very very poor. This lack of transfer of chirality between the smectic solvent and the reaction is discussed to understand better the requirements for more successful tailoring of such experiments.

1. Introduction

Many of the processes taking place in biological systems (such as enzymatic catalysis [1]) are determined not only by the chemistry of the individual reagents, products and biological catalysers, but also, by the specific interactions between these species with themselves and with their environment. That is why part of synthetic chemistry is today engaged in obtaining multi-molecular systems with a high degree of internal organization, able to reproduce the activity of molecules occurring in natural systems [2, 3], or able to be used as simplified models in order to study the effect of supramolecular parameters on the path of the reaction [4]. The reactivity of solute molecules can be modified within structurally organized solvents (such as liquid crystals [5–7], vesicles [8], micelles [9, 10] and membranes [11]). These reactivity controls can be considered as true catalytic effects and are determined by anisotropic restrictions exerted on the orientational and diffusional properties of the reagent molecules and in some cases also by preferential solubilities in structurally different regions inside the solution.

Being interested in performing asymmetric transformations assisted either by chiral auxiliaries or by a chiral medium, we decided to study the effects that smectic phases of liquid-crystalline solvents composed of chiral molecules could exert on the stereochemical outcome of properly chosen reactions.

The availability of chiral mesomorphic molecules exhibiting smectic phases is now increasing because of possible applications to the display industry. These materials can therefore be used also as solvents for organic reactions. We turned our search for asymmetric induction to smectic mesophases because our group recently demonstrated that S_B liquid crystals provide the most efficient way to carry out quaternization reactions of aminobenzene sulphonate esters [12]. We have demonstrated that S_B

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0267-8292/89 $3.00

solvents are able to catalyse reactions by forcing the translational diffusion of the guest reactant molecules to occur basically in two dimensions. The same type of reduction of dimensionality is one of the mechanisms by which nature handles problems of timing and efficiency in membranes and enzymes [13].

In addition nematic solvents have been widely used by others as solvents for reactivity studies: mostly to probe reaction mechanisms because of the weak effects they normally exert. Weiss *et al.* have investigated a broad series of molecular rearrangements looking for correlations between the mechanism of the rearrangement and the structure or the mesomorphic state of the solvent [14–18]. Their results have shown that the choice of a particular path for the reaction depends both on the relative shapes of the solvent and the reacting molecules as well as the type of mesomorphic phase in which the solvent molecules organize themselves.

In addition, recent works by Leigh *et al.* reported the use of liquid-crystalline solvents to control the relative stereochemistry in Diels–Alder reactions; all of the mesophases investigated display no ability in discriminating endo versus exo product formation, in either isotropic, cholesteric or smectic solvents [19–20].

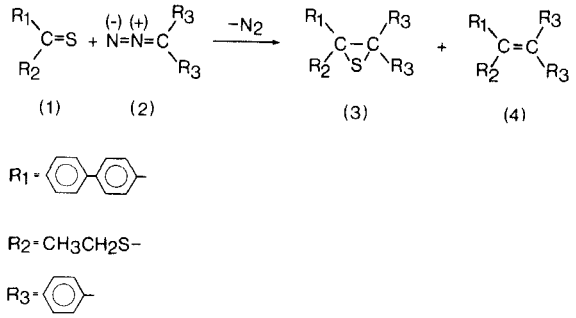
The higher ability of smectic phases, with respect to nematic or cholesteric solvents, to catalyze reactions and affect reactivity of guest molecules is due to their more rigid molecular packing and their layered structures. But at the same time this tight packing makes the requirements for guest solubility much stricter.

All these solvent effects can be also seen as the result of transferring linear anisotropy from the host structural organization to the reactant diffusion and orientation. Circularly anisotropic media also exist and they are able to discriminate between right and left circularly polarized light as well as between chiral enantiomeric molecules. Liquid crystals composed of chiral molecules are circularly anisotropic and their circular anisotropy could be transferred to interacting systems or processes which are structurally compatible with this chirality.

Chirality may thus be transferred from the solvent to guest reaction products. Basically discouraging results in this field have been obtained by several authors using cholesteric liquid crystals. In fact, whereas Pirkle *et al.* reported some promising results on the asymmetric transformation of racemic sulphoxides via their thermal inversion in cholesteric solution [21], Kagan *et al.* showed later that these and other results could not be substantiated by a careful reinvestigation [22]. Concluding his report, Kagan asked for further investigations, and also suggested the use of chiral smectic mesophases, as a better candidate as "a highly ordinated asymmetric solvent, capable of exerting considerable stereochemical control". To our knowledge this is the first report of a search for asymmetric induction within smectic phases. One bimolecular and one monomolecular reaction were chosen as probes.

2. Tailoring the bimolecular reaction probe

The reaction between a thiocarbonyl compound and a diaryl disubstituted diazomethane, depicted in scheme 1, leads to a chiral episulphide (3) as a reaction product when either the thiocarbonyl (1) or the diazo partner (2) bear a prochiral carbon. This kind of reaction has not been exploited for the synthesis of chiral episulphides (3), though it has been known for a long time [24] and was proved to be a general and efficient route to (3) and the related olefins (4) [25]. The stereochemistry of this reaction among others of diazoalkanes, has been examined by Turro [26]. This reaction appeared to fulfill the requirements of our approach also.



Scheme 1. Synthesis of episulphide (3) by reaction of dithioester (1) and diphenyldiazomethane (2).

The chiral liquid crystal chosen by us for this kind of bimolecular cycloaddition was CE3 (5) (figure 1): it has a S_C^* mesophase from 69 to 79°C. It is an optically active product, with $[\alpha]_D^{25} = +6{\cdot}7°$ (c = 3 in acetone).

Once the kind of reaction to be used as a probe and the solvent were chosen, we had to look for the maximum structural similarity between the molecules of the host-guest system. In addition the stability of the reactants must be taken into account in connection with the time required for the reaction to take place. This led us to the choice of diaryldiazoalkanes as the 1,3 dipolar partner.

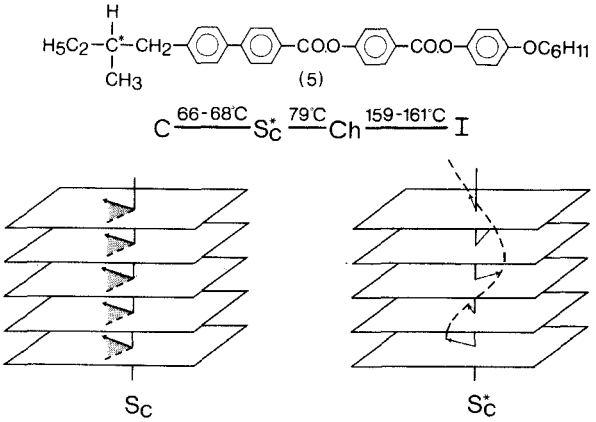


Figure 1. Structure of the liquid crystal CE3 and idealized representation of S_C^* mesophase.

The prochiral centre had thus to be placed in the thiocarbonyl reagent (1); but where? In this context it must be taken into account that chirality is a structural property of objects with pure rotational symmetries. The dimension of chirality spans the full range from the atomic size of a carbon asymmetrically substituted to the macro-size of cholesteric or smectic helices. We label these two different cases as micro- and macro-chirality. Host chiral liquid crystals exhibit both kinds of chiralities and in principle both chiralities can induce circular anisotropy to the guest reactions.

If polymer syntheses are carried out, the molecular dimension of the product is commensurable with the helical structure of the overall system: macro-chirality may thus be, in favourable conditions, transferred from the host to the reaction product.

In reactions where the reagents are incommensurable with the host macrochirality, only its local circular anisotropy can induce optical enrichment. In fact in

cholesteric mesophases the helical bias of the mesophase does not control the sense of an asymmetric transformation performed upon a chiral solute, even though this asymmetric transformation might happen [22]. The transfer of chirality from the solvent to the guest reaction relies in this case only on the guest-host packing. The location of the reaction centres must therefore be the closest possible to the centres or sources of the molecular chirality within the host structure.

We have managed to obtain at least one of the reagents preferentially localized near the chiral centre of CE-3. In order to achieve this, we decided to put into the molecular structure of the thiocarbonyl derivative (1) a biphenyl group directly bonded to the prochiral carbon of the thione function, the other substituent being an alkyl group. The biphenyl was suggested by the structure of the solvent molecules with their aromatic core. This structural similarity coupled with the layered smectic structure ought to promote the desired reagent localization without relying upon specific and stronger interactions, such as hydrogen bonding, charge transfer or metal coordinations. Therefore we synthesized biphenyl-methyl-thioketone and biphenyl-ethyl-thioketone, but neither was stable enough to allow attempts of cycloaddition with diphenyldiazomethane (2) in S_C^* CE-3. We resorted instead to the use of the ethyl dithioester of p-phenylbenzoic acid (DTE) (1) which is a very stable product with m.p. of 50–51°C. In fact we looked for reactants also melting at a temperature lower than that of the appearance of the S_C^* mesophase of CE-3 (55°C) in order to avoid any possible phenomenon of microcrystallization inside the solvent. That is why we chose as the 1,3 dipole diphenyldiazomethane (DFD) which melts at 29–30°C, in spite of its limited stability and its globular shape.

At this point, the chosen reaction was carried out in an isotropic solvent. DFD and DTE were dissolved in benzene (or petroleum ether) and refluxed under nitrogen in anhydrous conditions. The episulphide (3) was obtained (yield 45 per cent) and characterized by both spectroscopic techniques (N.M.R. and MS) and conversion to the corresponding olefin (4).

3. Experimental conditions for the bimolecular reaction probe and results

We have recently shown that studies of reactivity in smectic liquid crystals must always rely on a thorough knowledge of the specific solubilization processes which take place within the reactive mesomorphic solution [12]. Differential scanning calorimetry (D.S.C.) is mostly useful to study the loss of cooperativity between the solvent molecules due to the presence of the guest reactant. The reaction conditions in the S_C^* mesophase were therefore defined by applying the D.S.C. technique to the solution of reactants (DTE and DFD) at various concentrations in CE-3. The structural organization of the S_C^* solvent was found to be affected dramatically by the presence of the reactant. The peak relative to the smectic–cholesteric transition disappeared from the D.S.C. thermogram for concentrations of DTE and DFD higher than 2 per cent in weight. With the concentrations equal to 2 per cent, the S_C^* mesophase exists in a 1·5°C (with DTE) or 0·5°C (with DFD) range. It is noteworthy that DTE, because of its longer shape and its closer structural similarity to the liquid crystal, allows a larger temperature range over which the S_C^* mesophase does exist. Based on these results, we chose a concentration of 1·5 per cent (w/w) for DTE and a corresponding concentration for DFD so as to have a molar ratio of 1 : 1. The DSC analysis also determined the temperature at which the reaction should be carried out, this being 67 $\pm$ 0·5°C. This very critical variable was controlled during the reaction

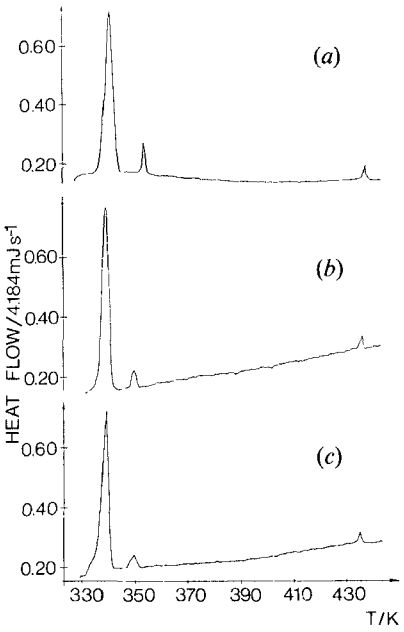


Figure 2. D.S.C. measurements of mixtures. (*a*) (5) alone, (*b*) (5) + (1) (1 per cent w/w), (*c*) (5) + (2) (1 per cent w/w).

Table 1. Reaction between (1) and (2) in S_C^* of CE3: test conditions and product yields.

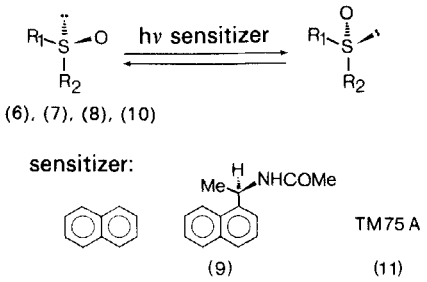
Run	Time/h	(3) per cent	(4) per cent	Unreacted (1)/ per cent	$[\alpha]_D$/°
1	53	41	20	Present	+7·5
2	64	40	35	Present	0
3	48	50	13	35	0

by the use of a high precision thermostat with a microprobe in the bulk of the reacting mesomorphic phase, mechanically stirred the whole time.

Another important detail of the preparation of the reaction pot is the mixing of the components. The two individual reagents DTE and DFD were dissolved in *n*-pentane then added to CE-3 in order to assure homogeneous dispersion; the solvent was then removed under vacuum. The reaction was performed under argon and in anhydrous conditions. The separation of the product was achieved by careful column chromatography followed by preparative TLC. The yield of products (3) and (4) obtained in various runs are reported in table 1, together with temperature and reaction times. The optical activity of the pure episulphide so obtained was tested in each case: only in run 1 did the episulphide (3) display a very small optical rotation, but in other runs it was practically zero.

4. Tailoring of the monomolecular reaction probe

The monomolecular reaction we chose was the pyramidal inversion of sulphoxides. It can take place either thermally [27] or photochemically [28]. In the latter case, the photoinversion must be sensitized, either intramolecularly by an aromatic

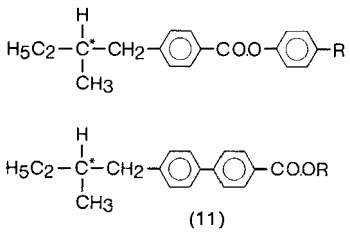


Scheme 2. Photosensitized inversion of chiral sulphoxides. (6) R_1 = *p*-Tol, R_2 = Me. (7) R_1 = *p*-Tol, R_2 = $PhCH_2$. (8) R_1 = Ph, R_2 = *t*-Bu. (10) R_1 = 1-Napht, R_2 = Me.

chromophore or by an external sensitizer (see scheme 2). Naphthalene is the most commonly employed; according to the results of Hammond, it acts through the formation of an exciplex between photoexcited singlet naphthalene and the unexcited sulphoxide, followed by energy-transfer and non-radiative decay [28]. Irradiation of optically active sulphoxides at wavelengths greater than 285 nm in inert solvents and with the presence of a sensitizer, thus leads to racemization. (Shorter wavelengths produce photocleavage of the sulphoxides.) The opposite experiment, i.e. the stereomutation of a racemic sulphoxide was carried out by Kagan [29]. He irradiated racemic p-tolyl methyl sulphoxide (6) employing R(+)α.(1-acetamido) ethyl naphthalene (9) as chiral sensitizer in ethereal solution. The recovered (6) showed only a feeble optical activity (o.p. 2 per cent). Later on, reinvestigating the reports of Pirkle [21], Kagan found that racemic methyl α-naphthyl sulphoxide (10) could not be optically enriched either by thermal inversion or by photoinversion in cholesteric mesophases [22]. Recently, Weiss looked for optical enrichment when racemic mixtures of products containing a labile stereogenic unit (such as 1,1′-binaphthyl) are allowed to interconvert either in cholesteric or in a chiral isotropic system [30]. The interconversions were obtained either thermally or photochemically. A very small and poorly reproducible photoresolution (less than 1 per cent) was found when racemic 1,1′ binaphthols were irradiated in cholesteric mesophases. These results thus confirm that enantiomeric enrichment can be obtained only when photochemically interconverting enantiomers interact strongly with the chiral medium.

In order to enhance as much as possible the stereoselection we had to run the photochemical stereomutation of our sulphoxides at the lowest possible temperature. The only chiral medium, available to us, which displayed a smectic phase down to room temperature was TM75A (11). Its chiral mesomorphic molecules form a S_A mesophase. The symmetry of this phase is not compatible with macrochirality. This did not bother us because monomolecular reactions of small molecules are certainly the least possibly affected by solvent macrochirality. Asymmetric induction effects must only rely on the best packing of the guest reaction centre with the local molecular microchirality of the host. TM75A is a mixture of esters of *p*-[(2-methyl)butyl] benzoic or *p*-phenyl benzoic acids (figure 3), with $[\alpha]_D^{20} = +4{\cdot}6°$ (c = 24·5 in acetone). Its S_A phase exists from well below 0°C up to 42°C. The sulphoxides (6) to (8) were obtained by known procedures (see experimental part).

As a first step, we performed the photoracemization of optically active benzyl p-tolyl sulphoxide (7) in an isotropic solvent, employing as photosensitizer either a small amount of (11) or naphthalene, which is known to be a good sensitizer for this reaction. The results are reported in table 2. Both naphthalene and TM75A



(11)

Figure 3. The structures of the components of the liquid-crystalline mixture TM75A (11); R = n-alkyl residues from C_6H_{13} to $C_{12}H_{25}$.

Table 2. Photosensitized racemizations carried out on optically active sulphoxides.

Sulphoxide	Sensitizer	Irradiation time/h	Recovered substrate/ per cent	Racemization/ per cent	Recovered sensitizer/ per cent
(6)	TM75A†	5	58	38	99
(7)	TM75A†	7	100	14	98
(7)	TM75A‡	8·5	63	63	97
(7)	naphthalene‡	4·5	64	21	91

† Test run in S_A mesophase; c = 5·5 per cent (w/w).
‡ Test run in isotropic solution (CH_2Cl_2); substrate/sensitizer 1 : 0·2 mol.

(containing a biphenylic chromophore) are efficient activators in the photoracemization of (7); also, this product is satisfactorily stable under the reaction conditions.

The next step was to test photoracemization directly in the S_A phase employing (7) or methyl p-tolyl sulphoxide (6). The experiments were performed in pyrex test tubes (cut-off at $\lambda < 300$ nm) at 15 ± 1°C. The products were then separated by chromatography and the optical activity measured. The results reported in table 2 show that the photoracemization also occurs in the S_A phase; the two sulphoxides (6) and (7) display different chemical and configurational stability, (6) being more labile with respect to both processes.

The most disappointing observation concerns the liquid crystal itself, which is quantitatively recovered, but partially degraded by U.V. radiation during the experiment. Even though the spectral characteristics of the recovered (11) are similar to those of the starting material, the S_A phase looses its rigidity on irradiating, as shown by the D.S.C. transition temperatures S_A–Ch displayed in figure 4. This phenomenon

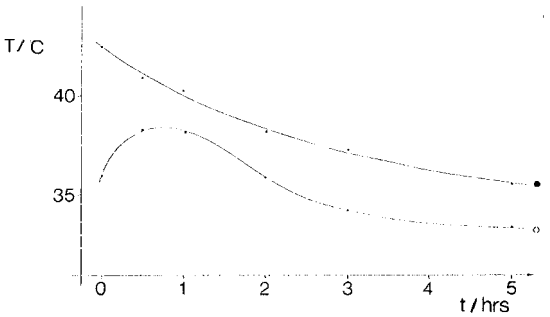


Figure 4. $S_A \rightarrow$ Ch transition temperature during the photoresolution. The points are relative to the maximum of the D.S.C. peaks. ●, TM75A alone; ○, TM75A + (6) (1·5 per cent w/w).

Table 3. Photointerconversion of racemic sulphoxides in a smectic A mesophase.

Sulphoxide	Concentration/ w total w^{-1}	Irradiation time/h	Recovered substrate/ per cent	Optical purity/ per cent	Recovered liq. cryst./ per cent
(6)	6·0	8·0	65	0·4	100
(6)	6·0	5·0	64	0	95
(7)	5·8	7·0	100	0	100
(8)	6·1	7·0	82	0	97
(6)	1·5	5·5	64	0	93
(6)	1·5†	5·5	73	0	94

† The liquid crystal employed as host was the denatured TM75A recovered from the preceeding tests.

limited the reaction running times. Nevertheless, we tried to obtain at least a partial photoresolution by irradiating the racemic sulphoxides (6), (7) and (8) in the S_A phase of (11). The optical activity of the recovered sulphoxides was tested by polarimetry and circular dichroism. The results are summarized in table 3: in only one case did we find a very small optical activity of the recovered (6), but this result could not be substantiated by further tests.

5. Conclusions

The basic aim of this investigation was that of probing the ability of the molecular packing of the smectic phases to exert, alone, asymmetric induction on prochiral solute molecules. In this case specific interactions which usually make asymmetric induction possible in isotropic media were not brought into play. The transfer of chirality from a smectic phase to the reactions examined by us was not operating to a measurable extent, in spite of our careful tailoring of the reagents and experimental conditions. The absence of asymmetric induction in smectic phases is strongly determined by the following three experimental peculiarities of this kind of investigation.

5.1. *Stability of the smectic phase*

The host molecular packing is affected by the reactant guest molecules according to their concentration and shape changes along the reaction coordinate. The solute disrupting effects in our cases increase along the reaction coordinate moving from the reactants towards the products. This was clearly shown by D.S.C. measurements at different times of the bimolecular reactive probe.

In the photochemical reaction the light led to degradation of the smectic solvent during the reaction course, thus altering the ordering of the mesophase as shown in figure 2. Particularly surprising was the temperature profile of the S_A–Ch transition of the reactant solution (figure 2). At the beginning it displays an upward curvature, which suggests the initial formation of a more ordered system. Subsequently, degradation occurs, basically with the same slope as the pure solvent.

5.2. *Partition of solute molecules between possible different sites within the internally inhomogeneous structure of a smectic liquid crystal, and between the smectic solvent and isotropic droplets induced by the solute*

The smectic order is characterized by an alternate sequence of rigid core and aliphatic tails sublayers. Solute expulsion processes from the cores to the chain layers

and also outside the solvent bulk are possible and must be taken into account [12, 31]. A very important and unfortunately negative role is played by the possibility of having biphasic equilibria between the smectic and isotropic or N nematic domains locally induced by the disruptive effects of the reactant solutes [32]. Their solubility in the latter, less ordered phases is higher than in the bulk smectic solvent. Solute molecules are thus taken away from the ordered chiral smectic solvent and left to react in a much less hindered environment. This is probably the main source of these negative results.

5.3. *Source of chirality within the host inducer*

In the cases investigated here it is an asymmetric carbon located in a flexible chain. The asymmetric bias of the 2-methyl butyl group is the worst possible source of chiral discrimination to be employed in an experiment of asymmetric induction. But nothing better was presently available. Axial chirality within the rigid core would be a much better source of circular anisotropy. No smectic medium is known, to our knowledge, whose constituent molecules are axially chiral.

The best option for forthcoming investigations is that of strengthening the guest-host packing by bringing into play stronger and specific interactions between the chirality inducer and the prochiral reaction centre.

6. Experimental

Optical activity of the products was checked either by polarimetry, employing a JASCO DIP-360 or a Bendix NPL 143-C automatic polarimeters, or by circular dichroism on a JASCO J-500 A spectropolarimeter; N.M.R. spectra were recorded on a Varian EM-360 L or on a Bruker CXP-300; I.R. spectra were obtained on a Perkin Elmer model 177 spectrometer; mass spectra were taken at 70 eV on a JEOL JMS-D100; U.V. spectra were recorded on a JASCO UVIDEC-650 spectrophotometer; DSC measurements were carried out on a Perkin Elmer model 2-C.

Melting points and chemical shifts are uncorrected.

6.1. *Ethyl(p-phenyl)dithiobenzoate (1)*

This was obtained according to the method of Mayer [33], reacting 2 g of biphenyl with 1·6 ml of ethyl dithiochloroformiate [34] in 1 ml dichloroethane in the presence of $AlCl_3$. Yield 1·24 g (37 per cent) after chromatography on silica gel (eluant petroleum ether). m.p. 50–51°C (from *n*-pentane); λ_{max} (*n*-hexane) 510 nm (ε = 200 ca); ν_{max} (CCl_4) 1052 cm^{-1} (C = S); δ_H ($CDCl_3$) 1·4 (3 H, t, CH_3), 3·36 (2 H, q, CH_2), 7·3–7·9 (9 H, m, aromatic protons); MS 258 (M^+), 230 ($M^+-C_2H_4$), 197 ($M^+-S-C_2H_5$), 165, 152 ($M^+-S-C_2H_5-CS-H$), 127, 115, 77.

6.2. *1-Ethylthio-1-(p-phenyl)phenyl-, 2,2,-diphenyl thiirane (3)*

Ethyl(p-phenyl)dithiobenzoate (0·1 g) was dissolved in anhydrous benzene (5 ml) under N_2, then added to 0·075 g of diphenyldiazomethane [35] in 5 ml of benzene and refluxed until decoloration takes place (about 45 min). The solvent was removed under reduced pressure and the residue chromatographed on silica gel, eluant petroleum ether/ethyl ether 10 : 1 recovering firstly unreacted (1) and (2) then a mixture of the product (3) and the corresponding olefin (4). This mixture was further purified by chromatography on preparative silica gel plates (20 × 20 cm, thickness 1 mm) eluant petroleum ether/ethyl acetate 10 : 1.

0·071 g (45 per cent yield on the starting reagent) were obtained: m.p. 115·55°C (from *n*-hexane) (correct, D.S.C. data); λ_{max} (cyclohexane) 214 nm; δ_H ($CDCl_3$) 1·11 (3 H, t, CH_3), 2·50 (2 H, q, J = 7·5 Hz, CH_2S), 6·9–7·8 (19 H, m, arom.. prot.); MS M^+ absent, 392 (M^+–S), 363 (M^+–S–C_2H_5), 347 (M^+–C_6H_5), 331 (M^+–2S–C_2H_5), 315 (M^+–2C_6H_5), 198 (M^+–S–2C_6H_5), 77, 29.

6.3. *1-Ethylthio-1-(p-phenyl)phenyl-, 2,2-diphenyl ethene (4)*

0·032 g of (3) and 0·020 g of triphenylphosphine were dissolved in 20 ml of anhydrous benzene and refluxed under N_2 till the disappearance of the starting episulphide (TLC). After evaporation of the solvent, the residue was chromatographed on preparative plates, eluant benzene, affording the olefin (4) as the fluorescent (green) fraction: 0·025 g (85 per cent); m.p. 139°C (from methanol); δ_H ($CDCl_3$) 1·44 (3 H, t, CH_3), 2·33 (2 H, q, J = 6 Hz, CH_2S), 6·9–7·6 (19 H, m, arom. prot.); MS 392 (M^+), 363 (M^+–C_2H_5), 331 (M^+–S–C_2H_5), 254 (M^+–S–C_2H_5–C_6H_5), 77, 29.

6.4. *Reaction of (1) with (2) in the smectic phase of CE-3*

CE-3, purified by repeated crystallizations from methanol, was placed in two distinct vessels (2·500 g in each of them) and left under vacuum. Then 0·0375 g (0·145 mmol) of (1) were added to the first portion and 0·0285 g (0·147 mmol) of (2) were added to the second. The mixtures were homogenized by dissolution in anhydrous *n*-pentane and transferred in a four-necked, 25 ml, round bottomed flask. The solvent was then removed by careful evaporation under vacuum and the flask, equipped with a mechanically driven stirring rod, an argon inlet and a thermocouple sealed to the glass, was put in a high precision thermostatic bath at 67 ± 0·1°C. The mixture was stirred under argon for 50 h; in this period it partly decolourizes. The reaction mixture was then subjected to chromatographic separation: first it was chromatographed on a large silica gel column (eluant benzene) affording an higher RF fraction, that contains unconverted (1) and (2) plus some of products (3) and (4), an intermediate fraction that contains products (3) and (4) plus liquid crystal CE-3 and finally a fraction containing pure CE-3. The mixed fractions were separated by chromatography on preparative plates (eluant petroleum ether/ethyl acetate 8 : 2) giving 0·0131 g (35 per cent) of unreacted (1); 0·0307 g (50 per cent) of the episulphide (3) and 0·0074 g (13 per cent) of the olefin (4). The product (3) shows the same physical and spectral features of the others previously described. An exception can be made for rotatory power, as the product obtained in the first run showed some optical activity, which could not be confirmed in subsequent runs: $[\alpha]_D^{20}$ = +7·5° (c = 0·85 in ethanol).

6.5. *Synthesis of sulphoxides (6), (7) and (8)*

The racemic sulphoxides (6), (7) and (8) were obtained by peroxidation of the corresponding sulphides according to the published procedures: (±) (6) (m.p.) 40–41°C (from *n*-hexane) [36]; (±) (7) m.p. 137–138°C (from ethanol) [37]; (±) (8) m.p. 56–57°C (from petroleum ether) [37].

The optically active sulphoxides (6) and (7) were obtained from (−) (S) (−) menthyl *p*-toluensulphinate, following the procedure of Andersen [38]: (+) (6) m.p. 74–76°C (from petroleum ether), $[\alpha]_D^{20}$ = +140·7° (c = 0·9 in acetone) (o.p. = 97 per cent) [39]; (+) (7) m.p. 165–167°C (from ethanol), $[\alpha]_D^{20}$ = +249° (c = 1·3 in acetone) (o.p. = 99 per cent) [40].

6.6. *Photoinversion of a chiral sulphoxide in the smectic A mesophase of TM75A*

0·5 g of TM75A and 0·03 g of the sulphoxide were placed in a pyrex tube with a stopcock. The mixture was homogenized by gently heating under argon, then degased at the vacuum pump and saturated with argon three times. The waxy mixture was then distributed on the surface of the tube as a thick film. The tube was placed in a thermostatic bath at 15 ± 1°C and irradiated with a Hanovia 125 W mercury vapour lamp; at intervals, the tube was removed and its content homogenized again by gentle heating. During irradiation, the consistence of the mixture changes from a white wax to a slight yellow syrup. After six hours, the reaction mixture was dissolved in chloroform and chromatographed on a silica-gel column, eluant petroleum ether/ethyl acetate, gradient from 3 : 7 to 0 : 1. Most of the liquid crystal was collected as the first fraction. The second fraction contains the impure sulphoxide, which was purified further by chromatography on silica gel plates (eluant petroleum ether/ethyl acetate 3 : 7). The product obtained was characterized by spectral techniques (^{1}H N.M.R., M.S.) and its optical activity was checked either by polarimetry or by circular dichroism. The results are reported in table 3 together with the recovered yields.

Generous gifts of CE-3 and TM75A from BDH Ltd. (England) are gratefully acknowledged. Sincere thanks are due to Professor G. Solladié (Strasbourg) for helpful suggestions and discussions. C.N.R. (Rome) supported this investigation.

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