Photopolymerization in Chiral Crystals. 1. The Planning and Execution of a Topochemical Solid-State Asymmetric Synthesis with Quantitative Asymmetric Induction[1]

Lia Addadi and Meir Lahav*

Contribution from the Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel. *Received August 20, 1977*

Abstract: The first solid-state asymmetric synthesis with quantitative diastereoisomeric yield, and with the asymmetric induction being entirely due to the chiral crystalline environment, has been designed and performed. Irradiation of crystalline enantiomerically pure (*S*)-(+)- or (*R*)-(−)-ethyl 2-cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl-(*E*)-propenoate (**1**) at 5 °C leads to the formation of chiral cyclobutane dimers, trimers, and oligomers in quantitative (>97%) diastereoisomeric yield, as established by ^1H and ^{13}C NMR spectroscopy. The absolute configuration of the products follows from the crystal structure of the reacting enantiomeric crystal. On the other hand, the corresponding enantiomerically pure **2**, in its β crystal modification, yields on irradiation chiral dimers with no detectable asymmetric induction; this is interpreted as being due to the quasi-racemic space group of the reactant crystal.

Introduction

Recently there has been an increased interest in exploiting chiral crystals as media for the performance of asymmetric syntheses. This approach aims to transform the chirality of the reactant crystal into chirality of the product molecules.[2]

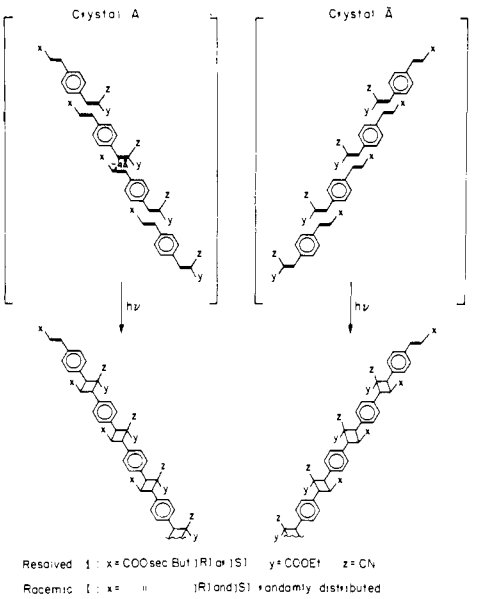
A number of such asymmetric syntheses have been described; among the successful ones, we may mention the solid state asymmetric polymerization of *trans,trans*-pentadiene embedded in the chiral inclusion complex of resolved perhydrotriphenylene[3] or in deoxycholic acid,[4] the addition of gaseous bromine to *p,p′*-dimethylchalcone in a chiral single crystal,[5] the solid-state bromination of *trans*-cinnamoyl alanines,[6] and the two-component photodimerization of diaryl butadienes in chiral mixed crystals.[7] The enantiomeric excesses in these reactions, when determined, range from 6 to 70%.

In the present study we aimed to design and perform an asymmetric synthesis leading to quantitative enantiomeric yield, where the sole asymmetric influence is due to the asymmetric environment of the crystal. Such a synthesis must involve transformation of achiral or racemic reactants into chiral products, with the conditions being such that only one of the two possible enantiomers can be generated. Resolved chiral reactants can be used, if the asymmetric influence of the chiral handle can be distinguished from that of the crystal.

Contrary to heterogeneous gas-solid reactions,[8] photochemical reactions in general are advantageous for our purpose, since by their use one may excite selectively molecules in the bulk, avoiding crystal destruction at low conversion.

One attractive photoreaction is that of $[2\pi + 2\pi]$ photocycloaddition which is known to proceed under topochemical control in many cases, without the difficulties of heat dissipation and volume contraction such as are met frequently in other cases of solid-state polymerization.[9] Further, in molecules of the type with which we shall deal, photocycloaddition takes place in the crystalline phase only, so that even if crystal destruction occurs during the reaction this will not lead to a lowering of the enantiomeric excess achieved. The conditions for utilization of $[2\pi + 2\pi]$ photocycloaddition reactions for the accomplishment of asymmetric syntheses have been discussed in detail previously.[10] It was suggested that only certain structural motifs are suitable for yielding reactions with quantitative optical yield; in one of these, which we have materialized in the present study (Scheme I), we start with an unsymmetrically substituted diene (similar to the symmetrical ones studied by Hasegawa, Nakanishi, et al.[9]), crystallizing in one of the chiral structures A or $\bar{A}$, in which molecules related by translation (5.5–7.0 Å) are so juxtaposed as to allow a topochemical photocyclodimerization and polymerization involving the nonequivalent double bonds (at a distance ≤4.0 Å apart).[10]

Scheme I



It can be seen from this model that if the sole contacts leading to reaction are within the translational stack, only one enantiomeric cyclobutane should be formed.

To guide our choice of a monomer molecule suited to crystallizing as shown in the scheme, we used a number of empirical facts: we avoided carboxylic acids and amides, since these generally pack in centrosymmetric or quasi-centrosymmetric structures;[11] we selected rather *p*-phenylenediacrylates, since in many crystals of these compounds there is observed a 4.0-Å spacing between double bonds, apparently resulting from an attractive interaction between superimposed phenyl and carbonyl groups of adjacent molecules.[12] Nonequivalence between the two reactive sites was introduced by adding a nitrile group on one of the ethylenic double bonds, and using two different ester groups. In order to assure a chiral space group and to avoid close contact between the two identical double bonds up a 4.0-Å translation axis (which would lead to a cyclobutane of symmetry *m*), we attached to one side of the diene a bulky chiral group. We thus ended up with the class of compounds

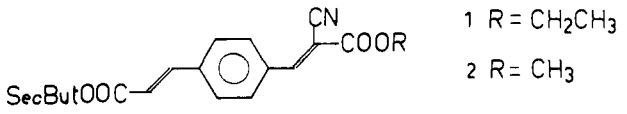
0002-7863/78/1500-2838$01.00/0

Table I. Cell Constants of Compounds **1** and **2** both as Pure Enantiomers and as Racemic Mixtures

Compd	*a*, Å	*b*, Å	*c*, Å	*β*, deg	Space group	*Z*
(*R*)-(−)- or (*S*)-(+)-**1**[a] (EtOH)	13.17	6.94	5.25	103.1 95.5 90.1	*P*1	1
Racemic **1** (melt or EtOH)	13.35	7.03	5.41	104 93 92	*P*1	1
(*R*)-(−) or (*S*)-(+)-**2**[a]						
Modification *α*	4.77	7.11	25.30	91	$P2_1$	2
Modification *β* (melt or EtOH)	9.67	25.73	8.15	57.3	$P2_1$	4
Racemic **2** (from EtOH)	9.67	25.73	8.15	57.3	Pseudo-$P2_1/a$[b] $P2_1/a$	4

[a] Both pure enantiomers have been measured on 90% optically pure samples. [b] The diffraction pattern is almost identical with the diffraction pattern of racemic **2**; thus space group is pseudo-$P2_1/a$.

reported below where R is a variable and where the *sec*-butyl group was chosen for reasons that will be clear later.



A number of homologues of this class have been synthesized and their reactions studied. The crystal photochemistries of two of these compounds are described here. Compound **1** has all the desired characteristics indicated in Scheme I.

Results and Discussion

Synthesis of Monomers and Their Solid-State Photopolymerization. All monomers were prepared by the same three-step synthetic route: *p*-phthalaldehyde was condensed with malonic acid to give *p*-formyl-*trans*-cinnamic acid, which was then condensed with the chosen *α*-cyanoacetate. The chiral *sec*-butyl group was attached in the last step, via an acidic esterification with 99% optically pure *sec*-butyl alcohol.

Crystals were grown, and their cell constants and space group determined. On the basis of the latter, we decided to focus our attention on compound **1**, which crystallizes in space group *P*1, *Z* = 1 with the cell constants reported in Table I. Both the (*R*)-(−) and (*S*)-(+) monomers were prepared and investigated. As expected they have mirror symmetric behaviors.[13]

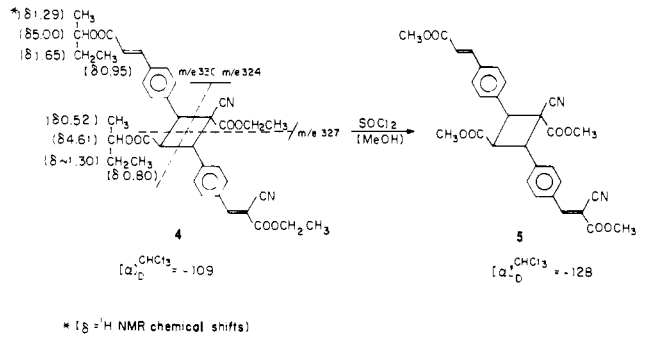
Since this is a multiphotonic polyaddition reaction, it is possible to control the product distribution by appropriate selection of the wavelength. Thus irradiation at $\lambda > 350$ nm, where the chromophore of dimer, trimer, and oligomers do not absorb, leads to the formation of dimers and trimers mainly. When oligomers were needed, the irradiation was carried out at $\lambda > 300$ nm.

Compound 1. Isolation of Products and the Determination of Their Structures. Irradiation of monomer **1** in the crystalline phase, at a temperature well below its melting point, affords a number of products that were identified as dimer, trimer, and oligomers.

The determination of the stereochemistries of dimer, trimer, and oligomers, starting from the (*S*)-(+) monomer, $[\alpha]_D$ ($CHCl_3$) +21°, follows.

Dimer 4 was isolated as an amorphous oil having $[\alpha]_D$ ($CHCl_3$) −109 ± 5°. The mass spectrum shows, in addition to the molecular ion peak *m/e* 654, peaks at *m/e* 327 (M/2, 100%), 324 (4.4%), and 330 (95%) due to asymmetric cleavage of the dimer ring, demonstrating the presence of a 1-3 diaryl disubstituted cyclobutane resulting from reaction between the two different double bonds (Scheme II). ^1H NMR spectra

Scheme II



confirm that two nonequivalent double bonds have been preserved in their original *E* symmetry (*δ* 6.43, doublet, *J* = 16 Hz, and 8.23, singlet). Of special interest in these spectra is the strong shielding by the *sec*-butyl *trans*-cinnamoylate group of the methyl (*δ* 0.52), methylene (*δ* 1.30), and methine (*δ* 4.61) hydrogens of the *sec*-butyl group attached directly to the cyclobutane ring, which shows that the dimer is not a 1-3 syn diaryl substituted cyclobutane.[14] Dimer **4** was transesterified with methanol containing catalytic amounts of thionyl chloride. The tetramethyl ester **5** obtained (Scheme II), after purification by preparative TLC, has the increased specific rotation $[\alpha]_D$ ($CHCl_3$) −128 ± 5°, demonstrating that the optical activity of **4** is mainly due to the new chiral centers created by reaction. This value of the specific rotation is not necessarily the maximum one, since the material contained some *sec*-butyl groups (5-10%) which were not replaced during transesterification.

Trimer 6 was obtained in the form of an oil having $[\alpha]_D$ ($CHCl_3$) −116 ± 5°. The presence of three monomeric units linked through two cyclobutane rings and their stereochemistry follows from the molecular ion peak at *m/e* 981, in addition to the peaks at *m/e* 654, 657, 327, and 330 due to symmetric and asymmetric cleavage at the rings. The NMR spectrum of the trimer is consistent with that of the dimer (Figure 2). The stereochemistry of the two ethylenic double bonds is preserved and again the hydrogens of the two methyls (*δ* 0.52 and 0.59) of the two *sec*-butyl groups on the cyclobutane rings are strongly shielded by the *sec*-butyl *trans*-cinnamoylate and phenyl groups.

Oligomers. The higher oligomers are isolable from the irradiation mixtures since they make up the sole fraction which is methanol insoluble. Part of this fraction is chloroform soluble and has $[\alpha]_D$ ranging from 54 to 66° depending on DP. The similarity of the ^1H NMR, ^{13}C NMR, and IR spectra of the various oligomers to those of dimers and trimers argues that the oligomers are constructed of units such as **4** and **6**. Results

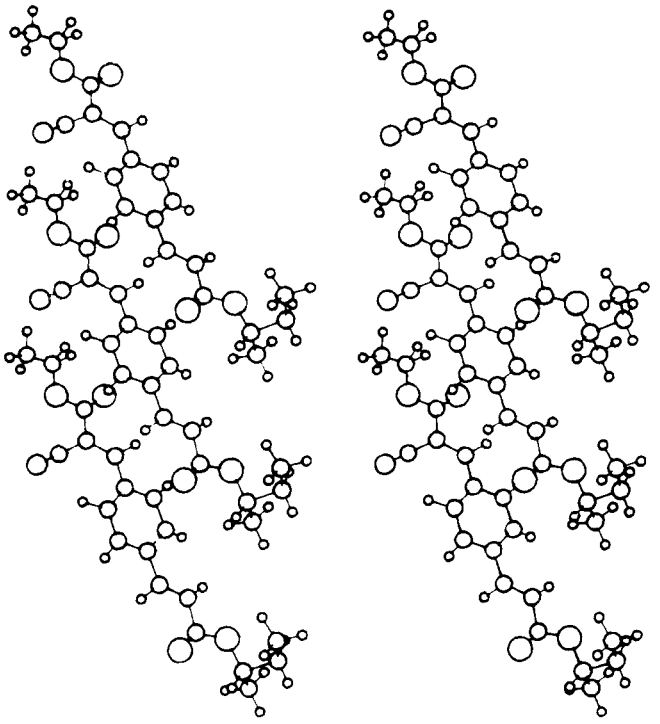


Figure 1. Stereoscopic view of the structure of (*S*)-(+)-**1** along the polymerization axis.

on various oligomers obtained by various methods of irradiation are summarized in Table II.

The molecular weight and degree of polymerization of the chloroform-soluble fraction were established by vapor pressure osmometry ($CHCl_3$) and UV titration of the end chromophores. The two independent methods are in good agreement.

An additional, $CHCl_3$-insoluble fraction is left in very small quantities (5%); this was not thoroughly investigated, but has the same IR spectrum as the oligomers, and higher reduced viscosity in HMPT (hexamethylphosphoric triamide), $[\alpha]_D$ (HMPT) −54°.

Table II. Molecular Weights and Specific Rotations of the Fractions Which Are MeOH Insoluble and $CHCl_3$ Soluble from the Irradiation Mixture from Resolved (+)-**1**

Irradiation conditions			Mol wt by		
Method	T, °C	Time	UV	Vapor pressure Osmometry	$[\alpha]_D^{CHCl_3}$, deg
a	5	2 weeks	2300	2380	−66
a	5	2 weeks	1825	1117	−62
b	−2	20 h	1720	1665	−64.5
b	−2	53 h	3390	3865	−59
b	+6	50 h	2360	2720	−63

[a] Irradiation through Pyrex with 4 × 40 W Westinghouse sunlamps. [b] Irradiation in suspension in methanol–water (1/10) with 450-W immersion lamp (Hanovia high-pressure Hg lamp).

Crystal Structure of (*S*)-(+) Monomer and Absolute Configuration of Products. Resolved (*S*)-(+) enantiomer **1** may in principle crystallize in each of the two diastereomeric motifs A and $\bar{A}$ in Scheme I. Reaction in these two crystals will lead to the formation of cyclobutane dimers, trimers, and oligomers with the same stereochemistry around the C_4 ring, but of opposite chiralities.

The two crystalline arrangements in the scheme are diastereoisomeric in nature, because of the chirality of the handle. Therefore **1**, when crystallized under controlled conditions, will appear in one of them preferentially. The absolute configuration of the stable phase can be determined by solving the crystal structure of a monomer of known absolute configuration. The absolute configuration of the dimer, trimer, and oligomers is then directly deducible from the structure of the reactant crystal. The crystal structure of the (*S*)-(+) monomer was solved,[15] and Figure 1 shows its packing arrangement seen along the *b* axis. From this figure we see that the packing of the monomer is in complete agreement with the schematic model suggested for this synthesis. Adjacent and partially overlapped molecules related by translation have the two different double bonds separated by a distance of 4.04 Å, leading to products with the stereochemistries reported above. The absolute configurations of the products, starting from enan-

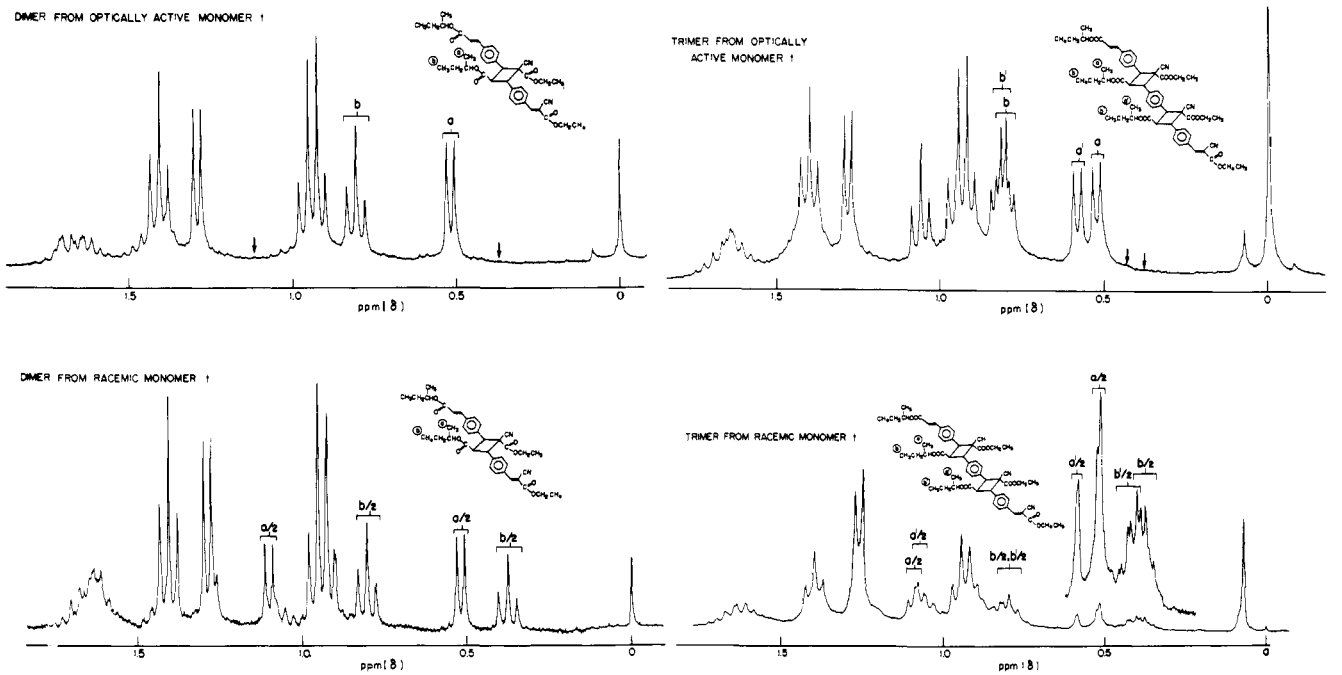


Figure 2. ^1H NMR spectra in the range 0–2 ppm of dimers and trimers obtained from resolved (*S*)-(+)- and racemic (*R,S*)-**1**.

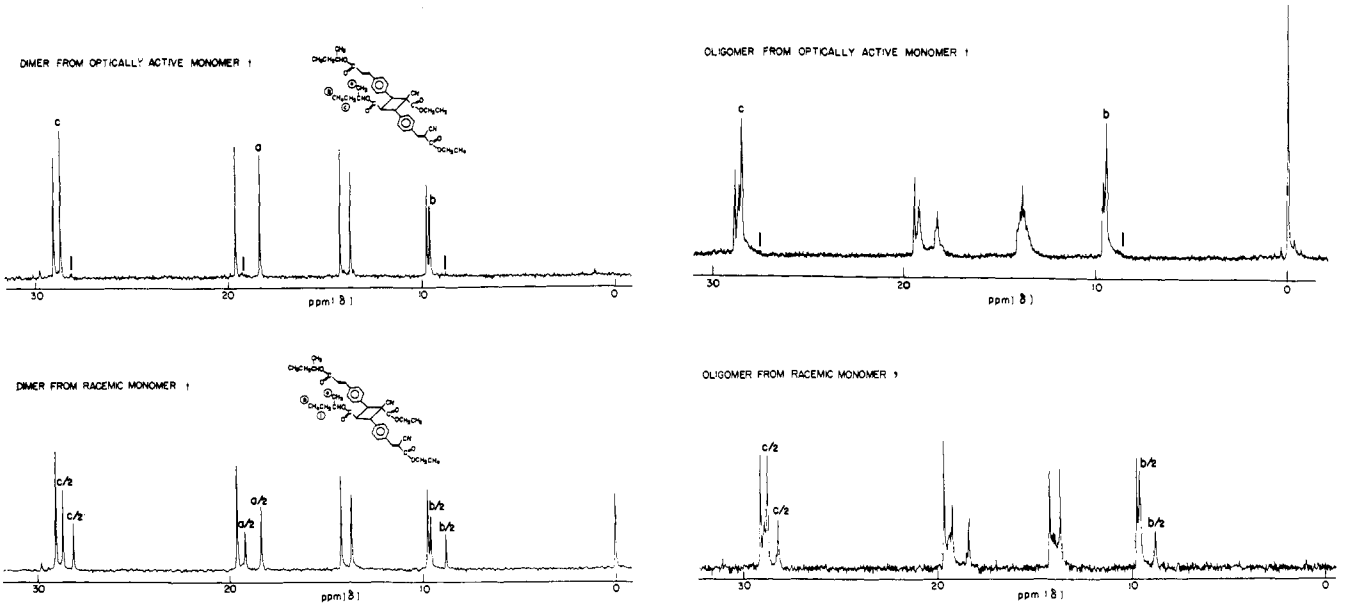
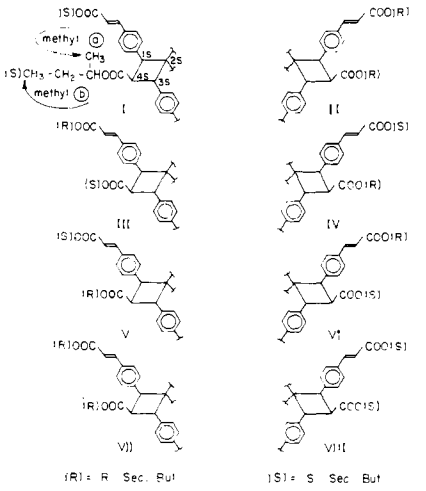


Figure 3. ^{13}C NMR in the range 0–30 ppm of dimers and oligomers obtained from resolved (*S*)-(+)- and racemic (*R,S*)-**1**.

Scheme III



tiomerically pure (*S*)-(+) monomer, are expected to be 1*S*, 2*S*, 3*S*, and 4*S* of Scheme III.

Determination of the Diastereoisomeric Excess of the Products. The packing arrangement of enantiomeric **1** suggests that only one diastereoisomer of the dimer, trimer, and oligomers should be formed, under the conditions of our topochemically controlled reactions. This will be true provided that the crystalline structure of the reactant monomer is unique; but a priori we do not know the energy difference between the two structures A and $\bar{A}$ (Scheme I). Therefore an independent determination of the diastereoisomeric excess of the products is necessary. For that purpose the diastereoisomers of the second class were synthesized and were shown to be absent in the product mixture. This synthesis was made possible by the following observation: racemic **1** crystallizes from the melt as a disordered solid solution of the two enantiomers in a crystal isostructural with that of pure enantiomer **1**. This conclusion was based on differential scanning calorimetric measurements on mixtures of (*R*)-(−)- and (*S*)-(+)-**1**, as well as on comparison of the cell constants of crystals of enantiomeric and racemic **1** which are very similar, but still detectably different, excluding the possibility of spontaneous resolution (Table I).

A schematic representation of the structure of the racemate is given too in Scheme I. The photodimerizable chromophores must be aligned as in the enantiomeric crystal, the sole difference being the presence of both enantiomeric *sec*-butyl handles in every crystal. We have demonstrated elsewhere that the distribution of these handles in the crystal is completely random.[16] The two arrangements of Scheme I, which were diastereoisomeric in the pure enantiomer, become on average enantiomeric in the racemate. As a direct consequence, irradiation of a racemic mixture leads to the formation of the eight diastereoisomeric dimers I–VIII (together with the corresponding trimers and oligomers) (Scheme III), instead of one (or possibly two) expected for the pure enantiomer (*S*)-(+) (I and VIII).

Comparative NMR studies on the dimers obtained from the pure enantiomer with those obtained from the racemate were performed. The ^1H NMR spectra of the dimers and trimers of both systems are shown in Figure 2. The most significant differences are observed for the two methyls of the *sec*-butyl group attached directly to the chiral centers of the cyclobutane ring, while all *sec*-butyl groups attached to the cinnamoyl group, and thus far from other chiral centers, are not distinguishable under our experimental conditions. Therefore for the sake of our NMR discussion, we shall divide the eight diastereoisomers into two groups, I–IV and V–VIII: I–IV have a doublet at chemical shift δ 0.52 (methyl a) and a triplet at δ 0.80 (methyl b) while V–VIII have a doublet at δ 1.10 (methyl a) and a triplet at δ 0.38 (methyl b). On the basis of these data we can conclude that, to the accuracy of our measurements, which we estimate to be >97%, diastereoisomer VIII is not produced by irradiation of the resolved monomer in the crystal.

By a similar comparative analysis we determined the diastereoisomeric excess of the trimer. In the case of the pure enantiomer, methyls a and a′ (Figure 2) of the two different *sec*-butyl groups appear as two doublets at δ 0.52 and 0.59 while methyls b and b′ appear as two triplets δ 0.80 and 0.82. The absence of the triplets at δ 0.38 and 0.43, observed for the trimer isolated from the racemate, demonstrates a quantitative asymmetric induction for the trimerization step too.

The determination of the diastereoisomeric excess of oligomers by ^1H NMR spectroscopy is naturally less accurate owing to broadening of the lines. Thus we shifted to ^{13}C NMR spectroscopy and performed similar comparative studies of dimers, trimers, and oligomers. Spectra are presented in Figure 3. The most significant differences are observed for carbons a (δ 18.3), b (δ 9.5), and c (δ 28.6). As for the ^1H NMR, the absence in the dimer, trimer, and oligomers obtained from the

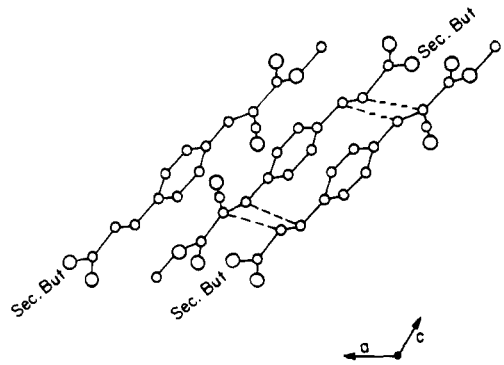


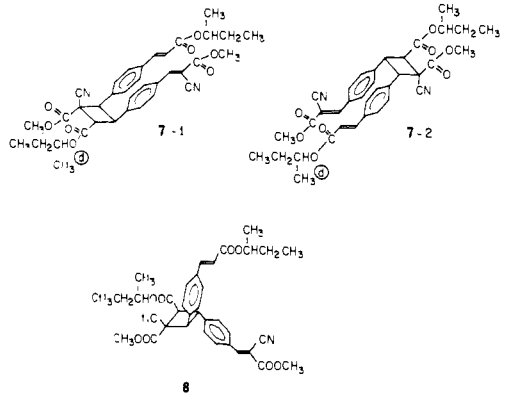
Figure 4. Schematic representation of the room temperature structure of (*R,S*)-**2**, β modification, in the *ac* plane. The *sec*-butyl group could not be located precisely because of disorder.

irradiation of the pure enantiomer of the additional peaks (a, δ 19.2; b, δ 8.8; c, δ 28.0) due to the diastereomeric products demonstrates that the control of the lattice is quantitative both for initiation and propagation steps.

Compound 2. Since we are interested in studying the influence of crystal chirality on the optical yield of the products of a topochemical reaction we shall consider now a second example of an enantiomerically pure monomer in which the asymmetric induction (in a pseudo-achiral crystal) is nil. Compound **2** is a good model for such behavior, since it packs in space group $P2_1$, $Z = 4$, and is isostructural with its racemic mixture ($P2_1/a$), with almost identical cell constants (Table I).

Isolation of Products and the Determination of Their Stereochemistry. Enantiomeric **2** is dimorphic. Form α is light stable; on the other hand, irradiation of the (*S*)-(+) monomer, $[\alpha]_D$ ($CHCl_3$) +23°, in its β form results in topochemical dimers, with $[\alpha]_D$ ($CHCl_3$) +12°, and structure as in **7** (Scheme IV), along with oligomers that have not been studied in detail.

Scheme IV



The stereochemistry of the dimers follows from their mass spectrum [*m/e* 626 (P), 313 (P/2), and 415 (asymmetric cleavage of the cyclobutane ring)] and ^{1}H NMR spectrum. The latter shows two carbomethoxy groups at δ 3.33 and 3.48, and, as in **1**, two different *E* ethylenic double bonds are conserved, confirming that the reaction takes place between two nonequivalent double bonds. No appreciable shielding of the groups linked to the cyclobutane ring is observed. The above information leaves us with either **7** or **8** as possible structures. The stereochemistry of the product is finally deduced from the crystal structure of racemic **2**,[17] which is isomorphous with the enantiomeric form β (see Table I) and has the same photobehavior, yielding cyclobutanes with the same NMR and mass spectra. The crystal structure of the racemate is reported in Figure 4. It could be demonstrated[16,17] that here again, as with racemic **1**, the crystal has no chiral recognition for the *sec*-butyl groups, thus explaining the isomorphism with the enantiomeric crystal. On topochemical grounds, we thus expect the formation of **7** from both the racemate and the enantiomer.

Determination of the Diastereoisomeric Excess of 7. On the basis of the packing arrangement of **2**, we expect the formation of the two diastereoisomers **7**-1 and **7**-2; their relative yields will reflect the reactivity of the two different reactive centers.

The ^{1}H NMR spectrum of the dimeric product shows two doublets of equal intensity corresponding to the two diastereomeric methyls d (Scheme IV). Furthermore, upon transesterification with protiated methanol, we obtain the corresponding tetramethoxy ester with no observable specific rotation, confirming the absence of measurable asymmetric induction in the reaction.

Conclusions

This communication describes the planning and successful performance of the first solid-state asymmetric synthesis with quantitative diastereomeric yield. Since we are dealing with a topochemical polymerization that occurs only within a crystalline arrangement, destruction of the lattice during the reaction is not associated with loss of control on the stereochemical course of the polymerization in its later steps, and indeed, we could prove the asymmetric induction to be quantitative both in initiation and propagation.

It was demonstrated by comparison of the two systems investigated that the presence or absence of measurable asymmetric induction is due only to the chiral environment of the reaction center in the crystal and not to the influence of the chiral *sec*-butyl group; this result suggests that even polymerization of polycrystalline monomer **1** of lower optical purity might give rise to products with quantitative diastereomeric yield. The limiting case is the racemic mixture, isomorphous with the pure enantiomer but composed of isoenergetic crystals of opposite chiralities. Under specific conditions we may expect to obtain crystals of one chirality in excess, and indeed, in several experiments,[1] specific rotations up to 30° were obtained after irradiation of large crystals of racemic composition (in principle in homochiral crystals a quantitative asymmetric induction is expected in this case too).

Finally, the same reasoning can be extended to any achiral compound of this same class of unsymmetrically substituted dienes, packing in the same chiral structure as **1**. In these last two cases, however, the absolute configuration of the products will vary from one experiment to the other, depending on which of the two isoenergetic enantiomeric structures appears under the crystallization conditions, whereas in enantiomerically enriched **1** the absolute configuration of the products is dictated by the chirality of the *sec*-butyl handle in excess.

The possibility of forming solid solutions between enantiomers furthermore suggests that we can use the system investigated as a solid matrix for inducing other molecules of the same family to crystallize in the same chiral structure. Studies based on the above conclusions are presently in progress, and will be the subject of further communications.

Experimental Section

Ethyl 2-Cyano-3-(*p*-3′-*E*-propenoic acid)phenyl-(*E*)-propenoate (3). *p*-Formyl-(*E*)-cinnamic acid[18] (0.026 mol) was dissolved in hot ethanol and condensed with ethyl cyanoacetate (0.052 mol) in the presence of 0.88 mL of piperidine. The reaction mixture was refluxed for 3 h. **3** crystallizes from the reaction mixture in the form of white crystals (65%): mp 245–247 °C; IR (KBr) 2220 (CN), 1725 (COOR), 1700 (COOH), 1650 cm^{-1} (C=C); ^{1}H NMR (Me_2SO) δ 1.32 (t, 3 H), 4.33 (q, J = 7 Hz, 2 H), 6.72 (d, J = 16 Hz, 1 H), 7.67 (d, J = 16 Hz, 1 H), 7.7–8.2 (complex m, 4 H), 8.42 (s, 1 H).

(*S*)-(+)-, (*R*)(−)-, and (±)-Ethyl 2-Cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl-(*E*)-propenoate (1). **3** was refluxed in $SOCl_2$ (5 h) to give the corresponding chloride; after removal of the remaining $SOCl_2$, the chloride was dissolved in dry benzene containing catalytic amounts of pyridine and a 50% excess of 99 or 90% optically pure (*S*)-(+)- or (*R*)-(−)-*sec*-butyl alcohol (Norse) or racemic *sec*-butyl alcohol, and refluxed for 3 h. The product was recrystallized from ligroin and ethanol (70%).

(*S*)-(+)-**1** has mp 105–106 °C (EtOH); $[\alpha]_D$ ($CHCl_3$) + 22.7°; IR 2220 (CN), 1730 (CO), 1700 (CO), 1630 cm^{-1} (C=C); UV λ_{max} (MeOH) 335 nm (ϵ 42 400); NMR ($CDCl_3$) δ 0.96 (t, J = 7 Hz, 3 H), 1.30 (d, J = 6 Hz, 3 H), 1.41 (t, J = 7 Hz, 3 H), 1.62 (m, 2 H), 4.43 (q, J = 7 Hz, 2 H), 5.03 (m, 1 H), 6.56 (d, J = 16.5 Hz, 1 H), 7.75 (d, J = 16.5 Hz, 1 H), 7.7–8.2 (m, 4 H, aromatics), 8.3 (s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 327 (31), 282 (10), 271, (100), 254 (63), 242 (23), 226 (23), 208 (20), 198 (13), 180 (18), 152 (20), 127 (13), 115 (7), 112 (10).

The monomer obtained by esterification with (*R*)-(−)-*sec*-butyl alcohol of enantiomeric purity 90% has $[\alpha]_D$ ($CHCl_3$) −21.0° and mp 102–103 °C. Racemic **1** has mp 90.5 °C and identical IR, UV, NMR, and mass spectrum.[19]

Irradiation and Isolation of Products from 1. Two irradiation methods were used. (a) The monomer was dispersed between two Pyrex plates and irradiated, with frequent mixing and grinding, under four Westinghouse sunlamps at 5 °C for periods of 1–2 weeks. (b) The monomer was suspended in a mixture of methanol–water (10%) and irradiated under continuous stirring with a 450-W immersion high-pressure Hg Hanovia lamp at −2 °C for periods of 20–60 h.

The approximate yields of products using the two different methods are the following: residual monomer, (a) 10%, (b) 2%; dimer(s), (a) 35%, (b) 23%; trimer(s), (a) 13%, (b) 10%; oligomers ($CHCl_3$ soluble), (a) 40%, (b) 60%; ($CHCl_3$ insoluble) (a) 0%, (b) 5%. By irradiating with λ >350 nm (filter Corning 7380) the yield of dimer can be increased up to 60%.

In both cases the lower oligomers were extracted from the reaction mixture with cold methanol, whereas the higher oligomers remain insoluble. From the methanol-soluble fraction dimers and trimers were separated by preparative TLC (silica gel, CH_2Cl_2) and then purified by a further fractionation (silica gel, benzene–ethyl acetate, 85:15); this last step allows us to get rid of small amounts of trans-cis isomerized products, formed in later stages of the reaction.

Determination of the Structure of Products from (*S*)-(+)-1. Dimer 4 was isolated in the form of an oil: IR 2960 (CH) 2210 (CN), 1720 (CO), 1620 cm^{-1} (C=C); UV ($CHCl_3$) λ_{max} 295–305 nm (ϵ 44 000); mass spectrum *m/e* (rel intensity) 654 (2), 330 (95), 327 (100), 324 (4); ^1H NMR (270 MHz) δ ($CDCl_3$) 0.52 (d, 3 H), 0.80 (t, 3 H), 0.92 (t, 3 H), 0.95 (t, 3 H), 1.29 (d, 3 H), 1.40 (t, 3 H), 1.65 (m, 2 H), ~1.30 (complex m, 2 H), 3.94 (q, 2 H), ~4.33 (q, 2 H), 4.40 (2 d, 2 H), 4.61 (m, 1 H), 4.98 (m, 1 H), 5.04 (q, 1 H), 6.45 (d, J = 16 Hz, 1 H), 7.65 (d, 1 H), 8.23 (s, 1 H), 7.3–7.6 and 7.98, 8.01 (m, 8 H, aromatics); ^{13}C NMR (270 MHz) δ ($CDCl_3$) 9.51, 9.73, 13.47, 14.07, 18.41, 19.61, 28.59, 29.04, 43.56, 47.15, 49.24, 49.54, 63.17, 63.62, 72.75, 74.10, 104.48, 115.70, 116.78, 120.35, 128.28, 128.73, 130.08, 131.43, 131.88, 135.45, 136.67, 141.01, 143.40, 154.18, 162.56, 166.46, 166.76, 169.75; $[\alpha]_D$ ($CHCl_3$) −109 ± 5°.

Transmethylation of Dimer 4. Dimer **4** (0.2 g) was refluxed in methanol with catalytic amounts of thionyl chloride for 72 h. The product was purified from residual partially reacted dimer by two successive separations on preparative TLC, silica gel, using methylene chloride and benzene–ethyl acetate in the ratio of 85:15. **5** was obtained in the fo. m of an oil (60 mg): NMR δ ($CDCl_3$) 3.45 (s, 3 H), 3.52 (s, 3 H), 3.83 (s, 3 H), 3.96 (s, 3 H), 4.44 (d, J = 8 Hz, 1 H), 4.53 (d, J = 4 Hz, 1 H), 5.11 (q, 1 H), 6.50 (d, J = 16.5 Hz, 1 H), 7.30–8.20 (m, 9 H), 8.33(s, 1 H); mass spectrum *m/e* (rel intensity) 542 (0.21), 511 (2), 271 (50), 246 (100), 240 (46); $[\alpha]_D$ ($CHCl_3$) −128°.

Trimer 6 was isolated in the form of an oil: IR 2960 (CH), 2220–2300 (CN), 1730 (CO), 1650–1600 cm^{-1} (C=C); UV ($CHCl_3$) λ_{max} 285 nm (ϵ 42 000); mass spectrum (70 eV) *m/e* (rel intensity) 981 (0.1), 908 (0.5), 654 (0.6), 657 (0.15), 581 (5), 330 (73), 327 (17), 324 (3), 271 (100), 254 (64); NMR δ ($CDCl_3$) 0.52 (d, 3 H), 0.58 (d, 3 H), 0.80 (t, 3 H), 0.82 (t, 3 H), 0.92 (t, 3 H), 0.95 (t, 3 H), 1.06 (t, 3 H), ~1.40 (2 m, 4 H), 1.29 (d, 3 H), 1.40 (t, 3 H), 1.66 (m, 2 H), 3.70–4.10 (complex m, 2 H), 4.10–4.55 (complex m, 6 H), 4.55–4.80 (m, 2 H), 4.80–5.20 (complex m, 2 H), 6.44 (d, 1 H), 7.2–7.6 and 7.98, 8.01 (aromatics, 12 H), 7.65 (d, 1 H), 8.24 (s, 1 H); ^{13}C NMR δ ($CDCl_3$) 9.55, 9.72, 13.60, 13.86, 14.15, 18.28, 18.39, 19.55, 28.56, 28.92, 43.23, 43.41, 46.83, 48.68, 48.94, 49.17, 49.30, 62.89, 63.38, 63.56, 72.49, 73.41, 73.72, 103.95, 115.26, 116.50, 116.86, 119.58, 127.35, 127.92, 128.29, 129.48, 129.80, 131.14, 131.44, 134.68, 134.90, 136.14, 136.79, 140.81, 143.35, 153.92, 162.29, 166.27, 166.41, 166.57, 169.35, 169.56; $[\delta]_D$ ($CHCl_3$) −116 ± 5°.

Oligomers. The methanol-insoluble fraction was partially dissolved in chloroform. Table II summarizes some typical data concerning these fractions; IR is very similar to that of dimers and trimers. ^{13}C NMR δ ($CDCl_3$) 9.5, 9.7, 13.6, 13.9, 14.1, 18.3, 19.3, 19.15, 28.6, 28.7, 28.9, 43.1, 43.3, 46.4, 46.7, 48.9, 49.3, 50.1, 62.8, 63.4, 64.5, 72.5, 73.4, 74.2, 103.8, 104.1, 115.3, 115.4, 116.6, 116.9, 119.8, 122.0, 126–132 (complex multiplet), 134–137 (complex multiplet), 140.8, 143.3, 153.7, 162.3, 166.3, 166.5, 169.4, 169.5.

Structure Determination of Products from Racemic 1. Dimers (9): mp 160–162 °C; IR, and UV, and mass spectrum almost identical with those of **4**; ^1H NMR (270 MHz) δ ($CDCl_3$) 0.38 (t, 3/2 H), 0.52 (d, 3/2 H), 0.80 (t, 3/2 H), 0.92 (t, 3 H), 0.95 (t, 3 H), ~0.95 (m, 2/2 H), 1.10 (d, 3/2 H), 1.29 (d, 3 H), 1.41 (t, 3 H), 1.65 (m, 2 H), 3.95 (m, 2 H), 4.31–4.51 (m, 4 H), 4.53–4.68 (m, 1 H), 4.95–5.1 (m, 2 H), 6.45 (d, 1 H, J = 16 Hz), 7.35–7.59 and 7.98, 8.01 (m, 8 H, aromatics), 7.63 (d, 1 H, J = 16 Hz), 8.24 (s, 1 H); ^{13}C NMR (270 MHz) δ ($CDCl_3$) 8.76, 9.56, 9.73, 13.65, 14.17, 18.34, 19.15, 19.57, 28.08, 28.64, 29.0, 43.34, 43.49, 47.07, 49.03, 49.36, 49.50, 62.88, 63.39, 72.53, 73.72, 73.93, 104.13, 115.26, 116.58, 119.85, 128.00, 128.38, 128.47, 129.86, 131.17, 131.57, 135.17, 135.07, 136.54, 136.64, 140.88, 143.26, 153.80, 153.87, 162.32, 166.22, 166.51, 169.39, 169.48.

Trimers (10): IR, UV, and mass spectrum identical with those of **6**; ^1H NMR (270 MHz) δ ($CDCl_3$) 0.38 (t, 3/2 H), 0.43 (t, 3/2 H), 0.53 (d, 3/2 H), 0.58 (d, 3/2 H), 0.80 (t, 3/2 H), 0.82 (t, 3/2 H), 0.92 (t, 3 H), ~0.95 (2 m, 4/2 H), 0.95 (t, 3 H), 1.02 (d, 3/2 H), 1.06 (t, 3 H), 1.10 (d, 3/2 H), 1.27 (d, 3 H), ~1.40 (2 m, 4/2 H), 1.41 (t, 3 H), 1.65 (m, 2 H), 3.70–4.10 (complex m, 4 H), 4.10–4.55 (complex m, 6 H), 4.55–4.80 (m, 2 H), 4.80–5.20 (complex m, 2 H), 6.44 (d, 1 H), 7.2–7.6 and 7.98, 8.01 (m, 12 H, aromatics), 8.24 (s, 1 H); ^{13}C NMR (270 MHz) δ ($CDCl_3$) 8.80, 9.55, 9.72, 13.61, 13.89, 14.14, 18.37, 19.33, 19.55, 28.09, 28.59, 28.74, 28.94, 43.29, 43.51, 46.56, 46.91, 48.79, 49.06, 49.42, 50.13, 62.91, 63.42, 63.56, 72.52, 73.46, 73.75, 104.09, 115.20, 116.60, 116.80, 128–132 (complex multiplet), 135.2, 136.6, 140.8, 143.3, 153.9, 162.3, 166.2, 166.5, 169.4.

Oligomers. IR and UV were almost identical with those of the oligomers isolated from enantiomeric **1**. ^{13}C NMR δ ($CDCl_3$) 8.75, 9.58, 9.71, 13.63, 13.86, 14.13, 18.29, 19.12, 19.53, 28.05, 28.57, 28.73, 28.92, 43.07, 46.1, 46.7, 48.5, 48.6, 49.1, 49.6, 62.2, 62.8, 64.0, 71.8, 73.0, 73.6, 103.8, 104.0, 115.2, 115.4, 116.6, 119.7, 126–132 (complex multiplet), 134–137 (complex multiplet), 139.1, 140.9, 143.3, 153.9, 162.2, 166.2, 166.4, 169.4, 169.5.

(*R*)-(−)-, (*S*)-(+)-, and (±)-Methyl 2-Cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl-(*E*)-propenoate (2). All three compounds have been prepared exactly as the ethyl homologue, using *sec*-butyl alcohol of optical purity 90%.

Enantiomeric **2** is dimorphic. Form α, mp 131–132 °C (EtOH). Form β was crystallized either from ethanol–water or directly from the melt, mp 129–131 °C. The crystallographic constants are reported in Table I. IR 2220 (CN), 1730–1700 (CO), 1630 cm^{-1} (C=C); mass spectrum *m/e* (rel intensity) 313 (15.8); NMR ($CDCl_3$) δ 0.95 (t, 3 H), 1.3 (d, 3 H), 1.62 (m, 2 H), 3.96 (s, 3 H), 5.03 (m, 1 H), 6.56 (d, ΔJ = 16 Hz, 1 H), 7.91 (d, ΔJ = 16 Hz, 1 H), 7.6–8.3 (4 H, aromatic), 8.26 (s, 1 H); (*S*)-(+) $[\alpha]_D$ ($CHCl_3$) +21°; UV λ_{max} 340 nm (ϵ 34 000) ($CHCl_3$). Racemic **2**, mp 125–127 °C (EtOH–H_2O). Cell constants in Table I.

Isolation and Structure Determination of Products from Form β of (*S*)-(+)-2. Form α is light stable. Form β reacts yielding products which are separated in the pure form by preparative TLC (silica, CH_2Cl_2, followed by a second separation with benzene–ethyl acetate, 85/15).

Dimers 7: mp 164–166 °C (EtOH); IR 2230 (CN); 1750–1725–1700 (CO), 1630 (C=C), 1600 cm^{-1}; UV λ_{max} 290 nm (ϵ 37 300); mass spectrum *m/e* (rel intensity) 626 (0.8), 570 (1.0), 553 (5.7), 524 (2.4), 496 (4.0), 465 (2.7), 415 (91), 359 (30), 342 (42), 313 (100); NMR δ (C_6D_6) 0.80 (t, 6 H), 1.12 (d, 3/2 H), 1.13 (d, 3 H), 1.16 (d, 3/2 H), 1.41 (m, 4 H), 3.33 (s, 3 H), 3.48 (s, 3 H), 3.95–4.3 (m, 2 H), 4.82 (m, 1 H), 5.05 (m, 2 H), 6.50–7.8 (m, 9 H), 7.83 (s, 1 H), 6.33 (d, ΔJ = 16 Hz, 1 H); $[\alpha]_D$ ($CHCl_3$) +12°.

Transesterification of the dimer was conducted as described for **4**,

yielding the tetracarbomethoxy dimer **11**: mass spectrum *m/e* (rel intensity) 542 (16), 511 (5), 373 (39), 271 (100), 240 (50); NMR δ ($CDCl_3$) 3.80 (s, 3 H), 3.86 (s, 3 H), 3.95 (s, 3 H), 4.00 (s, 3 H), 4.2-4.8 (m, cyclobutanes, 3 H), 6.4 (d, 1 H), 7-8 (m, 9 H, aromatics), 8.22 (s, 1 H). No measurable optical rotation could be obtained for this product.

Isolation and Structure Determination of Products from Racemic 2. Dimers obtained by irradiation of racemic **2** have been isolated exactly as for (*S*)-(+)-**2**, and have exactly the same NMR, IR, and mass spectrum as **7**.

Acknowledgments. We thank Dr. H. Nakanishi (Yokohama, Japan) for making available to us the crystal structure of *p*-phenylene di-δ-(*E*)-cyanoacrylic acid di-*n*-propyl ester, Professor M. D. Cohen for his support, Dr. L. Leiserowitz for his interest, and Dr. Z. Berkowitz-Yellin for making available to us the packing diagrams of the compounds described here before publication. We thank Mr. Mirchia Grinberg for his help with the NMR measurements. The authors acknowledge with thanks support of this work by a grant from the United States-Israel Binational Science Foundation (BSF), Jerusalem, Israel. L. A. acknowledges a Levi-Eshkol Fellowship.

References and Notes

(1) For preliminary reports see (a) L. Addadi, M. D. Cohen, and M. Lahav, *J. Chem. Soc., Chem. Commun.*, 471 (1975); (b) *Mol. Cryst. Liq. Cryst.*, **32**, 137 (1976).
(2) (a) B. S. Green, M. Lahav, and D. Rabinovich, *Acc. Chem. Res.*, in press; (b) B. S. Green and M. Lahav, *J. Mol. Evol.*, **6**, 99 (1975); (c) H. Morawetz, *Science*, **152**, 705 (1966); (d) F. Wudl, D. A. Lightner, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 4099 (1967); (e) R. S. Miller, D. Y. Curtin, and I. C. Paul, *Ibid.*, **94**, 5114 (1972); (f) R. E. Pincock, R. R. Pincock, R. R. Perkins, A. S. Ma, and K. R. Wilson, *Science*, **174**, 1018 (1971); (g) G. Wegner, *Chimia*, **28**, 475 (1974).
(3) M. Farina, G. Audisio, and G. Natta, *J. Am. Chem. Soc.*, **89**, 5071 (1967).
(4) G. Audisio and A. Silvani, *J. Chem. Soc., Chem. Commun.*, 481 (1976).
(5) (a) K. Penzien and B. M. J. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **8**, 608 (1969); (b) B. S. Green and L. Heller, *Science*, **185**, 525 (1974).
(6) (a) M. Lahav, E. Gati, L. Roitman, and L. Leiserowitz, in preparation; (b) S. Arlel, M. Lahav, and L. Leiserowitz, in preparation.
(7) A. Elgavi, B. S. Green, and G. M. J. Schmidt, *J. Am. Chem. Soc.*, **95**, 2058 (1973).
(8) G. Friedman, E. Gati, M. Lahav, D. Rabinovich, and Z. Shakked, *J. Chem. Soc., Chem. Commun.*, 491 (1975).
(9) F. Nakanishi and M. Hasegawa, *J. Polym. Sci., Part A-1*, **8**, 2151 (1970), and references cited therein.
(10) B. S. Green, M. Lahav, and G. M. J. Schmidt, *Mol. Cryst. Liq. Cryst.*, **29**, 187 (1975).
(11) L. Leiserowitz, *Acta Crystallogr., Sect. B*, **32**, 775 (1976).
(12) (a) H. Nakanishi, K. Ueno, M. Hasegawa, Y. Sasada, and T. Yurugi, preprint for the Symposium on Light Induced Polymerization Reactions, Philadelphia, Pa., July 1975; (b) Y. Bernstein, M. D. Cohen, and L. Leiserowitz in "The Chemistry of Quinonoid Compounds", S. Patai, Ed., Wiley, New York, N.Y., 1974, p 37.
(13) As 99% optically pure (*R*)-(−)-*sec*-butyl alcohol is not commercially available, the symmetric behavior of the enantiomers was tested in monomers in which the enantiomeric excess is only 90%.
(14) Prolonged exposure to light of the reaction mixture causes some cis-trans isomerization around terminal double bonds; no evidence, however, has been found for cis-trans isomerization prior to reaction, as no cis isomer was detected either in the recovered monomer or in the products of reaction after short irradiation periods.
(15) Z. Berkovitch-Yellin, private communication.
(16) L. Addadi, E. Gati, M. Lahav, and L. Leiserowitz, *Isr. J. Chem.*, **15**, 116 (1977).
(17) Z. Bercovitch-Yellin and W. Jones, private communication.
(18) R. H. Wiley and P. H. Hobson, *J. Am. Chem. Soc.*, **71**, 2429 (1949).
(19) Racemic **1** has two forms when crystallized from the melt: the stable form has mp 90.5 °C and the metastable mp ~87 °C. This point will be dealt with in detail in a further communication.

Chemistry of the Sulfur-Nitrogen Bond. 14.[1,2] Arenesulfenic Acids from *N*-Alkylidenearenesulfinamides (Sulfinimines)

Franklin A. Davis,* Arthur J. Friedman, and Upender K. Nadir

Contribution from the Department of Chemistry, Drexel University, Philadelphia, Pennsylvania 19104. *Received August 31, 1977*

Abstract: The synthesis of a novel class of reactive organosulfur-nitrogen compounds, *N*-alkylidenearenesulfinamides (sulfinimines), **1**, prepared by oxidation of the corresponding sulfenimines, **2**, is described. Thermally, these compounds rearrange via a concerted or nearly concerted mechanism to afford nitrile and arenesulfenic acid (ArSOH). The electronic effect of substituents on the rate of this reaction is negligible while steric factors are somewhat more important. The intermediate sulfenic acids were trapped with methyl propiolate and ethyl acrylate to afford **9** and **10** in good yield. Arenesulfenic acids prepared in this fashion decompose to yield disulfide and thiolsulfonate as major products. The corresponding sulfinic acids are obtained when the sulfenic acid contains electron-attracting groups. Possible reaction pathways for the formation of these products are discussed. In the presence of dimethyl sulfate **3g** affords a variety of methylated products, **15-18**, arising from the intermediate 3-nitrobenzenesulfenic acid.

Sulfenic acids (RSOH) have been proposed as key intermediates in a number of important chemical reactions including biological transformation.[3-7] Despite numerous attempts to isolate these species only a very few special examples are known. Four are derivatives of 1-anthraquinonesulfenic acid, first prepared in 1912 by Fries.[8] A stable azetidinone-(β-lactam) sulfenic acid was reported by Chou[4b] in 1974 and *tert*-butanesulfenic acid has been prepared in solution.[3b,c]

While 2-nitrobenzenesulfenic acid has been the subject of numerous investigations,[9] relatively few studies of simple arenesulfenic acids (ArSOH) have been reported.[10] Two methods are available to prepare arenesulfenic acids: the pyrolysis of sulfoxides (eq 1) and the hydrolysis of a sulfenyl derivative (eq 2). Neither of these methods affords isolable arenesulfenic acids.

$$\mathrm{Ar\text{-}S(O)CR_2CHR_2} \rightarrow \mathrm{ArSOH} + \mathrm{R_2C{=}CR_2} \quad (1)$$

$$\mathrm{Ar\text{-}S\text{-}X} + \mathrm{H_2O} \rightarrow \mathrm{ArSOH} + \mathrm{HX} \quad (2)$$

$$\mathrm{X = Cl, Br, NR_2, SAr}$$

The mechanism proposed for the pyrolysis of sulfoxides, which generally takes place in the temperature range 100-200 °C, is believed to involve a stereospecific cis elimination.[11] However, Hammett ρ values observed for the pyrolysis of aryl *tert*-butyl sulfoxides ($\rho = 0.65$)[3b] and aryl *n*-propyl sulfoxides ($\rho = 0.51$)[11b] suggest that the transition state for sulfoxide

0002-7863/78/1500-2844$01.00/0