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Photopolymerization in Chiral Crystals. 3.[1] Toward an "Absolute" Asymmetric Synthesis of Optically Active Dimers and Polymers with Quantitative Enantiomeric Yield

Lia Addadi* and Meir Lahav*

Contribution from the Department of Structural Chemistry, The Weizmann Institute of Science, Rehovot, Israel. *Received April 19, 1978*

Abstract: An "absolute" asymmetric synthesis of chiral dimers and polymers of variable optical yield and an asymmetric synthesis with quantitative enantiomeric yield starting from a monomer of low optical purity are described. Irradiation of polycrystalline ethyl 2-cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl(*E*)-propenoate (**1**) of 60% optical purity or above leads to the formation of chiral dimers and oligomers with quantitative enantiomeric yield. Carefully crystallized samples of **1** of 22–60% optical purity lead to enantiomeric excesses of 90% or above. Racemic **1** crystallizes from the melt either in the form of a stable eutectic mixture or in the form of an isomorphous, chiral, metastable phase of different microcomposition. A method for the characterization of the two phases, based on photodimerization and NMR analysis of the diastereomeric dimers, is described. Irradiation of samples of the chiral metastable phase with one enantiomorphous crystal form in excess leads to an "absolute" asymmetric synthesis with variable optical yield, of both signs. Possible routes to the achievement of an "absolute" asymmetric synthesis with quantitative enantiomeric yield, in systems related to **1**, are discussed.

Introduction

The achievement of asymmetric synthesis starting from racemic or achiral reagents and in the absence of any external chiral agent has long been an intriguing challenge to chemists.

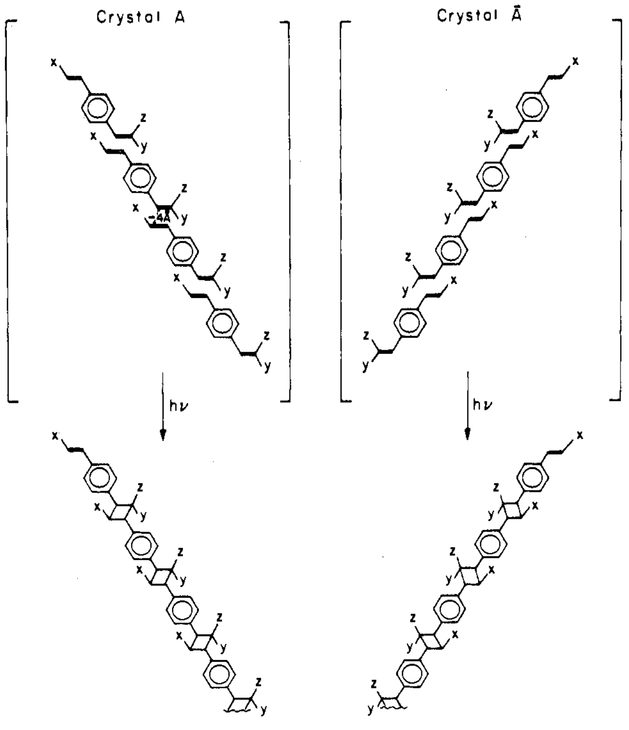
A number of such asymmetric syntheses have been recently described, which exploit the method of spontaneous asymmetric crystallization of achiral compounds coupled with topochemical transformations.[2-10]

In the present series of studies we are testing this approach by "engineering" crystals of appropriate monomers which upon photopolymerization can yield polymers with quantitative enantiomeric yield.

Recently we have described the planning and successful execution of an asymmetric synthesis of dimers and polymers with quantitative diastereomeric yield, starting from optically pure monomer ethyl 2-cyano-3-(*p*-*sec*-butyl-3′-(*E*)-propenoate)phenyl-(*E*)-propenoate (**1**), by a process involving crystallization of the monomer in a chiral crystal ($a = 13.17$ Å, $b = 6.94$ Å, $c = 5.25$ Å, $\alpha = 103.1°$, $\beta = 95.5°$, $\gamma = 90.1°$, $P1$, $Z = 1$), followed by a $[2\pi + 2\pi]$ topochemical photocycloaddition.[11,12] The reaction is schematically represented in Scheme I.

We have demonstrated that the optical yield in this reaction is quantitative both in the initiation and in the propagation steps and we presented experimental evidence which strongly suggested that the chiral induction in the various stages of the polymerization is entirely due to the asymmetric crystalline environment and not to the chiral handle itself. Racemic **1** is isostructural with the crystal of the pure enantiomer ($a = 13.35$ Å, $b = 7.03$ Å, $c = 5.41$ Å, $\alpha = 104°$, $\beta = 93°$, $\gamma = 92°$, $P1$, $Z = 1$), as can be seen from the identity in space group and from the similarity in crystallographic constants and X-ray diffraction intensities.[13] Therefore the chiral crystals of the racemate consist of a disordered solid–solution of the two enantiomers; while in the enantiomeric crystal all *sec*-butyl

Scheme I



Resolved 1 : x = COOsec But (R) or (S) y = COOEt z = CN
Racemic 1 : x = " (R) and (S) randomly distributed

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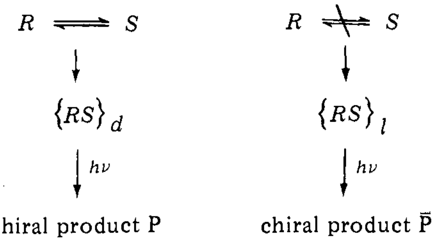
Table I

absolute confign of C_4 ring	absolute confign of *sec*-butyl group	methyl *a*[a] δ ($CDCl_3$)	methyl *b*[a] δ ($CDCl_3$)
SSSS	*S*	0.52	0.80
RRRR	*R*	0.52	0.80
SSSS	*R*	1.10	0.38
RRRR	*S*	1.10	0.38

[a] Methyls *a* and *b* are defined as in Scheme III.

Scheme II



groups are of the same chirality (Scheme I), in racemic **1** every single chiral crystal contains *sec*-butyl groups of both chiralities. Moreover, we have demonstrated by a chemical mass spectrometric method[1] that the antipodes are randomly distributed within the solid solution and that the original alignment of the polymerizing diene is left almost unchanged.

These observations suggest that, starting from racemic monomer **1**, an "absolute"[14] asymmetric synthesis with quantitative enantiomeric yield can be accomplished, provided that the compound can be crystallized as one single homochiral crystal (Scheme II).

The preparation of such a single chiral crystal, of 50% *R*, 50% *S* composition, under equilibrium conditions, demands solid solubility between the two enantiomers in all range) of compositions; partial immiscibility would be associated with the cocrystallization of the enantiomorphous phases in equal amounts in the form of an eutecticum.[15]

A deeper understanding of the system required therefore an accurate determination of the phase diagram between the two enantiomers of **1**.

Results

Phase Diagram. The phase diagram of *S*-(+)- and *R*-(−)-**1**, as experimentally determined from the DSC heating curves of mixtures of the two enantiomers in the whole range of compositions, is shown in Figure 1 (solid line). Particular care was taken in the preparation of the samples, in order to reach crystallization conditions near to equilibrium (details are described in the Experimental Section).

From this diagram we learn that the two enantiomers of **1** show complete solid miscibility in the ranges 100:0 to 60:40 and 0:100 to 40:60; an immiscibility gap in the range 60:40 to 40:60 divides the two enantiomeric *P*1 structures. As even small deviations from equilibrium in crystallization effect the correct evaluation of the solidus curve, the exact range of the eutecticum was confirmed by chemical means, as will be discussed in detail later.

An examination of the phase diagram shows two distinct ranges of composition that must be considered separately for the purpose of asymmetric synthesis. In range A, from 100:0 to 60:40 or 0:100 to 40:60, any polycrystalline sample crystallized from the melt under equilibrium conditions is composed of crystals of one chirality, dictated by the component present in excess, with an overall composition equal to the starting composition of the melt. In such a homochiral phase the diastereomeric yield of our topochemical reaction should be quantitative in spite of the fact that we start with a monomer of low optical purity. On the contrary, in range B, 60:40 to 50:50, the stable phase consists of a mixture of crystals of both chiralities. Every single crystallite has a composition fixed by the boundary of the eutecticum (~60:40). This, together with the overall composition in *R* and *S* enantiomers, defines the ratios between crystals of opposite chiralities. Since the total asymmetric induction results directly from this ratio, the overall optical yield of the reaction will decrease rapidly in this range and become 0 at 50:50 composition.

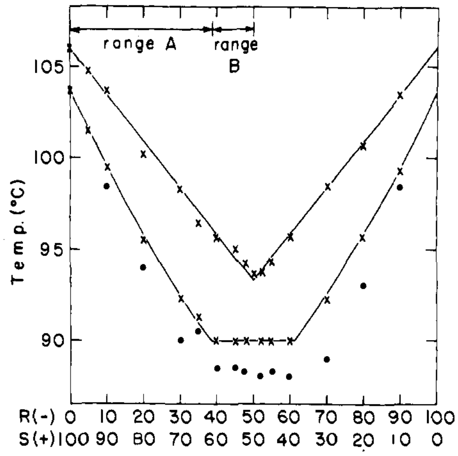


Figure 1. Phase diagram between *S*-(+)- and *R*-(−)-**1**.

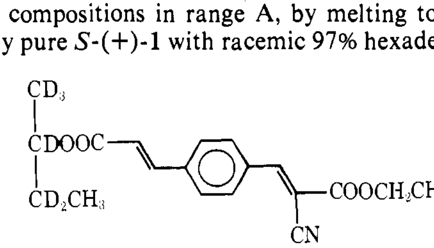
Solid-State Photochemistry of Mixtures of 1 of Different Optical Purities. Determination of the Enantiomeric Yield of the Dimerization Reaction.[16] The solid-state photochemistry of **1** has been analyzed in ranges A and B on the basis of the phase diagram discussed above.

Since we have shown[11] that the enantiomeric yields achieved on dimerization are conserved in the further propagation steps, for simplicity we concentrated here on the dimers alone.

The enantiomeric excesses[16] of the dimerization step of the reaction shown in Scheme I have been determined by ^1H NMR measurements on selectively deuterium labeled monomers. As already described in part 1,[11] the ^1H NMR of the *sec*-butyl groups linked to the cyclobutane ring in the dimers and oligomers is very sensitive to its chiral environment, owing to the strong shielding effect of the benzene rings (see Scheme III). The NMR pattern of the methyl of this group is reported in Table I.

By labeling methyl *a* of, for example, the *R sec*-butyl group with deuterium, we can follow directly by ^1H NMR of the protiated methyl *a* of the *S* antipode the diastereomeric ratio of the *SSSS* (*S*) and *RRRR* (*S*) dimers, which reflects the enantiomeric yield of the reaction.[17,18]

We have prepared mixtures of enantiomeric monomers of various compositions in range A, by melting together 99% optically pure *S*-(+)-**1** with racemic 97% hexadeuterated **2**.



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The samples were crystallized by slow cooling under controlled conditions (see Experimental Section) and irradiated at 5 °C with λ >310 nm; the mixtures of diastereomeric dimers were separated by preparative TLC from residual monomer and oligomers, and their 270-MHz NMR spectra recorded in $CDCl_3$ (one of these is reported in Figure 2). On these spectra

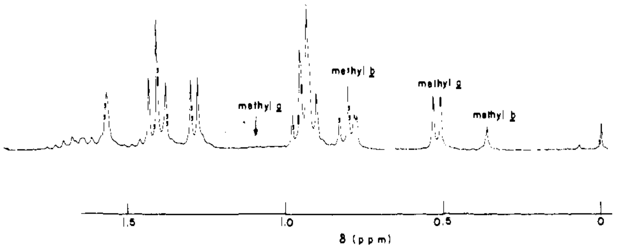
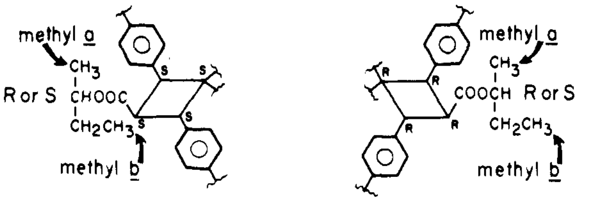


Figure 2. 270-MHz ^{1}H NMR spectrum ($CDCl_3$) of dimers obtained from partially deuterated monomer **1** of *S*/*R* ratio = 80/20 (see text), in the range 0–2 ppm.

Scheme III



R and S indicate the absolute configuration of the chiral centers

we measured the ratio between the doublet at δ 0.52 and the doublet at δ 1.10;[17] Table II summarizes the results obtained upon irradiation of monomeric samples of *S*/*R* ratio of 99/1, 80/20, 70/30, and 61/39.

Starting with monomers having an optical purity of at least 60%, a quantitative enantiomeric yield could be reached even without taking special precaution in the crystallization process. On the other hand, irradiation of monomers of optical purity of 22 and 40% was found to give dimers with enantiomeric yields as high as 94%, only provided that the crystallization process was carefully controlled. (The examples described here were crystallized and conditioned for 5 weeks prior to irradiation.) Therefore it can be concluded that in this region small deviations from ideality in crystallization cause coring of the crystal with consequent precipitation of part of the melt as eutecticum,[19] and this is responsible for lowering the enantiomeric yield of the reaction; this is confirmed by the metastable peak at about 93 °C observed in the DSC heating curve of non-perfectly-crystallized samples, recorded before irradiation.

The NMR technique we have used here is not accurate enough in range B, because of the small amount of the protiated enantiomer in excess; therefore we have followed the asymmetric induction in this range by specific rotation measurements. In Figure 3 are reported the values of $[\alpha]_D$ of the dimers as a function of the initial monomer *R*/*S* ratio, through the whole range of compositions.

Even though there is no one to one correlation between the absolute values of $[\alpha]_D$ and the enantiomeric yield of the reaction, owing to the varying contributions of the *sec*-butyl groups of opposite chiralities linked to the cyclobutane ring, we can see that the curve behaves almost linearly in range A, dropping rapidly to zero in range B. This behavior is consistent with the prediction formulated from the phase diagram.

It is worth pointing out that within the eutecticum range, tiny deviations from 50*R*:50*S* initial composition lead to relatively high enantiomeric yields in the products, with a defined absolute configuration.

Photochemistry of Racemic 1. A. Determination of the Microstructures of the Stable and Metastable Phases. Irradiation of racemic **1**, crystallized in the form of eutecticum, cannot lead to a net "absolute" asymmetric synthesis, owing to the coexistence of both enantiomorphous crystalline forms in equal amounts. However, crystallization induced under conditions deviating from equilibrium may lead to the precipitation of a metastable phase, composed of almost identical chiral crystallites, but with 50*R*:50*S* internal composition. The conditions of complete solid solubility of the two enantiomers present in this metastable phase would then allow precipitation of the enantiomorphous crystals in unequal amounts, and thus an "absolute" asymmetric synthesis could be accomplished.

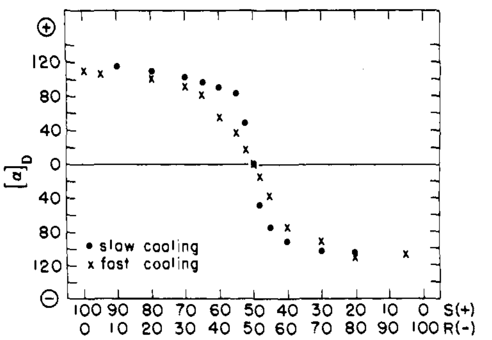


Figure 3. Measured specific rotations (~15 mg/mL $CHCl_3$) of dimers as a function of monomer *R*/*S* composition.

Table II. Measured Enantiomeric Excesses of Chiral Cyclobutane Rings in the Dimers Isolated after Irradiation of Crystalline Monomer **1** of Variable Initial Optical Purity

initial ratio of *S*/*R* monomers	initial enantiomeric excess	measured ratio of enantiomeric cyclobutanes (dimers)	enantiomeric excess of cyclobutanes
99/1	98	~100	~100
80/20	60	~100	~100
70/30	40	97.5/2.5	95.0
70/30	40	95.3/4.7	90.6
70/30	40	95.6/4.4	91.2
70/30	40	95.1/4.9	90.2
70/30	40	95/5.0	90.0
70/30	40	94.75/5.25	89.5
61/39	22	97.0/3.0	94.0
61/39	22	93.5/6.5	87.0
61/39	22	94.4/5.6	88.8
61/39	22	94.0/6.0	88.0
61/39	22	92.3/7.7	84.6

First support for the existence and nature of such a metastable phase comes from comparative DSC analyses of the same sample of racemic composition crystallized slowly and quickly (Figure 4A), and from the general behavior of the melting curves of undercooled samples as a function of composition (Figure 1, full circles), hinting at an enhanced solid solubility between the two enantiomers, in range B.

The expected microdistribution of enantiomeric monomers within the stable and metastable phases is summarized in Scheme IV.

We have demonstrated previously[1] that a 1:1 correspondence exists between the average enantiomeric microdistri-

Scheme IV[a]

$$R \rightleftharpoons S$$

$$\Big\downarrow \text{crystallization}$$

$$\{mR,nS\}_d + \{mS,nR\}_l$$

[a] The brackets designate the crystalline phases of arbitrary chirality *l* and *d* and *m*, *n* indicate the relative amounts of each enantiomer within the crystals. In the eutecticum: *m* ≉ *n*, and the amount of *d* = amount of *l*: in the pure metastable phase: *m* = *n*, and the amount of *d* ≉ or = the amount of *l*.

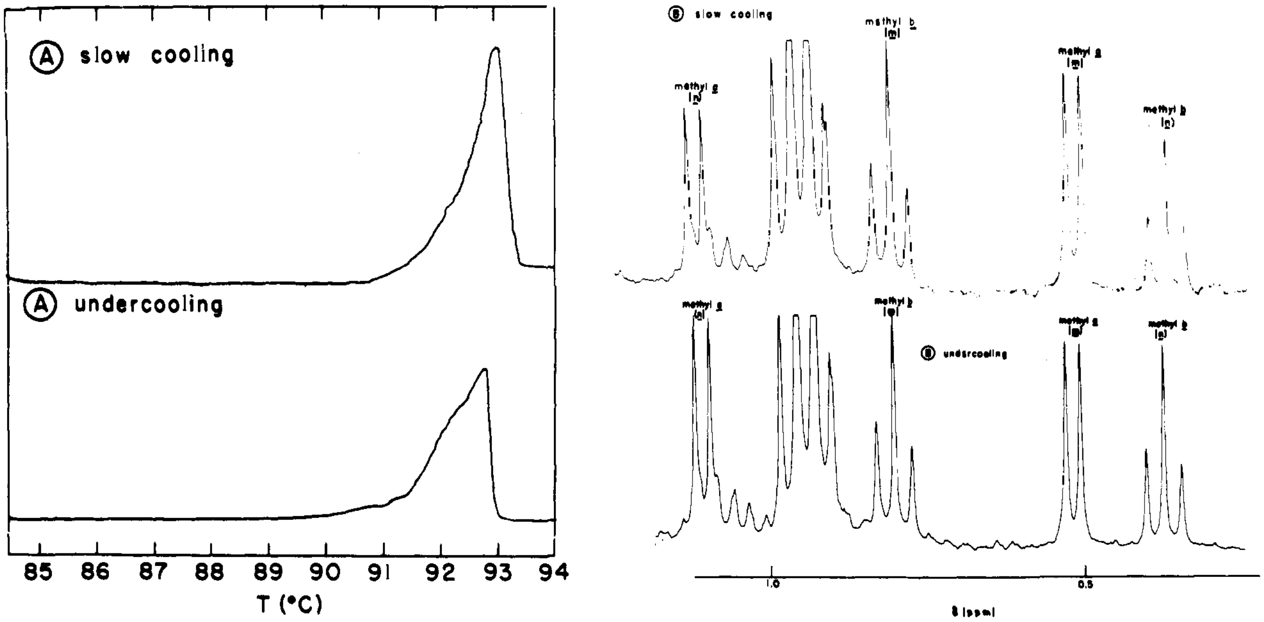


Figure 4. (A) DSC heating curves of monomers; (B) 270-MHz ^{1}H NMR spectra of dimers, in samples of racemic **1** crystallized slowly and undercooled, respectively.

bution of the monomers in the parent crystal, *m*/*n*, and the relative concentrations of the diastereoisomeric dimers formed after irradiation; therefore the ratio *m*/*n* can be directly measured by ^{1}H NMR of the dimers (see Table I). For convenience the peaks at δ 0.52 and 0.38 have been selected for integration.

Figure 4B shows the ^{1}H NMR spectrum of the dimers isolated from crystalline samples with melting behaviors as in Figure 4A. The results of three measurements on slowly cooled samples show *m*/*n* ratios of 61.1/38.9, 60.2/39.8, and 59.5/40.5, in agreement with the range of the miscibility gap deduced from the phase diagram and from the dependence of optical yield on composition.

On the other hand, significantly lower *m*/*n* ratios were obtained from undercooled batches: *m*/*n* = 52.2/47.8, 52/48, and 54/46, depending on the relative amounts of stable and metastable phase. This demonstrates unambiguously that, in the presence of the latter phase, the average internal composition of each chiral crystallite is shifted toward 50*R*:50*S*.

B. An "Absolute Asymmetric Synthesis". The above analysis suggests that the chances of achieving a net "absolute" asymmetric synthesis with quantitative enantiomeric excess depend on the successful preparation of a homochiral crystal of the undercooled phase.

The requirements for such an experiment are contradictory, since the preparation of a homochiral crystal demands growth under equilibrium conditions starting from a single nucleus, while undercooling is associated with fast crystallization. However, one can expect the existence of intermediate conditions in which it will be possible to obtain at least an excess of one of the enantiomorphous forms over the other.

For our purpose, we have used a modified Bridgman apparatus for crystal growth,[20] operated at variable temperatures and rates of growth. We have conducted about 20 experiments; the 8 successful ones are summarized in Table III. It can be seen from the table that specific rotations as high as 35° of both signs have been measured both in the entire irradiation mixture (with an average molecular weight of ~4000) and on the isolated dimers. No net rotation was detected in any of these experiments, either on part of the crystal dissolved before irradiation or on the monomer recovered from the irradiation mixture.

In three experiments the dimers have been isolated and their *m*/*n* ratios determined by ^{1}H NMR. The values obtained, reported in Table III, are in between 60/40 and 50/50, confirming the coprecipitation of the eutecticum together with the metastable phase.

Table III. Crystallization Conditions of Monomers and Specific Rotations of Products of Eight Successful "Absolute" Asymmetric Syntheses Out of 20 Total Experiments

rate of growth, mm/day	ΔT^a	wt of crystals, g	$[\alpha]_D{}^d$	*m*/*n*
9.9	110-82	0.006	$+5.8^b$	
9.9	110-82	0.015	-3.3^b	
9.9	110-82	0.010	-2.1^b	
9.9	110-82	0.010	-35.0^b	
33.4	110-69.4	0.500	$+4.3^c$	58.2/41.8
33.4	110-25	0.500	-6.5^c	58.4/41.5
40	110-80	2.000	-2.3^b	
40	110-80	2.000	$+30.3^c$	57.2/42.8

[a] For details of the crystallization conditions see Experimental Section. [b] Specific rotations measured on the mixtures of oligomers. [c] Specific rotations measured on the isolated dimers. [d] All $[\alpha]_D$ were measured in solutions containing 10-15 mg/mL $CHCl_3$.

The enantiomeric excesses obtained in these experiments can be roughly evaluated, from extrapolation of the $[\alpha]_D$ dependence on composition (Figure 3), as ranging between 0 and 37%.

Conclusions

In the present work, an asymmetric synthesis with quantitative enantiomeric yield and leading to a product of defined chirality has been accomplished, starting with a polycrystalline monomer of optical purity down to 60%. Small deviations from quantitative enantiomeric yield were observed upon irradiation of monomers of optical purities as low as 22%, crystallized under controlled conditions.

Furthermore, an "absolute" asymmetric synthesis of variable optical yield, up to 35%, and of both signs, was obtained starting from rapidly undercooled racemic monomer. The low optical yield is imputed to the metastable nature of the phase, which complicates the process of preparing a homochiral crystalline specimen; therefore the stabilization of that phase is a necessary condition for the accomplishment of an "absolute" asymmetric synthesis with quantitative enantiomeric yield. Since the existence of a stable eutecticum depends on the nonideal solid solubility of the two enantiomers, due to their unfavorable diasteromeric interaction within the chiral crystal,[15] a number of possible ways of removing or reducing these diastereomeric interactions can be conceived; one may attempt the design of an isomorphous achiral monomer of the same family of compounds, or the addition to the present system of a third achiral component, whose task would be to decrease the number of contacts between *sec*-butyl groups in the crystal.

Studies in these directions, under progress, will be the subject of further communications.

Experimental Section

Synthesis of monomers, irradiation methods, isolation of products, and their structural characterization have been described in detail in part 1.[11]

Deuterated monomer 2 was synthesized as protiated **1**, using 1,1,1,2,3,3-hexadeuterio-2-butanol in the last step of the synthesis. The alcohol was prepared by reduction of the corresponding pentadeuterated ethyl methyl ketone[21] with $LiAlD_4$: NMR δ ($CDCl_3$) 0.95 (s, 3 H), 1.42 (t, 3 H), 4.5 (d, 2 H), 6.67 (d, 1 H, J = 16.5 Hz), 7.86 (d, 1 H, J = 16.5 Hz), 7.7-8.3 (m, 4 H), 8.4 (s, 1 H); mass spectrum mol wt m/e 333.

All the NMR spectra of the dimers were recorded on a Bruker 270-MHz spectrometer.

Phase Diagram Determination. Batches (20 mg) of the various compositions were prepared by weighing and melting together the appropriate amounts of 90% optically pure and racemic monomer (99% optically pure compound was used for the determination of the pure enantiomer's melting range).

The batches were sealed in glass vials under N_2 flow and immersed in a thermostatic oil bath, the temperature of which was lowered at the rate of 2 °C/day for 10 days starting from 108 °C. Care was taken to ensure that no appreciable supercooling of the samples would occur.

After complete crystallization the samples were held in 88 °C for 3 more days. DSC heating curves were recorded on a Perkin-Elmer differential scanning calorimeter, at a heating rate of 1 °C/min, on ~5-mg samples.

Crystallization of the 300-mg batches for irradiation was carried out in a way similar to that just described while crystallization of the samples for enantiomeric excess determination was achieved by keeping the compound at a fixed temperature, in the middle of the melting range, for 1-2 weeks, followed by slow cooling at a rate of 1 °C/2-3 days, and final conditioning of the crystallized sample for an additional period of 2 weeks. The phase purity was checked in each case by DSC.

Single crystals were grown by the Bridgman technique in an apparatus envisaged by J. Sherwood;[20] the boule containing the compound is slowly lowered through a sharp gradient of temperatures ΔT (~10 °C/cm) established between two condensers by the vapors of two boiling liquids chosen at will, having boiling points above and below the melting point of the compound (see Table III). The lowering rate can be varied from 9 to 40 mm/day and the boule is additionally spun around at a spinning rate of ~30 rotations/min, changing direction every 0.5 min.

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(13) For the crystal structure data of pure *S*-(+)-**1**, see Z. Berkovitch-Yellin, *Acta Crystallogr.*, submitted for publication.

(14) The term absolute asymmetric synthesis is used to describe such processes which start with achiral materials and lead to nonracemic chiral products in the absence of external chiral agents. In this sense our coupled processes of crystallization and solid-state reaction provide such a synthesis; it is clear that the chirality is here in fact introduced in the crystallization step. The purist may object to the use of the word "absolute"; however, it is accepted by chemists in this context (I. N. Topchieva, *Russ. Chem. Rev.* (*Engl. Transl.*), **35**, 741 (1966)). A. P. Terenev and E. I. Klabunowskii in "The Origin of Life on the Earth", Pergamon Press, Elmsford, N.Y., 1959, p 95.

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(16) In the present study we define "enantiomeric yield" as the yield of enantiomeric cyclobutane rings of the dimers directly measured by NMR, ignoring the variable amounts of *sec*-butyl attached to them.

(17) Isotope effects have been ruled out both in crystallization and in the rate of formation of the products.[1]

(18) Starting with an excess of *S* monomers, cyclobutanes of absolute configuration *SSSS* are obtained.[11,13]

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