

Figure 2. Plot of cesium-133 chemical shift vs. C222B/CsBPh₄ mole ratio in different solvents. Concentration of CsBPh₄ is 0.01 M in all cases: (I) DMF, (II) PC, (III) Me₂CO, (IV) Me₂SO, (V) MeCN, (VI) PY.

gand to form a "sandwich" complex.⁴ In Me₂SO and MeCN solutions the ¹³³Cs resonance shifts only upfield with some indication of a weak "break" at 1:1 mole ratio. No clear-cut evidence for a 2:1 complex is observed. It should be noted, however, that the resonance continues to shift upfield, even after the formation of a 1:1 complex.

Cryptand C222B, with a tridimensional cavity, might be expected to form a stronger complex than does a two-dimensional crown. However, it is known⁵ that in methanol the complex between C222B and Cs⁺ ion is weaker than the corresponding dicyclohexyl-18-crown-6 complex. The variation of the chemical shift with ligand/Cs⁺ mole ratio is shown in Figure 2. In all solvents, except Me₂SO, the ¹³³Cs resonance shifts downfield with increasing concentration of the ligand. From the shape of the curves it can be concluded that the resulting complex is less stable than the 18C6 complex. However, the magnitude of the chemical shift upon complexation is much larger with the cryptand than with the crown. Similar results were observed in a study of Cs⁺ complexes with cryptand C222.⁶ Strong solvent dependence of the chemical shift of a 1:1 ligand/Cs⁺ mole ratio also indicates that, in contrast to the Li⁺-C211 case,^{1,7} the metal ion is not insulated from the solvent. These observations suggest that either the Cs⁺ ion is not completely enclosed in the ligand cavity or that the solvent can interact with Cs⁺ through the openings in the ligand.

With both ligands the extent of complexation is strongly dependent on the nature of the solvent. For example, it appears that in Me₂SO solutions the cryptand complex is much weaker than the crown complex and the binding ability of C222B is not strong enough to displace the primary solvation shell around the Cs⁺ ion (Figure 2). A similar behavior is observed for the Cs⁺-18C6 system in water (Figure 1).

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A New Method of Enantiomeric Purification via a Topochemical Photodimerization Reaction. Application to Three 1-Aryl Ethanols

Sir:

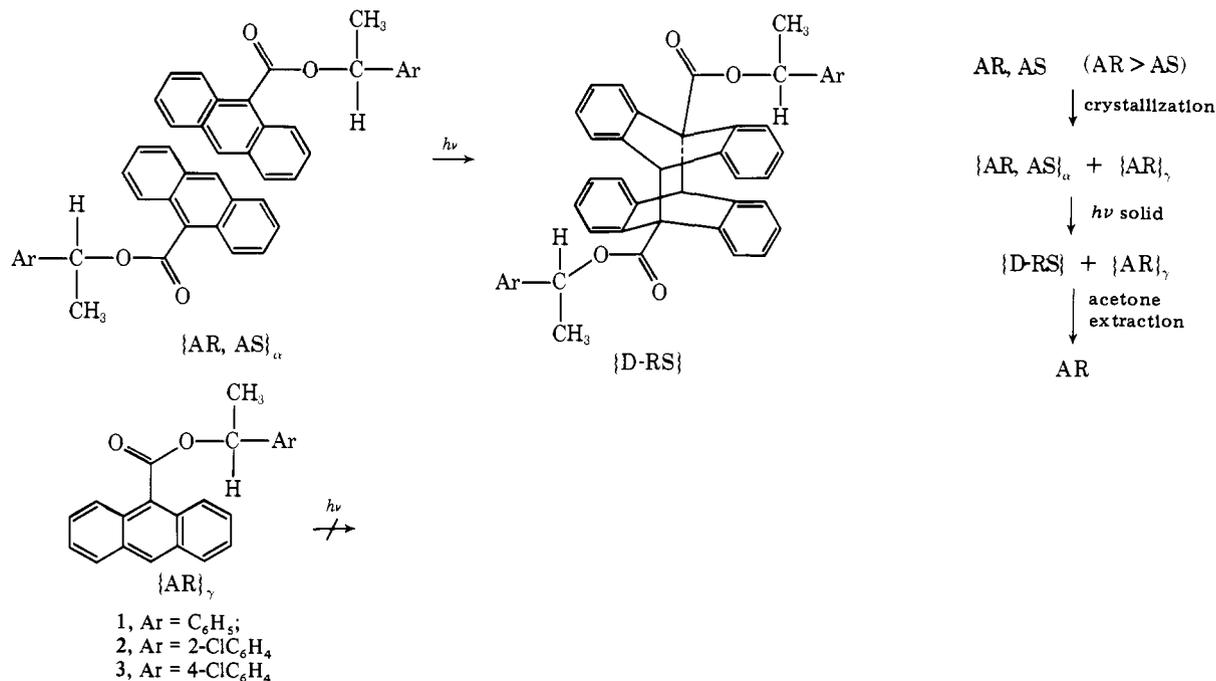
The preparation of enantiomerically pure products in the absence of a general method of resolution is still a challenge in synthetic organic chemistry.¹ We wish to describe here a novel method of enantiomeric purification based on the difference of a topochemical solid-state reaction of an enantiomeric crystal and the corresponding racemic compound.

Systematic studies on photodimerization of planar vinyl or aromatic molecules in the solid state have shown the necessity of a contact of about 4.0 Å between the reactive sites.² Such contacts may be achieved either via a short translation axis [β -type packing] or by antiparallel pairwise arrangement of the molecules, most commonly related by a crystallographic center of inversion [α -type packing]. Pairing via a twofold symmetry axis is very rarely observed^{2b} since it does not lead to a close packed crystal³ for a molecule of arbitrary shape. Photodimerizable molecules containing a chiral group may crystallize only in an α structure or in a light-stable γ structure, since a short distance of 4.0 Å [β -type packing] is precluded by the bulky nature of the chiral groups. A resolved sample of such molecules, which crystallize in a chiral crystal and thus in a structure lacking centers of inversion, will most probably appear in the light-stable γ form. On the other hand, a racemic compound may crystallize either in an α structure, where two heterochiral molecules make plane-to-plane contact across a center of inversion, or in a γ structure. Consequently, attachment of a photodimerizable handle to an enantiomerically enriched sample such as an alcohol, amine, acid, etc., will yield materials which may give a mixture of crystals in which the racemic compound appears in the photoactive α form and the enantiomer in the γ form. Upon irradiation of such a mixture the former will yield a meso photodimer, whereas the latter will remain unaffected, and will be easily separated from the reaction mixture.⁴

We describe here the use of this approach in the enantiomeric purification of three 1-aryl ethanols by condensing them with 9-anthroic acid to the corresponding anthroates 1-3, followed by irradiation and extraction (Scheme I).⁵ The crystallographic constants are summarized in Table I.

The anthracene handle was selected because its α form crystals, easily detected by a characteristic excimer emission, react almost quantitatively. The unaffected monomer may be simply extracted from the sparingly soluble dianthracenes.^{6,7} The dimer on heating at its melting point splits back to a monomer, and so allows a simple recovery of the anthracene reagent.

Partially enriched alcohols were obtained either by asymmetric reduction of the corresponding benzophenone with LiAlH₂(quinine)₂,^{8,9} or by partial resolution via the phthalic acid ester. These were treated with 9-anthroyl chloride and the crystalline esters exposed to uv irradiation at re-

Scheme I. Schematic Representation of Enantiomeric Purification via the Process of Topochemical Photodimerization^a

^a Brackets {} designate a crystalline phase.

Table I. Crystallographic Constants

Compound	Crystal form	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>β</i> (deg)	<i>Z</i>
1	Enantiomer	<i>P</i> 2 ₁ 2 ₁ 2 ₁	11.30	16.93	9.55		4
	Racemic compound	<i>P</i> 2 ₁ /a	11.72	19.69	7.80	93.5	4
2	Enantiomer	<i>P</i> 2 ₁ 2 ₁ 2 ₁	11.52	11.31	14.04		4
	Racemic compound	<i>P</i> 1̄	7.96	13.00	10.44	122.3 75.8 101.3	2
3	Enantiomer	<i>P</i> 2 ₁	14.40	7.77	8.85	96.0	2.0
	Racemic compound	<i>P</i> 2 ₁ /c	15.63	7.52	15.39	102.0	4

Table II. Specific Rotations and Material Balance of Compounds 1–3^a

Compound	Reaction mixture before photocyclodimerization		Recovered monomer		Specific rotation of pure chiral monomer
	Specific rotation, deg	Quantity, (g)	Specific rotation (deg)	Quantity (g)	
1	38.9	0.48	66.7	0.23	70
	53.3	0.50	67.1	0.38	70
2	-32.5	0.20	-38.3	0.14	38.3
	15.5	0.51	37.0	0.21	38.3
3	14.9	0.52	54.1	0.10	59.1
	30.5	0.55	57.8	0.25	59.1

^a Irradiation of samples of 1–5 g with Westinghouse sunlamps for 2–5 days. A parallel irradiation of the pure racemate was used as a blank experiment to determine the time of completion of the photodimerization. 1 racemate mp 91–93 °C, enantiomer mp 75–76 °C; 2 racemate mp 108–109 °C, enantiomer mp 119–120 °C; 3 racemate mp 114–115 °C, enantiomer mp 102–103 °C. The optical rotations were measured in CHCl₃ (*c* 25 mg/ml). Those for the extracted monomers were measured before recrystallization. The alcohols may be recovered either by hydrolysis or by reduction with LiAlH₄.

duced ambient pressure to avoid photooxidation. The unreacted monomer was extracted from the reaction mixture with cold acetone, or via a preparative TLC (Kiesel Gel H, and using benzene–hexane (1:1) as eluate), and thus easily separated from the sparingly soluble *meso*-dianthracenes. The photodimerizations in the three racemic compounds in-

vestigated are almost quantitative; enantiomeric purities of the recovered unreacted monomer are higher than 90% and its chemical yields higher than 80%. The results for compounds 1–3 are summarized in Table II.¹⁰

Fluorescence studies of racemic compounds 1, 2, and 3 show a characteristic [α-type] excimer emission, whereas

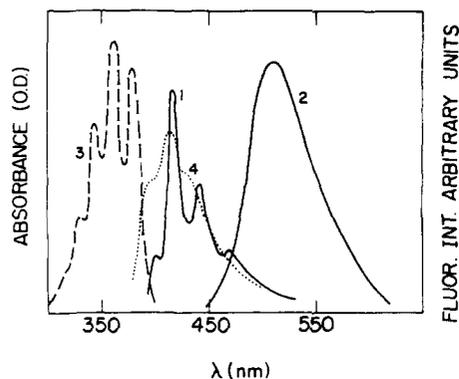


Figure 1. Absorption and corrected emission spectra of 1-[2-chlorophenyl]ethyl 9-anthroate (**2**): (1) Emission spectrum of chiral crystalline powder at 77 K, (2) emission spectrum of the racemic compound at 77 K, absorption (3) (300 K) and emission (4) (77 K) in ethanol (c 5×10^{-3} ; ϵ_{\max} 8×10^{-3} mol/l.).

the chiral enantiomer has a typical γ -type monomer emission, as demonstrated in Figure 1 for the 2-Cl derivative **2**, which indicates the validity of the suggested model.¹¹

We are also extending the method to additional systems and trying to engineer photodimerizable handles which will increase the probability of the racemic compounds crystallizing in α -type structures.

Beside the practical use of this approach for enantiomeric purification, this reaction might be of significance as a mode for possible routes for the amplification of optical activity under prebiotic conditions.¹²

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- (4) This method may also be applicable to the rare chiral crystal that contains parallel pairs, the two molecules of which are not related to each other by crystallographic symmetry. This enantiomer yields dimers *RR* or *SS* which can be separated from the reaction mixture provided either the racemate is light-stable or it forms the meso dimer. The method is not applicable to systems for which the racemate undergoes spontaneous resolution, to systems where the two enantiomers form continuous solid solutions, such as in the case of the *sec*-butyl substituted molecules (see ref 2c and also M. Lahav, L. Leiserowitz, and L. Reitman, to be submitted for publication), or to systems where both the racemate compound and the enantiomer crystallize in the light-stable γ form.
- (5) All new compounds have correct CH analyses as well as the expected NMR and mass spectra.
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- (10) Whereas the irradiation of the racemic compounds of **2** and **3** yield cleanly the head-to-tail *meso*-dianthracenes, some racemic dimer could be isolated from the reaction mixture of the racemic compound **1**. The head-to-tail structures of the solid-state photodimer were established by reduction with LiAlH_4 to the centrosymmetric 9,9'-dihydroxy-methylenedianthracene (**4**).⁶ Its meso stereochemistry follows from the

observation that it differs from the racemic head-to-tail dimers (TLC, ir), independently synthesized by photodimerization of the chiral anthracenes **1**, **2**, and **3** in benzene solutions. The reduction of these dimers with LiAlH_4 also yields **4**.

- (11) An analytical method for the determination of optical purity based on this difference of the fluorescence properties is presently being developed.
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The Ground Electronic State of Silaethylene. An Ab Initio Molecular Orbital Study of the Lower Electronic Manifold

Sir:

In the photochemical and thermal decompositions of silicon hydrides and alkylated silicon hydrides, the intervention of a variety of silicon free radicals and reactive intermediates has been demonstrated, largely on kinetic grounds.^{1a-d} In some instances a preference for the formation of a silaethylene structure, $\text{C}=\text{Si}$, has been shown to exist;^{1e-l} a clearly demonstrated case is the disproportionation reactions of silyl free radicals.² The value of the disproportionation to recombination rate constant of 0.046 obtained for the trimethylsilyl radical, for example, requires a rate increase in the order of 10^5 for the hydrogen-transfer reaction, $2(\text{CH}_3)_3\text{Si} \rightarrow (\text{CH}_3)_3\text{SiH} + (\text{CH}_3)_2\text{Si}=\text{CH}_2$, as compared with the case of the absence of a free spin on the silicon atom, such as in tetramethylsilane; $(\text{CH}_3)_3\text{Si} + (\text{CH}_3)_4\text{Si} \rightarrow (\text{CH}_3)_3\text{SiH} + \text{CH}_2\text{Si}(\text{CH}_3)_3$. This assistance must arise from the formation of either a singlet-state olefinic π -bond or a triplet-state 1,2-diradical in the resultant $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ moiety. The purpose of the present communication is to report the first ab initio type molecular orbital study addressed to the relative stability of singlet vs. triplet-state silaethylene and to show that the stability of the triplet 1,2-diradical is commensurate with the singlet π -bonded structure.

All calculations on silaethylene were carried out with s,p Gaussian-type functions contracted to a minimal (STO-4G) basis set³ using a version of the GAUSSIAN 70 program.⁴ The singlet closed-shell SCF problem was solved within the framework of Roothaan's restricted Hartree-Fock method, while the lowest triplet-state problem was solved using Pople's unrestricted Hartree-Fock method.

Four geometrically different structures of silaethylene were optimized starting from the recently published ab initio results on the study of the ir spectrum of silaethylene.⁵ These correspond to the absolute minima on the S_0 closed-shell singlet (I) and T_1 orbitally excited lowest triplet (II) conformational hypersurfaces as seen from the data presented in Figure 1 and Table I. The other two structures, III and IV, appear as transition states on the S_0 and T_1 conformational hypersurfaces, respectively. However, all four structures represent minima in the rotational cross sections associated with the *cis*-*trans* isomerization of silaethylene. These optimized points are shown as solid dots or solid triangles in the rotational cross sections of the S_0 and T_1 conformational hypersurfaces, Figure 1. The absolute minimum occurs at the skew position in the pyramidal T_1 state lying