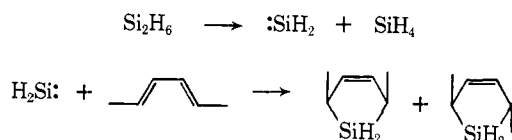
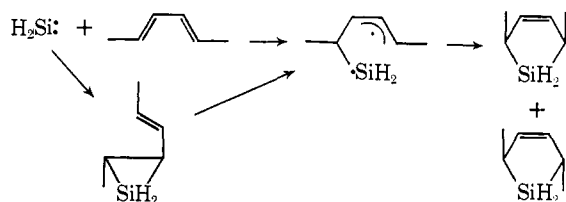


of disilane. Several minor products were formed in ca. 1% yield in addition to a high yield of silane from the disilane pyrolysis. Nuclear magnetic resonance, infrared, and mass spectra of the major products revealed their identity as the *cis* and *trans* isomers of 2,5-dimethyl-1-silacyclopent-3-ene. Characteristic ratios of vinyl-methyl-silyl hydrogens and the doublet splittings of the methyl hydrogens observed in the nmr spectra ensure that the two major products differ only in the *cis-trans* relationship of the methyl groups rather than in the location of the double bond. Each of the isolated products was subjected to pyrolysis under the original reaction conditions. While some decomposition (ca. 20%) occurred, no interconversion of the two isomers was detected. Thus formation of one isomer in a stereospecific reaction followed by rearrangement to the other isomer was excluded. Spectroscopic and chromatographic analysis of the recovered diene indicated that neither geometric isomerization of *trans,trans-* to *cis,trans-* 2,4-hexadiene nor structural isomerization of the reactant diene occurred during pyrolysis of the disilane.

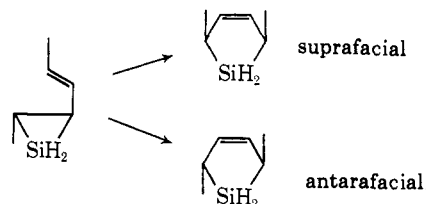
The reaction can be formulated



The formation of both stereoisomers in equal amounts (product ratio 1.0 ± 0.1) rules out a concerted 1,4-addition which would have yielded the *cis* product exclusively. Two reaction mechanisms are consistent with the observed stereochemistry. (1) A diradical is produced along the reaction coordinate either as the primary adduct or from ring opening of a vinylsilacyclopropane.³ (2) A vinylsilacyclopropane is formed in a



concerted addition and subsequently undergoes concerted antarafacial and suprafacial 1,3-sigmatropic rearrangements¹¹ with equal facility.



A diradical pathway seems more likely in view of the cumbersome transition state for concerted antarafacial rearrangement and the demonstrated participation of diradical intermediates in the all-carbon vinylcyclopropane rearrangements.^{12,13}

(11) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie and Academic Press, Weinheim, 1971, pp 121-122.

(12) M. R. Willcott and V. H. Cargle, *J. Amer. Chem. Soc.*, **89**, 723 (1967); **91**, 4311 (1969).

(13) P. H. Mazzocchi and H. J. Tamburin, *J. Amer. Chem. Soc.*, **92**, 7220 (1970).

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Use of Solid-Gas Reactions to Distinguish between Left- and Right-Handed Single Crystals of an Enantiomeric Pair

Sir:

From the separation by Pasteur of hemihedral crystals of racemic sodium ammonium tartrate,¹ the resolution of optical antipodes has been a continuing challenge to the organic chemist. Although it is now evident that few racemates can be expected to crystallize with hemihedral faces which would permit visual identification of the dextro and levo crystals, it is also generally recognized² that many substances crystallize as "conglomerates" or mixtures of crystals which taken individually are either dextro or levo. Although this phenomenon has been somewhat misleadingly called "spontaneous resolution," there is no practical resolution until the dextro and levo crystals have been identified and separated. A number of methods capable of identification of those crystals with a common chirality have been developed. In addition to the rarely applicable visual method of Pasteur, use has been made of polarimetric measurements of single crystals³ or solutions prepared from them,⁴ anomalous scattering of X-rays,⁵ etching,⁶ nucleation by a single crystal of one enantiomer of a second chiral substance,⁷ microscopic observation of the effect of a single crystal on a nematic liquid crystalline phase,⁸ nmr observation of interaction of the dissolved crystal with a chiral solvent⁹ or a chiral shift reagent,¹⁰ and relative rate of reaction in solution with a chiral reagent.¹¹ These methods, although cumbersome or limited in scope, have been or could be

(1) (a) L. Pasteur, *Ann. Chim. Phys.*, [3] 24, 442 (1848); see T. Martin Lowry, "Optical Rotatory Power," Dover Publications, New York, N. Y., 1964, p 28 ff; (b) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 41 ff.

(2) See, for example, A. Collet, M.-J. Brienne, and J. Jacques, *Bull. Soc. Chim. Fr.*, 127 (1972); S. H. Wilen, *Top. Stereochem.*, **6**, 107 (1971); R. E. Pincock and K. R. Wilson, *J. Chem. Educ.*, **50**, 455 (1973).

(3) N. H. Hartshorne and A. Stuart, "Crystals and the Polarizing Microscope," Edward Arnold, London, 1960, p 141 ff.

(4) For an example see P.-T. Cheng, C. H. Koo, I. P. Mellor, S. C. Nyburg, and J. M. Young, *Acta Crystallogr., Sect. B*, **26**, 1339 (1970).

(5) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," McMillan, New York, N. Y., 1968, p 425.

(6) See, for example, P. Groth, "Chemische Crystallographie," Vol. 3, Engelmann, Leipzig, 1917, p 304.

(7) For example, chiral single crystals of glycine [Y. Iitaka, *Acta Crystallogr.*, **13**, 35 (1960); *ibid.*, **14**, 1 (1961)] can induce the specific crystallization of D- or L-asparagine; the configuration of the asparagine thus apparently providing a means of identification of the chirality of the glycine crystal used to inoculate the crystallization [R. M. Secor, *Chem. Rev.*, **63**, 306 (1963)].

(8) P. Gaubert, *Bull. Soc. Fr. Mineral.*, **66**, 293 (1943); *Chem. Abstr.*, **39**, 5146⁷ (1943).

(9) W. H. Pirkle and S. D. Beare, *J. Amer. Chem. Soc.*, **91**, 5150 (1969); *ibid.*, **93**, 2817 (1971).

(10) M. D. McCreary, D. W. Lewis, D. L. Wernick, and G. M. Whitesides, *J. Amer. Chem. Soc.*, **96**, 1038 (1974).

(11) See ref 1b, p 65.

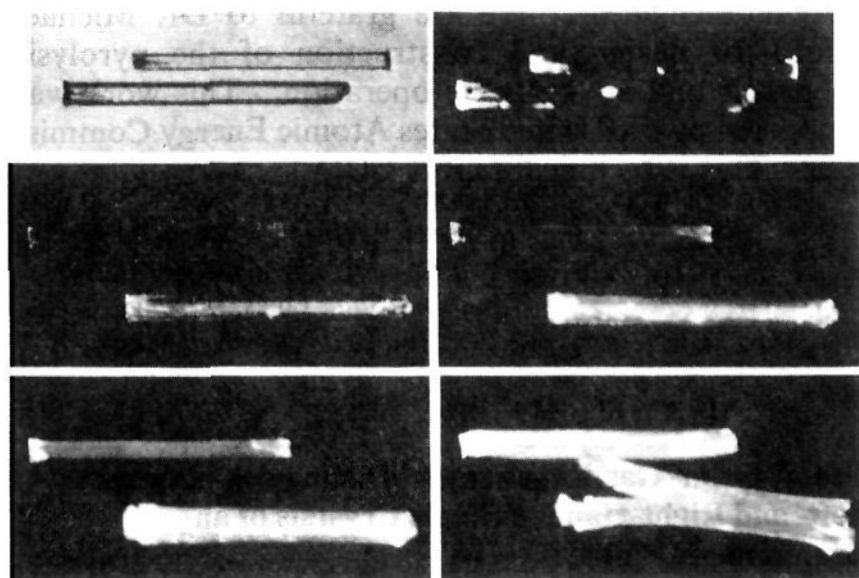


Figure 1. Reaction of (+)-1-phenylethylamine with a (+)-(upper) and a (-)-(lower) crystal of 2,2-diphenylcyclopropane-1-carboxylic acid: top left, before reaction, transmitted light; top right, before reaction, crossed polarizing filters; middle left, 5 min; middle right, 20 min; bottom left, 1 hr; bottom right, 24 hr.

employed to sort the crystals of such a conglomerate and so to effect a resolution.

In this communication is described a method which is certainly simpler to apply and hopefully more general than many of those listed above. It depends on the selectivity of reaction of a chiral gas exposed to a mixture of dextro and levo crystals. Previous studies of related solid-gas reactions have been reviewed elsewhere.¹²⁻¹⁴

(+)- and (-)-Enantiomeric single crystals of an optically active carboxylic acid were placed side-by-side in a cell formed from two microscope slides separated by a metal ring 5 mm thick with an inside diameter of 7.5 mm. Three drops of one of the enantiomeric 1-phenylethylamines were placed next to the crystals with a barrier formed from a small amount of stopcock grease to prevent the liquid amine from coming into contact with the crystals. Although the amine has bp 188°, its vapor pressure at room temperature is sufficiently high to permit a relatively rapid gas-solid reaction. The assembly, placed on a microscope stage between crossed polarizing filters was photographed at regular intervals. In Figure 1 are shown a series of photographs of crystals of (+)- and (-)-2,2-diphenylcyclopropane-1-carboxylic acid^{15,16} with (*S*)-(+)-1-phenylethylamine vapor. It is apparent that the top surface of the (-)-acid crystal has become opaque after only 5 min due to the formation of microcrystallites of the product salt. However, at the same time the (+)-acid crystal has remained essentially unchanged. This difference in reactivity is evident throughout the entire 24-hr period the reaction was followed. A similar experiment in which (-)-amine was used showed the same selectivity, except that the (+)-crystal was attacked preferentially. Similar enantiomer specificity was shown in competitions of (+)- and (-)-crystals of

(12) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, in press, and references cited therein.

(13) C.-T. Lin, I. C. Paul, and D. Y. Curtin, *J. Amer. Chem. Soc.*, **96**, 3699 (1974).

(14) I. C. Paul and D. Y. Curtin, *Science*, in press.

(15) This acid was prepared and resolved by the method of Walborsky and his collaborators.¹⁶ In addition we are indebted to Dr. Walborsky for providing samples of those acids.

(16) H. M. Walborsky, L. Barash, A. E. Young, and F. J. Impastato, *J. Amer. Chem. Soc.*, **83**, 2517 (1961); H. M. Walborsky and A. E. Young, *ibid.*, **86**, 3288 (1964).

Table I. Relative Reactivities of (+) and (-) Optically Active Carboxylic Acids with (+)- or (-)-1-Phenylethylamine

	Sign of rotation		Relative rate obsd ^a	Composition and mp (°C) of product
	Acid	Base		
2,2-Diphenylcyclopropane-1-carboxylic acid	(+)	(+)	Slow ^b	1:1, 201-203
	(-)	(+)	Fast ^b	1:1, 190-192
Mandelic acid	(+)	(-)	Fast	
	(-)	(-)	Slow	
Tartaric acid	(+)	(+)	Fast	1:1, 109-111
	(-)	(+)	Slow	1:1, 176-178
	(+)	(-)	Slow	
	(-)	(-)	Fast	
	(+)	(+)	Slow	1:2, 179-182
	(-)	(+)	Fast	1:2, 175-178
	(+)	(-)	Fast	
	(-)	(-)	Slow	

^a Based on the rate of development of opacity observed microscopically. ^b The results of visual observation were confirmed by interrupting the reaction of a pair of crystals each weighing 0.3 g (after 3.5 hr of reaction with the amine) and submitting each entire crystal for microanalysis. The calculated % reaction was 18 for the (+) crystal and 51 for the (-) or a ratio of (-)/(+) of 2.8.

mandelic acid and tartaric acid for (+)- or (-)-1-phenylethylamine. The results are summarized in Table I.¹⁷

The limited information available at present^{12,13,18} makes it impossible to predict or even to explain the preference shown by a particular enantiomer of the amine for one enantiomer of a crystalline acid. However, our work suggests that such solid-gas reactions may provide a general method for readily sorting a conglomerate of (+)- and (-)-crystals obtained from crystallization of a racemic substance and so providing an additional means of resolving optically active compounds.

Acknowledgment. The authors would like to thank the National Science Foundation (Grant GH-33634) for support of this work.

(17) It should be observed that the selective attack of the top (major) face of the crystals reported here is different from the behavior reported previously for a number of reactions of ammonia gas with other acids. The nature of the anisotropic behavior has not yet been seriously examined with the compounds studied here.

(18) R. S. Miller, D. Y. Curtin, and I. C. Paul, *J. Amer. Chem. Soc.*, in press.

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Application of Chemically Induced Dynamic Nuclear Polarization to a Study of Acylsilane Photolysis

Sir:

The stereochemistry and chemical reactivity of silyl radicals has been the focus of several recent investigations.¹⁻⁵ It has been suggested, for example, that the

(1) A. G. Brook and J. M. Duff, *J. Amer. Chem. Soc.*, **91**, 2118 (1969).

(2) H. Sakurai, M. Murakami, and M. Kumada, *J. Amer. Chem. Soc.*, **91**, 519 (1969).

(3) L. H. Sommer and L. Ulland, *J. Org. Chem.*, **37**, 3878 (1972).

(4) (a) R. A. Jackson, *Advan. Free-Radical Chem.*, **3**, 231 (1969);

(b) S. W. Bennett, C. Eaborn, A. Hudson, R. A. Jackson, and K. D. J. Root, *J. Chem. Soc. A*, 348 (1970).

(5) A. G. Brook, P. J. Dillon, and R. Pearce, *Can. J. Chem.*, **49**, 133 (1971).