

for the Re and Si prochiral faces of the monomer.

$$F_R = \frac{r_1 + 1}{r_1 + r_2 + 2} \quad (5)$$

With $[Re] = [Si]$, $r_1 = k_{RR}/k_{RS}$ and $r_2 = k_{SS}/k_{SR}$. Substitutions in eq 5 from eq 1-4 and rearrangement yields F_R in terms of the substitution probabilities:

$$F_R = (1 - P_{SS}) / (2 - P_{SS} - P_{RR}) \quad (6)$$

Similarly,

$$F_S = (1 - P_{RR}) / (2 - P_{SS} - P_{RR}) \quad (7)$$

As an example, the probability of an $RRRRR$ stereosequence during chain growth at a particular catalyst site (a m mmmm pentad) is obtained by substitution into eq 8

$$P_{RRRRR} = [F_R][P_{RR}][P_{RR}][P_{RR}][P_{RR}] \quad (8)$$

The sequence distributions of the polymers made at either enantiomeric site are identical. The total intensity of the m mmmm pentad in the general case is obtained as the sum of $RRRRR$ and $SSSSS$ contributions produced by a particular site. To avoid an implication of chirality in polymer chains detached from the catalyst the parameters P_{RR} , F_R , P_{SS} , and F_S are relabeled P_a , F_a , P_b , and F_b , respectively

$$m\text{mmmm} = F_a[P_a]^4 + F_b[P_b]^4 \quad (9)$$

The pentad equation simplifies to the chain-end control model when

$$k_{RR} = k_{SS} \quad (10)$$

and

$$k_{RS} = k_{SR} \quad (11)$$

Substituting from eq 10 and 11 into eq 1 and 3 results in

$$P_a = P_b = P \quad (12)$$

Substitution of P in eq 6 and 7 gives

$$F_a = F_b = 0.5 \quad (13)$$

Substitution into eq 9 from eq 12 and 13 gives

$$m\text{mmmm} = P^4 \quad (14)$$

From the probability of a meso dyad

$$m = 0.5P + 0.5P = P \quad (15)$$

Atactic polymers have $m = 0.5$. The equations simplify to the enantiomeric-site control model when, at each chiral site,

$$k_{SR} = k_{RR} \quad (16)$$

$$k_{RS} = k_{SS} \quad (17)$$

Substitution from eq 16 and 17 into eq 2 and 3 shows

$$P_{SS} = P_{SR} = (1 - P_{RR}) \quad (18)$$

Substitution from eq 18 into eq 6 yields

$$F_a = P_a = \beta \quad (19)$$

Similarly, eq 7 gives

$$F_b = (1 - P_a) = P_b = (1 - \beta) \quad (20)$$

Substituting from eq 19 and 20 into eq 9

$$m\text{mmmm} = \beta^5 + (1 - \beta)^5 \quad (21)$$

or

$$m\text{mmmm} = 5\beta^4 - 10\beta^3 + 10\beta^2 - 5\beta + 1 \quad (22)$$

The equations for the other pentads for each mechanism can be obtained similarly.

Registry No. $\text{Cp}_2\text{Ti}(\text{Ph})_2$, 1273-09-2; *meso*-Et[Ind]₂TiCl₂, 91606-02-9; *rac*-Et[Ind]₂TiCl₂, 91685-21-1; Cp_2ZrCl_2 , 1291-32-3; $(\text{Me}_3\text{Cp})\text{CpZrCl}_2$, 81476-73-5; (*cis*-CD₃CD=CHD)-(propylene) (copolymer), 91586-05-9; propylene, 115-07-1; isotactic polypropylene (homopolymer), 25085-53-4; polypropylene (homopolymer), 9003-07-0.

Absolute Configurations, Maximum Rotations, and Kinetics of Thermal Racemization of the 1-Phenyl-2-deuteriocyclopropanes

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Abstract: From precursors of known absolute configurations and optical purities have been prepared (1*S*,2*R*)-(-)-*cis*-1-phenyl-2-deuteriocyclopropane and the (1*R*,2*R*)-(+)-*trans* isomer. The predicted kinetics of racemization for the (-)-*cis* isomer at 309.3 °C based on the known rate constants for all four distinct modes of stereomutation interconverting 1-phenyl-1,2,3-trideuteriocyclopropanes have been experimentally confirmed, providing an independent validation of those rate constants and the mechanistically informative conclusion they support: one-center epimerizations are decisively dominant in the thermal stereomutations of phenylcyclopropane.

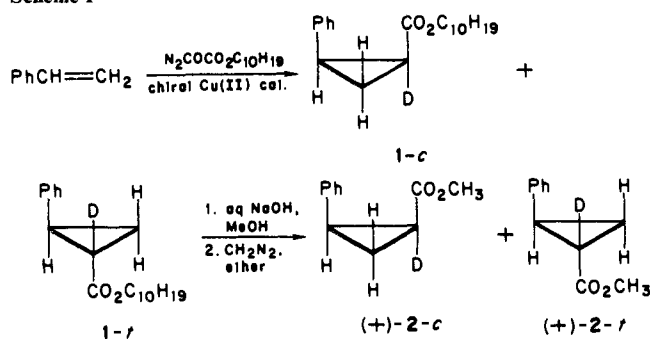
The thermal stereomutations of cyclopropanes¹ have been the subject of numerous experimental and theoretical studies since 1958, the year when Rabinovitch, Schlag, and Wiberg disclosed the thermal interconversion of *cis*- and *trans*-1,2-dideuteriocyclopropane.² At least three factors have sustained this unusually prolonged and intensive study of the reaction: it has relevance to the structure and chemistry of trimethylene, one of the simplest

localized biradicals;³ it involves a hydrocarbon small enough to be explored meaningfully by theoretical methods of reasonable

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(1) For major reviews and references to early work in this area see: Berson, J. A. *Annu. Rev. Phys. Chem.* 1977, 28, 111-132. Berson, J. A. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 1, pp 311-334. Borden, W. T. In "Reactive Intermediates"; Jones, M.; Moss, R. A., Eds.; Wiley: New York, 1981; Vol. II, pp 176-188. Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981, pp 27-35. Dervan, P. B.; Dougherty, D. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; pp 107-149.

Scheme I



sophistication,⁴ and it has proved remarkably resistant to final or even proximal elucidation.⁵ It has remained a durable challenge to those curious about 1,3-diradicals, concerned with the interrelations between experimental observables and theoretical predictions for potentially complicated reactions and convinced that generally valid understandings of the reaction type may yet be attained.

Cyclopropanes undergo stereomutations through both one-center (k_i) and two-center (k_{ij}) epimerizations. The task of an experimentalist seeking to measure every k_i and k_{ij} rate constant for a given cyclopropane—and hoping to see mechanistically illuminating insights in the pattern of rate constants observed—depends sensitively on the degree of substitution. For monosubstituted cyclopropanes, there are only four kinetic parameters to measure, and with suitable isotopic substitution they may be determined. But this task has not proved easy: the problem was clearly stated in 1964⁶ and solved only in one instance, 20 years later. For phenylcyclopropane, the several practical and conceptual barriers to obtaining these rate constants have been surmounted: at 309.3 °C in the gas phase the rate constants ($\times 10^5$ s) are $k_1 = 0.36 \pm 0.03$, $k_2 = 0.87 \pm 0.02$, $k_{12} = 0.20 \pm 0.01$, and $k_{23} = 0.0$.⁷

Yet this claimed solution to a long-standing problem might be considered with some reserve, for it conflicts markedly with an earlier partial kinetic treatment of the stereomutations of 1-phenyl-2-deuteriocyclopropanes which provided the rate constants ($\times 10^5$ s, at 309.5 °C) $k_1 = 0$, $k_{12} = 0.96$, and $(k_2 + k_{23}) = 0.19$.⁸ These rate constants point toward synchronous two-center epimerization as the major pathway and make plausible interpretations invoking an orbital symmetry controlled ring opening–ring closing sequence.⁹

The rate constants and mechanistic implications from the two experimental efforts^{7,8} cannot both be accurate. This paper reports further synthetic and kinetic work designed to test rigorously the reliability of the conflicting investigations.

Results

Syntheses. The experiment we believed would provide that rigorous test and discriminate between the two sets of incompatible rate constants required chiral samples of the cis and trans isomers of 1-phenyl-2-deuteriocyclopropane of known relative configuration

(2) Rabinovitch, B. S.; Schlag, E. W.; Wiberg, K. B. *J. Chem. Phys.* **1958**, *28*, 504–505.

(3) Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533–6542. Goldberg, A. H.; Dougherty, D. A. *Ibid.* **1983**, *105*, 284–290. Yamaguchi, Y.; Osamura, Y.; Schaefer, H. F., III *Ibid.* **1983**, *105*, 7506–7511.

(4) Horsley, J. A.; Jean, Y.; Moser, C.; Salem, L.; Stevens, R. M.; Wright, J. S. *J. Am. Chem. Soc.* **1972**, *94*, 279–282.

(5) "Despite intense experimental and theoretical effort directed toward understanding cyclopropanes, these simple molecules obdurately continue to hide the secrets of their behavior".^{1b}

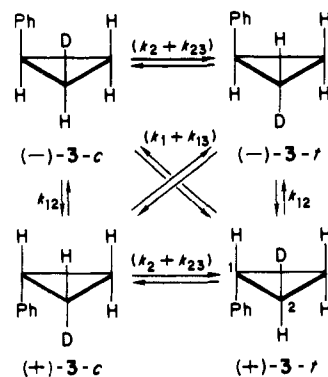
(6) Setser, D. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1964**, *86*, 564–569.

(7) Baldwin, J. E.; Patapoff, T. W.; Barden, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 1421–1426. Baldwin, J. E.; Barden, T. C. *Ibid.* **1984**, *106*, 5312–5319.

(8) Berson, J. A.; Pedersen, L. D.; Carpenter, B. K. *J. Am. Chem. Soc.* **1975**, *97*, 240–242; **1976**, *98*, 122–143; **1977**, *99*, 7399.

(9) Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

Scheme II



and optical purity. Kinetic studies based on polarimetry using materials having comparatively small specific rotations caused only by deuterium substitution necessitate fairly large samples of the hydrocarbons with a high degree of stereochemically discrete deuterium incorporation. The synthetic methodology developed for our earlier work⁷ proved suitable to this new requirement.

Styrene was condensed with *dl*-menthyl α -deuteriodiazoacetate in the presence of a chiral copper catalyst^{7,10,11} (Scheme I) to produce the *cis*- and *trans*-menthyl carboxylates **1** (69% after Kugelrohr distillation). This mixture of menthyl esters was converted in two steps to the corresponding mixture of methyl esters **2-c** and **2-t** which were shown by NMR analysis to be present in a 1:6 ratio. The *cis*- and *trans*-menthyl esters were separated by low-pressure column chromatography to give samples of each better than 99.5% isomerically pure, as determined by capillary VPC.

The diazoester:styrene condensation in the presence of this chiral copper catalyst occurs with high asymmetric induction.^{7,11} The optical purities of **2-c**, $[\alpha]_D +36.1^\circ$ (CHCl_3), and **2-t**, $[\alpha]_D +281^\circ$ (CHCl_3), were found to be 86% and 89%, respectively, through the use of NMR spectroscopy and the chiral shift reagent $\text{Eu}(\text{hfc})_3$.¹²

The absolute configurations of esters **(+)-2-c** and **(+)-2-t** follow from assignments in the literature for the undeuterated analogues.¹³ The specific rotation for optically pure methyl (1*S*,2*R*)-**(+)-cis**-2-phenylcyclopropanecarboxylate is $[\alpha]_D +40^\circ$ (CHCl_3),¹⁴ while the 1,2,3-trideuterated (1*S*,2*S*)-*trans*-methyl ester has $[\alpha]_D +337^\circ$ (CHCl_3).¹¹ On the basis of these literature values and our measured rotations, the methyl esters **(+)-2-c** and **(+)-2-t** are estimated to be 90% and 83% optically pure, in fair agreement with the results of the chiral NMR shift reagent analyses.

The same sequence of three reactions converted **(+)-2-t** to **(-)-3-c** and **(+)-2-c** to **(+)-3-t** (52% and 39% overall, respectively). Aldehydes were generated from **(+)-2-t** and **(+)-2-c** by reduction with LiAlH_4 followed by oxidation with pyridinium chlorochromate. With a stoichiometric amount of Wilkinson's catalyst, chlorotris(triphenylphosphine)rhodium(I), these two aldehydes underwent decarbonylation with extremely high stereospecificity to give hydrocarbons **(-)-3-c** and **(+)-3-t**. The two isomers were purified by preparative VPC to 99.9% and 99.8% structural homogeneity, according to capillary VPC analyses. The specific rotations for these two hydrocarbons, measured with concentrated

(10) Cf.: Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1975**, 1707–1710; **1977**, 2599–2602.

(11) Baldwin, J. E.; Carter, C. G. *J. Am. Chem. Soc.* **1982**, *104*, 1362–1368.

(12) Tris[3-((heptafluoropropyl)hydroxymethylene)-*d*-camphorato]europium(III) from Aldrich Chem. Co., also abbreviated $\text{Eu}(\text{hfc})_3$.

(13) Inouye, Y.; Sugita, T.; Walborsky, H. M. *Tetrahedron* **1964**, *20*, 1695–1699. Aratani, T.; Nakanishi, Y.; Nozaki, H. *Ibid.* **1970**, *26*, 1675–1684.

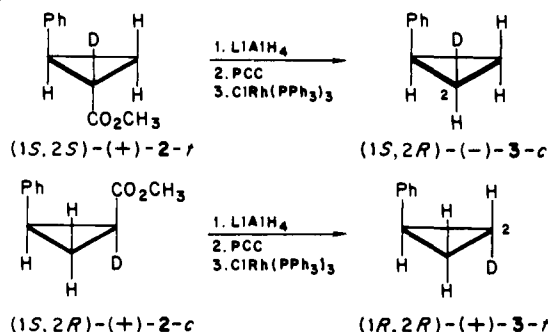
(14) The maximum rotation for the (1*R*,2*S*) *cis* acid is $[\alpha]_D^{25} -28^\circ$ (CHCl_3) [Elling, G. R.; Hahn, R. C.; Schwab, G. *J. Am. Chem. Soc.* **1973**, *95*, 5659–5662], and (1*S*,2*R*) *cis* acid of $[\alpha]_D^{20} +22.9^\circ$ (CHCl_3) has been converted with diazomethane to the corresponding methyl ester having $[\alpha]_D^{20} +32.8^\circ$ (CHCl_3) [Krieger, P. E.; Landgrebe, J. A. *J. Org. Chem.* **1978**, *43*, 4447–4452].

Table I. Calculated Specific Rotations at 365 nm for 1-Phenyl-2-deuteriocyclopropanes from (-)-3-*c*, $[\alpha]_{365} -5.15^\circ$, at 309.3 °C

ref	rate constants ^a		
	$\frac{[\alpha]_c^{\max}}{[\alpha]_t^{\max}}$	$[\alpha]_{365}$ at 300 min	$[\alpha]_{365}$ at 800 min
7 ^b	2.30	-3.80	-2.30
8 ^c	2.30	-2.81	-1.07
8 ^c	0.78 ^d	-2.46	-0.69

^a In all cases the approximation $k_{12} \approx k_{13}$ was utilized. ^b Rate constants ($\times 10^5$ s): $k_{12} = 0.20$, $(k_1 + k_{13}) = 0.56$, and $(k_2 + k_{23}) = 0.87$. ^c Rate constants ($\times 10^5$ s): $k_{12} = 0.96$, $(k_1 + k_{13}) = 0.96$, and $(k_2 + k_{23}) = 0.19$. ^d Reference 8.

isooctane solutions at 24 °C, were $[\alpha]_{365} -5.15 \pm 0.01^\circ$ and $[\alpha]_{365} +2.16 \pm 0.02^\circ$. These $[\alpha]_{365}$ values showed no substantial dependence on concentration. From them and knowledge of optical purity of the precursors one calculates $[\alpha]_{365} -5.79^\circ$ and $[\alpha]_{365} +2.52^\circ$ as maximum specific rotations for the optically pure compounds.



Kinetic Predictions. The thermal stereomutations shown by the 1-phenyl-2-deuteriocyclopropanes are summarized in Scheme II. The evolution of the system of isomers with time is dictated by three kinetic parameters. The specific rotation of the mixture of four isomers as a function of time may be calculated from initial isomer concentrations, maximum specific rotations for the cis and trans forms, knowledge of relative stereochemistry, and the three kinetic parameters.¹⁵

Predicted values of $[\alpha]_{365}$ for the mixture of isomers derived from (-)-3-*c*, $[\alpha]_{365} -5.15^\circ$, after 300 and 800 min at 309.3 °C are given in Table I for three sets of kinetic and rotational parameters. The predicted rotational values are sufficiently different to be encouraging: an experimental determination of racemization kinetics may give an independent basis for preferring one over the other two sets of kinetic parameters.

The substantially different values for the ratio of maximum rotations for cis and trans isomers obtained here and in earlier work⁸ do not have an overwhelming influence on the predicted racemization kinetics. Both the second and the third set of predictions based on the rate constants reported for 1-phenyl-2-deuteriocyclopropanes⁸ are substantially distinct from the predicted $[\alpha]_{365}$ values derived from our rate constants.⁷

Kinetic Results. With predictions made, the experimental test was run. Two samples of (-)-3-*c*, $[\alpha]_{365} -5.15^\circ$, were heated in the gas phase, one for 300 min and the other for 800 min. Each sample was reisolated by preparative VPC and subjected to polarimetric analysis. The first had $[\alpha]_{365} -3.82 \pm 0.01^\circ$ while the second had $[\alpha]_{365} -2.35 \pm 0.02^\circ$.

Discussion and Conclusions

The close correspondence between the first set of predicted specific rotations (Scheme II; Table I) and the experimentally observed rotations confirms our earlier kinetic work on 1-phenyl-1,2,3-trideuteriocyclopropanes and a chiral phenylcyclopropane-2-¹³C,1,2,3-²H₃.⁷ Insofar as the earlier studies did not

rely on any polarimetric measurements to derive rate constants, this experiment constitutes a rigorous test of the reliability of that prior work: predictions firmly set before any results based on the new experimental probe for following reaction kinetics became available were confirmed to very close tolerances. This outcome also serves to validate the multiple labeling and stereochemical tactics applied to decipher and solve the monosubstituted cyclopropane kinetic problem.⁷

The second and third sets of predictions for the racemization of (-)-3-*c* do not agree at all closely with the experimental results, and it is clear that the rate constants in the calculations rather than the values used for rotations of optically pure isomers are largely responsible for the discord. Our present work and the earlier synthetic efforts of Berson, Pedersen, and Carpenter⁸ agree on associations between absolute stereochemistry and sign of rotation, but our magnitudes of rotation are substantially higher for both cis and trans isomers, $[\alpha]_{365} -5.79^\circ$ and $+2.52^\circ$ for (-)-3-*c* and (+)-3-*t* as compared with $\alpha_{365} -1.112^\circ$ (neat, 1 dm) for (-)-3-*t* and $\alpha_{365} +1.114^\circ$ (neat) for a 56.2:43.8 mixture of (+)-3-*c* and (+)-3-*t*.⁸

Whatever the grounds for these discrepancies in the magnitudes of rotations, they do not by themselves provide a rationale for the much larger rates of racemization reported in 1975–1976.⁸

It also appears that secondary deuterium kinetic isotope effects on the stereomutations of phenylcyclopropane are not large enough to be of major significance. This qualitative inference was drawn earlier⁷ when a rate constant from a kinetic study of 1-phenyl-2,3-dideuteriocyclopropanes, $(k_2 + k_{12} + k_{23}) = 1.10 \times 10^{-5} \text{ s}^{-1}$ at 309.5 °C, was found to be in excellent agreement with the same parameter calculated from the 1-phenyl-1,2,3-trideuteriocyclopropane rate constants for stereomutations, $(1.07 \pm 0.02) \times 10^{-5} \text{ s}^{-1}$ at 309.3 °C.⁷

The present experiments, being wholly consistent with the rate constants for the stereomutations of phenylcyclopropane derived independently,⁷ reiterate the mechanistically significant result: one-center epimerizations are dominant, a characteristic of stereomutation reactions thoroughly compatible with a diradical view of alternative transition structures. The comparatively minor net two-center epimerization at C(1) and C(2) may well result from uncoordinated epimerizations at each end of the diradical, rather than from an orbital symmetry controlled ring opening and ring closing.

Experimental Section

Proton NMR spectra were measured on a Varian XL-100 instrument; chemical shifts are reported in ppm (CDCl₃ solutions) relative to Me₄Si (δ 0.0) as internal standard. Polarimetric measurements were made on a Perkin-Elmer 141 polarimeter at 24 °C with a 1-dm cell. A Varian A90-P3 Aerograph gas chromatograph was employed for preparative-scale separations and purifications. Analytical VPC measurements were secured with a Hewlett-Packard 5790A series gas chromatograph, a 3.05 M fused silica capillary column (cross-linked dimethylsilicone fluid), and a model 3390A integrator. Detailed synthetic procedures for reactions entirely analogous to those utilized in this work and general remarks on solvents have been provided.⁷

Methyl 2-Phenylcyclopropane-1-carboxylates-1-²H (2-*c* and 2-*t*). Menthyl α -deuteriodiazoacetate (24.0 g, 106 mmol) was added by syringe pump (1.0 mL/h) to a preheated (74 °C) cyclohexane (200 mL) solution of commercial styrene (14.5 g, 139 mmol) and freshly prepared chiral copper(II) catalyst^{7,11} (609 mg, $[\alpha]_{346} +500^\circ$ (c 0.18, ethanol)). After the addition was complete, the solvent was removed by rotary evaporation and the product (1-*c* and 1-*t*; 22.13 g, 69%) was collected by Kugelrohr distillation (90–140 °C, 0.2 torr). This mixture of esters was saponified with 25% aqueous NaOH (50 mL) and methanol (70 mL) at reflux to give 10.08 g of crude carboxylic acids. Esterification with CH₂N₂ gave the corresponding *cis*- and *trans*-methyl esters (9.9 g) in a 1:6 ratio as determined by ¹H NMR spectroscopy. Low-pressure liquid chromatography on silica gel (1:9 ethyl acetate/hexanes as eluant) provided 1.2 g of *cis* ester (+)-2-*c* and a 4.3-g sample of *trans* ester (+)-2-*t*. Isomeric purity for these *cis* and *trans* esters was established by capillary VPC (150 °C, column pressure 10 psi) to be 99.5% and 99.9%, respectively. Small samples of each were collected by VPC (2-m Carbowax

(15) Exact integrated expressions for the concentrations of the isomers of Scheme II as a function of time, initial concentrations, and kinetic parameters are derivable, and a corresponding computer program was used.

(16) Wood, J. T.; Arney, J. S.; Cortès, D.; Berson, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3855–3860.

20 M, 20% on Chromasorb W-HP, 180 °C) for characterization.

Cis ester (+)-2-*c* had $[\alpha]_D +36.1^\circ$ (*c* 1.85, CHCl₃); according to NMR analysis with the aid of the chiral shift reagent Eu(hfc)₃, this ester was 86% optically pure and the downfield -OCH₃ singlet was predominant. The ¹H NMR spectrum showed signals at δ 7.27 (s, 5 H), 3.45 (s, 3 H), 2.58 (d of d, *J* = 7, 9 Hz, 1 H), 1.70 (d of d, *J* = 5, 8 Hz, 1 H), 1.32 (d of d, *J* = 5, 9 Hz, 1 H); signal intensity due to residual proton at C(1) was conspicuously absent.

Trans ester (+)-2-*t*, $[\alpha]_D +281^\circ$ (*c* 2.69, CHCl₃) was 89% optically pure according to Eu(hfc)₃ analysis, with the downfield -OCH₃ signal strongest; NMR δ 7.02-7.20 (c, 5 H), 3.72 (s, 3 H), 2.53 (d of d, *J* = 6, 9 Hz, 1 H), 1.59 (d of d, *J* = 5, 9 Hz, 1 H), 1.30 (d of d, *J* = 5, 6 Hz, 1 H), and no residual proton at C(1) was seen.

(1*S*,2*R*)-*cis*-2-Phenylcyclopropanemethanol-1-²H. The cis ester (+)-2-*c* (1.20 g, 6.8 mmol) was reduced with LiAlH₄ (0.28 g, 7.3 mmol) in ether (40 mL) at reflux. A standard workup followed by drying (MgSO₄), filtration, and rotary evaporation gave 0.94 g of colorless oil (94%). The alcohol was used without further purification to avoid any possibility of optical fractionation. The crude product had NMR δ 7.27 (s, 5 H), 3.37 (d of d, *J* = 11, 20 Hz, 2 H), 2.28 (m, 1 H), 1.29 (br s, 1 H), 0.78-1.20 (c, 2 H).

(1*R*,2*R*)-(+)-*trans*-2-Deuterio-1-phenylcyclopropane ((+)-3-*t*). The alcohol prepared immediately above (0.94 g, 6.3 mmol) was oxidized with pyridinium chlorochromate (PCC, 2.24 g, 10.4 mmol) in CH₂Cl₂ (25 mL) to give 0.87 g of an aldehyde with the anticipated characteristic NMR singlet at δ 8.68. No signal at δ 9.32 for trans aldehyde was evident. This cis aldehyde (0.87 g, 5.3 mmol) was decarbonylated with Wilkinson's catalyst (5.01 g, 5.41 mmol) in benzene (50 mL) at reflux. Final purification by VPC was accomplished with a 2.5 × 0.62 cm Apiezon L column (14% on 60/80 mesh Chromasorb G-HP) at 160 °C to give 316.2 mg (42% from the alcohol) of deuteriohydrocarbon (+)-3-*t*. Capillary VPC (130 °C, column pressure 5 psi) showed that this material was 99.8% pure with three impurities present: α -methylstyrene-²H (0.05%) plus two unidentified impurities (0.05% and 0.1%). The hydrocarbon had $[\alpha]_{365} +2.16 \pm 0.02^\circ$ (*c* 28.4, isooctane) [lit.⁸ $[\alpha]_{365} +1.053^\circ$ (neat)]; NMR δ 6.98-7.36 (c, 5 H), 1.72-1.98 (m, 1.0 H), 0.92-1.02 (m, 1.0 H), 0.60-0.92 (m, 2.0 H).

(1*S*,2*S*)-*trans*-2-Phenylcyclopropanemethanol-1-²H. Ester (+)-2-*t* (1.53 g, 8.63 mmol) was reduced with LiAlH₄ (0.48 g, 12.6 mmol) in

ether (50 mL) to give 1.28 g (99%) of trans alcohol; NMR δ 6.98-7.20 (c, 5 H), 3.58 (br s, 2 H), 1.86 (br s, 1 H), 1.71-1.90 (m, 1 H), 1.89-1.02 (m, 2 H).

(1*S*,2*R*)-(-)-*cis*-2-Deuterio-1-phenylcyclopropane ((-)-3-*c*). The alcohol prepared immediately above (1.28 g, 8.58 mmol) was oxidized to the corresponding aldehyde with PCC (3.15 g, 14.6 mmol) in CH₂Cl₂ (30 mL). The product (1.20 g, 95%) had the expected NMR singlet at δ 9.32 and no detectable signal at δ 8.68. The aldehyde (1.12 g, 7.61 mmol) was then decarbonylated with Wilkinson's catalyst (7.34 g, 7.94 mmol) in benzene (40 mL) at reflux. Capillary VPC analysis showed that only two compounds were present in the VPC-purified product (483.3 mg, 53%) from the alcohol; $[\alpha]_{365} -5.15 \pm 0.01^\circ$ (*c* 43.5, isooctane): hydrocarbon (-)-3-*c* (99.9%) and α -methylstyrene (0.1%). The cyclopropane was reisolated and repurified by VPC and found to have $[\alpha]_{365} -5.16 \pm 0.02^\circ$ (*c* 15.9, isooctane), demonstrating that concentration has a negligible effect on the measured rotation and confirming that no significant racemization occurs during VPC purification. The product had NMR δ 6.98-7.38 (c, 5 H), 1.72-2.00 (m, 1.0 H), 0.92-1.00 (m, 2.0 H), 0.60-0.92 (m, 1.0 H).

Gas-Phase Pyrolyses of (-)-3-*c*. A 180- μ L sample of (-)-3-*c* and 70 μ L of dry pentane were heated at 309.3 °C for 300 min.^{7,11,17} The pyrolysate was recovered by vacuum transfer, and the phenylcyclopropane was reisolated by VPC. Similarly, 190 μ L of (-)-3-*c* and 60 μ L of dry pentane were heated for 800 min at the same temperature followed by VPC reisolation. The sample heated for 300 min had $[\alpha]_{365} -3.82 \pm 0.01^\circ$ (*c* 14.9, isooctane), while the latter, heated for 800 min, had $[\alpha]_{365} -2.35 \pm 0.02^\circ$.

Acknowledgment. We thank the Research Corporation and the National Science Foundation for partial support of this work.

Registry No. 1, 91760-01-9; (1*S*,2*S*)-(+)-2-*t*, 91760-02-0; (1*S*,2*R*)-(+)-2-*c*, 91839-88-2; (1*S*,2*R*)-(-)-3-*c*, 91839-89-3; (1*R*,2*R*)-(+)-3-*t*, 54516-61-9; (1*S*,1*R*)-*cis*-2-phenylcyclopropanemethanol-1-²H, 91760-03-1; (1*S*,2*S*)-*trans*-2-phenylcyclopropanemethanol-1-²H, 91839-90-6; methyl α -deuteriodiazoacetate, 80594-25-8; styrene, 100-42-5.

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Kinetics and Mechanism of the Pyrolysis of Allyltrimethylsilane

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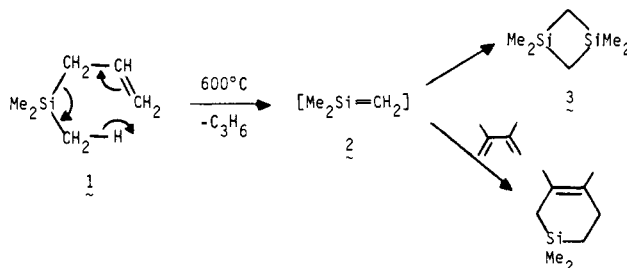
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Abstract: The gas-phase thermal decomposition of allyltrimethylsilane has been reinvestigated by using deuterium labeling and kinetic studies of variable pressure. Trimethylvinylsilane, the major product at high pressures, is found not to be a primary product of unimolecular decomposition. Silyl radical trapping allowed kinetic separation of the two competitive primary processes of decomposition: a concerted retroene elimination of propene to directly produce a silene and Si-C bond homolysis.

The gas-phase thermal decomposition of allyltrimethylsilane (1) has received periodic attention from several research groups since 1969 when Bailey and Kaufmann¹ reported that at temperatures above 600 °C this molecule underwent a retroene elimination of propene to produce transient 2-methyl-2-silapropene (2). The formation of 2 was inferred from the formation of the usual² heat-to-tail silene dimer, 3, and by "4 + 2" trapping with 2,3-dimethyl-1,3-butadiene.

A full account of this work was never published. Indeed, the retroene conversion of 1 to 2 appeared to be discredited when in



1970 Sakurai, Hosomi, and Kumada³ reported that thermolysis of 1 at 500 °C in a nitrogen stream produced no dimer 3, and

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