Supplemental Material Available. Experimental details will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-936.

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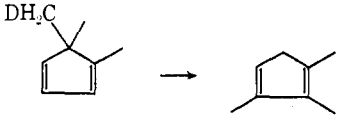
Intermolecular Methyl Transfer during Pyrolysis of 1,5,5-Trimethylcyclopentadiene

Sir:

Sigmatropic (1,5) hydrogen shifts in substituted dienes are thoroughly documented,[1] and the intramolecularity of the reaction is firmly established.[2–4] A corresponding (1,5) methyl shift has characteristics which, by every previous experimental test, were also consistent with intramolecular processes.[5–6] We report here a new investigation, pyrolysis of a monodeuterated trimethylcyclopentadiene, which reveals a previously undetected intermolecular component in the (1,5) sigmatropic methyl shift.

Deuterium labeled 1,5,5-trimethylcyclopentadiene (**1**)[7] was pyrolyzed at 350° for 20 min in a stirred flow reactor. The partial pressure of **1** was *ca.* 10 Torr in a 1 atm N_2 stream. Isotropic analysis of **1** and of vpc purified **2** by low-voltage mass spectroscopy revealed the label distribution shown in eq 1.[8] The average deuterium content was 1.0 atom/molecule in every case.



(1)

	1	2
d_0	5.4	23.0
d_1	90.5	60.0
d_2	3.7	15.0
d_3	0.4	2.0

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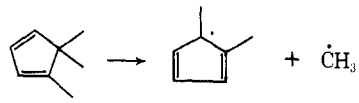
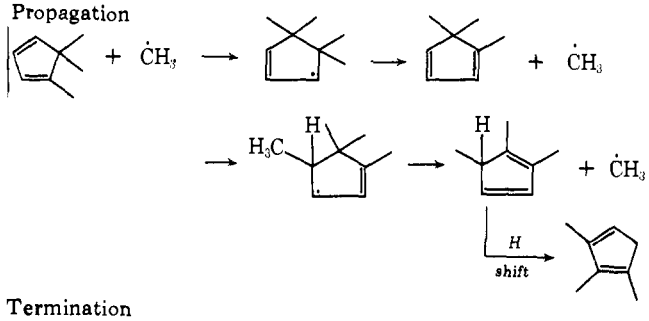
These results, incompatible with intramolecular methyl migration, suggest the following radical chain reactions

Initiation



Propagation



Termination

$$\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6$$

The observed exclusive appearance of trimethyl products[5,6] is assured by the propagation steps we have written here, and propagation by transfer of methyl groups limits the deuterium distribution to discrete units of CH_2D (*i.e.*, the labels must be d_0, d_1, d_2, or d_3). A degenerate 1,5,5- to 1,5,5-trimethylcyclopentadiene rearrangement reconciles the appearance of d_0 and d_2 deuterium labels in this compound. Finally, the preponderance of the 1,2,3 isomer in the reaction mixture is readily justified by the stability of the allylic radical involved in its formation. This scheme, internally consistent for our results, is not in conflict with previous experimental work. Indeed, the rates of disappearance of starting materials and product distribution accord well with those reported by Kloosterziel for the cyclopentadienes.[5]

A subtlety of this class of rearrangement is pointed out by a more quantitative consideration of the isotope distribution. The 60% d_1 label of the 1,2,3 isomer can only result from incomplete intramolecular mixing.[9] Even though an isotope effect could be postulated as the cause, it would be unprecedentedly large. We prefer to think the discrepancy in the distribution is due to the superposition of a radical chain (intermolecular) and concerted (intramolecular) reaction path. This then forces the conclusion that the two paths are finely balanced in this case.[10] The stabilization energy of 20 kcal/mol for the cyclopentadienyl radical[11] can be coupled with known bond dissociation energies in neopentane (80 kcal/mol)[11b] to provide a predicted activation energy of 60 kcal/mol for the bond homolysis reaction. The kinetics of the dimethyl substituted cyclopentadienes are no longer easy to interpret since two processes must be separated. A consistent explanation is that the E_a for the concerted path is near 42 kcal/mol while that for the radical path

(9) The rigorous analysis of the expected deuterium distribution is nontrivial, but a simple analysis, made by counting the number of ways the reactions in the radical chain can occur, predicts 50% d_1, and 25% each d_0 and d_2 labels.
(10) Our attempts to suppress or to divert the radical chain have failed thus far. This feature is under continuing investigation. For a discussion of the experimental problem involved in rate inhibition for this particular case see ref 12.
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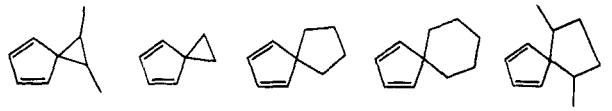
is estimated at 50–56 kcal/mol.[12] Suppression of the radical chain reaction by incorporating the dialkyl substituents in a ring can be seen in the spiroheptadienes **3**[13] and **4**.[14] Both of these compounds give reactions characteristic of cyclopropanes: loss of ring stereochemistry for **3**[13] and H migration for **4**.[14] Spiro nona- and decadienes **5** and **6** both contain virtually strain-free fused alicyclic rings, and give reaction



3 4 5 6 7

products and rates which are sensible only in terms of a concerted reaction. The activation energies are lower (35 and 45 kcal/mol for **5** and **6**) than any estimated bond homolysis step by a substantial amount.[15] The most cogent argument for a concerted path is provided by the observation of a high stereosopecificity in the (1,5) sigmatropic shift of *cis*- and *trans*-**7**.[16]

In summary, the thermal chemistry of 5,5-disubstituted cyclopentadienes now provides examples or radical, diradical, and concerted rearrangements. Future experiments and interpretations must be designed with some attention to these possibilities.

Acknowledgment. Professor R. G. Bergman provided helpful discussions which we acknowledge with pleasure. This work was supported in part by the Robert A. Welch Foundation (Grant E-183).

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(17) One of us (M. R. W.) thanks the Guggenheim Foundation for a fellowship, and the Division of Chemistry at Caltech for a stimulating environment in which to pursue these studies.
(18) NDEA Fellow 1967–1971.

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Stereospecificity of Proton Uptake in the Enzymatic Conversion of Sphinganine 1-Phosphate to Ethanolamine 1-Phosphate[1]

Sir:

Sphingolipid bases are major constituents of a variety of biologically important classes of compounds including ceramides, sphingomyelins, gangliosides, cerebrosides, and other glycosphingolipids. The enzymatic degradation of one of the sphingolipid bases, sphinganine (I, C_{18}-dihydrosphingosine, Figure 1), has been shown to be initiated by an ATP-dependent phosphorylation to yield sphinganine 1-phosphate (II).[2,3] Stoffel, *et al.*,[4,5] have reported the degradation of II involves conversion to palmitaldehyde and ethanolamine 1-phosphate (III). Recent results from the same laboratory indicate that the enzyme responsible for this catalysis (sphinganine 1-phosphate lyase) is specific for the D-*erythro*-(2*S*,3*R*) isomer of II.[6] We have directed our attention to the following questions. First, is a hydrogen atom from the solvent incorporated into III in the enzymatic degradation of II, and, second, if this is the case, is the incorporation of the hydrogen atom also stereospecific?

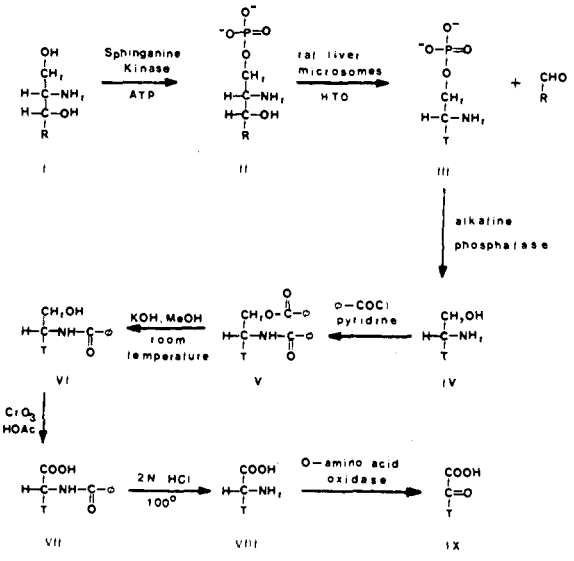

Figure 1. Enzymatic degradation of sphinganine. Stereospecificity in the conversion of sphinganine 1-phosphate to ethanolamine 1-phosphate (R = $C_{15}H_{31}$).

Accordingly, we have incubated II (2.5 μmol, prepared by chemical synthesis[7]) with rat liver microsomes in the presence of HTO (2 Ci).[8] ^{3}H-Labeled III was isolated by chromatography on a Dowex-1-formate column, preparative paper chromatography, and rechromatography on a Dowex-1-formate column. Identity and radiopurity of the labeled III was established by paper radiochromatography and gas–liquid radiochromatography (of the trimethylsilylated product). In two separate incubations, the recovery of labeled III was 2.76×10^5 and 3.24×10^5 cpm. Treatment of [^{3}H]-III with alkaline phosphatase[9] gave [^{3}H]ethanolamine (IV) (~44% yield) which was purified by preparative paper chromatography and its identity and radiopurity was established by paper and thin-layer radiochromatography. Treatment of [^{3}H]-IV with benzoyl chloride in pyridine gave (~77% yield) [^{3}H]-*N*,*O*-dibenzoylethanolamine (V) which was isolated by silicic acid column chromatography and whose radiopurity was established by thin-layer radiochromatography. [^{3}H]-V was converted to [^{3}H]-*N*-benzoylethanolamine (VI) by mild alkaline hydrolysis and the

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(9) Sigma Chemical Co., Type IV.