

lecular orbital calculations on molecules of the type $C_5H_5M(CO)_3$ give tiny barrier values.³ Thus, it is unlikely that the differences in the activation energies between **1** and **4**, for example, are due to electronic effects. Therefore these differences are probably due to the relative steric interactions between the three types of substituents on the platinum atom and the ring. Relative contributions for $C(O)CH_3$ (0.6 kcal/mol) and for C_2H_5 (0.3 kcal/mol) with respect to CH_3 can be derived from comparing **1**, **2**, and **5** and used to calculate activation energies for **4** (5.5 kcal/mol) and for **3** (6.1 kcal/mol) which agree well with the measured values.

Mechanical spectroscopy appears to be a promising technique with which to examine ring rotation in organometallic compounds. It has the advantage that both solid and liquid compounds can be examined if they are soluble in benzene (and most are). The temperature used to mold the sample ($\sim 80^\circ C$) is low enough not to cause decomposition.¹⁶ The polystyrene environment is probably close to being isotropic with respect to nonbonded intermolecular interactions allowing comparisons of a series of molecules to be made. Finally the instruments are fairly simple and inexpensive making this method most attractive.¹⁷

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References and Notes

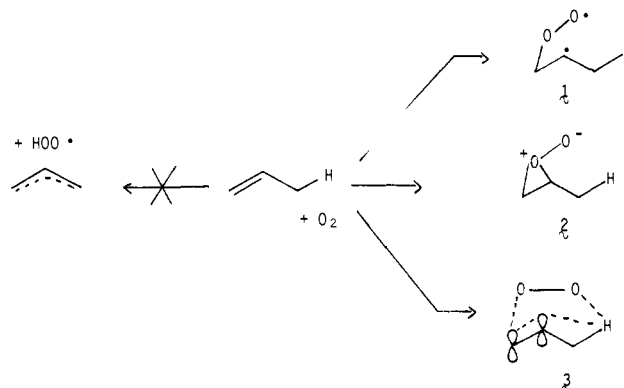
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- (a) There is evidence that energy barrier data for certain organic molecules obtained by both dielectric studies on polystyrene matrices and by NMR studies on solids are similar.^{10a} A preliminary study^{14b} on benzenetricarbonylchromium gave an activation energy of 4.8 kcal/mol in fairly good agreement with the NMR value¹³ of 4.2 kcal/mol. (b) T. Tsutsui, A. Eisenberg, and A. Shaver, work in progress.
- A slight concentration dependence of the peak temperatures for **2** suggests that the physical state of the matrix may have some influence on the barrier to ring rotation. Since the comparison is done at uniform concentration (10%), this should not affect the relative differences.
- All of the complexes **1-6** are air stable; thus inert atmosphere techniques were not used but they could easily be applied.
- Both of the instruments used in this study were designed and built within our department at an estimated total price of \$15,000.
- Department of Materials Science and Technology, Kyushu University, Fukuoka, Japan.

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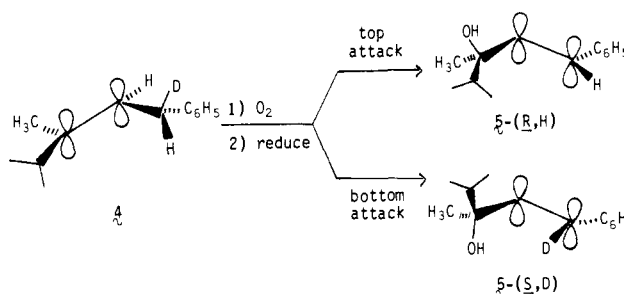
Stereochemistry of the Singlet Oxygen Olefin-Ene Reaction

Sir:

Most of the convincing demonstrations of mechanism in potentially concerted reactions have involved combinations of kinetic-energetic considerations and stereochemical studies. In the singlet oxygen-ene reaction, the finding of low activation enthalpies¹ (<10 kcal/mol) eliminates rate-determining hydrogen abstraction, but is less useful in deciding between other competing mechanisms, e.g., diradical **1**, perepoxide **2**, or concerted pathway **3**. We report here a study of reaction ste-



reochemistry and isotope effects for this reaction. The reactive trisubstituted olefin, **4**, is ideally suited for this purpose. Compound **4** can be prepared in high geometrical and known optical purity.² The product, **5**, is obtained in high yield (only 18% $-CH_3$ hydrogen abstraction and no isopropyl CH abstraction) and only the trans-allylic alcohol shown is found in the mixture. The expectations for a concerted, or similarly highly organized, reaction pathway are shown. Approach of oxygen from above would form the *R* tertiary alcohol, and to produce trans olefin, would remove D. Approach from below would form the *S* alcohol and remove H. These two products are labeled **5-(R-H)** and **5-(S-D)**. With this mechanism, one



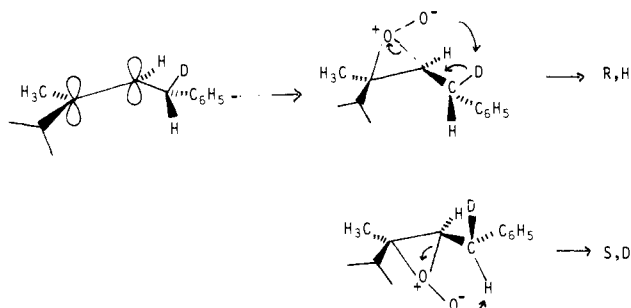
could obtain crossover products (*R-D* and *S-H*) only to the extent that the other olefin isomer or opposite enantiomer is present in the starting material.

Examination of both the methyl and the olefinic protons of **5** by NMR reveals that both are measurably diastereotopic in the presence of $Eu(tfc)_3$, even at 60 MHz. Thus, it is simple to demonstrate that one enantiomer of the product **5** has only H at the crucial vinyl position, while the other has only D. High analytical precision can be claimed in this measurement, since, starting with materials of lower optical and geometrical purity, we find precisely the expected quantity of the "crossover products", *R-D* and *S-H*, in the resulting allylic alcohol.

We find no isotope discrimination in this reaction, *R-H* and *S-D* being produced in equal yield. Thus, while the reaction is highly stereospecific, it does not display the isotope effect one might anticipate for a normal ene reaction.

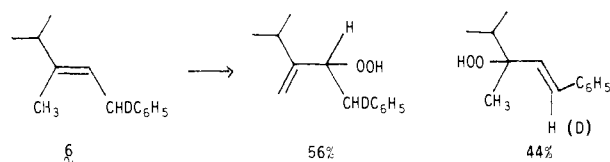
A conceptually simple way of viewing this result is via irreversibly formed perepoxide intermediates. One would an-

ticipate, in such a formulation, equivalent attack on the top and the bottom olefin faces, leading to equal yields of the two intermediates. Completion of the sequence would thus lead to

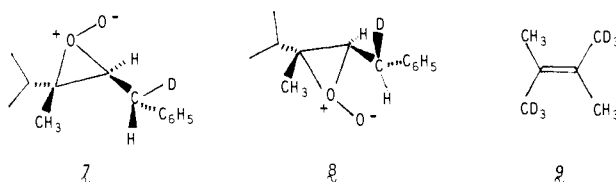


equal yields of the two products, with no apparent isotope effect or enantiomeric excess.

Singlet oxygenation of the opposite geometrical isomer, **6**, of this olefin leads to interestingly different results. The methyl group is now placed on the reactive disubstituted side³ of the olefin π system and competes efficiently with the chiral center.

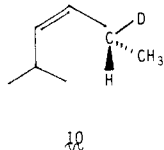


In this case one now anticipates, and finds, an isotope discrimination. Again, using the formalism of the peroxide for purposes of discussion, one sees that, in **7**, the system has a choice of abstracting D from the chiral center or reacting with methyl C-H bonds and, in **8**, a choice of -H or the methyl C-H. We find an isotope effect of 1.2. This is exactly half the effect (1.4) found for the system **9**, which is ideally suited for



cis competition on both top and bottom faces. Again, in this case the enantiomeric ratio in the products (1.2) matches the isotopic ratio.

In our earlier study⁴ on **10**, below, we reported completely analogous results when this reaction was carried out in acetone;



R/S and *D/H* ratios matched and were near unity for the allylic alcohol products. We also reported a novel solvent effect in which methanol was postulated to participate in the hydrogen abstraction step, while acetone did not. This provided an explanation for the high isotope effects (~ 2), but low enantiomeric ratios in the products obtained in methanol. This result can be duplicated in the present trisubstituted series if galvinoxyl is omitted from the reaction medium. Thus we believe that these results can be attributed to radical-chain processes (i.e., a hydrogen abstraction-allyl radical sequence) and are unrelated to the singlet oxygen mechanism.

The present results confirm that the singlet oxygen-ene reaction is a highly stereospecific suprafacial process. The absence of an isotope effect of any significant magnitude makes it difficult to argue for a traditional concerted transformation. We use the peroxide here for discussion purposes only. We

will present a comprehensive mechanism shortly which we believe is consistent with all recent data.

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2,4-Methano-2,4-dehydroadamantane.

A [3.1.1]Propellane¹

Sir:

We report the first synthesis and characterization of 2,4-methano-2,4-dehydroadamantane² (**1**), a derivative of [3.1.1]propellane. This is the smallest carbocyclic propellane system which has been prepared.

Small-ring propellanes possess three rings fused together at the central bond containing two carbons with inverted tetrahedral geometry.³ Decrease in ring sizes parallels increase in *p* character of the central bond, which approximates a *p-p* σ bond in smallest ring propellanes.³⁻⁵ Carbocyclic propellanes containing three, four, and five bridge carbons ([1.1.1], [2.1.1], [3.1.1], and [2.2.1]) have not been synthesized so far. Propellane systems containing six bridge carbons, ([4.1.1],⁶ [3.2.1],³ and [2.2.2])⁷ have been prepared rather recently and found to be very reactive. Large-ring propellanes, however, contain no inverted carbon and behave chemically like "normal" polycyclic hydrocarbons.⁸

2,4-Methano-2,4-dehydroadamantane (**1**) was prepared by the intramolecular cycloaddition of 4-methylene-2-adamantylidene (**2**) to the olefinic bond. Thus, treatment of 4-hydroxy-2-adamantanone⁹ with methyl Grignard reagent, followed by Jones oxidation and acid-catalyzed dehydration, afforded 48% 4-methylene-2-adamantanone¹⁰ (**3**). Pyrolysis of the dry sodium salt of the tosylhydrazone derived from ketone **3** (**3a**) at 180 °C and 0.02 mmHg produced 70% **1**. The

