(particularly ^{2}H, ^{15}N, ^{34}S, and ^{54}Fe substitution) are required to clarify the reasons for this observation and to understand the differences between the TRP and PDO spectra. We are currently pursuing these studies.

Cyclopropane Stereomutation Catalyzed by One-Electron Oxidants

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Cyclopropane cation radicals are proposed intermediates in the cis ⇌ trans isomerization of 1,2-diphenylcyclopropane under photooxidation conditions.[1,2] The cation radicals do not isomerize directly, however. Instead, chemically induced dynamic nuclear polarization (CIDNP) studies[2] reveal that back electron transfer from the sensitizer anion radical to the cyclopropane cation radical leads to the intermediate responsible for isomerization: a triplet 1,3-diphenyltrimethylene biradical. It was ultimately concluded that interconversion of the *cis*- and *trans*-1,2-diphenylcyclopropane cation radicals was slow even at room temperature.[2c,3]

*We have discovered that cis-1-p-anisyl-2-vinylcyclopropane (**1**) is rapidly isomerized by one-electron chemical oxidants at temperatures as low as −90 °C.* The thermodynamics of electron transfer exclude a biradical mechanism and isotopic labeling experiments bound considerably the mechanistic possibilities for stereomutation.
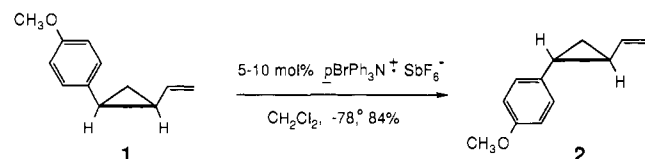
1[4] was isomerized to *trans*-cyclopropane **2** (84%) by 5–10 mol % *p*-BrPh$_3$N$^{\bullet+}$SbF$_6^-$ (**3**)[5] in CH$_2$Cl$_2$ at −78 °C or in CH$_3$CN at −40 °C (88%). The reaction was similarly catalyzed by O$_2^{\bullet+}$SbF$_6^-$ (**4**)[6] albeit in lower yield (48%). Above −78 °C in CH$_2$Cl$_2$, polymerization competed with isomerization using either catalyst but was effectively inhibited by the addition of 2,6-di-*tert*-butylpyridine, which had no effect on cyclopropane isomerization.

The isomerization half-life measured at −90 °C in CH$_2$Cl$_2$ with 10 mol % **3** was ≈10 min. A comparison with the extrapolated thermal cis → trans rearrangement rate of 1-phenyl-2-vinyl-cyclopropane[7] $(t_{1/2}^{-90\ °C} \approx 10^{25}$ min) reveals that the *p*-

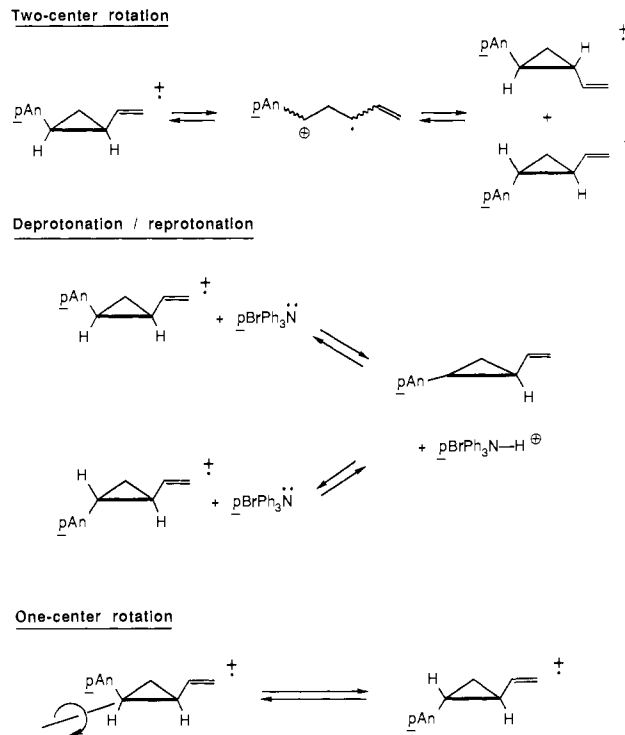(1) (a) Murov, S. L.; Cole, R. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1968**, *90*, 2957. (b) Hixson, S. S.; Boyer, J.; Gallucci, C. *J. Chem. Soc., Chem. Commun.* **1974**, 540.
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Figure 1. Three stereomutation mechanisms.

BrPh$_3$N$^{\bullet+}$SbF$_6^-$ catalyzed isomerization is accelerated by a factor of ≈10^{24}!

We propose a cation radical chain mechanism for isomerization based upon the one-electron oxidation chemistry of **3**[8] and **4**.[6] Excluded from this mechanism is the trimethylene biradical. The one-electron reduction of intermediate cyclopropane cation radicals by the strongest available reductant, *p*-BrPh$_3$N, does not provide enough energy to populate the biradical.[9] The energetics of electron transfer further permit **3** to be a reversible one-electron oxidant but not **4**.[10] Thus **4** can only serve as a chain initiator for isomerization. Shown below is a unified mechanism which utilizes both **4** and **3** in this fashion. The propagation steps then involve **1**, **2**, and their cation radicals.[11]
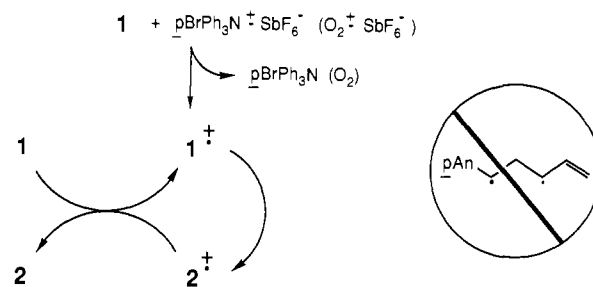
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(9) The oxidation potentials (E_p vs. SCE) of **1** (1.43 V), **2** (1.46 V), and **3** (1.12 V) were obtained by cyclic voltammetry in CH$_3$CN with *n*-Bu$_4$N$^+$-ClO$_4^-$ as the supporting electrolyte. Thus back electron transfer from **3** to **1**$^{\bullet+}$ or **2**$^{\bullet+}$ is exothermic by ca. 7–8 kcal/mol. The energetic requirements for the isomerization initiated by O$_2^{\bullet+}$SbF$_6^-$ are even more stringent. Here, electron transfer from **1** to **2**$^{\bullet+}$ is exothermic by ca. 0.7 kcal/mol. We assume the biradical energy is comparable to the thermal activation enthalpy for cis → trans isomerization of 1-phenyl-2-vinylcyclopropane, 32 kcal/mol.[7]
(10) Reduction of **1**$^{\bullet+}$ or **2**$^{\bullet+}$ by O$_2$ would be endothermic by ca. 90 kcal/mol. This was calculated using the oxidation potentials of **1**[9] and **2**[9] and the calculated electrode potential for O$_2$ (5.3 V vs. SCE). The latter was obtained from Miller's empirical equation (Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916), using the ionization potential of O$_2$ measured by photoelectron spectroscopy (12.08 eV: Collin, J. E.; Delwiche, J.; Natalis, P. *Int. J. Mass Spectrom. Ion Phys.* **1971**, *7*, 19) and converting the Ag/Ag$^+$ potential so obtained to the SCE potential by adding 0.34 V.

If cyclopropane cation radicals are intermediates in the isomerization, how do they interconvert? We consider three stereomutation mechanisms, called "two-center rotation", "deprotonation/reprotonation", and "one-center rotation" (Figure 1). The first of these has ample analogy in neutral cyclopropane chemistry.[12] It nonetheless suffers from one weakness. It does not readily accommodate an important experimental observation: the consistent failure to form 4-*p*-anisylcyclopentene under any of the experimental conditions explored. The other two mechanisms do. The second mechanism is additionally recommended by the high acidity estimated for arene cation radicals.[13] The last mechanism recognizes that reactivity may be controlled by the bonding changes that occur upon one-electron oxidation. If the singly occupied MO in the cation radical shares sufficient character with the antisymmetric ($^2B_2$) Walsh[14] MO, then the *two* cyclopropane bonds adjacent to the most electron-donating substituent (*p*-anisyl in this case) will be weakened.

The specifically deuterated cyclopropane **5**[15] was synthesized to distinguish between these possibilities. The one-center rotation and the deprotonation/reprotonation mechanisms predict that isomerization will produce a single trans isotopomer, **6**. In contrast, the two-center rotation mechanism predicts that a mixture of the two trans isotopomers **6** and **7** will be formed.

5

6

7

8
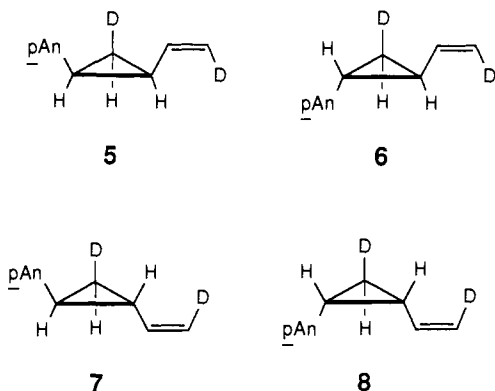
In practice, partial isomerization (15–80%) of **5** with **3** or **4**, in either CH_3CN or CH_2Cl_2, resulted in the formation of nearly equal amounts of the two deuteriated *trans*-cyclopropanes **6** (48 ± 6%) and **7** (52 ± 6%). The near random distribution of deuterium did *not* result from prior automerization of **5** nor from a rapid automerization of **6** or **7** under the isomerization conditions. The former was excluded by ^1H and ^2H NMR analysis of recovered *cis*-cyclopropane, after 67% cis → trans conversion, which revealed a mixture consisting of 85% of **5** and 15% of **8**. The latter was excluded by the results of a similar control experiment. ^1H and ^2H NMR analysis of recovered *trans*-cyclopropane, after 57% cis → trans isomerization of an initial 63:37 mixture of **5** and **6**, revealed a nonequilibrium composition of the trans isotopomers **6** (62%) and **7** (38%).

The combined labeling results exclude the deprotonation/reprotonation and the one-center rotation mechanisms.[16] Correlated two-center rotation,[17] a subset of the two-center rotation mech-

anism, is similarly excluded; it would only permit the interconversion of the two cis isotopomers **5** and **8**. Only the two-center *uncorrelated* rotation mechanism remains.[18] The fact that the rotations must be uncorrelated, i.e., random, further suggests that the ring-opened cyclopropane cation radical is an intermediate on the potential energy surface for isomerization, rather than a transition state.

It is now apparent that the isomerization mechanism for cyclopropanes using one-electron chemical oxidants can differ from that using photochemical oxidants. The inability of the 1,2-diphenylcyclopropane cation radicals produced by photooxidation[2] to isomerize is likely dictated by the relative rates of back electron transfer to isomerization. This conclusion may be general and suggests opportunities for the discovery of other cation radical reactions.

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(18) Not considered here are two-center rotations which involve cleavage of either of the two less substituted cyclopropane bonds (C1–C3 or C2–C3). Experiments are in progress to test these possibilities.

Dehydration of Silica–Aluminas Monitored by High-Resolution Solid-State Proton NMR

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Knowledge of the acid sites on silica–aluminas and zeolites has been addressed by various techniques.[1–9] With a combination of multiple-pulse techniques[10,11] and magic-angle spinning (MAS)[10–13] one can obtain high-resolution ^1H NMR spectra of solid samples.[14] In this paper we report the initial results of a study of the dehydration of silica–alumina, silica gel, and γ-alumina by the ^1H CRAMPS (combined rotation and multiple-pulse spectroscopy)[14] NMR technique.

Silica–alumina samples SA-14 (containing 14% Al_2O_3 and 86% SiO_2 by weight) and SA-25 (containing 25% Al_2O_3 and 75% SiO_2

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(11) Amine cation radical–arene complexes are plausible isomerization intermediates when **3** is used as the initiator. The fact that **4** is also an initiator permits these complexes but does not require them.

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(15) Prepared as a separable mixture with **6** by cyclopropanation[4b] of (Z,Z)-1,3-butadiene-*1,4-d₂* (Stephenson, L. M.; Gemmer, R. V.; Current, S. P. *J. Org. Chem.* **1977**, *42*, 212).

(16) Also consistent with the labeling data are competing one-center rotations at any two of the three cyclopropane carbon atoms or similarly competing deprotonations. Both of these hypotheses are unlikely since they would each require two heterotopic processes with essentially identical activation barriers over a wide range of temperature (−90 to −40 °C) and in two different solvents (CH_2Cl_2 and CH_3CN).

(17) Correlated rotation may occur in a conrotatory or a disrotatory fashion. These experimentally indistinguishable processes are not considered separately.

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