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# The kinetics, stereochemistry, and deuterium isotope effects in the α-pinene pyrolysis. Evidence for incursion of multiple conformations of a diradical

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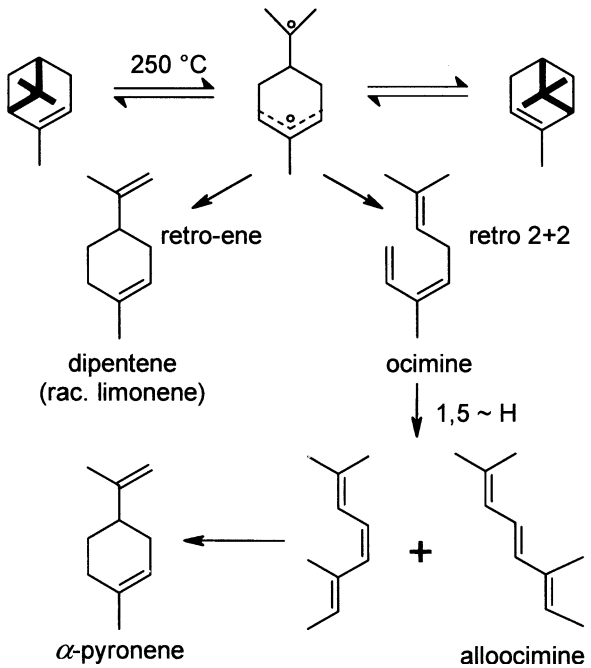
**Abstract**—Pyrolysis of optically active α-pinene gave 95% racemic limonene (dipentene), alloocimine, racemic α-pinene, α-pyronene. Activation parameters are reported. Pyrolysis of (*S*) *syn*-6-trideuteriomethyl α-pinene at 256.7°C for 2400 s gave dipentene with twice as much deuterium as hydrogen transfer with $k^{H}/k^{D}$=1.49 and alloocimine with a *Z* and *E* trideuteriomethyl ratio of ca. 5 with $k^{H}/k^{D}$=0.89. The isotope effect on loss of starting material was 1.16. Separation of the enantiomers of α-pinene from 3600 s pyrolyses at 256.7°C followed by NMR analysis revealed that the ratio of the *R-syn* to *R-anti* to *S-anti* isomers is 4.6:3.7:1 at roughly two half-lives. Kinetic analysis reveals that the previously proposed mechanism for all conversions involving slow interconversion of two diradicals with $C_s$ symmetry is not consistent with the distribution of the α-pinene isomers, particularly the formation of more suprafacial-retention product (*R-anti*) than bond-rotated isomer (*S-anti*). Inclusion of another $C_s$ species (ignoring the deuteriums) that would be intermediate between the originally proposed $C_s$ species, appears more consistent with the observations. 

## 1. Introduction

α-Pinene has been subjected to pyrolysis long ago and found to give the retro-ene product limonene, the retro 2+2 product alloocimine after a 1,5-hydrogen shift in the initially produced ocimine, as well as racemization presumably via a 1,3-sigmatropic shift of carbon.[1] Among the minor products formed in the reaction is α-pyronene, which is formed by electrocyclization of the *Z* isomer of alloocimine. Because the limonene produced is racemic,[1a,b] it has been postulated that homolysis of the C1–C6 bond gives a diradical which can be responsible for all the products (Scheme 1).[1c]

It seemed appropriate to examine the stereochemistry and deuterium isotope effects in the reactions to distinguish between concerted and diradical pathways and to better characterize the diradical responsible for dipentene (racemic limonene).[2] It was also of concern to determine the stereochemistry of the 1,3-shift of carbon because these have been a central focus in organic thermal chemistry. Forbidden (by the Woodward Hoffmann rules) to occur in a concerted manner if the overall stereochemical pathway is the suprafacial use of the allylic moiety with retention at the migrating atom.[3] Nonetheless, this pathway often occurs along with the usually dominant 'W-H allowed' suprafacial-inversion pathway.[4] So the question often asked is whether a concerted pathway is competing with a non-concerted diradical pathway or whether the overall pathway is totally diradical with some stereochemical bias resulting from recombination steps being competitive with bond rotation that might randomize the stereochemistry. For instance, the vinylcyclopropane rearrangement occurs with almost, but




**Scheme 1.** Pyrolysis products of α-pinene and mechanistic rationale.

*Keywords*: pyrolysis; alloocimine; dipentene; pinene; 1,3-sigmatropic shift.

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**Table 1**. Pyrolysis of (*S*)-(−)-α-pinene (91.2% ee)—percentages of products

| Temperature (°C) | Time (s) | α-Pinene | Limonene | Alloocimine | α-Pyronene | *R*-α-pinene | *S*-α-pinene |
|---|---|---|---|---|---|---|---|
| 256.7 | 2400 | 37.0 | 35.9 | 24.1 | 1.2 | 17 | 81 |
| 256.7 | 4800 | 13.4 | 49.2 | 32.1 | 1.7 | 27 | 66 |
| 241.7 | 7800 | 36.9 | 36.8 | 23.6 | 1.0 | 17 | 81 |
| 226.7 | 27,000 | 37.7 | 37.2 | 22.6 | 0.9 | 15 | 83 |

not completely random stereochemistry in the parent case,[5] however, suprafacial inversion stereochemistry dominates the rearrangement of the alpha-*tert*-butyl material.[6] In cases where steric effects might reasonably raise the energy of the suprafacial-inversion pathway over that of the suprafacial-retention pathway, the 'W-H forbidden' pathway is utilized to a great extent.[7]

Further complicating the mechanistic picture is the suggestion that dynamical effects may promote formation of the 'allowed' suprafacial-inversion product in less substituted cases.[8] The origin of these effects in 1,3-shifts is argued to be the continuing rotation about a bond after cleavage that which keeps spinning in one direction until it is stopped by product formation. Herein we report the full details of pyrolysis of α-pinene and more recent studies that bear on the question of the mechanism of the 1,3-shift.

## 2. Results and discussion

It was found that in a well-conditioned 2 L glass bulb pretreated with dimethyldichlorosilane then diisopropylamine, gas phase pyrolysis of α-pinene proceeded to give the products previously reported.[1c] Table 1 lists the percentages of the major products determined from multiple runs at various times and temperatures starting with 99+% pure, 91.2% (ee) *S*-α-pinene.

The Arrhenius parameters for loss of racemic α-pinene are $\log k\ (s^{-1})=14.2-42{,}700/2.303RT$. The Arrhenius parameters for the three reactions, retro-ene, retro 2+2, and enantiomerization are $\log k\ (s^{-1})=13.6-41{,}800/2.303RT$, $14.1-43{,}300/2.303RT$, and $14.4-45{,}000/2.303RT$, respectively,[9] with standard deviations of the order of 0.5% in every value except for those for the enantiomerization which are roughly 5%. The latter determination was made on an α-cyclodextrin on Celite packed g.c. column while the former determinations were made on a DB-5 capillary column from pyrolyses conducted over a 30°C temperature range measured accurately with a Platinum resistance thermometer. When a sample of (−)-*S*-α-pinene (91.2% ee) was pyrolyzed for 2400 s at 256.7°C, which represents roughly 25% enantiomerization, the limonene isolated and found to be 99.1% pure had $[\alpha]_D=-3.98°$ (cyclohexane) which represents roughly 5% preservation of optical purity considering the extent of racemization of the starting material. Thus at most, only 5% of the limonene can be formed by a concerted retro-ene mechanism; the rest of the retro-ene product, properly termed dipentene, must be formed from a $C_s$ symmetric intermediate or equilibrating set of intermediates of effectively $C_s$ symmetry. All of the data thus far is consistent with the simple mechanism previously postulated[1] involving mostly C1–C6 bond homolysis to a $C_s$ symmetric 1,4-diradical followed by either hydrogen atom shift, central bond cleavage, or recombination to racemic α-pinene (Scheme 1).

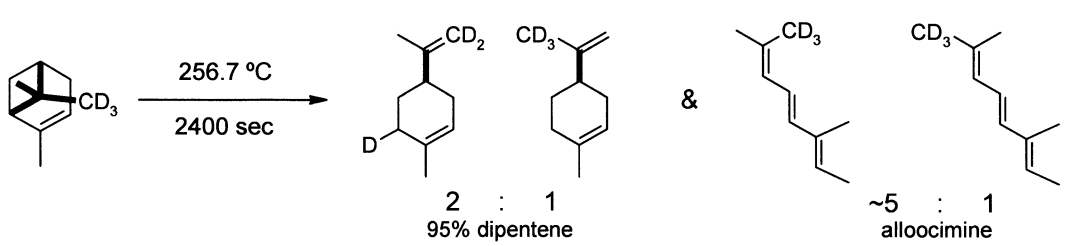
**Table 2**. Pyrolysis of *syn*-6-trideuteriomethyl-α-pinene—percentages of products

| Temperature (°C) | Time (s) | α-Pinene | Limonene | Alloocimine | α-Pyronene |
|---|---|---|---|---|---|
| 256.7 | 2400 | 42.4 | 25.4 | 29.1 | 1.56 |

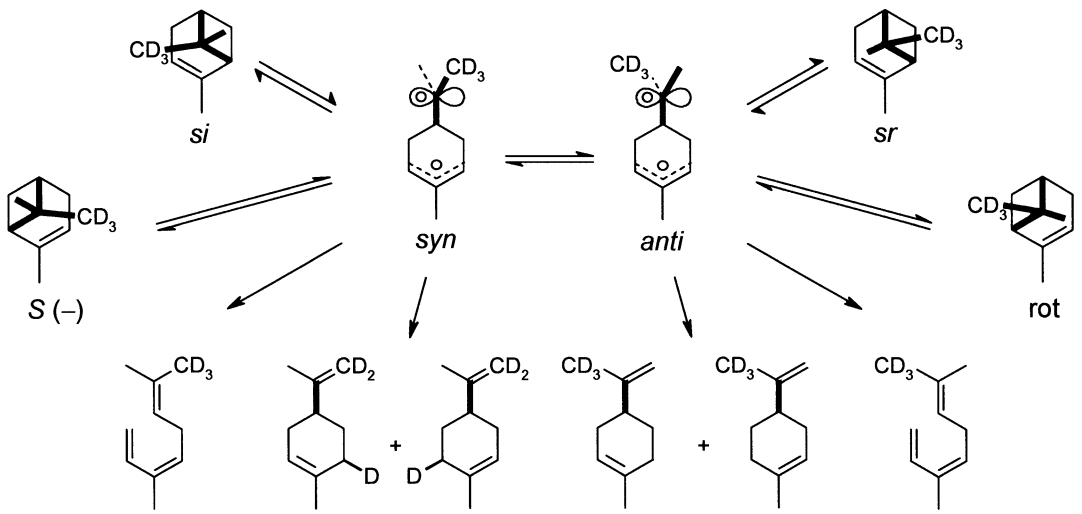
To further define the mechanism of reaction optically pure (−)-*S*-*syn*-6-trideuteriomethyl-α-pinene was pyrolyzed at 256.7°C for 2400 s, Table 2.

The rate constant for of loss of starting material allowed determination of $k^H/k^D=1.16$. However, $k^H/k^D$ for formation of dipentene is 1.49 and that for formation alloocimine is 0.89. Further, by deuterium NMR twice as much deuterium relative to hydrogen was transferred to the six membered ring in the retro ene reaction to form dipentene, and the *Z* to *E* ratio of trideuterio methyl group in alloocimine is roughly 5:1 by deconvolution of the *Z* and *E* methyl peaks and integration (Scheme 2).[10]

The *Z* and *E* methyl proton chemical shifts of alloocimine were assigned by first identifying the carbon and proton resonances of each of the four methyl groups by a 2D correlation experiment. The 6.9 Hz doublet methyl at δ 1.74 having a carbon chemical shift of 14.7 ppm must be C8. The methyl group at δ 1.85 with a carbon shift of 28.0 ppm is assigned C10 attached to C6 because the proton intensity is the same in both protio alloocimine and in the alloocimine obtained from pyrolysis of the *syn*-6-trideuteriomethyl α-pinene. The methyl group at δ 1.80 and a carbon shift



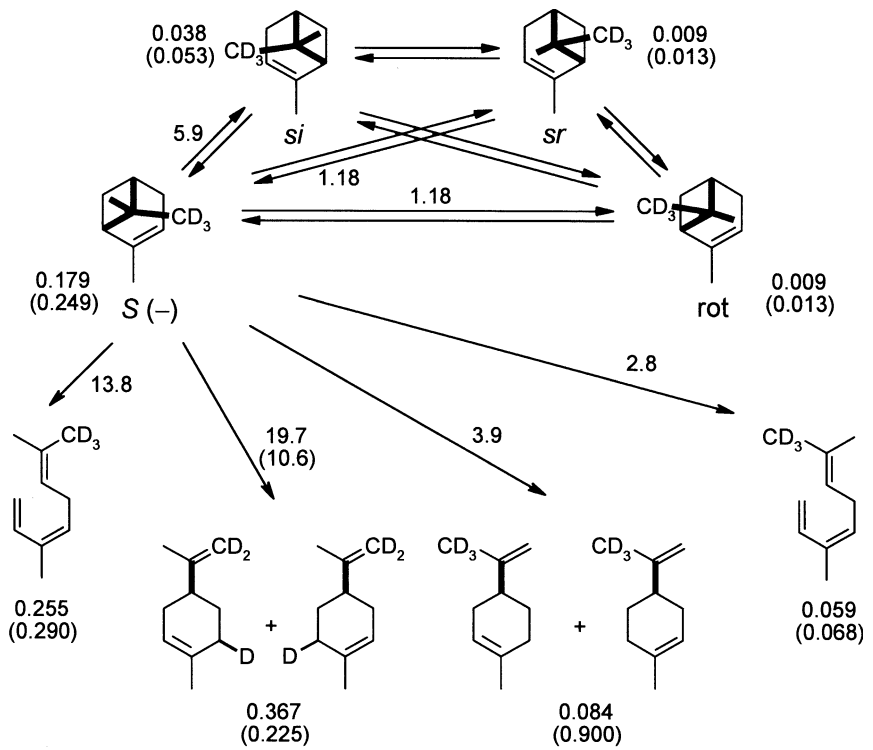

**Scheme 2.**




**Scheme 3.** $C_s$ diradical pathway.

of 20.1 ppm was assigned to be C9, the *Z* methyl group, because the upfield carbon in such terminal geminal dimethyl olefinic systems is the *Z* carbon due to shielding by the attached chain.[11] Therefore the *E* methyl group must give rise to the proton resonance at 1.81 ppm.

The simplest mechanistic rationalization for all of these observations (Scheme 3) revolves about initial formation, as the dominant rate determining step, of a diradical of $C_s$ symmetry having a half-chair cyclohexenyl moiety with an axial dimethylcarbinyl radical positioned along the symmetry plane. If this species were formed by a least motion pathway, it would have the trideuteriomethyl group *syn* to the allylic moiety and be poised to transfer deuterium to either allylic site to give dipentene (racemic limonene) and undergo cleavage to ocimine with a *Z* trideuteriomethyl group. Competing with these reactions would be rotation of the radical carbon bearing the geminal dimethyl groups to give the stereoisomeric *anti* $C_s$ symmetric diradical with the perprotiomethyl group arrayed to transfer hydrogen to either side of the allylic radical and undergo cleavage to ocimine with an *E*-trideuteriomethyl group. This rotation necessarily must be a slower reaction that directs product formation from the original diradical. The greater ratio of *Z* to *E*




**Scheme 4.** Calculated product fractions from *S*-α-pinene after 3600 s at 256.7°C with the rate constants indicated (in units of $10^{-4}$/s) assuming five times as much reaction via the *syn* diradical as via the *anti* diradical in H case. The $CD_3$ values are in parentheses. All other pinene isomers are reacting with the appropriate rate constants which are not shown for sake of clarity. The calculated percentages after 2400 s at 256.7°C provide the following ratios: $k^{H}/k^{D3}$ (ocimine)=0.91, found 0.89; $k^{H}/k^{D3}$ (ocimine)=1.48, found 1.49; *Z*/*E* $CD_3$ ocimine=4.6, found ~5; D/H transfer (dipentene)=2.5, found 2.0; $k^{H}/k^{D3}$ (-total α-Pinene)=1.24, found 1.16.

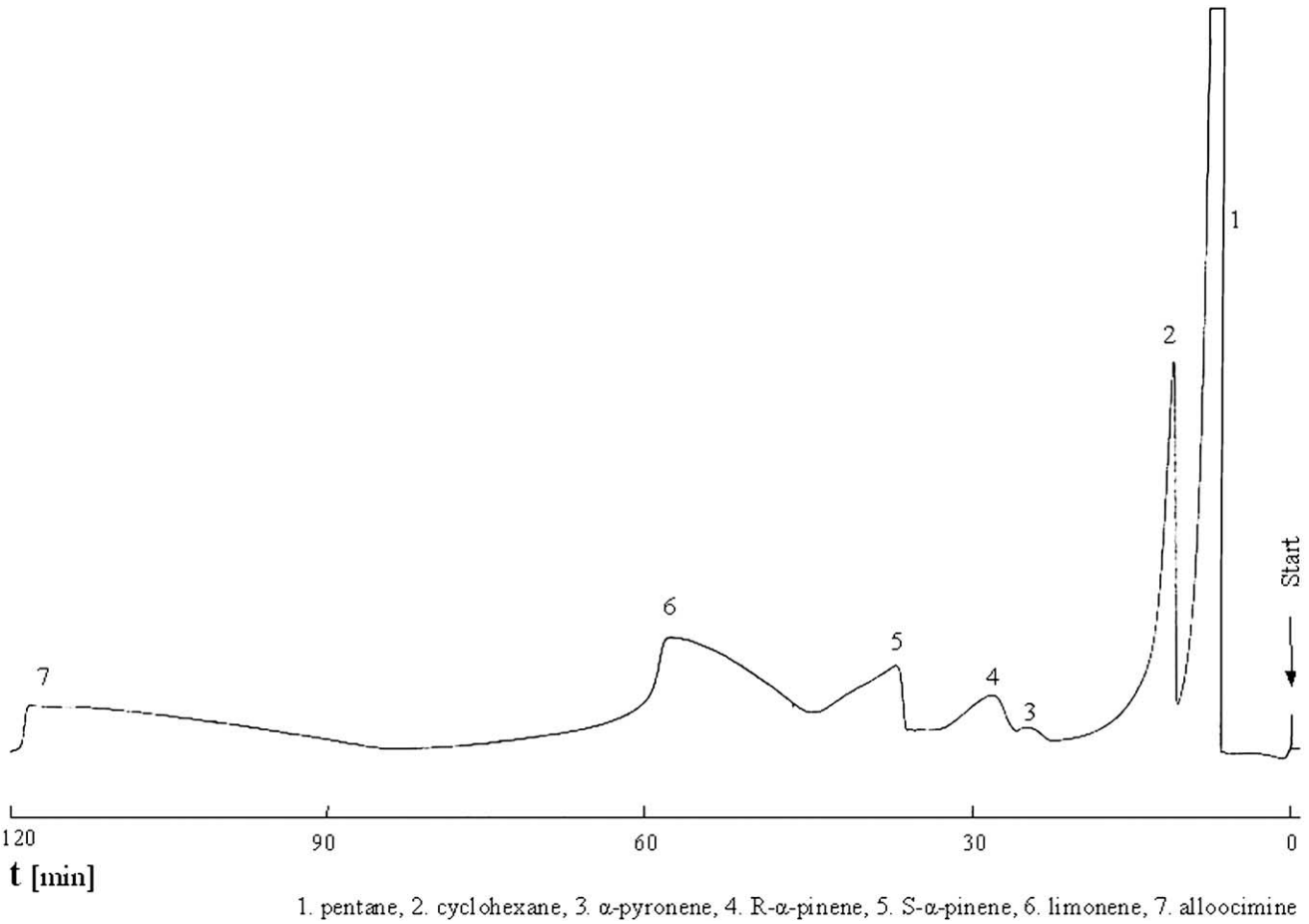



**Figure 1.** Chromatogram of solution of *syn*-6-trideuteriomethyl-α-pinene pyrolysate in pentane/cyclohexane obtained at 65°C on column filled with α-cyclodextrin on celite.

trideuteriomethyl ocimine (ca. 5) than that for dipentene resulting from deuterium rather than hydrogen atom transfer (2.0) is not inconsistent with this explanation.

The activation parameters are consistent with rate determining formation of a diradical, but more importantly, the different activation energies for formation of the various products indicate partitioning of the diradical via steps that are governed by statistical, i.e. Boltzmann, factors rather than dynamic ones.

To model the kinetics and isotope effects in system, a numerical integration program was used that calculates the mole fractions of stable species as a function of time from assumed first order rate constants. These rate constants, of course, must reflect the observed rate constants and the deuterium distributions observed. However, such programs cannot easily include unstable species like diradicals because the large rate constants then require very short time steps which make difficult achieving the overall reaction. Nonetheless, the relative utilization of the *syn* and *anti* $C_s$ symmetric diradicals becomes a crucial consideration. The results from various attempts suggested that the best choice was 5:1. Scheme 4 depicts the products derived from the *syn* and *anti* $C_s$ symmetric diradicals, the rate constants and the distribution of products expected at 256.7°C after pyrolysis of the $D_3$-α-pinene for 3600 s (roughly two half-lives). Further, it was assumed that the rate of formation of the suprafacial-retention 1,3-shift product, *R*(+) with an *anti* $CD_3$ group, is the same as formation of the bond-rotated enantiomer, *S*(−) with an *anti* $CD_3$ group since both should be formed with equal probability from the *anti* $C_s$ diradical. It should be noted that the rate constant for formation of the suprafacial-inversion product, *R*(+) with a *syn* $CD_3$ group is five times that for formation of the former stereoisomers since it is formed from the *syn* $C_s$ diradical. Also reported in Scheme 4 are the kinetic isotope effects and deuterium product ratios expected at 2400 s, the time period for the determinations. The agreement is remarkable considering that the only rate constant changed upon deuteration is that for formation of the deuterium transferred limonene, and this was adjusted to reproduce the observed kie for dipentene formation. Further, the numerical integration scheme does not consider intermediates, so the larger calculated kie for loss of α-pinene results from a primary isotope effect on the formation of the deuterium transferred limonene product, yet this product must be formed from an intermediate because it is mostly racemic. Given diradical intermediate and that reformation of α-pinene is slow compared with other product forming processes, the rate determining step should be ring opening which should result in no primary isotope effect on the loss of α-pinene. There may, however, be a hyperconjugative secondary isotope effect on the ring opening of α-pinene which may account for the kie of 1.16. Nonetheless, at least some of the deuterated α-pinene that

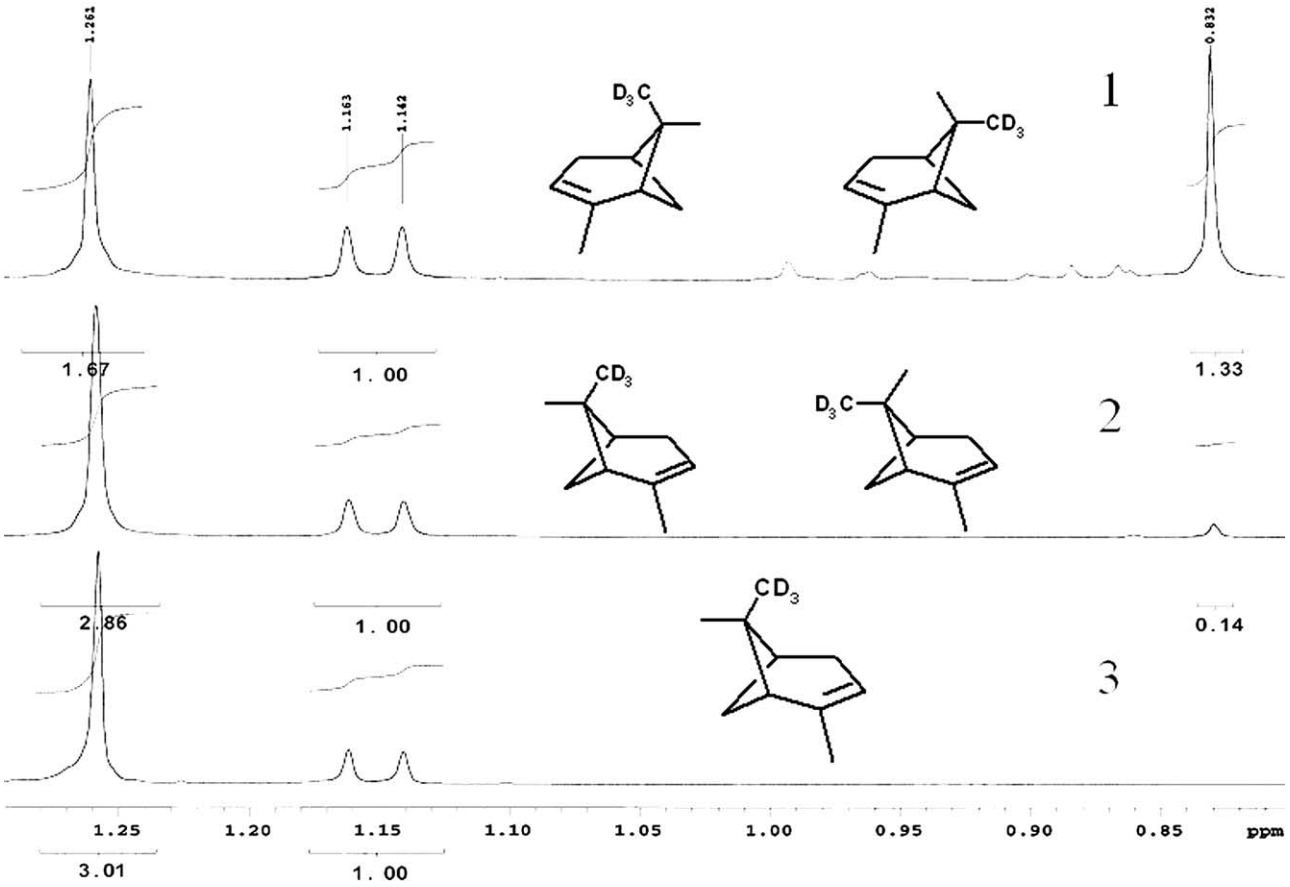



**Figure 2.** Samples of many $^1$H NMR spectra to determine the ratio *syn*- to *anti*-$CD_3$ in *R* (1) and *S* (2) α-pinene after 60 min pyrolysis at 256.7°C and $^1$H NMR of starting material (3).

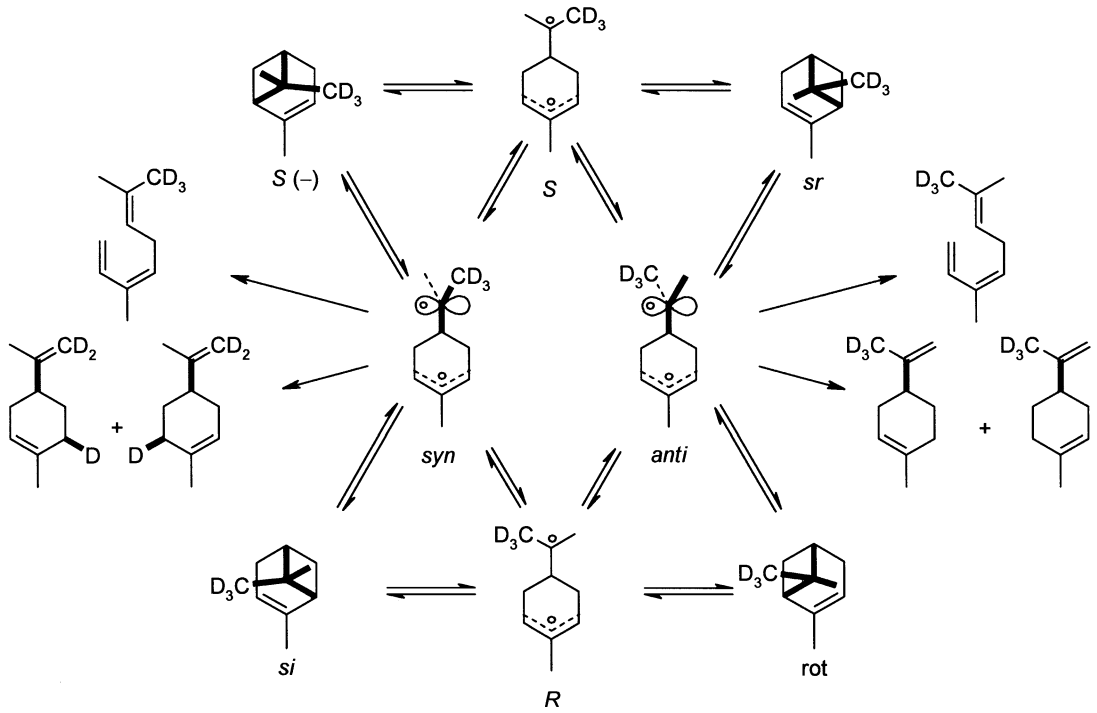
does not react according to Scheme 4 should be giving the products from the *anti* $C_s$ diradical, namely hydrogen transferred dipentene and *E*-trideuteriomethyl ocimine. This should alter some the ratios calculated in Scheme 4 to more nearly those observed.

Missing from this analysis is an experimental determination of the distribution of α-pinene isomers involved in the racemization reaction, the 1,3-sigmatropic shift. If the α-pinene isomers were formed from the same two diradicals postulated above, initially there would be a 5:1:1 distribution of isomers resulting from the three stereopathways: *si*, *sr*, and reformation of the same enantiomer of α-pinene with interchange of the trideuteriomethyl and perprotiomethyl groups, i.e. the bond-rotated isomer. The rest of the α-pinene would, of course, be of the configuration of the starting material. Interestingly, the ratio of the three geometric isomers changes only slowly with time according to the calculation since each isomer is also undergoing the same reactions as starting material with overall rates that not only differ only by a small isotope effect on the loss of α-pinene, but all are substantially faster than racemization. Indeed, Scheme 4 also includes the calculated amount of the various α-pinene isomers after roughly two half-lives. It therefore was important to determine the ratio of the α-pinene isomers to verify the proposed diradical pathway.

Thus 99% optically pure (1*S*)-(−)-α-pinene-9-(*syn*)-$d_3$ was prepared as described previously from 99% optically pure β-pinene, and 80–120 mL samples were pyrolyzed at 256.7°C for 3600 s in vacuum in a 2 L glass bulb which had been 'conditioned' with dichlorodimethylsilane. The samples were removed and separated on a 18 ft×1/4 in. GC column packed with α-cyclodextrin on 80–100 mesh celite, Fig. 1.

The ratio of *syn* and *anti* $CD_3$ methyl groups in each enantiomer could be determined from the $^1$H NMR peak ratios at $\delta$ 0.85 (*syn* methyl) and 1.28 (*anti* methyl). The ratio of *syn* to *anti* in the *R* isomer was 1.24±0.07 (average of eight runs), and that in the *S* isomer was 19±0.6, Fig. 2. The ratio of *S* to *R* α-pinene recovered was determined to be 2.4±0.2 which allowed calculation of the ratio of *si* to *sr* to rotation products of 4.6:3.7:1, respectively. The error in these values is estimated to be 20% due to incursion of minor unknown impurities and tailing of the solvent peak in the GC. Extraordinary means were taken to provide accurate NMR integrations (see Section 4).

The results of the pyrolyses, GC separation of α-pinene enantiomers, and NMR analysis of each enantiomer make it clear that the mechanism of Scheme 3 proposed previously cannot be correct for the formation of the geometric isomers of α-pinene. Schemes 3 and 4 require a 4.1:1:1 ratio of α-pinene stereoisomers from suprafacial-inversion, suprafacial-retention, and bond-rotated isomer pathways, respectively. The ratio of *si* to bond-rotated product observed (4.6:1) might be within experimental error of the calculated




**Scheme 5.** Mechanistic rationale for the pyrolysis products of α-pinene.

value since it proved difficult to integrate a small peak relative to a large one in the NMR. Further, the comparison required good integration of enantiomers from the optically active GC column, a task that was complicated by base-line drift due to solvent. However, there is no way to manipulate the rate constants of Scheme 4 to provide more suprafacial-retention product without ignoring the symmetry of the diradical intermediates. The ratio of *si* to *sr* product involves NMR integration of two nearly identical sized peaks so this value, 1.24, has a standard deviation of only 3%. Thus the hypothesis of Schemes 3 and 4 is inconsistent with the data unless there is an additional, separate suprafacial retention pathway that intervenes to the extent of 25–30% of the total pathway responsible for geometric isomerization.

The simplest scheme required by an extra *sr* reaction pathway would be exactly like Scheme 3 with the addition of an equilibrium pathway connecting the starting α-pinene and its *sr* 1,3-shift isomer as well as one connecting the *si* 1,3-shift isomer with the bond-rotated isomer. Justification of such a pathway is not provided by the Principle of Conservation of Orbital Symmetry which would favor a suprafacial-inversion pathway for a 1,3-shift of carbon. A more reasonable mechanistic formulation would recognize that the *sr* product could arise from the species responsible for interconversion of the two diradicals of Scheme 3, namely, the other $C_s$ symmetric diradical (ignoring the deuterium labels). This species exists as enantiomers due to the presence of the $CD_3$ group; however, one of them, *S* (in Scheme 5), is more accessible from the α-pinene starting material of the *S* configuration via a least motion pathway. If these latter species were responsible only for additional α-pinene product and not the other isomeric products, then Scheme 5 is a possible scenario. That these chiral species, *S* and *R*, could not easily form the other products is not unreasonable considering the geometry and overlap requirements for the retro 2+2 reaction to form ocimine and the ene-like reaction to form the dipentene. It is important to recognize that both types of diradicals, the *syn* and *anti* $C_s$ species and the *S* and *R* $C_s$ species (in the absence of D) must be formed directly from the appropriate α-pinene. However, the species *S* need provide only 1/4 of the α-pinene product.

The mechanistic Schemes 3 and 5 have focused on a conformation of the diradicals that would place the dimethylcarbinyl radical group on the axial position in a half-chair geometry for the cyclohexenyl radical. Unknown is the extent to which the half-chair undergoes a 'flip' to place the dimethylcarbinyl radical equatorial. However, where this to occur, no product could be formed from it recognizing the geometric requirements for formation of the observed products. Nonetheless, it would randomize the stereochemistry of the dimethylcarbinyl group and could be responsible for all products attributed to the *S* and *R* and *anti* diradicals of Scheme 5 as well as an equal amount of the products attributed to the *syn* diradical of Scheme 3. Thus, up to 50% of the total product might be attributed to this conformational interconversion with the rest proceeding via the *syn* species. However, if this were the case then an equal amount of *sr* and bond rotated α-pinene isomers should be formed, and this is not the case. Perhaps, at best, the extent of involvement of the equatorial substituted half chair diradical is measurable by the relative extent of formation of the bond rotated α-pinene isomer. This is probably less than 10% once there is consideration of the observed reformation of the *S* enantiomer of α-pinene.

Finally, it should be noted that the diradicals drawn in Scheme 5 may not be the actual structures responsible for products. They may merely represent a set of rapidly interconverting conformations of the diradicals. Hopefully detailed quantum mechanical calculations will reveal such

behavior. Lastly, there might be concern that the product distributions obtained in the pyrolyses are controlled by dynamic as opposed to statistical factors.[8] The nearly complete formation of racemic limonene would suggest a diradical intermediate which can partition to both enantiomers of limonene argues against dynamical control at least in the formation of dipentene. Further, there is no evidence for dynamical control on the ratio of retro-ene to retro 2+2 to racemized α-pinene products since differences in activation energies are primarily responsible for the distribution. Nonetheless, it could be argued that the α-pinene stereoisomer distribution is dominated by dynamical factors since it has not be ruled out by a direct experiment which, unfortunately, would require examining the stereoisomer distribution as a function of temperature. A sufficiently precise distribution has been difficult to obtain, vide infra.

## 3. Summary

The stereochemistry of the 1,3-shift which thermally racemizes α-pinene is most easily rationalized by simultaneous formation of two extreme conformations of a diradical. One diradical is responsible for inversion at the migrating carbon in the 1,3-shift as well as the formation of racemic dipentene and of ocimine. The other is responsible for retention at the migrating carbon in the 1,3-shift as well as for the interconversion of the two stereoisomers of the other diradical when substituted with both methyl and trideuteriomethyl groups but not for formation of dipentene and ocimine due to geometric constraints (see Scheme 5).

## 4. Experimental

### 4.1. General

$^1$H NMR spectra were obtained on a Nicolet 360 MHz and a Varian VXR 400 (400 MHz) spectrometer. Chemical shifts are reported in delta units relative to TMS in chloroform-d solution where chloroform-h is the reference, which is assumed to be at delta 7.28 ppm. Capillary gas chromatography was performed on a Varian 3700 FID gas chromatograph equipped with a 30 m×0.25 mm DB-5 fused silica capillary column. A Hewlett Packard 3390A was used for electronic integrations. Preparative GC was performed using a Varian 4700 gas chromatograph equipped with a thermal conductivity detector and a 15 ft, 1/4 in. column packed with 20% Carbowax 20 M on 60/80 mesh Chromosorb P. Starting 1*S*-(−)-β-pinene (99%) and other reagents were purchased from commercial sources and used without further purification. The solvents used were dried and distilled by standard procedures. All glassware for addition reactions was flame-dried under vacuum with an $N_2$ purge.

**4.1.1. Pyrolyses of α-pinene.** 'Gold label' (1*S*)-(−)-α-pinene (Aldrich) was distilled from lithium aluminum hydride under nitrogen and used directly. The pyrolysis apparatus has been described previously.[6] Analyses were performed by capillary GC and reported in Table 1. The products were separated on the Carbowax 20 M column. In order of increasing retention times the $^1$H NMRs are: α-pyronene, δ 0.86 (d, *J*=7.0 Hz, 3H), 0.96 (s, 3H), 0.97 (s, 3H), 1.69 (q, *J*=7.0 Hz, 1H), 1.76 (s, 3H), 5.25 (d, *J*=9.4 Hz, 1H), 5.51 (d, *J*=5.0 Hz, 1H), 5.72 (dd, *J*=9.4, 5.0 Hz, 1H); α-pinene, δ 0.84 (s, 3H), 1.17 (d, *J*=8.5 Hz, 1H), 1.27 (s, 3H), 1.64–1.70 (m, 3H), 1.90–1.98 (m, 1H), 2.04–2.38 (m, 1H), 2.17–2.20 (m, 1H), 2.20–2.25 (m, 1H), 2.30–2.38 (m, 1H), 5.17–5.22 (m, 1H); dipentene, δ 1.40–1.55 (m, 2H), 1.66 (s, 3H), 1.75–2.20 (m, 5H), 1.73 (s, 3H), 4.7 (m, 2H), 5.41 (d, *J*=2.1 Hz, 1H); alloocimine, δ 1.75 (d, *J*=7 Hz, 3H), 1.80 (s, 3H), 1.81 (s, 3H), 1.85 (s, 3H), 5.39 (q, *J*=7 Hz, 1H), 5.95 (dd, *J*=9.4, 1.2 Hz, 1H), 6.35–6.55 (m, 2H).

A 0.081 g sample of dipentene obtained from a pyrolysis of 91.2% ee (1*S*)-(−)-α-pinene at 256.7°C for 2400 s was diluted to 1 mL with cyclohexane. GC analysis showed the dipentene to be 99.1% pure, and $[\alpha]_D^{27}=-3.98°$.

**4.1.2. Pyrolysis of α-pinene-9(*syn*)-$d_3$.** Pyrolysis of α-pinene-9(*syn*)-$d_3$[12] at 256.7°C for 2400 s followed by preparative GC separation provided dipentene and alloocimine. Dipentene DMR (carbon tetrachloride): δ 4.67 (s, 4.00D), 1.90 (d, *J*=1.4 Hz, 1.92D), 1.64 (s, 2.88D). In the deuterated alloocimine, the 1.80 ppm resonance line is a shoulder on the 1.81 ppm signal which, with Gaussian deconvolution, provides a integral of ca. 1:5, respectively, but with an uncertainty estimated to be 40%. The proton resonance lines were assigned by a 2D correlation with the carbon-13 resonances of the methyls which could be assigned—see text.

**4.1.3. Pyrolysis of optically active *S*(−)-α-pinene-9(*syn*)-$d_3$.** Pyrolysis of optically pure *S*(−)-α-pinene-9(*syn*)-$d_3$[12] was conducted on 50–100 mL samples at 256.7°C which were removed after 3600 s. The samples were then diluted with 100 μL of cyclohexane and separated on a GC column packed with α-cyclodextrin on celite prepared by the method of Sybilska and Koscielski[13] as follows: α-Cyclodextrin hydrate (4.77 g) (Aldrich) was suspended in 10 mL of distilled water, then mixed with 11.7 g freshly distilled formamide and stirred. Distilled water was added until the α-cyclodextrin completely dissolved. The solution was added slowly to 45 g 80–100 mesh celite (Alltech Gas chrom S) in a 250 mL flask under vigorously shaking. After being subjected to rotatory evaporation at 50°C overnight under aspirator vacuum, the solid was used to pack an 18 ft×1/4 in. copper column which was conditioned overnight at 70°C. GC separation was accomplished by injecting 70 μL samples of the pyrolysate in cyclohexane into the column which was operated at 65°C. The injector temperature was 160°C and the detector temperature was 200°C. Near baseline separation between the pinene enantiomers was achieved (at 20ψ He flow, the retention times were 27 and 46 min for the *R* and *S* enantiomers, respectively; however, the peaks were broad).

The ratio of enantiomers was achieved by weighing the peaks in the chromatogram, Fig. 1.

### 4.2. NMR analysis of the enantiomers

The distribution of *anti* and *syn* deuterium labeled isomers

was determined by integration of methyl singlets at 1.28 and 0.85 ppm, which are the *anti* and *syn* methyls, respectively, Fig. 2. Spectra were phased, but not base-line corrected. In the case of overlapping impurity peaks, the integration value of each peak was determined by deconvolution or by subtraction of spectra of solvents. The integration results were compared with values obtained after applying resolution-enhancing filter (combination of gaussian, shifted gaussian, exponential, sine, sine squared, and shifted sine functions) to the Free Induction Decay.

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