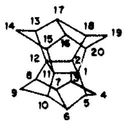
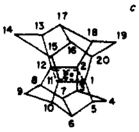
Table I. ^{1}H and ^{13}C NMR Spectroscopic Data on Pagodane (1) and Pagodane Dication (5)

structure	^1H, δ[a]	^{13}C, δ[a]
	[b] H_4,H_9,H_{14},H_{19} = 1.58 (AB, 8 H); $H_3,H_5,H_8,H_{10},H_{13},H_{15},H_{18},H_{20}$ = 2.24 (br, 8 H); H_6,H_7,H_{16},H_{17} = 2.60 (br, 4 H)	C_1,C_2,C_{11},C_{12} = 62.8 (s); C_6,C_7,C_{16},C_{17} = 59.6 (d, J_{C-H} = 137.8 Hz);$C_3,C_5,C_8,C_{10},C_{13},C_{15},C_{18},C_{20}$ = 42.6 (d,J_{C-H} = 140.6 Hz); C_4,C_9,C_{14},C_{19} = 41.9 (t, J_{C-H} = 129.8 Hz)
	[c] H_4,H_9,H_{14},H_{19} = AX spin system; H_{endo} = 3.68 (d, J_{H-H} = 13.2 Hz, 4 H);[d] H_{exo} = 2.72 (d, J_{H-H} = 13.2 Hz, 4 H);[d] H_6,H_7,H_{16},H_{17} = 2.39 (br, 4 H); $H_3,H_5,H_8,H_{10},H_{13},H_{15},H_{18},H_2O$ = 3.37 (br, 8 H)	C_1,C_2,C_{11},C_{12} = 251.0 (s); C_4,C_9,C_{14},C_{19} = 65.3 (t, J_{C-H} = 141.9 Hz); $C_3,C_5,C_8,C_{10},C_{13},C_{15},C_{18},C_{20}$ = 57.2 (d, J_{C-H} = 148.0 Hz); C_6,C_7,C_{16},C_{17} = 52.3 (d, J_{C-H} = 152.8 Hz)

[a] Chemical shifts are in ppm from external capillary tetramethylsilane. [b] In $CDCl_3$ solution at 25 °C. [c] In SbF_5/SO_2ClF solution at −80 °C. [d] Endo and exo assignments are only tentative. Multiplicities: s = singlet, d = doublet, t = triplet, br = broad.

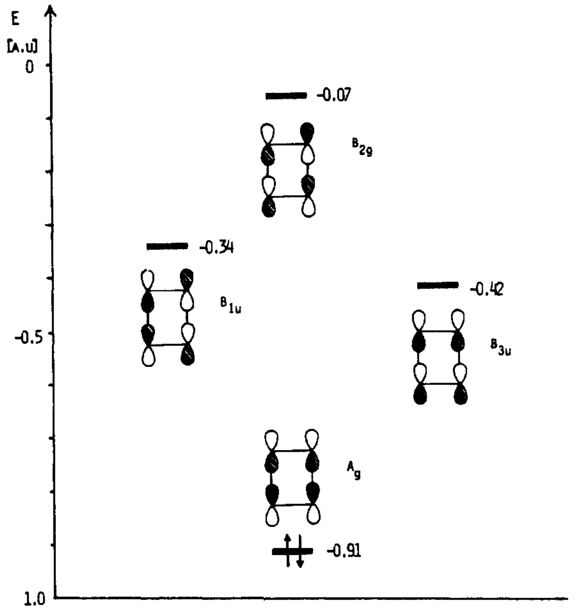


Figure 2. MO diagram of distorted cyclobutane dication.

for such a structure 5 also comes from the MINDO/3 theory. Olah, Schleyer, and Dewar[11] in 1973 rationalized the stability of the related 1,4-bicyclo[2.2.2]octanediyl dication[12a] through such pseudo-2π aromatic overlap.

We also carried out ab initio calculations at the STO-3G level[12b,c] on the parent cyclobutane dication. To simulate the strain, which is imposed by the pagodane framework, the geometry was optimized in a D_{2h} symmetry. The calculations reveal that the cyclobutane dication has a rectangular structure 9. The shorter C–C bonds with 1.447 Å in 9 seem to indicate a bond order between C–C single and C–C double bonds, whereas the other two bonds with considerably longer length (2.020 Å) imply a bond order around 0.5 (i.e., less than a C–C single bond). In contrast to the well-known cyclobutadiene dication,[13] the π-orbitals which are delocalized lie in the plane of the cyclobutane ring (structure 5a). The π-MO's of 9 are shown in Figure 2 with lowest bonding MO occupied with 2 electrons which provide the aromatic stabilization.

An accessible experimental test for aromatic system is the detection of a ring current. A ring current effect in the pagodane dication seems to be indicated at positions 6,7 and 16,17. Both ^{1}H and ^{13}C NMR shifts at these positions are shielded compared to pagodone (by 7.3 ppm for carbons and 0.21 ppm for the protons). It is noted that the cyclobutanoid carbons in 5 are much more deshielded than those observed in the isoconjugate tetramethylcyclobutadiene dication[13] (by 41.3 ppm). However, it is improper to compare these chemical shifts in view of the different types of π-bonding. We are continuing our studies to find other examples of 2π-aromatic dications in similarly disposed cyclobutane-containing system.[14,15]

Acknowledgment. Support of this work at USC by the National Science Foundation is gratefully acknowledged. R.H. thanks the Alexander von Humboldt Foundation for a Feodor Lynen Fellowship.

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(11) Olah, G. A.; Liang, G.; Schleyer, P. v. R.; Engler, E. M.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6829.

(12) (a) The assumed long-lived 1,4-bicyclo[2.2.2]octanediyl dication has been recently reinvestigated and found to be only the monocation monodonor acceptor complex: de Meijere A.; Schallner, O.; Gölitz, P.; Weber, W.; Schleyer, P. v. R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.*, in press. Nevertheless the theoretical argument put forward in ref 11 seems valid in regard to the presently studied pagodane dication: (b) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) Binkley, J. S.; Whiteside, R. A.; Krishnan, R.; Seeger R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406. Van Kamper, P. N.; Smiths, G. F.; De Leeuw, F. A. M.; Altona, C. *QCPE* **1982**, *14*, 437.

(13) Olah, G. A.; Staral, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 6290 and references cited therein. The cyclobutanoid carbons in tetramethylcyclobutadiene dication are observed at δ ^{13}C 209.7.

(14) Cyclic voltammetric measurements (SO_2, −40 °C, TBA·PF_6) reveal an ECE mechanism for the oxidation of 1 to a dication at 1.2 V (vs. Ag/AgCl). 1 reacts with tris(*p*-bromophenyl)amminium hexachloroantimonate or with bromine ($CDCl_3$, 20 °C) to give exclusively the dichloride 7 (X = Cl) and the dibromide 7 (X = Br), respectively. Their ^{1}H and ^{13}C NMR spectra strongly support the assignment of the dimethoxy/dihydro structures 7 (X = OCH_3/H) (Prinzbach, H.; Bulusu, A. R. C. M.; Fessner, W.-D.; Heinze, J.; Mortensen, J., unpublished results).

(15) 1e$^-$ oxidations on strained σ-bonds are known: Gassman, P. G.; Olson, K. D. *J. Am. Chem. Soc.* **1982**, **104**, 3740.

Gas-Phase Pyrolysis of Isotopically and Stereochemically Labeled α-Pinene: Evidence for a Nonrandomized Intermediate

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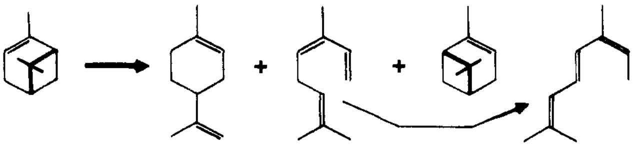
Liquid- and gas-phase pyrolysis of α-pinene leads to dipentene (racemic limonene), alloocimine (the 1,5-hydrogen shift product of ocimine, the likely primary product), and enantiomeric α-pinene. These materials are derived by retro-ene, retro 2 + 2, and 1,3-sigmatropic shift reactions, respectively. The mechanistic question is whether all three are separate, perhaps concerted processes, or if there is a common biradical intermediate.

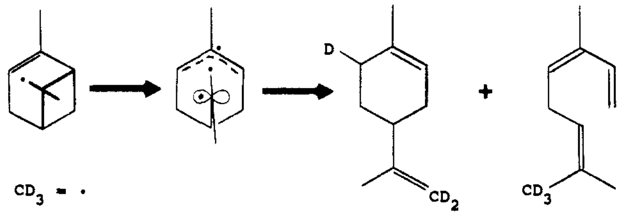


The original (liquid phase) kinetics were reported by Fuquitt and Hawkins[1] who found first-order behavior for all three reactions. A common biradical intermediate was proposed by Burwell.[2] This interpretation was popularized by Frost and Pearson[3] despite the very low activation energy and preexponential term for the formation of dipentene ($\log k = 11.47 - 37000/2.3RT$). Finnish workers studied the reaction in the gas phase and obtained different activation parameters, specifically, a higher activation energy and entropy for the formation of dipentene $\log k(\text{dipentene}) = 13.30 - 40900/2.3RT$ and $\log k(\text{alloocimine}) = 14.70 - 44500/2.3RT$; these workers did not examine the racemization reaction.[4] We report here a reinvestigation of the gas-phase kinetics, including that for racemization, as well as a study of the primary hydrogen isotope effect in the kinetics of formation of products and the position of the label in the major products.

Pyrolyses of (−)-(*S*)-α-pinene (91.2 ± 0.1% optically pure) were conducted in the vapor phase in a vessel pretreated with dichlorodimethylsilane then with diisopropylamine. Without this conditioning, a myriad of products, presumably the same as those observed on GC injector pyrolyses,[5] were observed. Often rate constants drifted upward with concomitant formation of additional products, but the rate constants could be restored to the reported values by reconditioning. The temperature dependence of the rate over a 30 °C range led to the Arrhenius parameters $\log k(\text{dipentene}) = 13.70\ (\pm 0.1) - 42000\ (\pm 200)/2.303RT$, $\log k(\text{alloocimine}) = 14.40\ (\pm 0.1) - 44000\ (\pm 200)/2.303RT$, and $\log k(\text{enantiomer}) = 14.5\ (\pm 0.9) - 45200\ (\pm 2000)/2.303RT$, where the error limits are one standard deviation. The racemization was followed by GC on an α-cyclodextrin column.[6] The limonene formed had $[\alpha]_D$ −4°; thus, 4% of the *S* enantiomer and 96% of a racemic mixture (dipentene) were formed. It is important to note that the Arrhenius parameters for formation of dipentene are higher than in all previous reports.

When *syn*-7-(trideuteriomethyl)-α-pinene[8] was pyrolyzed at 256.7 °C, the rate of loss of starting material slowed by only 15 ± 15%, yet the ratio of dipentene to alloocimine dropped by a factor of 1.70 (±0.05). Since a primary hydrogen isotope effect is expressed in the product distribution but not in the rate, there must be an intermediate formed after the rate-determining step unless there is an unprecedented inverse kinetic isotope effect on the retro 2 + 2 reaction. The slight rate retardation is probably the result of some additional reclosure of the intermediate back to α-pinene, a reaction of significance as judged by its occurrence with a rate roughly 15% that of the other two processes.

A biradical is the likely intermediate for the two major processes, so its structure is of concern. Three observations bear on this question: (a) the dipentene is nearly racemic; (b) the deuterium distribution in the dipentene reveals that twice as much deuterium is transferred as hydrogen; (c) the alloocimine has more than 90% of the deuterium in the *Z* methyl group.[9] The preferential transfer of deuterium is unprecedented *if both C-6 methyls were equally disposed to transfer hydrogen.* It can only be concluded that the syn methyl resides over the allylic radical on the bisector of this necessarily achiral species.



Simple stretching of the C-1,C-6 leads to nearly the correct biradical geometry. What little twist is necessary about the C-5,C-6 bond is in the same sense as in all cyclobutane ring openings that appear to be nonconcerted on the basis of activation energies being comparable to the estimated dissociation energy of the bond being broken.[10] While not specifically determined, the stereomode of the 1,3-shift to give enantiomerized α-pinene is probably the suprafacial-inversion mode if the biradical described above closes to the 1,3-shift product with least motion control. The observation of such stereochemistry, however, could not be attributed to conservation of orbital symmetry in a concerted reaction unless such control is expressed in the ring opening only and is relinquished necessarily, vide infra, in the form of an intermediate whose least motion ring closure would give what would appear to be the "allowed" product. Such an ad hoc rationalization, however, could not be applied to the suprafacial-inversion 1,5-carbon shift in bicyclo[4.1.1]octa-2,4-diene.[8]

Acknowledgment. We thank the National Science Foundation for generous financial support, Prof. W. T. Borden for experimental details to prepare the trideuterio-α-pinene, Professor P. Magnus for nopinone, and Prof. W. R. Dolbier, Jr., for a copy of Dr. Fuguitt's Ph.D. Thesis at the University of Florida.

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(3) Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; pp 373–378.

(4) Riistoma, K.; Harva, O. *Finn. Chem. Lett.* **1974**, 132.

(5) Crowley, K. J.; Traynor, S. C. *Tetrahedron* **1978**, *34*, 2783.

(6) Sybilska, D.; Koscielski, T.; Jurczak, J. *J. Chromatogr.* **1983**, *280*, 131. Sybilska, D.; Koscielski, T. *J. Chromatogr.* **1983**, *261*, 357.

(7) Aldrich Catalog/Handbook of Fine Chemicals, 1984–1985.

(8) Borden, W. T.; Lee, J. G.; Young, S. D. *J. Am. Chem. Soc.* **1980**, *102*, 4841.

(9) The double bond in allocimine is *E* as judged by the large proton coupling constant. A heteronuclear 2D NMR experiment revealed that the upfield methyl ^{13}C resonance was associated with the deuterium, and the *Z* methyl resonance is normally the upfield one. Further, the proton resonances of the double-bond methyl groups have been assigned in a variety of related materials (Bellamy, A J.; Crilly, W. *J. Chem. Soc., Perkins Trans. 2* **1973**, 122] and are consistent with the assignments above.

(10) Gajewski, J. J. "Hydrocarbon Thermal Isomerizations"; Academic Press: New York, 1981; p 220.

A Transacylase Partial Mimic[1]

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The serine transacylases combine a complexing site with three cooperating functional groups: a serine hydroxyl, a histidine imidazole, and an aspartate carboxyl. In past work, compounds **1** and **3** were prepared in an incremental approach to serine transacylase mimics.[2] Compound **3** in $CDCl_3$ with R_3N–R_3NHClO_4 buffer at 25 °C reacted with **8** with an estimated second-order rate constant $\sim 10^{11}$ times that of nonbonding model compound **9**. A thirty-step synthesis of **5** has now been completed which also provided **4**, **6**, **7**, and **11**. Other studies provided **2**.[4]

Here we report that **5** and **9** very rapidly reacted at 0.012 M in 20% pyridine-d_5–80% $CDCl_3$ (by volume) to produce **12**, which $\sim 10^2$ more slowly gave **13**.[5] Only the N-3 nitrogen of the imidazole can accept and donate the acyl group without strain in the **5·8** complex (CPK molecular model examination).[6,7] Table

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(1) We thank the U. S. Public Health Service for Grant GM 12640, which supported this research.

(2) (a) Cram, D. J.; Katz, H. E. *J. Am. Chem. Soc.* **1983**, *105*, 135–137. (b) Cram, D. J.; Katz, H. E.; Dicker, I. B. *Ibid.* **1984**, *106*, 4987–5000.

(3) Cram, D. J.; Lam, P. Y.-S. *Tetrahedron*, in press.

(4) Miesch, M.; Cram, D. J., unpublished results, compound fully characterized.

(5) Formation and disappearance of **12** was followed at 25 °C with the ^1H NMR signal at δ 8.52 due to the C-2 proton of acylated imidazole.

(6) Attempts to isolate **13** free of hydrolysis product failed, although a FAB-MS (Xe) of impure **13** gave a strong peak for **13** + H_2O − ClO_4.

0002-7863/86/1508-0839$01.50/0