

PYROLYSIS OF STEREOTOPICALLY TWISTED CYCLOBUTANE RINGS. STEREOCHEMISTRY OF THE THERMAL CLEAVAGE OF ISOMERIC 5,6-DIMETHYLBICYCLO[2.1.1]HEXANES TO 2,6-OCTADIENES

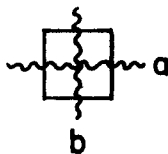
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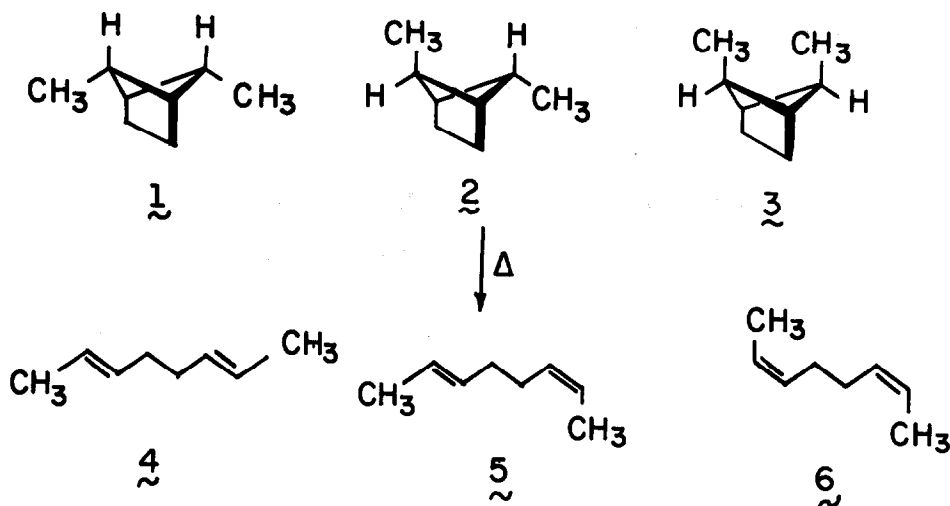
Cyclobutane derivatives which can adopt a planar or nearly planar conformation seemingly experience thermal fragmentation via singlet 1,4-diradical intermediates.^{2,3} In contrast, quantum mechanical considerations denote that the geometry associated with severely twisted four-membered rings is highly favorable to the operation of the concerted [$\sigma_a^2 + \sigma_b^2$] pathway.⁴ If 1,4-butanediyl formation were circumvented in such systems, then appropriate stereochemical labeling should give evidence of inversion at one constituent ring carbon and retention at the remaining three.

To test this theory most simply, it would be advantageous if one of the two possible modes of cleavage of the four-membered ring could be maximized relative to the other. Far better,



however, is the situation in which the twisted cyclobutane is provided with sufficient symmetry to render paths a and b equivalent. These conditions are met in the stereoisomeric 5,6-dimethylbicyclo[2.1.1]hexanes 1-3, the fragmentations of which were considered destined⁵ to give rise to one or more of the three possible 2,6-octadienes (4-6) of well established configuration.⁶

Efficient synthesis of a mixture of 1 (30%) and 2 (70%) began with the convenient triplet-sensitized photocyclization of dimethyl octa-2,6-diene-1,8-dioate to the stereochemically related bicyclic esters.⁷ Lithium aluminum hydride reduction and reaction with methanesulfonyl chloride in pyridine led to the epimeric dimesylates, final hydride reduction of which gave the hydrocarbons. These were readily separated on a 20% β, β' -oxydipropionitrile column at 60°. ⁸



Stereospecific synthesis of $\underset{\sim}{3}$ was achieved by sequential ozonolysis and esterification of $\underset{\sim}{1}$,⁹ followed by a comparable three-step reduction of the resulting diester (8).⁸

The gas-phase pyrolyses were conducted to partial completion (Table I) in a Vycor reactor packed with quartz chips at temperatures of approximately 385° and atmospheric pressure (N_2 flow rate 7 ml/min, residence time ca 3 min). Not unexpectedly, the reactivity order ($\underset{\sim}{3} > \underset{\sim}{2} > \underset{\sim}{1}$) parallels the strain inherent in the individual isomers. The experimental results reveal further the operation of configurational inversion at one of the substituted carbons in $\underset{\sim}{1}$ - $\underset{\sim}{3}$, the extent of which at 385-386° likewise increases incrementally with added steric strain. These isomerizations can plausibly arise by homolytic cleavage of a cyclobutane bond with formation of a diradical capable of experiencing bond rotation-cyclization at a rate decidedly competitive with diene formation. The efficiency with which these diradicals undergo cyclization despite adverse strain factors is qualitatively concordant with the low degree of through-bond coupling¹⁰ arising from the rigid geometry structurally enforced upon these intermediates.

Although the mixtures of dienes produced upon pyrolysis of $\underset{\sim}{1}$ and $\underset{\sim}{2}$ are indistinguishable within experimental error, $\underset{\sim}{3}$ gives rise to significantly greater quantities of cis,trans-diene $\underset{\sim}{5}$ and lesser amounts of cis,cis isomer $\underset{\sim}{6}$. These results suggest that $\underset{\sim}{1}$ and $\underset{\sim}{2}$ undergo initial fragmentation to give trans diradical $\underset{\sim}{9}$ while $\underset{\sim}{3}$ gives cis diradical $\underset{\sim}{10}$. That $\underset{\sim}{2}$ undergoes preferential C-C bond cleavage to $\underset{\sim}{9}$ is suggested by the fact that this hydrocarbon

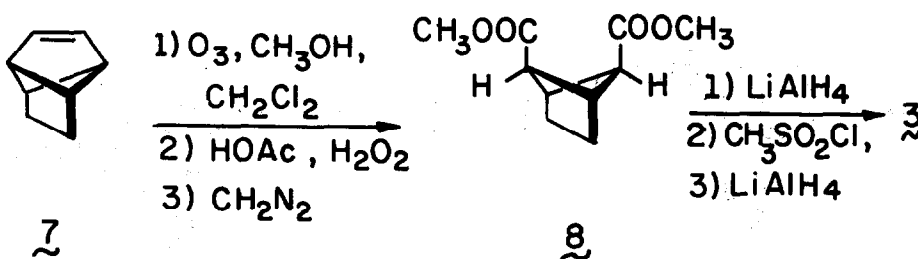


Table I. Pyrolysis Products

Reactant	Temp, °C	Bicyclic-diene ratio	Recovered bicyclics, % ^b			Dienes, % ^{c,d}		
			<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
<u>1</u>	385 ^a	92:8	95	5	--	59	30	11
<u>2</u>	385 ^a	77:23	15	85	--	63	28	9
<u>3</u>	382	67:33	--	47	53	57	39	4
	386	54:46	--	55	45	56	39	5
	390	49:51	--	62	38	57	38	5

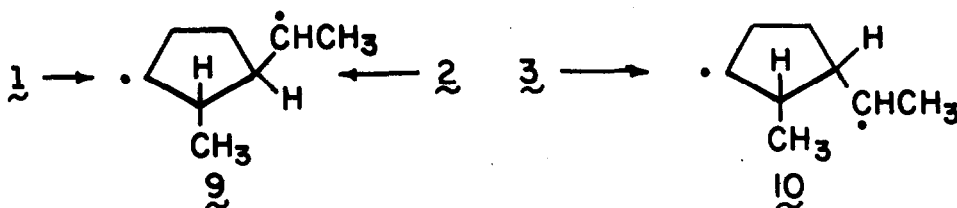
^aAverage of two independent runs. ^bCompositions determined through a combination of vpc analysis on a 20 ft x 0.25 in column packed with 20% β, β' -oxydipropionitrile at 60° and nmr techniques. ^cAnalyses achieved by an adaptation of the method described in ref. 6.

^dControl experiments with 4-6 indicated no significant isomerization of the t,t and c,t isomers, but 2% conversion of 6 chiefly to 4. Since 6 is a minor product, the contribution of this thermal isomerization to the final diene composition is minimal (see also ref 6).

fails to generate 3 and fragments to a mixture of dienes similar to that obtained from 1.

Also, its conversion to the trans diradical relieves more strain than formation of the cis diradical. Rotation about the $\text{>CH}-\overset{\bullet}{\text{C}}\text{HCH}_3$ bond in 9 and 10 leads to loss of stereochemistry at one center while inversion of the trigonal ring carbon atom leads to ultimate loss of stereochemistry at the second double bond.

The comparable (after allowance is made for strain differences) activation energies for the fragmentation of bicyclo[2.1.1]hexane (55.9 kcal/mol)⁵ and cyclobutane (62.5 kcal/mol)¹¹ attest to the absence of a kinetic advantage in the first instance. Thus, even when the cyclobutane ring is prestrained in a highly energetic torsional sense, the symmetrical stretching of two diametrically opposed bonds to give rise in concert to two olefin components



does not operate. Consequently, that idealized geometric situation where the axes of the developing π orbitals are pretwisted orthogonally with respect to the breaking bonds remains inadequate to promote the incursion of the ($\sigma_a^2 + \sigma_s^2$) cycloreversion. Interestingly, the microscopic reverse of the pyrolysis reaction reported here has recently been found to obtain in the thermal cyclization of 1,8-divinyl naphthalenes to twisted cyclobutanes via diradical intermediates.^{12,13}

FOOTNOTES AND REFERENCES

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