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MECHANISMS OF THERMAL REARRANGEMENTS OF BICYCLO[3.2.1]OCTA-2,6-DIENES; STERIC EFFECTS AS A TOOL TO DISTINGUISH BETWEEN COMPETING PERICYCLIC AND DIRADICAL PROCESSES

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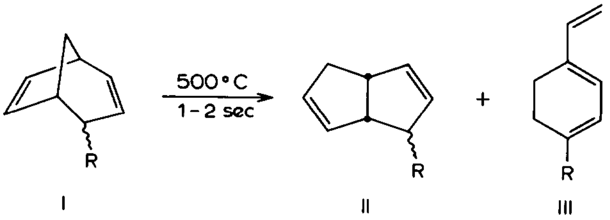
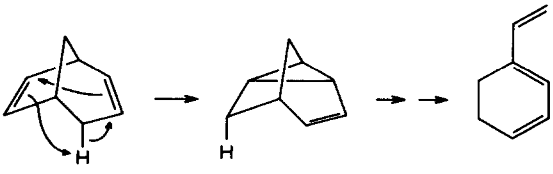
In order to gain some insight into the mechanisms of the thermal transformations I ⟶ II and I ⟶ III[1] the rearrangements of several substituted bicyclo[3.2.1]-octa-2,6-dienes were studied. Results are given in Table 1.



a: R = D
b: R = CH_3
c: R = cyclo-C_3H_5

Upon exposure to the reaction conditions products were not affected to more than a few percent. The pronounced differences of the product ratios observed with epimeric pairs of starting materials (entries 2 and 3, 4 and 5) show that under the conditions of reaction these materials do not equilibrate with each other faster than they react, and that the role of intermediates common to the reaction paths of both epimers must be relatively unimportant. Substrates lacking an endo-hydrogen at C-4 do not yield III. It is most probable therefore that the formation of III starts with a homo-[1,5]-hydrogen shift:



IV

The known[2] thermal rearrangement of tricyclo[3.2.1.0^{2,7}]oct-3-ene (IV) to vinylcyclohexadiene was proven to occur under the conditions of the transformation I → III. Thermolysis of bicyclo[3.2.1]octa-2,6-diene deuteriated specifically at the 3-position did not yield bicyclo[3.3.0]octa-2,6-diene carrying deuterium at the bridgehead positions. This observation excludes the intermediacy of 3,4-homotropilidenes, which are known to form bicyclo[3.3.0]octadienes[3] and which, in the present case, would have resulted from [1,3]-migration of C-8. The result is in accord however with [1,3]-migration of C-4.

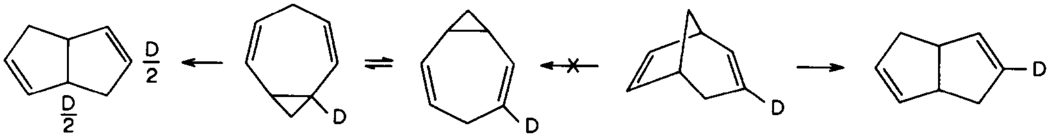


Table 1[*]

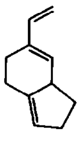
Entry	Substrate	II			III
		% of product mixture	$\frac{\text{endo-II}}{\text{exo-II}}$	$\frac{\text{inversion}}{\text{retention}}$ at C-4	% of product mixture
1	exo-Ia	ca. 40	1.85	1.85	ca. 30
2	exo-Ib	ca. 3	[**]	--	ca. 97
3	endo-Ib	ca. 100	0.43	2.3	--
4	exo-Ic	ca. 20	0.8	0.8	[***]
5	endo-Ic	ca. 85	0.43	2.3	--

[*] Details of syntheses and proofs of structure will be given in the full paper.

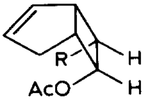
[**] Not determined.

[***] The main product (80%, tentative structure i) is assumed to have resulted from further rearrangement of IIIc.

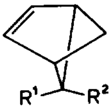
Contrary to the profound changes in the inversion:retention ratio that are caused by the substitution of an <u>endo</u>-hydrogen by an <u>endo</u>-methyl group on the migrating carbon atom in corresponding rearrangements of bicyclo[3.2.0]hept-2-enes[4] and bicyclo[2.1.1]hex-2-enes[5], such substitution hardly affects the



i



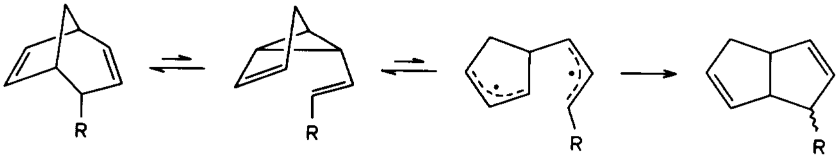
	inversion:retention
R = H :	19 : 1
R = CH_3:	1 : 7



	inversion:retention
R_1=H, R_2=CH_3:	197 : 1
R_1=CH_3, R_2=H:	2.2: 1

stereochemistry of the rearrangement I ⟶ II. Also, no change in stereoselectivity is observed on going from endo-4-methyl to endo-4-cyclopropyl. Their different response to variation of steric effects therefore seems to place the thermal [1,3]-carbon shifts of I into a mechanistic class, different from that of the [1,3]-carbon shifts of bicyclo-[3.2.0]hept-2-enes and of bicyclo[2.1.1]hex-2-enes. Whereas in the latter cases competing reaction pathways of the Woodward-Hoffmann and the Berson-Salem type may be invoked (those of the Berson-Salem type being less prone to steric hindrance and therefore gaining in importance on going to the endo-methyl derivatives)[6] the present results are more in line with a diradical mechanism. In the reactant-like transition states that interconnect diradicals and II steric effects are expected to play a minor role.

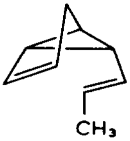
Below, a possible reaction mechanism is depicted, which leads, stereospecifically, from endo-I to diradicals VI, carrying R in the trans-position. The transition states leading from VI to II are expected to show little response to variation of R.[7]



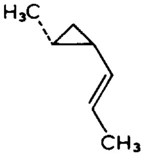
I V VI II

The Cope-rearrangement of V to I is well-known[8]. At the temperatures used in the present investigation it can be expected to be reversible. V thus formed can undergo homolysis of its activated cyclopropane bond thereby producing diradicals VI. It was found[9] that at higher temperatures (ca. 400°C) the Cope-rearrangement of (cis-R)-V loses some of its stereospecificity. Apparently unfavorable steric effects in the transition state of the concerted rearrangement lead to the emergence of less specific diradical processes. Since the reverse reaction exo-Ib(c) ⟶ V must be affected similarly the stereoselectivities of the transformations exo-Ib(c) ⟶ IIb(c) are not amenable to interpretation, since mixtures of *cis*- and *trans*-diradicals may be formed[10].

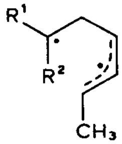
Concerning the transformation V$\longrightarrow$II competing one-step processes of the antarafacial/retention (a/r) type (Woodward-Hoffmann) and of the suprafacial/retention (s/r) type (Berson-Salem) might be invoked as an alternative to the diradical mechanism proposed. The inversion:retention ratios given in Table 1 would then correspond to the ratios a/r:s/r. Assuming again, that a/r and s/r transition states are apt to respond to changes in R quite differently, we are inclined to uphold our diradical hypothesis. It is noteworthy that in the vinylcyclopropane-cyclopentene rearrangement of *trans*-1-methyl-2-(*trans*-1-propenyl)-cyclopropane a very similar ratio of a/r:s/r has been found.[11]



a/r:s/r
1:2,3



a/r:s/r
1:2,75



A

The near-equality of these ratios raises the question, whether both systems initiallyy yield the same type of diradical (A), whose partitioning among the various possible pathways of cyclisation is rather independent of the nature of R^1 and R^2.[12]

References

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2) W.R. Roth and B. Peltzer, Ann., 685, 56 (1965).
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4) J.A. Berson and G.L. Nelson, J. Amer. Chem. Soc., 89, 5303, 5503 (1967).
5) W.R. Roth and A. Friedrich, Tetrahedron Letters, 1969, 2607.
6) J.A. Berson, Acc. Chem. Res., 5, 406 (1972).
7) For a reaction sequence encompassing the steps postulated here in reversed order, see: J.A. Berson, T. Miyashi, and G. Jones, J. Amer. Chem. Soc., 96, 3468 (1974).
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9) J. Japenga, Dissertation, Vrije Universiteit, Amsterdam, 1976; see also: J.M. Brown, Chem. Comm., 1976, 638.
10) Kinetic data of the related degenerate [1,3]-carbon shift in bicyclo[3.3.1]nona-2,6-diene (R. Bishop, W. Parker, and I. Watt, Tetrahedron Letters, 1977, 4345) are consistent with a diradical mechanism.
11) G.D. Andrews and J.E. Baldwin, J. Amer. Chem. Soc., 98, 6705 (1976).
12) Insensitivity of stereoselectivity towards variation of steric effects has also been observed (and ascribed to the intervention of diradicals) in the (2+2)-cycloaddition of benzyne to olefins: A.T. Bowne, T.A. Christopher, and R.H. Levin, Tetrahedron Letters, 1976, 4111.