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DIRADICALS IN THE VINYLCYCLOPROPANE REARRANGEMENT OF BICYCLO[3.1.0]HEXANE DERIVATIVES

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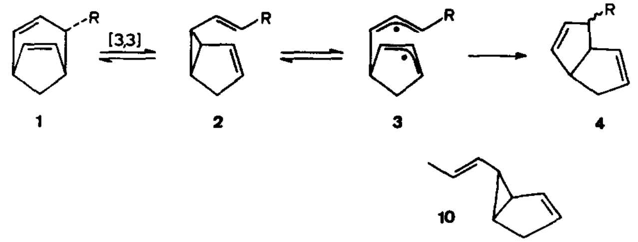
Abstract Product ratios and their insensitivity to steric effects indicate the title reactions to occur through diradicals with limited rotational freedom.

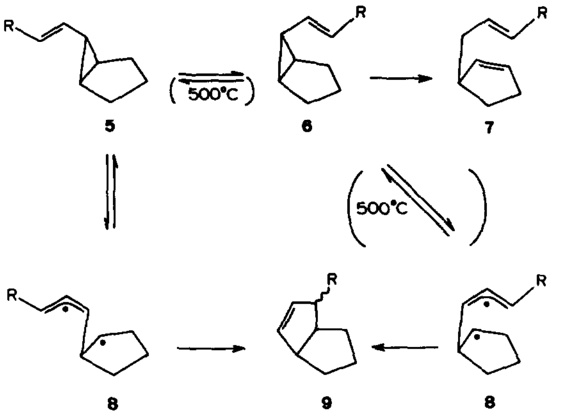
The mechanism of the thermal vinylcyclopropane rearrangement is still a matter of controversy.[1] The absence of steric effects that might be caused by substituents R of differing size has led us to suggest that diradicals 3a-c are intermediates in the rearrangement of 1 *via* 2 to 4 (see Scheme 1).[2]



a: R = D; b: R = Me; c: R = *cyclo*-C_3H_5; 500°C; 1-2 sec
Scheme 1

In order to narrow down the scope of such behaviour we have studied the thermolyses of 5 (Scheme 2). Diradicals 8 derived from these substrates are less stable than 3 and therefore concerted rearrangement might take over and manifest itself by substituent dependent stereoselectivity. For further reference 6b and 10 were studied, too. The results are given in Table 1.

At 325-350°C 5a-c rearrange to a 20:1 mixture of 7a-c and 9a-c (see entries 1-3). Geometric isomerisation to 6a-c is the fastest reaction of 5a-c; 7a-c arise from 6a-c by homo-[1,5] hydrogen shift. It was proven[3] that under the conditions of thermolysis the latter reaction quantitatively removes 6a-c. The minor products 9a-c must therefore be formed from 5a-c. At 500°C 9b was also obtained from 6b (see entry 5). The value *endo/exo* was the same as observed for 5b (entry 4), indicating that at 500°C 5 and 6 interconvert rapidly and that the Curtin-Hammett principle applies. In order to supplement our earlier work the system of Scheme 1 was extended by using the *trans*-divinylcyclopropane 10 as the starting material. At 325°C (1-2 sec) the main product was 1b resulting from geometric isomerisation of 10 to 2b followed by Cope-rearrangement. It was accompanied by a very small amount[4] of 4b in an *endo/exo* ratio that was closer to one than the one observed with 1b $\rightleftharpoons$ 2b at 500°C (see entries 6 and 7). Most probably reactions at 500°C are under Curtin-Hammett control, whereas at 325°C equilibrium between 2b and 10 is not established due to the irreversible conversion of 2b to 1b.



a: R = D; b: R = Me; c: R = i-Pr; 325-350°; 1h

Scheme 2

Table I Thermolysis products of 1b, 5a-c, 6b and 10[a]

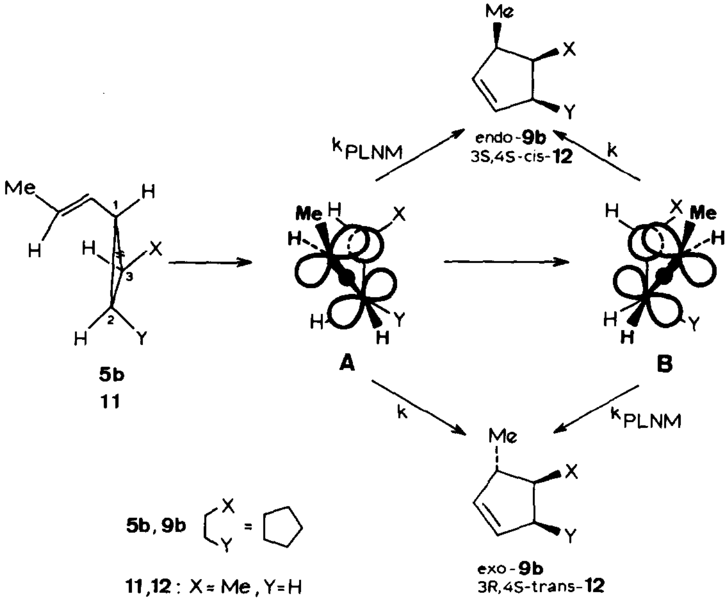
Entry	Substrate	Temp. °C	time	Products	%	*endo/exo*
1	5a	350	1h	7a	95	-
				9a	5	2.5/1
2	5b	350	1h	7b	95	-
				9b	5	2.6/1
3	5c	325	1h	7c	95	-
				9c	5	3.8/1
4	5b	500	1-2 sec	7b	75	-
				9b	25	2.1/1
5	6b	500	1-2 sec	7b	92	-
				9b	8	2.0/1
6	10	325	1-2 sec[b]	1b	>99.5	-
				4b	<0.5	1/1.2
7	1b	500	1-2 sec	4b	100	1/2.3

a: Entries 1-3: carried out in the gas phase in evacuated ampoules; entries 4-7: carried out in a flow system, as described elsewhere.[5]

b: Under these conditions 1b is stable

The near invariance of the stereoselectivity of the rearrangement 5a-c → 9a-c when R is changed from deuterium to isopropyl (Table 1, entries 1-3) indicates transition states which are little susceptible to the size of R. Diradicals 8 which would close to *endo*- and *exo*-9 *via* reactant-like transition states satisfy this condition. Product formation *via* competing concerted [1,3] carbon shifts is expected to show a decrease of *endo/exo* upon increase of the size of R (the *sr* transition state leading to *endo*-9 being more sensitive to steric hindrance by R than the *ar* transition state leading to *exo*-9)[6]

The moderate, yet nearly substituent-independent stereoselectivity of 8a-c is in line with the principle of least nuclear motion (PLNM). In Scheme 3 the operation of the PLNM is illustrated for the formation of 9b from two conformations, A and B, of 8b. Assuming that $k_{PLNM} : k$ of both A and B be greater than 1 the values of *endo/exo* (Table 1, entries 1-3) indicate that the mole fraction of 9 formed from 8A must be greater than 0.5 for any ratio $(k_{PLNM} : k)_A : (k_{PLNM} : k)_B$.[7] Thus it appears that the majority of diradicals 8A arising from 5 collapse to 9 *before* they can complete a rotation of more than 90°. [Homolysis of 5 with *anti*-clockwise internal rotation (of the diradicals as depicted in Scheme 3) is not expected to yield 9 but to result in geometric isomerisation, exclusively].[8,9] The partial conservation of optical activity observed for the rearrangement of (+)-(1S,2S)-*trans*-1-(*trans*-1-propenyl)-2-methylcyclopropane (11) by Andrews and Baldwin[10] has led these authors to propose that the four possible modes of concerted [1,3] carbon shift compete in this reaction.



Conformations A and B of diradicals involved in vinylcyclopropane rearrangements. A and B are viewed down the C^1C^2 bond axis shown in the starting cyclopropane. For the sake of clarity the circle denoting the rear atom in conventional Newman representation is omitted. The circle between H and X portrays the 2p orbital on C^3.

However, their results can also be accommodated by a scheme analogous to the one proposed for 5. In fact, the ratio of products that can be ascribed to PLNM controlled ring closure of diradicals A and B is very similar for 5b $[(endo\text{-}9b : exo\text{-}9b)_{350^\circ} = 2.6]$ and 11 $[(3S,4S\text{-}cis\text{-}12 : 3R,4S\text{-}trans\text{-}12)_{296.5^\circ} = 2.75]$. PLNM controlled five-membered ring formation competitive with internal rotation has been implied for orthogonal 2,2'-bis(allylmethane) formed on thermolysis of 1,3-dimethylene cyclopentane.[11]

References

1. *Cf*. J.J. Gajewski, Israel J. Chem. 21, 169 (1981).
2. J. Japenga, G.W. Klumpp, M. Schakel, Tetrahedron Letters 1978, 1869.
3. Independently synthesized 6a-c rearranged at 325-350°C exclusively and quantitatively to 7a-c.
4. Greater preference for 1,3-ring closure over 1,5-ring closure of 3 compared to 8 is also found if these diradicals (R=H) are generated from pyrazolines:
   M. Schneider, I. Merz, Tetrahedron Letters 1974, 1995;
   M. Schneider, G. Mössinger, Tetrahedron Letters 1974, 3081;
   M. Schneider, A. Erben, I. Merz, Chem. Ber. 108, 1271 (1975).
5. J. Japenga, G.W. Klumpp, M. Kool, Recl. Trav. Chim. Pays-Bas 97, 7 (1978).
6. *Cf*. J.A. Berson, G.L. Nelson, J. Am. Chem. Soc. 92, 1096, (1970);
   W.R. Roth, A. Friedrich, Tetrahedron Letters 1969, 2607.
7. $\gamma_A = \dfrac{(m+1)(n^{-1}-N)}{(N+1)(n^{-1}-m)}$, γ_A = mole fraction of product derived from A;
   $m = (k_{PLNM} : k)_A$; $n = (k_{PLNM} : k)_B$; $N = ([endo\text{-}9] : [exo\text{-}9])_{overall}$.
8. *Anti*-clockwise rotation moves CHMe to its maximal distance from CHX (see Scheme 3). Right after passing through this conformation overlap propitious to 1,3-closure starts to develop rapidly while CHMe and CHX are still far away from each other. Evidence suggesting that closure of 1,3-diradicals is fast compared with bond rotation is discussed in ref.1.
9. Another path to geometric isomerisation is provided by diradicals substituted *trans,trans* in their allylic side chain.
10. G.D. Andrews, J.E. Baldwin, J. Am. Chem. Soc. 98, 6705 (1976).
11. J.J. Gajewski, J.D.C. Salazar, J. Am. Chem. Soc. 103, 4145 (1981).

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