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THERMOLYSIS OF SPIRO[4.4]NONADIENE-1,3 AND SPIRO[4.5]DECADIENE-1,3

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As part of a study on the possible occurrence of thermal, suprafacial, sigmatropic 1,5 shifts of alkyl groups in geminally substituted cyclopentadienes (1,2) we report here the title reactions.

Spiro[4.4]nonadiene-1,3 (1a), diluted with nitrogen, is converted at 280°C - 380°C (residence times 30-140 sec) by first-order kinetics to one major (>90%, by GLC) product 2a, an isomer (by massspectrum). Spectral (UV: λ_{max} = 255.5 nm, ϵ = 2740 in isooctane; IR: characteristic absorptions of cyclopentadiene and cyclohexene rings; NMR: δ = 6.22-6.12 ppm, δ = 2.76 ppm, δ = 2.3-2.1 ppm, δ = 1.7-1.5 ppm, relative areas 2:2:4:4) and chemical (H_2, PtO_2 yields trans- and cishexahydroindane) evidence proves that 2a is 1,2-cyclopenta-1',3'-dienocyclohexene.

Spiro[4.5]decadiene-1,3 (1b), diluted with nitrogen, is converted at 380-445° (residence times 40-180 sec) by first-order kinetics to one major (90% by GLC) product 2b, an isomer (by massspectrum). Spectral (UV: λ_{max} = 246 nm, ϵ = 3050 in isooctane; IR: characteristic absorptions of cyclopentadiene and cycloheptene rings; NMR: δ = 5.90, δ = 2.77, δ = 2.42, δ = 1.65, relative areas 2:2:4:6) evidence shows that 2b is 1,2-cyclopenta-1',3'-dienecycloheptene.

The data yielded the activation parameters given in the Table.

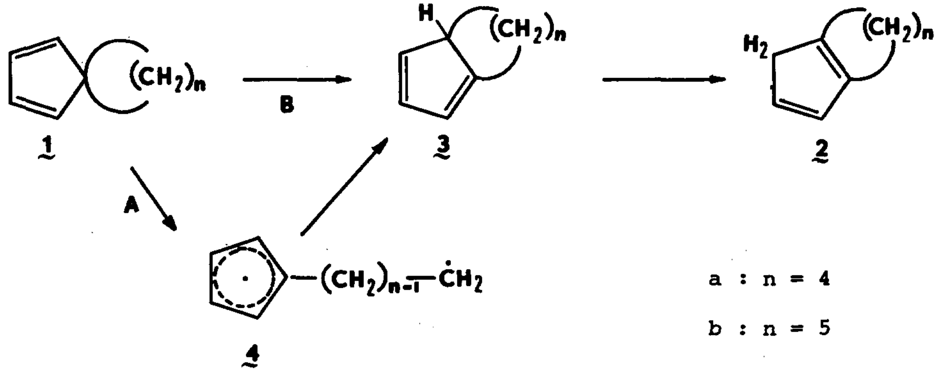
<u>Table.</u>

Reaction		^{10}log A	E_a (kcal/mol)	$\Delta H^{\neq}$ (kcal/mol)	$\Delta S^{\neq}$ (cal/mol.degr)	$\Delta G^{\neq}$ (kcal/mol)
1a	2a	13.32	35.6	34.6	-1	35.0
1b	2b	15.09	46.7	45.5	+6	41.8

Since 1,5 shifts of hydrogen in cyclopentadiene (3→2) are relatively fast (3), the observed rates and the crucial question on the mechanism of the isomerization of 1 pertain to the conversion of 1 into 3. Two possible processes are to be considered:

Path A: a two-step process involving ring opening to a biradical 4 followed by a ring closure.

Path B: a one-step sigmatropic reaction giving directly ring expansion.



a : n = 4

b : n = 5

In the preceding letter it was concluded that thermolysis of spiro [2.4] heptadiene-1,3 (1 with n=2) involves both paths A and B with, accidentally, comparable rates (in this case, n=2, path A does not lead to 3). The data on the energy of activation, $\Delta H^{\neq}$, and the rate (expressed as $\Delta G^{\neq}$ at 600°K) for 1 with n=2 will serve as a basis to discuss the present results.

We assume that the transition state for path A involves a total release of the ring strain associated with the (n+1) ring of 1 and that the transition state for path B involves one half of the difference between the ring strain of the (n+1) ring of 1 and that of the (n+2) ring of 3.

<u>Path A</u> *for* spiro [2.4] heptadiene-4,6 has the values $\Delta H^{\neq} = 45.8$ and $\Delta G^{\neq}_{600} = 44.2$ kcal/mol. We assume that the relative ring strains (4) of 1 with n=2, 4 and 5 are given by the difference between the ring strain of cyclopropane (= 27.6) and those of cyclopentane (=6.5) and cyclohexane (= o kcal/mole). Then the calculated values for 1a are: $\Delta H^{\neq} = 45.8 + 27.6 - 6.5 = 67$ and $\Delta G^{\neq}_{600} = 65$ kcal/mol. Similarly for 1b: $\Delta H^{\neq} = 73$ and

$\Delta G^{\neq}_{600} = 72$ kcal/mol. The values thus arrived at differ by about 30 kcal/mol with the experimental data (Table).

Path B for spiro[2.4]heptadiene-4,6 has the values $\Delta H^{\neq} = 36.8$ and $\Delta G^{\neq}_{600} = 46.2$ kcal/mol. We assume that the relative differences between the ring strains of 1 and 3 are given by the ring strain of the appropriate (n+1) and (n+2)-cycloalkanes (4). Then the calculated values for 1a are $\Delta H^{\neq} = 36.8 + \frac{1}{2}(146.5 - 145.4 + 140.8 - 146.9) = 34$ en $\Delta G^{\neq} = 44$ kcal/mol.

Similarly for 1b: $\Delta H^{\neq} = 41$ and $\Delta G^{\neq} = 50$ kcal/mol.

The values thus arrived at differ by 1 to 8 (average 4) kcal/mol with the experimental data. In view of the crudeness of the assumptions, we conclude that thermolysis of 1a and 1b involves suprafacial, sigmatropic 1,5 shifts of an alkylgroup (5). The stereochemistry of these reactions is currently under investigation (6).

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(5) Thermochemical data (4) indicate that the similar reaction of 1 with n = 3 should be relatively fast (calculated $\Delta H^{\neq} = 28$ kcal/mole). Though the formation of 1 (n = 3) from cyclopentadiene and 1,4-dibromopropane in the presence of a base has been reported (7), we and others (8) have failed to obtain 1 (n = 3) in this manner.

(6) After completion of this work the thermal conversion of 1a to 2a was reported without kinetic data (9).

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