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THERMOLYSIS OF THE [n.2.2]PROPELLANES. MECHANISMS FOR THE THERMOLYSIS OF BICYCLO[2.2.0]HEXANES.

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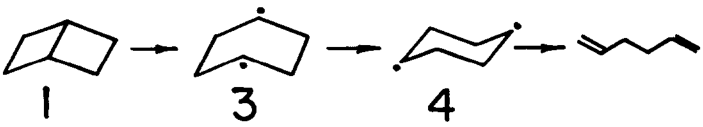
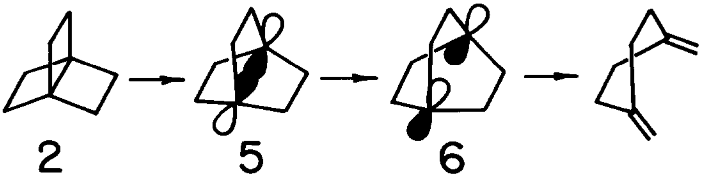
Abstract: The thermolysis of the [4.2.2]propellene proceeds with good first order kinetics and gives E_a = 46 kcal/mole. The increase in E_a over that for bicyclo[2.2.0]hexane and the [2.2.2]propellane provides evidence for the mechanism of these thermolyses.

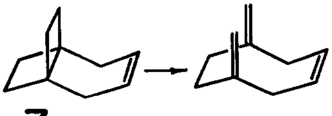
The thermolyses of bicyclo[2.2.0]hexane, (1)[1-3] and the [2.2.2]propellane (2)[4,5] have received considerable study. Despite the similarity in structure, and in the products of thermolysis, the reactions are suggested to proceed via different mechanisms. The reaction of 1 is believed to involve the formation of the boat cyclohexane-1,4-diradical (3) which isomerizes to the chair diradical (4). This, in turn, forms the product diene via an orbital symmetry allowed reaction. The mechanism accounts for the thermal inversion of 1 (E_a = 35 kcal/mole)[2] as well as the stereochemistry of the overall reaction[2,3] (E_a = 36 kcal/mole).[1,2]

The reaction of 2 is believed to proceed again via a 1,4-diradical (5). Here, it is proposed that the antibonding diradical (6) is of lower energy, and is formed from 5 in the rate determining step. A rapid cleavage of 6 to the product via an orbital symmetry allowed process completes the reaction.[5] A remarkable difference between the thermolyses of 1 and 2 is found in the low activation energy for the reaction of 2 (22 kcal/mole).[4]





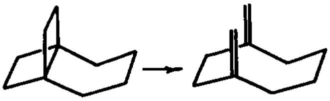
In order to explore the reasons for the differences between these two reactions, we have examined the thermolyses of the [4.2.2]propellene-3 (7) and [4.2.2]propellane (8), as well as the [3.2.2]propellane derivatives 9 and 10. Both 7 and 9 are readily prepared by the Diels-Alder reaction of $\Delta^{1,4}$bicyclo[2.2.0]hexene with butadiene, or cyclopentadiene respectively.[6] This is followed in the case of 8 and 10 by diimide reduction. The rates of their reactions were determined using a stirred flow reactor,[7] and gave good first order kinetics.[8] The products,[9] relative reactivities (310° C.) and activation energies (± 1 kcal/mol) are shown below:



7

$k_{rel} = 1$

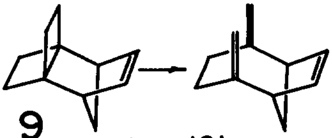
$E_a = 46$



8

$k_{rel} = 5$

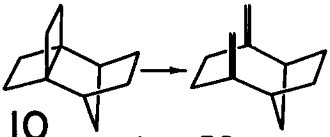
$E_a = 41$



9

$k_{rel} = 101$

$E_a = 41$



10

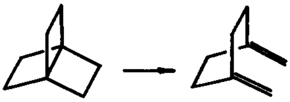
$k_{rel} = 56$

$E_a = 44$

1

$k_{rel} = 1670$

$E_a = 36$



2

$k_{rel} = 59000$

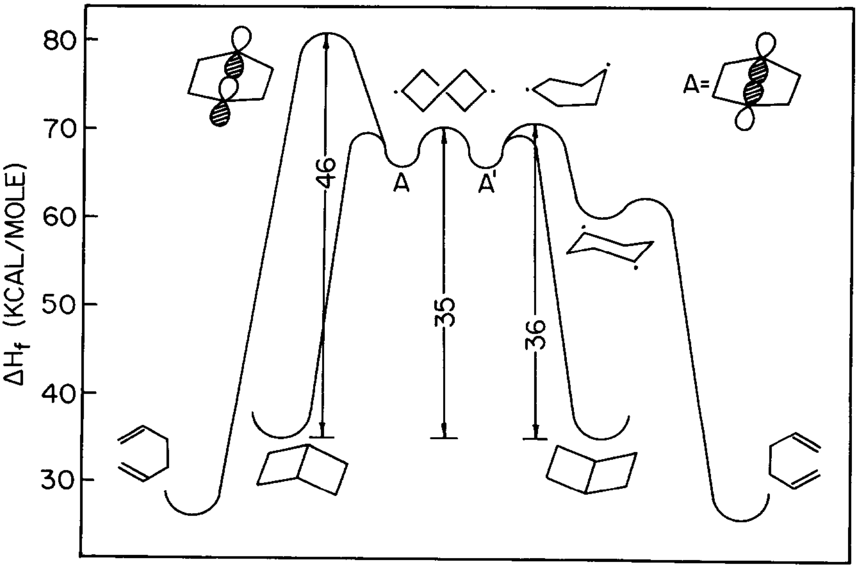
$E_a = 22$

The decrease in reaction rate in going from 1 to the propellanes 7-10 is striking, and can only result from the geometrical restraint preventing the formation of a chair cyclohexan-1,4-diyl in the latter cases. Thus, the reaction which proceeds via the boat activated complex is strongly disfavored. The activation energy for the thermolysis of 7 was 10 kcal/mole greater than that for the thermolysis of 1. The changes in rate through the series 7-10 are in accord with expected strain energies.[10] The SE of 7 should be close to that of 1. The known structure of 8[11] indicates that the bicyclohexane unit is considerably distorted to accommodate the torsional angles in the saturated 4-carbon chain. The SE of 9 should be greater than that of 7 or 8 because of the shorter distance between the bridging carbons forced by the smaller bridge. The double bond in 10 should decrease the distance even more leading to further destabilization.

The thermolysis of 2 must proceed via an activated complex which has a geometry similar to that for 7-10. Why is its activation energy so much smaller than that for 7? The answer cannot be found in a difference in flexibility, for 7 could form an extended 1,4-diradical, allowing an antibonding ground state, as well as 2. Although 2 has three σ^* orbitals which may help stabilize the antibonding diradical whereas 8 has only two, it is difficult to see how this difference could account for the large difference in activation energy.

A major difference between 2 and 7 is in the strain energy. The replacement of the six membered ring in 7 with the four membered ring in 2 should increase the strain by at least 20 kcal/mole. The resultant destabilization of the ground state must lead to a marked reduction in the activation energy, and certainly is a major factor in accounting for the large difference in activation energy.

These results allow one to summarize all of the results on the thermolysis of bicyclo[2.2.0]hexanes as indicated in Figure 1. The twist diradical is suggested by the calculations of Dewar, et. al.[12] to be the activated complex for the interconversion of the two boat diradicals, leading to the conformational inversion of 1. The half-chair diradical is probably the activated complex for the conversion of the boat to the chair diradical, and leads to the 36 kcal/mol activation energy for conversion of 1 to 1,5-hexadiene.[13]



If the rearrangement to the diene is forced to proceed via the boat diradical, the reaction will have an activation energy on the order of 46 kcal/mol (i.e., that of 7). The remaining problem is that of separating the effects of strain and σ^* orbital participation in the series: cyclobutane, 1 and 2.[14] This will be discussed at a later time.

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References

1. C. Steel, R. Zand, P. Hurwitz and S. G. Cohen, J.Am.Chem.Soc., 86, 679 (1964); R. Srinivasan, Intern.J.Chem.Kinet., 1, 133 (1969).
2. M. J. Goldstein and M. S. Benzon, J.Am.Chem.Soc., 94, 5119 (1972).
3. L. A. Paquette and J. A. Schwartz, J.Am.Chem.Soc., 92 , 3215 (1970); A. Sinnema, F. v. Rantwijk, A. J. De Koning, A. M. v. Wijk and H. v. Bekkum, Tetrahedron 32, 364 (1973). R. Wehrli, D. Bellus, H.-J. Hansen and H. Schmid, Chimia, 30, 416 (1976).
4. P. E. Eaton and G. E. Temme, III, J.Am.Chem.Soc., 95, 7508 (1973).
5. W.-D. Stohrer and R. Hoffmann, J.Am.Chem.Soc., 94, 779 (1972); M. D. Newton and J. M. Schulman, J.Am.Chem.Soc., 94, 4391 (1972).
6. K. B. Wiberg, G. J. Burgmaier and P. Warner, J.Am.Chem.Soc., 93, 246 (1971); K. B. Wiberg, W. F. Bailey and M. E. Jason, J.Org.Chem., 39, 3803 (1974); K. B. Wiberg and M. E. Jason, J.Am.Chem.Soc., 98, 3393 (1976).
7. E. S. Lewis and W. C. Herndon, J.Am.Chem.Soc., 83, 1955 (1961); W. C. Herndon, M. B. Henly and J. M. Sullivan, J.Phys.Chem., 67, 2842 (1963); W. C. Herndon and L. L.Lowry, J.Am.Chem.Soc. 86, 1922 (1964); W. C. Herndon, J.Chem.Ed., 41, 425 (1964).
8. The reaction was followed by gas chromatography, and the relative response factors were determined. Good first order kinetic plots were obtained in each case.
9. The thermolyses of 7-10 gave one product in each case, which was identified by comparison of its spectrum with that previously reported (D. Tatarsky, M. Kaufman and D. Ginsberg, Israel.J.Chem., 9, 715 (1971); C. S. Dean, D. A. Jonas, S. H. Graham, D. O.Lewis, J.Chem.Soc. Pt.C 24, 3045 (1968); H.-D. Beckhaus, C. Heller, B. Mayer, Chem.Ber. 11, 2589 (1980)).
10. The low activation energy for 8 may be due to the distortion introduced into the bicyclohexane ring by the four-carbon bridge in order to minimize torsional interactions.[11] Correspondingly, the low log A factor may result from low frequency vibrations introduced by this bridge, which will in part be lost on going to the activated complex. A similar change in activation parameters was found with 1,4-dimethylbicyclo[2.2.0]hexane (R. Srinivasan, Int.J.Chem.Kinet. 1, 133 (1969)).
11. J. V. Silverton, G. W. A. Milne, P. E. Eaton, K. Nyi and G. H. Temme, III, J.Am.Chem.Soc. 96, 7429 (1974).
12. M. J. S. Dewar, G. P. Ford, M. C. McKee, H. S. Rzepa and L. E. Wade, J.Am.Chem.Soc., 99, 5069 (1977); Cf. A. Komornicki and J. W. McIver, ibid. 98, 4553 (1976).
13. The calculations of R. V. Lloyd, J. G.Causey and F. A. Momany, J.Am.Chem.Soc. 102, 2260 (1980) suggest that cyclohexyl radicals have approximately the same conformational preferences as cyclohexane itself. It is not clear to what extent the radical sites would interact in the diradical. If the interaction is not large, or is similar between conformations, the ralative energies of the chair and boat diradicals may be approximately the same as those for cyclohexane. The postulate that the half-chair diradical is the activated complex for conversion of 1 to 1,5-hexadiene would resolve the thermochemical dilemma posed by J. J. Gajewski and N. D. Conrad, J.Am.Chem.Soc., 100, 6268 (1978). This conclusion has been reached independently by Prof. R. W. Alder (private communication).
14. The similarity in E_a between 10 and tetracyclo[4.2.1.1^{2,5}.0^{1,6}]octane (E_a=47 kcal/mol, D. H. Aue and R. N. Reynolds; R. H. Reynolds Ph.D. Thesis, University of California, Santa Barbara, 1977) suggests that σ^* orbital participation may have only a small effect on the rate of thermolysis.

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