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THERMAL CHEMISTRY OF A BICYCLIC BENZOCYCLOBUTENE

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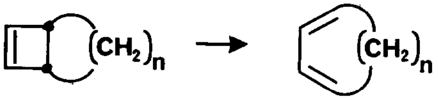
The preferred nature of the "allowed" conrotatory electrocyclic ring openings of cyclobutenes has been extensively documented by both theory and experiment, the conrotatory path being favored over alternative disrotatory or biradical(oid) mechanisms by an estimated 15 kcal/mol.[1-5] This preference has been dramatically observed in the thermal ring openings of bicyclo[n.2.0]-alkenes. Vapor phase activation energies of some representative compounds are shown in the Table. There are apparently two major factors at work in producing the observed energies,[1] strain in the starting cyclobutene and strain in the "allowed" E,Z diene product. For large n the activation energies should approach that of cis-3,4-dimethylcyclobutene[6] (34.3 kcal/mol), and the maximum in activation energies occurs when n=3.

Table:



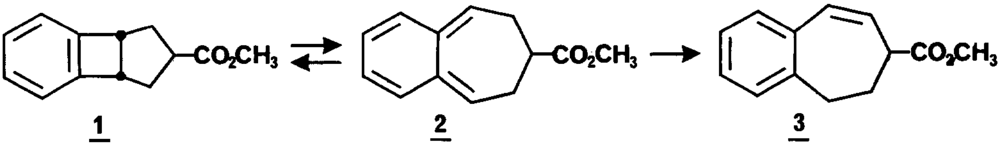
n:	1	3	4
$E_{act.}$ (kcal/mol):	26.88[2]	45.51[10]	43.18[8]

The mechanisms(s) involved in these transformations have received considerable attention since the products observed in the vapor phase, for n=1 to 4, are the Z,Z dienes and must result from either a "forbidden" disrotatory or a biradical(oid) process.[1-5,7,8] There is evidence that in solution for n=4 the mechanism involves rapid formation of the E,Z diene in an "allowed" conrotatory process ($\Delta H^{\dagger}$=32.6 kcal/mol) followed by a rapid 1,5 suprafacial hydrogen shift to the Z,Z diene,[9] however, this mechanism apparently does not hold in the vapor phase. When n=3 the similarity of the vapor phase and solution (45.86 kcal/mol)[10] activation energies, along with the considerable strain anticipated for E,Z-1,3-cycloheptadiene make this mechanism unlikely and thermochemical estimates of the activation energies are consistent with a biradical pathway.[3,7]

Very little quantitative work has been done on the related thermal ring openings of benzocyclobutenes to *ortho*-quinodimethanes. This transformation is of considerable interest both from the standpoint of mechanistic studies and from the synthetic potential[11] of the reactive product. Extensive studies on *cis*- and *trans*-1,2-diphenylbenzocyclobutene have shown that the thermal ring openings are stereospecific[12,13] and in accord with orbital symmetry predictions; however, the photochemical ring openings are only stereoselective.[14] $\Delta H^{\dagger}$ for the *trans* and *cis* ring openings are 20.6 and 25.2 kcal/mol respectively.[13] The activation energy for the ring openings of 1-methoxybenzocyclobutene has been estimated at 31 kcal/mol,[15] and the activation energy for the parent molecule should no doubt be similar.

Because of the recent interest in these transformations, we decided to investigate the thermal and photochemical ring opening of a bicyclic benzocyclobutene in which the influences of starting material strain and "allowed" tetraene product strain would be manifest. We have therefore chosen for investigation benzocyclobutenes corresponding to n=3, methyl benzobicyclo[3.2.0]-hepten-3-*exo* and *endo*-carboxylates (1).[16] In addition to the effects noted, the ring opening now involves disruption of the benzene resonance and formation of a reactive and in this case a highly strained *ortho*-quinodimethane (2). The strain in the product is due to the constraint that the product be in the all Z configuration and must therefore be substantially twisted from planarity. This product should only be "allowed" in the photochemical reaction and the thermal reaction should therefore show a large activation energy. The *exo*- and *endo*-carbomethoxy groups serve as stereochemical probes and should have no effect on the reaction course and/or energetics.

Thermolysis of the *exo* and *endo* epimers in benzene results in quantitative conversion to methyl 1,2-benzo-1,3-cycloheptadiene-5-carboxylate (3) and based on previously published work, we postulate the intermediacy of (2) which



rapidly undergoes a 1,5-hydrogen shift.[16] The fact that no interconversion of epimers is observed indicates that reclosure of the intermediate is slow under the reaction conditions. This result is expected as reclosure to give a cis fused bicyclic benzocyclobutene is "forbidden" and the competing 1,5 hydrogen shift is facile even at low temperature.[16]

Thermolysis of the exo epimer was studied at six different temperatures between 241.6°C and 292.5°C and a least-squares treatment of the reaction rates yielded an activation energy of 45.35 kcal/mol (correlation coefficient 0.992) for the ring opening.[17] The activation energy for the endo epimer was not determined but as expected this ring opening was slightly more facile.

The similarity between the activation energies of 1 and bicyclo[3.2.0]-hept-6-ene is remarkable.[18] The latter reaction is exothermic by approximately 13 kcal/mol while the former is estimated to be endothermic by at least 15 kcal/mol.[19] Thus, the transition state for the ring opening does not feel the influence of the relatively large heat of formation of the product. This is consistent with the biradical model which has been proposed for the ring openings in bicyclic cyclobutenes and an estimate of the activation energy expected for a biradical mechanism in this case,[19] assuming that approximately half of the potential benzylic stabilization is available in the transition state,[20] gives a value of 47 kcal/mol. This excellent agreement indicates that, as with bicyclic cyclobutenes, the biradical model for disrotatory ring opening is consistent with the observed energies.[2-4,7,8,10]

The photochemistry of both epimers of 1 has also been investigated; however, no products have been obtained with either direct (254 nm) or sensitized (acetone, 313 nm) irradiation conditions.

In conclusion, the thermal ring opening of methyl benzobicyclo[3.2.0]-hepten-3-carboxylate to an ortho-quinodimethane occurs with a large activation energy, which is consistent with either a biradical or a "forbidden" concerted mechanism.

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