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DERIVATIVES OF TETRACYCLO $[4.3.0.0^{2,9}0^{5,7}]$ NON-3-ENE: SYNTHESIS AND THERMAL REARRANGEMENTS

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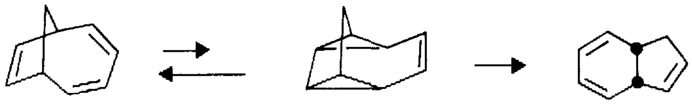
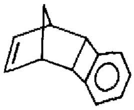
The pyrolytic transformation of bicyclo[4.2.1] nona-2,4,7-triene 1 and its thermal precursors to *cis*-9,10-dihydroindene 3 has prompted a number of recent mechanistic investigations.[1] It seems generally agreed that the unstable tetracyclic olefin 2 formed via intramolecular Diels Alder cycloaddition is ultimately converted into 3. The mechanism of the subsequent transformation of 2 has alternatively been described in terms of sequential 1,5-hydrogen shifts ("hydrogen rebound")[1a] for the parent system and carbon-carbon bond cleavage and reorganization[1b] for 3,4-disubstituted derivatives. Further mechanistic investigation has been hampered until now by the unavailability of stable derivatives of 2 for subsequent pyrolytic studies.



1 2 3

Recently Martin and coworkers[2] have reported the preparation of 7 from the pyrolysis of either 4 or 5. Independently, we have prepared and characterized 7 by the same route and have extended the generality of the transformation to the preparation of the hetrocyclic derivative 8[3] from the quinoxaline 6.[3] We now report on the thermal transformation of 7 and its consequent mechanistic implications.



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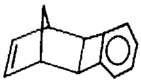

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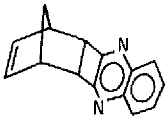

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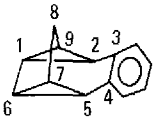

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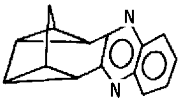

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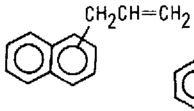
The cycloadduct 7 was remarkably stable thermally and could be recovered unchanged from refluxing xylene (18hr). It was similarly unreactive toward electrophilic reagents capable of cycloadding to quadricyclane derivatives[4] and was unchanged after heating (10hr,140°) with maleic anhydride or dimethylacetylene dicarboxylate. However, gas phase pyrolysis of 7 in a flow system (475°,1mm) produced a mixture of 1 and 2-allylnaphthalene 9 (24%)[5] and cis-3a,9b-dihydro-3H-benz[e]indene 10 (56%).[6] The allylnaphthalenes were shown to arise from the subsequent thermolysis of 10 under the reaction conditions.[7]



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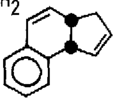

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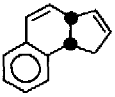

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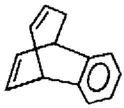

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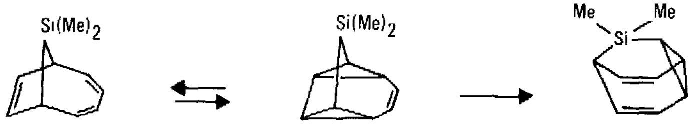
The regioselective production of 10 seemed initially most compatible with the mechanistic suggestion of DeSelms.[1b] However, lower temperatures (400°,58% conversion) led to the appearance of another isomeric hydrocarbon subsequently identified as benzobarbaralane 12 (17%) in addition to 10 (30%). The generation 10 and 12 was reminiscent of a report by Tsuji and coworkers[9] who isolated the same compounds from the pyrolysis (231°,hexane) of the isomeric 6,7-benzobicyclo[3.2,2] nona-2,8-diene 13 and raises the question whether 13 could be an intermediate in the pyrolysis of 7. Glpc examination of the crude pyrolysate of 7 failed to reveal any significant quantity of 13. However, interpretation of this result is complicated by the thermal lability of 13[10] under the conditions coupled with the possibility that it could be generated vibrationally "hot" in the gas phase via an exothermic bis-homo 1,5-sigmatropic rearrangement resulting in the opening of both strained cyclopropane rings. As a result, samples of 7 and 13 were simultaneously pyrolyzed in n-decane at 261°(91hr) and analyzed. Under these conditions, 13 produced 12 and 10 in the relative ratio 1.2 (84% conversion). As expected, the decomposition of 7 was slower (24% conversion) and the ratio 12/10 rose to >9. Glpc analysis of the latter sample showed that the triene 13 comprised <2% of the reaction mixture. This data implies that 13 is not a significant intermediate in the pyrolysis of 7. In a similar fashion, the observed increase in the ratio of 12/10 with decreasing contact times in the gas phase coupled with the almost exclusive formation of 12 in solution, suggests that it is the major primary thermal product in the pyrolysis of 7 and is the origin of 10 in the gas phase. Consistently, the pyrolysis of 12 (400°,1mm) led to the regioselective generation of 10 as the major volatile product (71%,85% conversion). Mechanistically the generation of barbaralane 12 is most simply reviewed as a homolytic cleavage of the weak 1,2(5,6) bond in 7 and subsequent 1,2-alkyl migration. Energetically this is an attractive suggestion, since it proceeds via a stabilized intermediate with no attending lost in aromaticity. A similar suggestion has recently been made by Barton and Juvet[11] as one possible pathway for the conversion of 9,9-dimethyl-9-silabicyclo[4.2,1] nona-2,4,7-triene 14 into the silabarbaralane derivative 16.



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While the mechanism for the subsequent conversion of 12 into 10 is still uncertain, the regioselectivity of this transformation renders a diradical process such as has been suggested for the conversion of barbaralane itself into cis-9,10-dihydroindene suspect.[12] Further work is continuing in this area.

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7. Both regioisomers 9 and 10[6] are converted to the same mixture of allylnaphthalenes upon pyrolysis (600°,0.25mm).

8. Less than 12% of a product with the same retention time on two columns as authentic 10 could be detected in the pyrolysate.

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10. At 400°(1mm) 13 is converted (80%) to a mixture of 9 and 12. A small amount (10%) of an as yet unidentified product is also generated.

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12. Alcyclic Compounds, W. Parker ed., (University Park Press, Baltimore, MD, 1973), p. 196.