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DIELS-ALDER REACTIONS OF TROPYLIUM ION.[1]
AN EMPIRICAL FORCE FIELD STUDY

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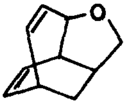
Summary: New Diels-Alder reactions of tropylium ion are studied, and empirical force field calculations are used to explain the regio- and stereoselectivities of these reactions.

In an earlier report[2] we described the Diels-Alder condensation of tropylium ion with allyl alcohol and the subsequent cyclization and rearrangements of the allylic ions thus formed to yield products **1-3**. We have now begun to explore the limits of this reaction as a potential synthetic approach to novel polycyclic ring systems and to elucidate the factors that control the course of these processes.



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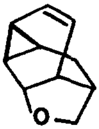

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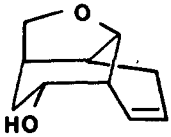

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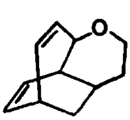

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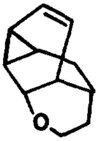

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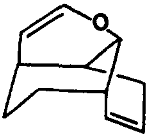

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Tropylium ion reacts with 3-buten-1-ol at room temperature to yield ethers **4** and **5** analogous to exo and endo ethers **1** and **2**.[3] Because of the high strain energy associated with the cyclopropyl ring in **5**, the observed **4**:**5** product ratio of 1.2 indicates that they were not formed in equilibrium concentrations. However, when a mixture of **4** and **5** (produced at 25°) was treated with dilute acid at room temperature, no change in this ratio was found after 48 hr as indicated by GC-MS analysis. Thus the product ratio observed in reactions at room temperature would appear to reflect rather the ratio in which the initial allylic ions are produced before being irreversibly trapped in a kinetically controlled process to yield **4** and **5**.

The trapping of both endo and exo allylic ions could also lead to the formation of regioisomers **7** and **8**, but in neither case were additional products obtained in isolable amounts. Empirical force field calculations[4] indicate that in each case these alternatives are appreciably more strained. Thus, **7** is calculated to be 13.05 kcal higher in energy than **4**, while **8** is 4.23 kcal higher than **5**. To the extent that these energy differences are reflected in the corresponding isomeric transition states, irreversible trapping of the ions by the hydroxyl group would lead to preferential formation of **4** and **5**.

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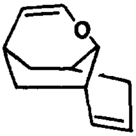

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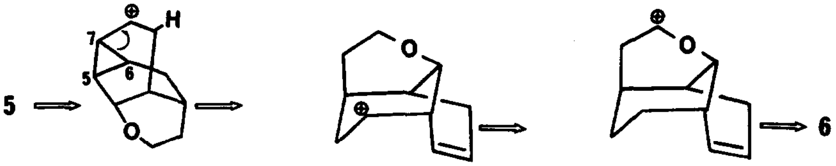
When the Diels-Alder reaction was carried out at 65°, an ether isomeric with **4** and **5** was obtained rather than a rearranged hydration product analogous to **3**. This new product showed an enhanced olefin absorption in the IR and a characteristic doublet/triplet pattern in the vinyl region of the ^{1}H NMR that confirmed its structure as the enol ether **6** (the regisomer **8** would have produced **9** in a similar manner).[5,6] If **6** arises *via* a mechanism similar to that previously suggested for the formation of **3** from **2**, then a remarkable 1,5 hydride shift in the



10 **11** **12**

intermediate cation **11** is required. The calculated geometry for this ion indicates,however, that such a process should be quite facile. As illustrated in Figure 1, that conformation of ion **11** which is calculated to be the most stable places the migrating hydrogen directly over the cationic center, the distance between the two being only 2.4 A. Thus, rearrangement to the resonance-stabilized ion **12** is highly favored. On the other hand nucleophilic attack by solvent at the top face of the ion is thereby sterically blocked while attack from the bottom is prevented by homallylic resonance with the adjacent double bond. An hydration-rearrangement reaction as observed for **2** is thus retarded.

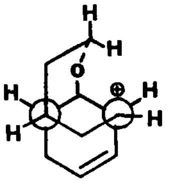


Figure 1. Ion **11**

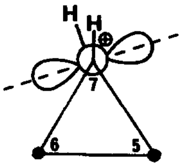


Figure 2. Ion **10**

The rearrangement of **5** to **6** proceeds, as does that of **2** to **3**, with a very specific opening of the cyclopropyl ring at the 6,7 bond. Again, empirical force field calculations suggest a reason. The calculated geometry for the cyclopropylcarbinyl ion formed on protonation of **5** (**10**) is distorted from the stable bisected structure[7] (Figure 2) in a way which strongly favors interaction of the p orbital of the ion with the 6,7 bond of the cyclopropyl ring rather than the 5,7 bond. Further, the 6,7 bond is calculated to be the longest and most strained of the three cyclopropyl bonds and hence the most readily cleaved.

Tropylium ion does not react with the relatively electron-deficient dienophiles cinnamic acid, diethyl or monomethyl furmate, or vinyl acetic acid under any of the reaction conditions used above. It thus appears, not surprisingly, that electron-rich dienophiles are required to react with the cationic tropylium ion. When such dienophiles also contain nucleophilic substituents, then novel polycyclic systems can be produced.

References and Footnotes

1. Taken in part from the M.S. thesis of MSM, Bowling Green State University, June, 1990.

2. Clemans, George B. and Dobbins, Michael A. *Tetrahedron Lett.* **1982,** *23*, 387-390.

3. Reaction conditions and yields were essentially those reported earlier for the formation of **1** and **2**. The assigned structures of compounds **4** and **5** are in accord with spectroscopic data as described previously.

4. Empirical force field calculations were carried out using Allinger's program MM2 (Program No. 395 available from QCPE, Department of Chemistry, Indiana University, Bloomington, IN 47450, USA). See Burkert, U. and Allinger, J.L. *Molecular Mechanics, ACS Monograph 177*: American Chemical Society: Washington, D.C., 1982.

5. For enol ether **6**: MS (m/z) 162 (M^+); IR (cm^{-1}) 3023, 1645, 1080, 1040; NMR ($CDCl_3$) δ 4.29 (m, 1H), 4.68 (t, 1H), 5.53 (t,t, 1H), 5.73 (d,t, 1H), 6.48 (d, 1H).

6. The distinction between enol ethers **6** and **9** was made by catalytic hydrogenation to the corresponding saturated compound. The product obtained showed three clearly non-equivalent downfield hydrogens in the H NMR, an observation inconsistent with the more symmetrical structure **9**.

7. **Rhodes, Y. E., and DiFate, V.G.,** *J. Amer. Chem. Soc.* **1972,** *94*, 7582.

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