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STEREOSELECTIVITY IN THE DIELS-ALDER REACTIONS OF TROPYLIUM ION[1]

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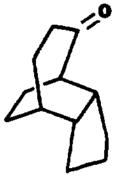
Abstract: New Diels-Alder reactions of tropylium ion are studied, and the observed stereoselectivities suggest that solvent effects determine the steric course of these reactions.

Troplylium ion (1) has been found to undergo a number of Diels-Alder type reactions with high endo selectivity.[2] In aqueous dioxane, for instance, it reacts with cyclopentene to yield products which on oxidation and catalytic hydrogenation give endo ketones such as 2 and 3 but only minor amounts of the exo product 4. Other dienophiles react with similar selectivity. The pronounced stereoselectivity of these reactions is not well understood, however, having been rationalized both in terms of electrostatic repulsions[3] and π-alkyl attractions in the transition state.[2b] Nonetheless, tropylium ion is well suited for the study of the variety of electronic factors that govern the steric course of polar cycloadditions generally. We have therefore initiated an investigation of new Diels-Alder reactions of this ion in hopes of further clarifying these effects.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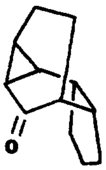
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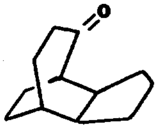
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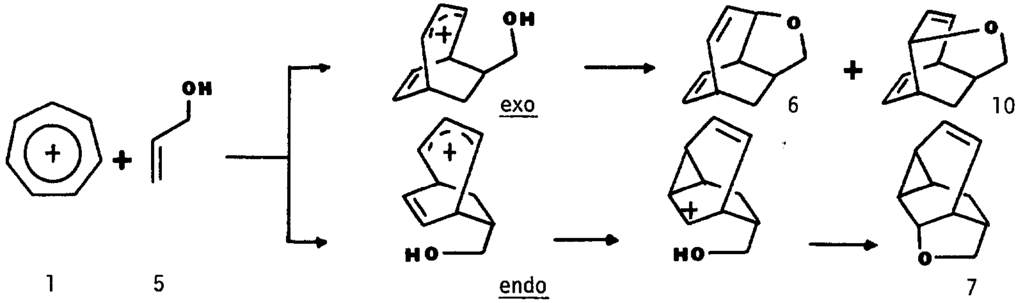
The initial dienophile selected for study was allyl alcohol (5), the first acyclic dienophile to be so studied in this reaction. This particular substrate should permit the development of electrostatic attractions in the transition state which might drastically alter the consistent preference for endo products. Further, it should be capable of trapping the intermediate cations via internal nucleophilic attack by hydroxyl, thereby generating new ring systems of potential synthetic interest.

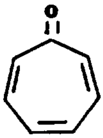
Treatment of tropylium tetrafluoroborate[4] with allyl alcohol at room temperature in water gave ethers 6 and 7 in addition to small amounts of tropone (8)[5,6] and unidentified materials.

In the presence of added acid these same products were obtained in approximately the same ratio.[7] At 65° in water the hydroxy ether 9, arising from the hydration of 7, was also obtained. Under acidic conditions the relative proportion of this hydration product was increased significantly.[8a] These results are summarized in Table 1.



(1)

All products were readily separable by preparative gas-liquid chromatography, and each gave spectroscopic data (^{1}HNMR, ^{13}CNMR, IR, and MS) consistent with the structures assigned.[8b] Extensive decoupling and shift reagent studies further confirmed these assignments. Product 6 was accompanied by small amounts of its regioisomer 10 which could not be removed. The assignment of 6 to the major component of this mixture was based on an examination of molecular models which suggested that it was significantly less strained than 10. The remaining two products (7 and 9) were formed isomerically pure and were distinguished from their regioisomers 11 and 12 as follows. The hydroxy ether 9 was oxidized[9] to the corresponding ketone 13. Treatment[10] of this product with K_2CO_3/D_2O led to the rapid incorporation of two deuteria into the molecule, an observation that is consistent only with structure 13, thus confirming the assignments of 7 and 9 as well.[11]



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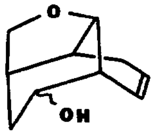

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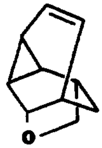

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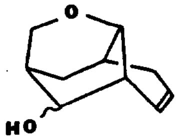

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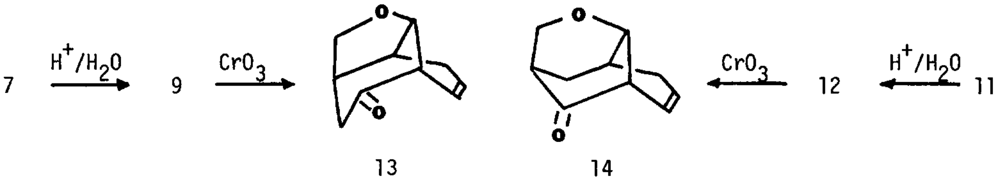


(2)

An examination of Table 1 reveals profound differences between the reactions reported here and previously observed Diels-Alder processes of tropylium ion. Most notably, of course, stereoselectivity is low, and a slight preference for exo products is actually observed.

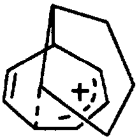
Further, internal trapping of the ionic intermediates has indeed been achieved, ethers 6 and 7 arising from the corresponding exo and endo cations by nucleophilic attack of the hydroxyl group (Equation 1).[12] An alternative mechanism invoking the prior formation of allyl tropyl ether is unlikely and can be ruled out, since heating this ether[13] at 65° in aqueous THF yielded tropone and ditropyl ether[14] as the only detectable products.

The results reported here suggest that the stereoselectivity of the Diels-Alder reactions of tropylium ion is largely a result of differential solvation of the isomeric transition states. Cyclic dienophiles, such as those used in all previous studies, strongly screen one face of the developing allylic cation in the exo transition state (15), thus sharply reducing the possibility of solvent stabilization. A similar loss of solvation does not occur in the endo transition state (16), hence the endo mode of reaction is greatly favored. Acyclic dienophiles like allyl alcohol are much less effective in screening the developing charge in either transition state (eg. 17), and therefore neither the endo nor exo mode of reaction is to be preferred. Stereoselectivity will be low in these cases as observed. To test this hypothesis the reaction was carried out in a less polar solvent, 20% aqueous tetrahydrofuran. As anticipitated, stereoselectivity remained low, but a shift toward normal endo selectivity was observed (see Table 1). It thus appears that solvent effects play a dominant role in determining the steric course of Diels-Alder reactions of tropylium ion. We are continuing to investigate the theoretical and synthetic aspects of these reactions.

Table 1

Reactants (Equivs.)			Time (Hrs.)	Temperature (°C)	Total Yield (%)	Products (%)				
1	5	TsOH				6	7	8	9	Other
1	5	0	44	25	51[a]	58	35	5	0	2
1	5	0	22	65	27[a]	20	18	5	49	8
1	5	0.8	44	25	37[a]	66	28	0	0	6
1	5	0.8	22	65	47[a]	15	9	0	75	1
1	5	0	22	65	35[b]	11	22	52	0	15

a) Reaction run in water. b) Reaction run in 20% (v/v) aqueous tetrahydrofuran.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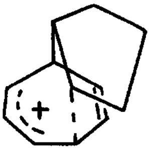
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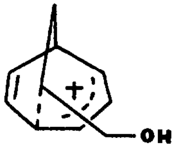

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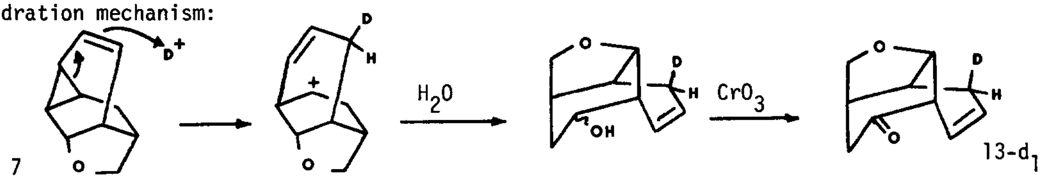
References and Notes

1. Taken in part from the Masters Thesis of MAD, Bowling Green State University, March, 1981.
2. (a) S. Ito, and I. Itoh, *Tetrahedron Lett.*, 2969 (1971); (b) S. Ito, I. Itoh, I. Saito, and A. Mori, *ibid.*, 3887 (1974); (c) S. Ito, A. Mori, I. Saito, K. Sakan, H. Ishiyama, and K. Sasaki, *ibid.*, 2737 (1973).
3. C. K. Bradsher, F. H. Day, A. T. McPhail, and P. S. Wong, *Chem. Commun.*, 156 (1973).
4. Prepared by the method of H. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, **25**, 1442 (1960).
5. Tropone was identified by spectroscopic comparison (IR and ^{1}HNMR) with an authentic sample prepared by the method of P. Radlick, *J. Org. Chem.*, **29**, 960 (1964).
6. Tropone presumably is formed in this reaction by a disproportionation between tropylium ion and tropyl alcohol (or ditropyl ether). See, for instance, A. P. TerBorg, R. van Helden, A. F. Bickel, W. Renold, and A. S. Dreiding, *Helv. Chim. Acta*, **43**, 457 (1960).
7. Both 6 and 7 were shown to be stable in aqueous solution at room temperature even in the presence of added acid.
8. (a) When 7 was treated with D^+/D_2O at 65° and the resulting alcohol oxidized,[9] the ketone produced was monodeuterated at the allylic methylene as evidenced by the expected partial collapse of the vinyl proton splitting pattern. This is consistent with the following hydration mechanism:



(b) For example, for 6: MS (m/e) 148 (M^+); δ ($CDCl_3$) 5.31 (d,d,1H), 5.97 (d,d,1H), 6.26 (d, d,1H), 6.64 (d,d,1H) vinyl H's; $\nu_{max}^{CCl_4}$ (cm^{-1}) 3020, 1120. For 7: MS (m/e) 148 (M^+); δ ($CDCl_3$) 5.90-6.06 (2H) vinyl H's; $\nu_{max}^{CCl_4}$ (cm^{-1}) 3034, 1068. For 9: MS (m/e) 166 (M^+); δ ($CDCl_3$) 5.67 (2H) vinyl H's; $\nu_{max}^{CCl_4}$ (cm^{-1}) 3523, 3018, 1061. For 13: MS (m/e) 164 (M^+); δ ($CDCl_3$) 5.60 (q,t,1H) 5.93 (d,t,1H) vinyl H's; $\nu_{max}^{CCl_4}$ (cm^{-1}) 3023, 1725, 1072.
9. R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).
10. H. W. Whitlock, Jr., and M. W. Siefken, *J. Amer. Chem. Soc.*, **90**, 4929 (1968). Although deuterium exchange has been observed at bridgehead positions, it occurs only very slowly and under more drastic conditions than used here.[11]
11. See, for instance, J. P. Schaefer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965).
12. Other products that might have been formed from these intermediate ions were not found, possibly reflecting their instability under the conditions used.
13. Allyl tropyl ether was prepared by the method of C. Cupus, W. Schumann, and W. E. Heyd, *J. Amer. Chem. Soc.*, **92**, 3237 (1970).
14. Ditropyl ether was identified by comparison (^{1}HNMR and GC) with an authentic sample prepared by the method of W. Doering and L. H Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

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