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THE CONCERTED CYCLOADDITION OF CYCLOOCTATETRAENE AND MTAD; A BIS-PERICYCLIC PROCESS

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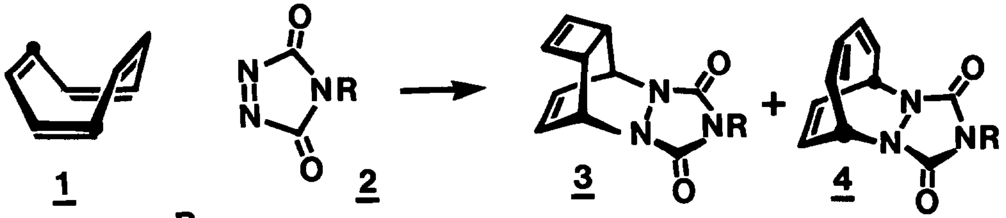
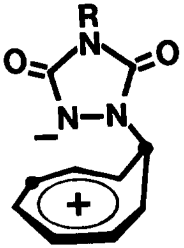
Cyclooctatetraene (COT, 1) is reluctant to participate in cycloaddition reactions leading to a Diels-Alder type product. Ordinarily the tetraene delivers the analog of the tetracyclic adduct 3 via its valence tautomer, bicyclo(4.2.0)-octatriene.[1] However 1 and certain monosubstituted derivatives combine slowly with triazolinediones 2 in low yield to give tricycle 4 often accompanied by 3 depending on the temperature.[2] The presumed electrophilicity of 2 has led Huisgen, Konz and Schnegg to suggest that the transformation proceeds by way of a zwitterionic homotropylium intermediate 5.[2b]





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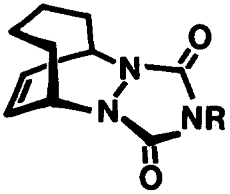

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In order to test the proposed incursion of a charge-separated species in the formation of 4, we have measured the rate of reaction between cyclooctatetraene and MTAD (2, R = CH_3) as a function of solvent at 20.0° where the bicyclic isomer does not intervene.[1a,2b] For comparison the adduction of MTAD and cyclooctadiene (COD) to give 6[3] has been similarly studied. The absence of extended conjugation for the diene prevents the operation of a dipolar structure such as 5. The rates are all second order and have been obtained by following the disappearance of MTAD at 525-538 nm (Table).

For both COT and COD the reaction rate is essentially solvent independent, although similar small rate fluctuations are evident over a wide range of solvent polarity. At the extremes $k_{CH_3CN}/k_{C_6H_6}$ = 0.83 and 0.68 for the diene and the tetraene respectively. The intervention

TABLE. Second order rate constants for the cycloaddition of cyclooctatetraene and cyclooctatriene to MTAD as a function of solvent (20.0°).[a]

			COD[b]		COT[c]	
	ε	E_T	10^2k $1\ mol^{-1}s^{-1}$	$\Delta G^{\dagger}$ kcal/mole	10^2k $1\ mol^{-1}s^{-1}$	$\Delta G^{\dagger}$ kcal/mole
benzene	2.3	34.5	1.8 ± 0.003	19.5	0.0028 ± 0.0002	23.3
chlorobenzene	5.6	37.5	4.3 ± 0.04	19.0	0.0063 ± 0.0002	22.8
CH_2Cl_2	8.9	41.1	13.0 ± 0.4	18.3	0.012 ± 0.0001	22.4
acetone	20.5	42.2	0.34 ± 0.002	20.4	0.0035 ± 0.0006	23.1
CH_3CN	26.0	46.0	1.5 ± 0.03	19.6	0.0019 ± 0.00005	23.5

a) All rate measurements were performed in duplicate. The rate constant plots show an average correlation coefficient of 0.9997. Error limits for k's have been taken as one-half the range between each pair of duplicate measurements giving a maximum error in $\Delta G^{\dagger}$ of ± 0.2 kcal/mole.

b) The rates were obtained during the last 50-95% of reaction with $[MTAD]_o$= 0.009-0.015 M and $[COD]_o$= 0.04-0.10 M.

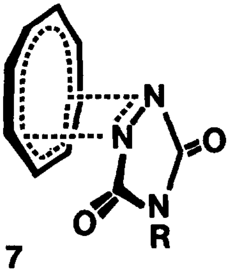
c) The rates were determined from 30 to 65% conversion; $[MTAD]_o$= 0.007-0.10 M, $[COT]_o$= 0.08-0.3 M.

of a zwitterionic intermediate in the cycloaddition of TCNE and enol ethers leads to a rate enhancement of 1200-11,000 (k_{CH_3CN}/k_{CCl_4}) and 200-1000 (k_{CH_3CN}/k_{Et_2O}) for a comparable difference in solvent ε and E_T values respectively.[4] Furthermore the absolute values of the rate constants for COD and the magnitude of the rate increments with a change in solvent are similar to the Diels-Alder behavior of MTAD with deactivated dienes.[5] In sum the rate-solvent relationship argues persuasively for a concerted ($_{\pi}4_s$ + $_{\pi}2_s$) cycloaddition between MTAD and both cyclooctadiene and monocyclic cyclooctatetraene.[6]

Methoxy COT reacts with TCNE[7] and PTAD[2c] (2, R = C_6H_5) to give positional isomers of the analog of 4. The exclusive formation of triene from these reactions and the ability of $-OCH_3$ to stabilize a cationic center have been offered as additional evidence for the involvement of a homotropylium intermediate.[7] For substituted COT derivatives a changeover in mechanism from a concerted to a zwitterionic process is conceivable. It is more likely, however, that structural modification leads to a complex interplay of the COT/bicyclo(4.2.0)-octatriene equilibrium composition,[1a,8] the energy of the highest occupied COT molecular orbital,[9] and the conformational barrier to ring inversion.[10-12] All of these probably contribute to the ultimate cycloaddition partition of 3 and 4.[13]

With regard to the latter conformational factor, it is of interest that for any given solvent MTAD combines with COT 100-1100 times slower than with COD corresponding to a $\Delta\Delta G^{\dagger}$ =

2.7-4.1 kcal/mole (20.0°, Table). The energy barrier difference is nicely accommodated by consideration of the conformational behavior of the eight-membered rings as they travel to the cycloaddition transition state. The dihedral angles between adjacent double bonds in COD and COT are 40-60°[14,15] and 58-60°[14,16] respectively. Thus to achieve a reasonable cycloaddition transition state, the diene system must approach a near planar conformation. For cyclooctadiene the energy cost amounts to ca. 9 kcal/mole at -40°,[17] while flattening of cyclooctatetraene at -10° requires 13.7 kcal/mole.[10] Correction to 20°[18] leads to an energy barrier difference of $\Delta\Delta G^{\dagger}$ = 4.4 kcal/mole in close agreement with the measured $\Delta\Delta G^{\dagger}$ (COT-COD).



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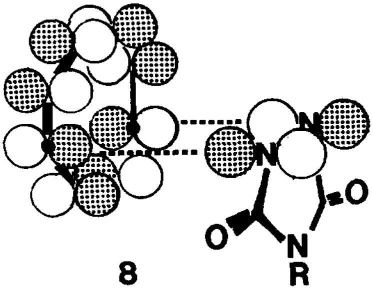

8

Finally we would like to point out that the cyclooctatetraene/MTAD union is an example of a bis-pericyclic process in which one fragment of the transition state is a formal 6-electron, aromatic (or "allowed") cycle, the other an 8-electron, anti-aromatic (or "forbidden") cycle, 7. It has been argued[19] that the latter ought to oppose the former leading to a higher energy transition state relative to a model without the 8-electron component, e.g. the cyclooctadiene cycloaddition. Consequently one might conclude that $\Delta\Delta G^{\dagger}$(COT-COD) arises from the "partly-forbidden" COT adduction. This viewpoint, however, is an artifact of representing pericyclic transition states in terms of isolated, monocyclic π-ground state isoelectronologs.[20] An appropriate analysis requires a model wherein all interacting components of the key molecular orbitals of each fragment are explicitly considered. The MTAD/COT reaction undoubtedly involves the initial transfer of electrons from the diene to the dienophile, i.e. a "normal" Diels-Alder process. The relevant frontier orbitals (COT-HOMO/MTAD-LUMO) are depicted in 8. Planarization of cyclooctatetraene permits a symmetry acceptable interaction between the addends. Clearly no energetically unfavorable factor arises from this primary association. By the principle of microscopic reversibility, a similar situation obtains for chelotropic fragmentation.[19]

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