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SOME FACTORS CONCERNING DIELS-ALDER REACTIVITY OF HYDROCARBONS CONTAINING UNSATURATIVELY BRIDGED SMALL RINGS.

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In the recent literature several reports have appeared that indicate unanticipated differences in reactivity for hydrocarbons containing unsaturatively bridged small rings towards Diels-Alder cycloaddition.[1-5] A particularly moot example is found with 1,2,5,6-tetramethyl-3,4 dimethylenetricyclo[3.1.0.$0^{2,6}$] hexane 1 which reacts instantaneously with tetracyanoethylene (TCNE) in chloroform solution at room temperature to give the 1,4 cycloaddition product[2], whereas the analogous reaction of 1,4,5,6-tetramethyl-2,3 dimethylenebicyclo[2.1.1]hexane 2 with TCNE requires several hours refluxing in chloroform solution for completion.[4] We offer here some explanations for this difference in reactivity as a function of structure.

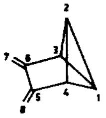

1


2

— = CH_3

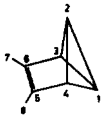
Several theoretical approaches regarding Diels-Alder cycloaddition reactions have been formulated. The principle of conservation of orbital symmetry[6] allows a prediction of the geometry of the transition state but does not automatically lead to an explanation for a difference in reactivity among dienes. Perturbation theory[7] as applied to the frontier orbitals[8] leads to a better understanding of chemical reactivity.[9] More recently the low Diels-Alder reactivity of 2 was predicted[10] on the basis of qualitative considerations of orbital interactions between the cyclobutane ring and the butadiene and ethylene bridge, respectively. This conclusion was corroborated by Extended Hückel calculations.

In order to explain the Diels-Alder reactivity of 1 compared to that of 2 we have carried out ab initio calculations on the model systems 3, 4, 5, 6, bicyclobutane, cyclobutane, cis-butadiene and cis-butene-2. The numbering of the carbon atoms, as used in the calculations, is the one given in the model systems (3, 4, 5 and 6).



3

— = CH_3



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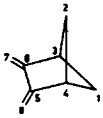

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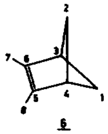

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The calculations were performed on the University's CDC CYBER 74-16, using the program system SYMOL, developed by Dr. G.A. van der Velde.[11] This program takes optimal advantage of any molecular symmetry available, thus allowing the use of fairly large basis sets of gaussian type orbitals (GTOs). The actual basis set used consisted of 6s and 9p primitive GTOs on each carbon atom contracted to 4 and 6 basisfunctions, respectively. For each hydrogen atom 3s GTOs were contracted to 2 basisfunctions.[12] For all species C_{2v} symmetry was assumed. Relevant geometrical details, taken from ref 13, are as follows. In species 3 and 4 the dihedral angle (143, 432) and the C-C distances (12) and (34) were taken as 71°, 1.452, and 2.704 Å, respectively. For species 5 and 6 the values for these parameters were 125°, 1.947 Å, and 2.173 Å. In all species the angle (856) was 127°, the distance (45) 1.503 Å, and the lenght of the remaining C-C single and double bonds (56) was fixed at 1.484 Å, and 1.338 Å, respectively.

If we consider the orbital interactions between ring and bridge in 3 and 4 by looking at the frontier orbitals of bicyclobutane and cis-butene-2 or cis-butadiene, respectively, it turns out that the HOMO and LUMO of bicyclobutane have the proper symmetry to mix with the LUMO and HOMO, respectively, of cis-butene-2, whereas the HOMO of cis-butadiene has the same symmetry as the HOMO of bicyclobutane. The HOMO-LUMO mixings in the first case have a stabilizing effect, but the HOMO-HOMO interaction in the second case are destabilizing (overlap repulsion).[14,10] These qualitative considerations suggest a preference for cis-butene-2 over cis-butadiene as a bicyclobutane bridging group. In the case of cyclobutane the opposite conclusion could be drawn as was reported.[10]

The isodesmic reaction which replaces the cis-butene-2 bridge in 4 by cis-butadiene is calculated to be exothermic by about 7 kcal/mole. For the same reaction with 6 an exothermicity of 17 kcal/mole was calculated which agrees with reported results.[10] Although no quantitative significance should be attached to these values, one can accept the trends as indicating that the Diels-Alder adduct derived from 3 should be more stable as compared to 3 than that from 5 as compared to 5. This makes a fast preequilibrium in the reaction of 1 with maleic anhydride in the presence of silver perchlorate and sodium carbonate[3] unlikely.

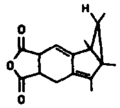
Replacing the cis-butadiene moiety in 3 and 5 by a cis-butene-2 moiety affects also the bonding in the bicyclobutane and cyclobutane parts of the molecules. (table)

C atom pairs	net overlap populations			
	3	4	5	6
12	2.810	2.828	-.231	-.259
14	.405	.400	.142	.144
15	-.135	-.185	-.338	-.398
17	-.002	.002	-.007	.002
34	-.271	-.388	.047	-.090
35 + 36	.382	.437	.351	.398
37 + 38	-.098	-.080	-.035	-.028
56	3.271	5.043	3.020	4.922
57 + 58	1.061	.451	1.065	.415
78	-.431	.067	-.446	.074

Table: Net overlap populations from a Mulliken population analysis for symmetry - unique groups of atoms. Negative values indicate antibonding.

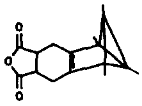
The positive overlap population between rings and bridges is increased in going from 3 to 4 and from 5 to 6, respectively, indicating that the cis-butene-2 fragments are more strongly bonded. However, the negative overlap populationsbetween carbon atom pairs (34) and (15) is increased as is the positive overlap population between the bridge atoms. The changes in these two types of interaction lead to an enhancement of strain in the ring fragment in 4 as compared to 3. Frame work model inspection suggest that, as a result, the central bond in the bicyclobutane system in 4 is compressed as compared to that in 3, whereas the sidebonds are weakened. The overlap populations indicate the same trends.[15]

This supports the suggestion that compound 7 which is isolated in the reaction of 1 with maleic anhydride is formed from 8 by breaking one of the side bonds of the bicyclobutane moiety accompagnied by a hydrogen shift.[5]



7

— = CH_3



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In going from 5 to 6 all interactions are similar except C(12) and C(14). The C(12) repulsion becomes stronger and the interaction between C(14) tends to become more bonding. The "π bond order"[10] between adjacent carbons of rings and bridges is found to be + .019, + .013, -.001 and -.027 for 3, 4, 5 and 6, respectively.[16]

There is another way of comparing the reactivity of 1 and 2 in Diels Alder cycloadditions. In the normal Diels-Alder cycloaddition[17] the interaction between the LUMO of the dienophile and the HOMO of the diene is the dominant stabilizing factor.[18] The HOMO in the model system 3 lies about 25 kcal/mol above that of 5. Both HOMO's have the proper symmetry to interact with the LUMO of a dienophile and have their highest coefficient on C(7) and C(8)[19]. Because of the lower energy separation between the HOMO and a fixed LUMO of a dienophile this interaction is more favourable for 3 than for 5, which may explain the high reactivity of 1 compared to 2 in Diels-Alder cycloadditions.

References and notes.

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12) Detailed information about the calculations is available on request.
13) a) J.F. Chang, J. Amer. Chem. Soc. 93 5044 (1971),
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14) M.J. Goldstein and R. Hoffmann ibid, 6193 (1971).
15) Actually in 3 we used the relevant geometrical parameters as they appear in benzvalene[13b] which certainly is not the optimal geometry for the species at hand. We expect that a geometry optimisation would reveal more strongly the changes in the overlap population for the C(12) and C(14) bonds in going from 3 to 4. Support for this expectation comes from microwave structural studies.[13b] It turns out that the sidebonds in the parent bicyclobutane are considerably longer than in benzvalene whereas the central bond is shorter.
16) Strictly speaking, a "π bond order" cannot be defined for non-planar systems. The numbers quoted here refer to the p_x contributions (x perpendicular to the plane 345) to the net overlap population. This contribution is certainly not the dominant part of the numbers in line "35 + 36" in the table. Hence, we feel it not justified to discuss the differences in reactivity in terms of this "π bond order" only.
17) J. Sauer, Angew. Chem. 79, 76 (1967).
18) R. Sustmann Tetrahedron Lett. (1971) 2721 see also ref 7, 8, 9.
19) The orbital energies of the HOMO's in 3 and 5 are computed to be -.270 A.u. and -.310 A.u., respectively.