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SUBSTITUENT EFFECTS ON THE SYMMETRY-DISALLOWED THERMAL RING OPENING OF TETRAMETHYLBICYCLO[2.2.0]HEX-2-ENES

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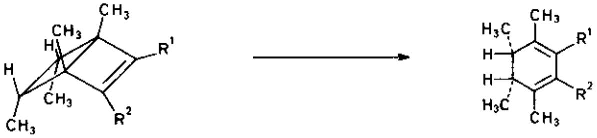
The theoretical aspects of symmetry-disallowed pericyclic reactions have received considerable attention recently[1-3]. When such reactions proceed with concerted breaking and making of bonds, an anti-aromatic transition state is involved. The amount of energy required for such a process has been overestimated[4,5] because configuration interaction had not been taken into account[1,5]. The resulting lowering of the energy of the transition state depends strongly on the relative energies of the molecular orbitals of the transition state. On this basis, it has been predicted that substitution of one component of the pericyclic reaction with electron releasing groups - raising the MO's of that component - and of the other component with electron-withdrawing substituents - lowering the MO's - will effectively reduce the energy barrier of disallowed processes[6].

A convenient way of verifying this prediction would be to examine the effect of substituents on a system which is constrained to a disallowed pericyclic reaction mode for geometric reasons. Consider the thermal $[{}_{\sigma}2_s + {}_{\pi}2_s]$ ring opening of bicyclo[2.2.0]hex-2-ene. We have investigated the easily accessible[7] 1,4,5-endo,6-endo-tetramethylbicyclo[2.2.0]hex-2-enes **1-4**, in which the σ-component is substituted with two methyl groups, and the π-component with methyl, methoxycarbonyl or phenyl groups[8].



1 – 4

1 $R^1 = R^2 = Me$
2 $R^1 = COOMe,\ R^2 = Me$
3 $R^1 = R^2 = COOMe$
4 $R^1 = COOMe,\ R^2 = Ph$

The thermal ring opening reaction of 1-4 was studied at 90-210°. In each case the product expected for $[{}_{\sigma}2_s + {}_{\pi}2_s]$ cycloreversion was selectively formed, as shown by ^1H NMR. Approximate values of the activation parameters are compiled in the Table. The enthalpy of activation is found to decrease by 17-19 kJ mole^{-1} for each methoxycarbonyl group (reaction in heptane)[9]. The activation enthalpy correlates with the π,π^* transition of the ethylenic double bond[6,10]. The values of the activation entropy would seem to reflect the restricted rotation of the methoxycarbonyl and phenyl groups in the transition state compared wtih the ground state. In DMSO similar trends are observed.

Table. Activation parameters for the ring opening of 1 - 4[a]

Solvent	heptane			DMSO	
Compound	$\Delta S^{\neq}$ gibbs mole^{-1}	$\Delta H^{\neq}$ kJ mole^{-1}	λ_{max} nm	$\Delta S^{\neq}$ gibbs mole^{-1}	$\Delta H^{\neq}$ kJ mole^{-1}
1	+ 5	154	210	-18	143
2	-14	135	229	-41	119
3	-27	119	241	-41	108
4	-30	129	229	-16	131

[a] In sealed glass, 5% solution.

A similar substituent effect is observed for the disrotatory cleavage of the bridge in Dewar-benzenes: hexamethylbicyclo[2.2.0]hexa-2,5-diene (liquid phase), $\Delta S^{\neq}$ = +31 gibbs mole^{-1}, $\Delta H^{\neq}$ = 152 kJ mole^{-1}[11]; 1,4,5,6-tetramethyl-2,3-dimethoxycarbonylbicyclo[2.2.0]hexa-2,5-diene (in carbon tetrachloride, 90-120°), $\Delta S^{\neq}$ = -17 gibbs mole^{-1}, $\Delta H^{\neq}$ = 112 kJ mole^{-1}[12].

The energy difference between disrotatory and conrotatory ring opening of cyclobutene has been estimated[5] at 13 kcal mole^{-1} (57 kJ mole^{-1}). The substituent effect for 3 amounts to a reduction of the activation enthalpy by 35 kJ mole^{-1}. Whilst this effect does not amount to removal of the symmetry-imposed energy barrier, it is non the less very considerably reduced.

References and notes

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7 For the preparation of 1 see H.C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas* 86, 1356 (1967) and H. van Bekkum, F. van Rantwijk, G. van Minnen-Pathuis, J.D. Remijnse and A. van Veen, *Ibid.* 88, 911 (1969). For 2-4 see F. van Rantwijk, G.J. Timmermans and H. van Bekkum, *Ibid.* 95, 39 (1976).

8 Substitution of the 1- and 4-positions with electron-delocalizing substituents should further stabilize the transition state, due to stabilization of the partially bonded centers (cf. ref 1); accordingly, the ring opening of 2,3-dimethyl-1,4-dimethoxycarbonylbicyclo-[2.2.0]hex-2-ene proceeds readily, D. Seebach, *Chem. Ber.* 97, 2953 (1964).

9 Destabilization of the ground state of 2-4 by methoxycarbonyl and phenyl groups is not expected. A small stabilizing effect would result from the interaction between the anti-symmetric cyclobutane MO and the π^* orbital, cf. W.L. Jorgensen, *J. Am. Chem. Soc.* 97, 3082 (1975).

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12 We thank mr. P.R. Salwiczek for this result.