CHEMISTRY LETTERS, pp. 89-92, 1976. Published by the Chemical Society of Japan

A MULTI-CYCLIC INTERACTION EFFECT
ON SYMMETRY-IMPOSED STEREOSELECTION RULE.
ANTI-BISALLYLIC SYSTEM

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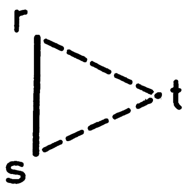
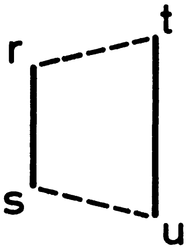
The symmetry-imposed stereoselection rule is partially modified on the basis of orbital interaction. The modification is required for multi-cyclic interactions. The mechanisms of "symmetry-forbidden" 1,3-migration in bisallylic compounds were discussed successfully.

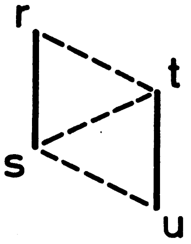
The stereoselection rule based on orbital phase relationship[1,2] has been developed and applied to the chemical reactions characterized by a mono-cyclic interaction between two molecules or between two parts in a molecule. These interaction patterns are schematically represented by I and II. We present a theoretical argument about a new interaction pattern, offering a modification of the stereoselection rule. The interaction pattern of our present interest is one where two conjugate systems are allowed to interact at three pairs of sites (r-t, s-t, and s-u in III).



(I)



(II)



(III)

The selection rule is derived from molecular orbital perturbation theory. To the frontier orbital approximation, the stabilization energy, ΔE, depends on the magnitude of $|\sum_{rt}\sum C^{f}_{Ar}C^{f}_{Bt}|$, that is,

$$|C^{f}_{Ar}C^{f}_{Bt} + C^{f}_{As}C^{f}_{Bt}| \qquad \text{for I,}$$

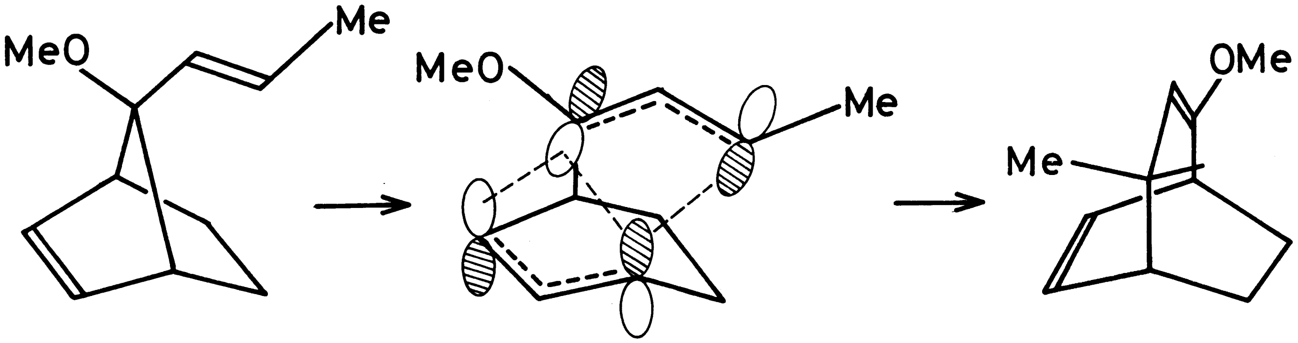
$$|C^{f}_{Ar}C^{f}_{Bt} + C^{f}_{As}C^{f}_{Bu}| \qquad \text{for II,}$$

$$|C^{f}_{Ar}C^{f}_{Bt} + C^{f}_{As}C^{f}_{Bt} + C^{f}_{As}C^{f}_{Bu}| \qquad \text{for III,}$$

where C^f_{Ar} denotes the coefficient of the r-th atomic orbital of the frontier orbital of molecule A. In symmetry-disfavored reactions the two dominant products of AO coefficients for I or II have the opposite signs; ΔE^f_I or $\Delta E^f_{II} \sim 0$.

The interaction pattern III contains both types of mono-cyclic interactions, I and II. It is evident that $\Delta E^f_{III} \neq 0$ even if the stabilization energies coming from each mono-cyclic interaction happen to be zero, that is, if $|C^f_{Ar}C^f_{Bt}+C^f_{As}C^f_{Bt}|=0$, $|C^f_{As}C^f_{Bt}+C^f_{As}C^f_{Bu}|=0$, or $|C^f_{Ar}C^f_{Bt}+C^f_{As}C^f_{Bu}|=0$. This suggests that some multi-cyclic interaction systems are stabilized even if each mono-cyclic interaction is disfavored in terms of the orbital phase continuity. Some seemingly "symmetry-forbidden" reactions can take place stereoselectively in this case.

The modification of the selection rule is exemplified by some 1,3-sigmatropic reactions of the bisallylic systems in the anti-geometrical relation. The high stereoselectivity was observed in the rearrangement of anti-7-trans-propenyl-syn-7-methoxynorbornene (1) to 4-endo-methyl-2-methoxybicyclo[3.2.2]-nona-2,6-diene (2), a formally "symmetry-forbidden" reaction[3]. The endo-isomer (2) is the predominant product of the pyrolysis of 1 (95% of the products including 3,3-sigmatropic products). The stereospecificity of the formal 1,3-sigmatropic shift is higher than 99% . The thermal rearrangement of tricyclo-[3.3.0.0^{2,6}]octa-3,7-diene (3) to semibullvalene (4)[4] is also regarded as a similar 1,3-sigmatropic shift of an anti-bisallylic system.



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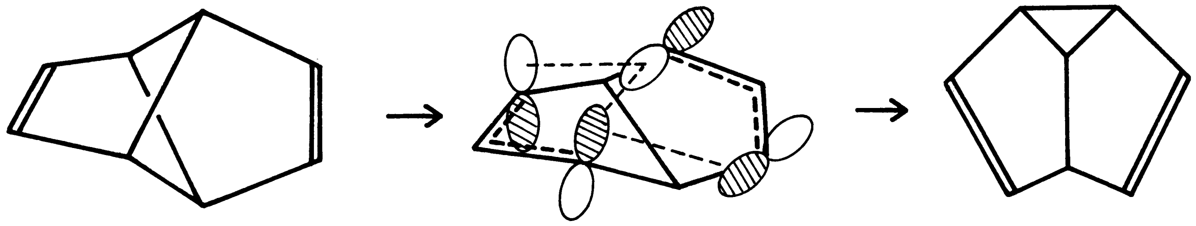

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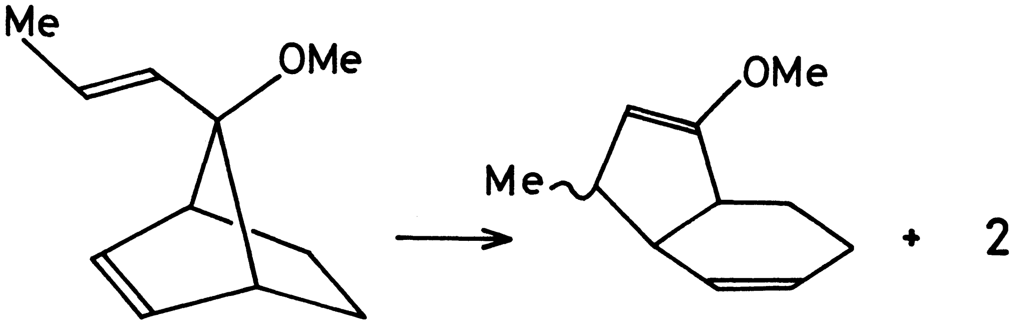
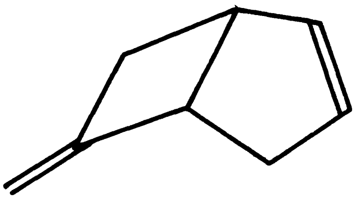
It is interesting in comparison with the thermal rearrangement of 1 that the pyrolysis of syn-7-trans-propenyl-anti-7-methoxynorbornene (5), an isomer of 1, undergoes 3,3-sigmatropic shift predominantly to 6 (70~74%) and 1,3-sigmatropic shift exclusively to 2.3) The difference between 1 and 5 in the favorable reaction course may be attributed to a steric inaccessibility to the transition state of an anti-bisallylic interaction in case of 5. The related bicyclic dienes, 6-methylenebicyclo[3.2.0]hept-2-ene (7)5) and 6-methylenebicyclo[3.2.1]oct-2-ene (8)6) are thermally transformed mainly to the Cope rearrangement products. The lack of the effective anti-bisallylic interaction may similarly be responsible for the preference of the 3,3-sigmatropic shift over the 1,3-sigmatropic shift.



5 6



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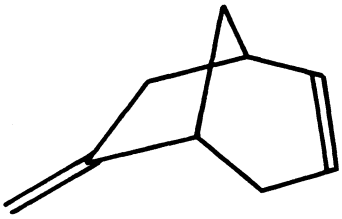

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The multi-cyclic interaction effect should be distinguished from other effects on the modification of the stereoselection rule, i.e., the pseudo-excitation7), the three-system interaction effects including the role of catalysts8) and substituents9), and the "subjacent orbital effect" proposed by Berson and Salem10).

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(Received December 2, 1975)