A CLASSIFICATION OF THE PHOTOCHEMICAL ELECTROCYCLIC REACTIONS

OF HETEROATOM CONJUGATED SYSTEMS

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Abstract: Photochemical electrocyclic reaction mechanism of a variety of heteroatom conjugated systems has been elucidated by a unique concept. The proposed classification of the reaction, which is based upon the number and types of electrons involved in the reaction centers, takes into account the participation of the lone-pair electrons and gives the correct description of the electron behavior during the electrocyclic reaction process.

The electrocyclic reaction of all-hydrocarbon conjugated systems has well been elucidated on the basis of the orbital symmetry arguments.[1] Little attention, however, has been paid upon the electron behavior in the formal electrocyclic reaction of the heteroatom conjugated system, in which one of the terminal methylene groups in the all-hydrocarbon system is replaced by a heteroatom. In our previous calculation on the photochemical isomerization of acrolein into oxetene,[2] the reaction path *via* zwitterion was shown to exist. This path is much different from that for the corresponding all-hydrocarbon system. It is emphasized here that the path involved therein is characteristic of the heteroatom conjugated system and the photochemical electrocyclic reaction mechanism of a variety of hetero-atom conjugated systems can be understood by a unique concept.

Let us consider the two-stage path in which the photo-induced rotation of the terminal methylene is followed by the ring closing between the terminal atoms. It is noted that the argument presented here is valid even for the concerted path in which the rotation of methylene and the ring-closing occur simultaneously, since the concerted path can be

D Z_+ Z_- 1   2
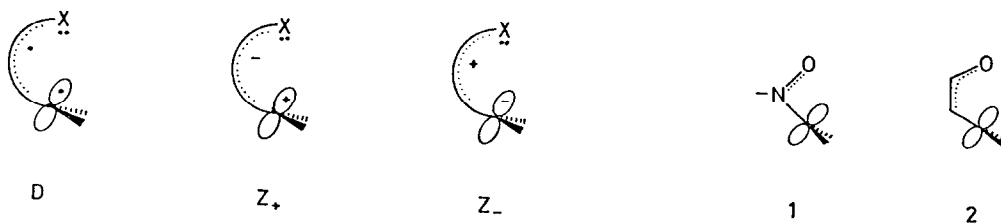
understood by the superposition
of the two independent steps.
The rotation of methylene gives
the twisted molecule. The
relative energies of three
electronic states of the
twisted structure,[3] diradical,
$D_{\sigma\pi}$, and two zwitterions, Z_+
and Z_-, are determined by the
electronic property of the π
sub-structure in the twisted
molecule. In the case of
cyclization of nitrones into
oxaziridines, the anti-bonding
π^*_{NO} orbital of the twisted
structure, 1, lies much higher
than the σ AO of the terminal

Fig. 1. Two typical correlation diagrams
between the twisted and cyclic structures.
(a) $E(Z_+) > E(Z_-)$, (b) $E(Z_+) < E(Z_-)$.

carbon atom; the Z_+ state is higher than the Z_- one.[4]   On the other hand,
the Z_+ state of the twisted acrolein, 2, is lower than the Z_- state.[2]
Depending upon the ordering of these electronic states, a variety types of
potential curves will be obtained along the two-stage path.   However, as
may be seen from the state correlation diagrams[5] between the twisted
structure and the cyclization product (Fig. 1), the Z_+ state[6] always
correlates with the ground state of the cyclization product independent of
the ordering of these three states.   The cyclization is expected to occur
from the Z_+ state.   This is due to the important participation of the
lone-pair electrons of the terminal heteroatom during the ring-closing step
and is characteristic of the heteroatom conjugated system.

   The above analysis of the electron behavior suggests that the electron
reorganization during the formal electrocyclic reaction of nitrones, 3→4,
is represented in terms of two π electrons and two lone-pair electrons by
$\pi^2_{NC} + n^2_O \rightarrow \pi^2_N + \sigma^2_{CO}$, or simply by $\pi^2 + n^2 \rightarrow \pi^2 + \sigma^2$.   For the case of acrolein,
5→6, the representation would be $\pi^2_{CC} + \pi^2_{CO} + n^2_O \rightarrow \pi^2_{CC} + \pi^2_O + \sigma^2_{CO}$ or $\pi^4 + n^2 \rightarrow \pi^4 + \sigma^2$.
These representations involve the important role of the lone-pair electrons
in the reaction process and can not be derived by the analogy of all-hydro-
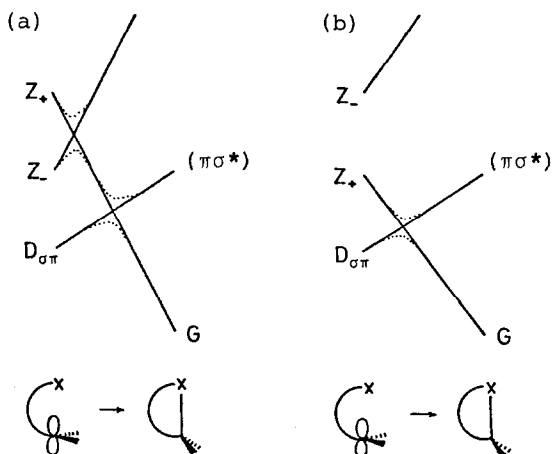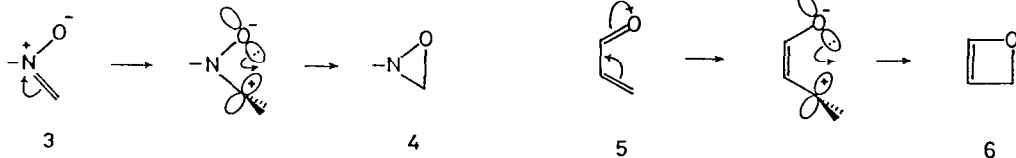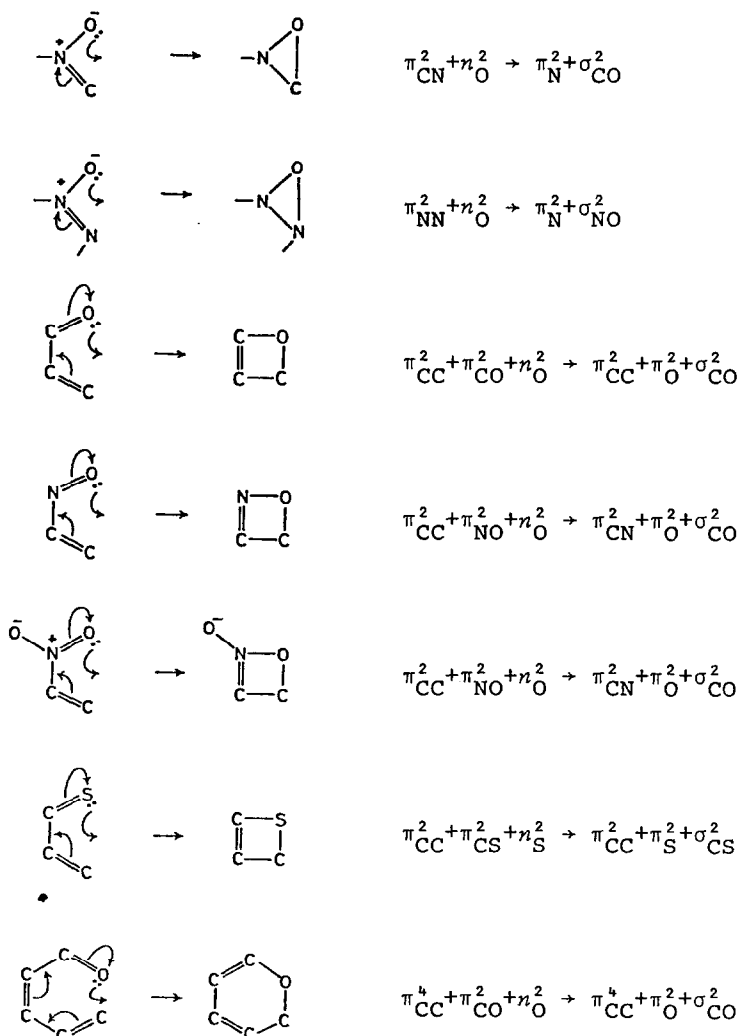carbon conjugated systems; the simple analogy of the all-hydrocarbon

3   4   5   6

systems gives the representation of $\pi^4 \rightarrow \pi^2+\sigma^2$ for both $\underline{3}\rightarrow\underline{4}$ and $\underline{5}\rightarrow\underline{6}$ reactions.[7]

The present argument is general one which can be applied to any heteroatom conjugated system. Thus the photochemical electrocyclic reactions of heteroatom conjugated systems may be conveniently classified by indicating the number and types of electrons involved in the reaction. Several examples, of which the experimental evidences have been reported in literature,[8] are shown in Scheme I. The classification in Scheme I is clearly different from that for the all-hydrocarbon conjugated systems.[7] It gives the correct electron behavior and the uniform understanding for

Scheme I

$$\pi^2_{CN}+n^2_O \rightarrow \pi^2_N+\sigma^2_{CO}$$

$$\pi^2_{NN}+n^2_O \rightarrow \pi^2_N+\sigma^2_{NO}$$

$$\pi^2_{CC}+\pi^2_{CO}+n^2_O \rightarrow \pi^2_{CC}+\pi^2_O+\sigma^2_{CO}$$

$$\pi^2_{CC}+\pi^2_{NO}+n^2_O \rightarrow \pi^2_{CN}+\pi^2_O+\sigma^2_{CO}$$

$$\pi^2_{CC}+\pi^2_{NO}+n^2_O \rightarrow \pi^2_{CN}+\pi^2_O+\sigma^2_{CO}$$

$$\pi^2_{CC}+\pi^2_{CS}+n^2_S \rightarrow \pi^2_{CC}+\pi^2_S+\sigma^2_{CS}$$

$$\pi^4_{CC}+\pi^2_{CO}+n^2_O \rightarrow \pi^4_{CC}+\pi^2_O+\sigma^2_{CO}$$

a variety of heteroatom conjugated systems.

  The classification in Scheme I can not answer the question which state of the heteroatom conjugated system is the most important for the formation of the cyclic product. This problem may be solved by the analysis of the calculated potential surfaces for each reaction. In the case of the 5→6 reaction, for example, the photochemical cyclization is expected to occur from the $\pi\pi^*$ singlet state of acrolein.[2]

References and Notes

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3) The electronic structures of diradicals and zwitterions have well be documented: L. Salem and C. Rowland, Angew. Chem. Int. Ed., 11, 92 (1972); W. Dauben, L. Salem, and N.J. Turro, Acc. Chem. Res., 8, 41 (1975); L. Salem, ibid., 12, 87(1979).

4) This was confirmed by the MINDO/3 CI calculation.

5) The state correlation diagram can simply be obtained by counting the σ and π electrons on the reaction centers. See Ref. 3.

6) The $D_{\sigma\sigma}$ diradical has the symmetry property same as the Z_+ zwitterion. When the $D_{\sigma\sigma}$ state is close to the Z_+ state, the substantial mixing occurs between these two states. In that case, the formation of the zwitterion Z_+ may not clearly be observed during the reaction.

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