Tetrahedron Letters No.22, pp. 1885-1888, 1970. Pergamon Press. Printed in Great Britain.

THE CYCLOADDITION OF $n \to \pi^*$ EXCITED DIMETHYL MALEATE TO 1,2-DIDEUTERIOCYCLOHEXENE[x]. A "HALF ALLOWED" REACTION

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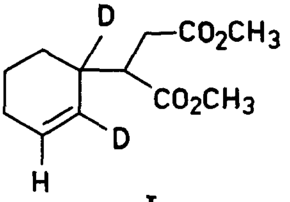
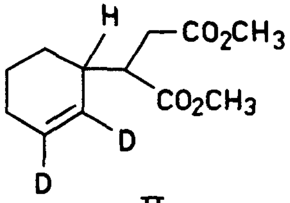
(Received in UK 1 April 1970; accepted for publication 9 April 1970)

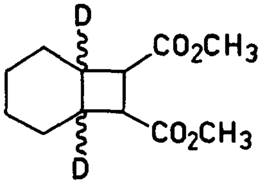
The photo-induced addition of dimethyl maleate to cyclohexene is symmetry allowed according to the Woodward-Hoffmann rules in their simplest formulation (1). Nevertheless, the addition appears to be largely non-concerted (2-4). To determine if the ene-addition, which is reported as a major side reaction, is also non-concerted we have studied the photoaddition of dimethyl maleate to 1,2-dideuteriocyclohexene. One part each of the ene-adducts (I) and (II) were formed together with two parts of the cycloadduct (III) (5). The photo-induced ene-addition is thus non-concerted and probably involves cyclohexenyl radicals that are partly free as is indicated by the formation of dicyclohexene. In contrast, the thermal addition gave only the "true" ene-adduct (I) (6). It is interesting to note that the formally related ene-addition of dimethyl diazenedicarboxylate (azoester) to 1,2-dideuteriocyclohexene is a radical reaction both photochemically and thermally (8).



I



II



III

It is quite conceivable that the photochemical ene-addition should be a radical reaction

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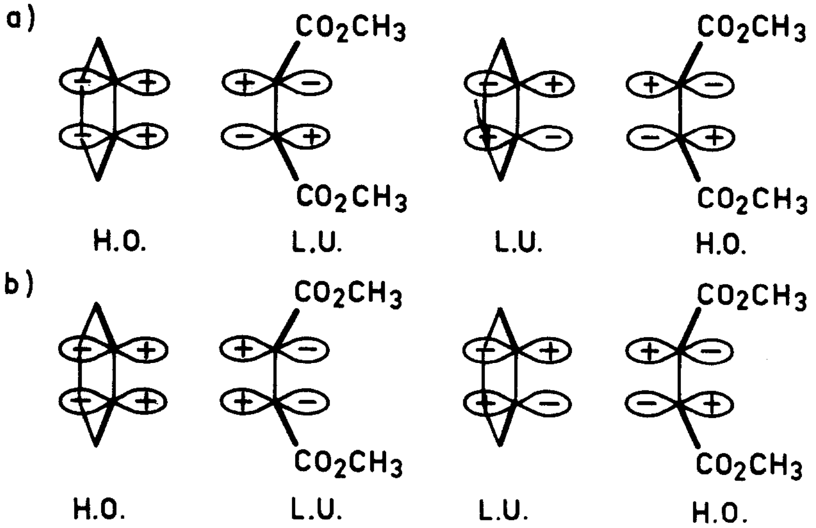
[x] Cycloaddition reactions, part 3. Presented at Organikerdagarna, Uppsala, Sweden, June 1969. Parts 1 and 2: Refs (7,8).

since only the thermal reaction should be symmetry allowed (9,10). However, it is less obvious why the photocycloaddition of dimethyl maleate to cyclohexene is non-concerted. One possible reason is indicated by a simple perturbation treatment of the orbital interactions between dimethyl maleate and cyclohexene (cf. 11-13). It is probable that the $n \rightarrow \pi^*$ excited state is the main state involved in the photoaddition (4). For this state, the interaction between the highest occupied orbital (HO) of the maleate and the lowest unoccupied (LU) orbital of cyclohexene is symmetry allowed. However, the interaction between the LU orbital of the maleate and the HO orbital of cyclohexene is disallowed (fig. 1a). It seems reasonable to assume that concerted addition is possible only when both interactions are symmetry allowed. The "half-allowed" addition of $n \rightarrow \pi^*$ excited maleate to cyclohexene should therefore be non-concerted, which is in accordance with experiment. By contrast, cycloaddition involving $\pi \rightarrow \pi^*$ excited maleate should be concerted since both orbital interactions are symmetry allowed (fig. 1b, cf. ref. 1).

Fig. 1. Relative symmetries of the interacting orbitals in the transition state for addition of excited dimethyl maleate to cyclohexene.
a) $n \rightarrow \pi^*$ b) $\pi \rightarrow \pi^*$ excited state

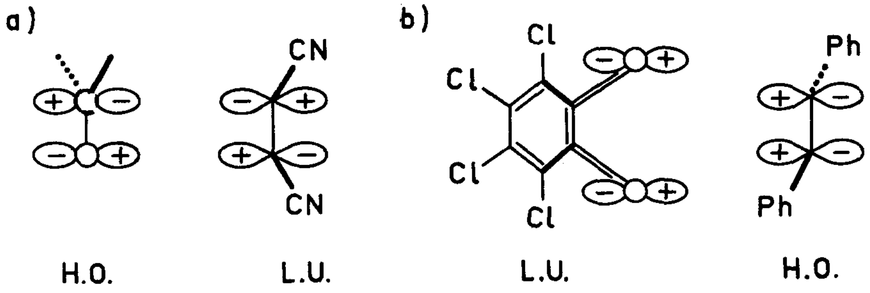


An allowed reaction appears to require 10-20 kcal lower activation energy than a disallowed reaction, other factors being equal (14, 15). This lowered activation energy probably results from the fact that both orbital interactions in the transition state are symmetry allowed (e.g. fig. 1b). For a "half allowed" reaction the "decrease" in activation energy should be smaller since there is only one symmetry allowed interaction in the transition state (fig. 1a). If there is charge transfer interaction in the transition state this should predominantly involve only one of the two orbital interactions. The symmetries of the two reactant orbitals that participate in this interaction should determine the decrease in activation energy relative to a disallowed reaction. Depending on the direction of the charge transfer "half allowed" reactions ranging from essentially allowed to essentially disallowed should therefore exist.

In the case of $n \rightarrow \pi^*$ excited maleate-ground state cyclohexene, charge transfer should occur from the HO cyclohexene orbital to the LU maleate orbital. Since the interaction between these orbitals is symmetry forbidden (fig. 1a), the addition should be essentially disallowed. The triplet excited state of the maleate should have at least 10 kcal/mol lower energy than the singlet state. Since the decrease in activation energy due to symmetry allowed overlap should be small for the singlet reaction, the non-concerted triplet reaction should be favoured by about 10 kcal/mol (16, 17).

In the addition of $n \rightarrow \pi^*$ excited acetone to ground state fumaronitrile the charge transfer should be from the HO orbital of acetone to the LU orbital of fumaronitrile. The interaction between these two orbitals is symmetry allowed (fig. 2a). "Nearly" concerted addition involving the excited singlet state should therefore be possible. The addition indeed proceeds stereospecifically as required for a concerted addition (18, 19).

Fig. 2. Examples of systems where the symmetry allowed interactions are favoured due to charge transfer. (Only the allowed interaction is shown in each case).



These simple predictions can probably be generalized to more complex systems. For example, for a 4+2 system, $n \rightarrow \pi^*$ excited tetrachloro-o-benzoquinone and stilbene, charge transfer should make the symmetry allowed interaction (quinone LU-stilbene HO orbital fig. 2b) dominate, leading to the highly stereoselective addition observed (20).

Financial support from the Swedish Board for Applied Research is gratefully acknowledged.

References and Footnotes

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5. Addition of copper(I) bromide gave rise to a "charge transfer" band at 310 nm and led to a more rapid and clean reaction. The ratio between the adducts (I), (II) and (III) remained unchanged, indicating that copper(I) functions largely to facilitate population of the photo-reactive state. It also seems probable from this result that ene-addition and cycloaddition take place from the same excited intermediate.
6. Equal amounts of *exo* and *endo* adducts are formed when maleic anhydride is used in place of dimethyl maleate, indicating low steric preference also in the latter case.
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16. The $n\rightarrow\Pi^*$ triplet state of the maleate is probably less than 77 kcal above the ground state (G.S. Hammond *et al.*, *J.Am.Chem.Soc.* **86**, 3197 (1964).
    Since dimethyl maleate is essentially transparent above 300 nm, the corresponding singlet must be more than 87 kcal above the ground state.
17. When a singlet state has more than 20 kcal/mol higher energy than the corresponding triplet (e.g. in organometallic compounds) a non-concerted triplet reaction may be preferred even when a totally symmetry allowed reaction path is available.
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