The Representation of Electronically-excited Intermediates in Photochemical Reactions

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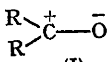
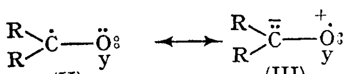
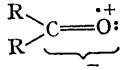
RECENTLY, much interest has been directed towards the photochemistry of carbonyl compounds. It is recognised that the starting point of many of the reactions is the lowest triplet $\pi\pi^*$ state, and two methods of representing this excited state have been proposed. The polar-state concept proposed by Chapman[1] represents this excited state by (I), which encourages the rationalisation of photochemical reactions in terms of ionic processes. A disadvantage of this description is that it is also a canonical structure of the ground state molecule, and in a reaction sequence using this symbolism it is not clear at what stage demotion to the ground state must occur. An alternative proposal by Zimmerman[2] represents the excited state by the structures (II) and (III), in which the various symbols distinguish between electrons in different orbitals. This description permits rationalisation of the subsequent reaction in terms of single electron shifts.

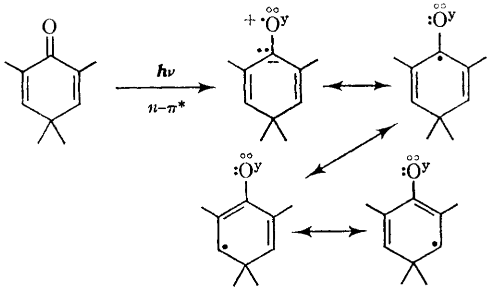

(I)


(II) (III)

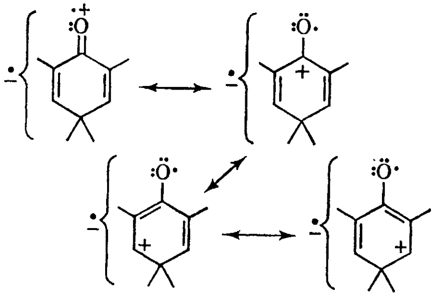

(IV)

Both of these representations are unsatisfactory, since both strongly imply the absence of a π-bond and therefore suggest a $\pi\pi^*$ state. The representation (IV), in which the electron in the π orbital is not incorporated at any specific part of the bonding framework of the molecule, is proposed as a more satisfactory alternative since it preserves both bonds between carbon and oxygen and emphasises the radical and electrophilic character of the oxygen atom simultaneously.

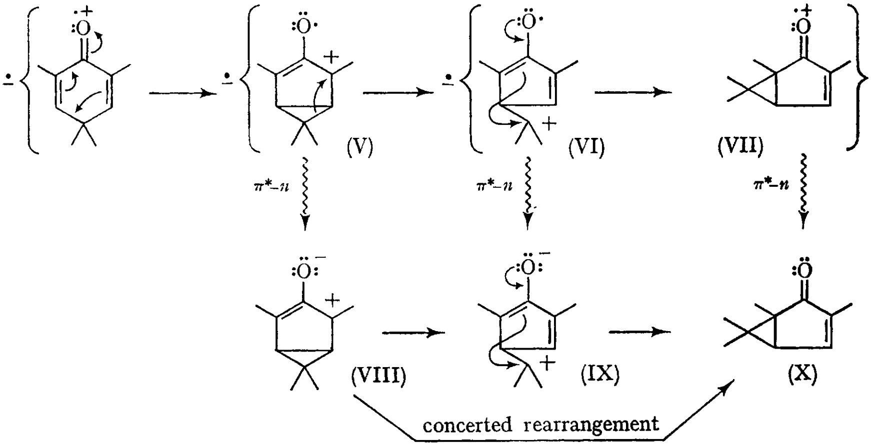
The application of this representation to the rearrangement of dienones shows some possible advantages. Zimmerman[2] has described the excited species by the alternative structures:

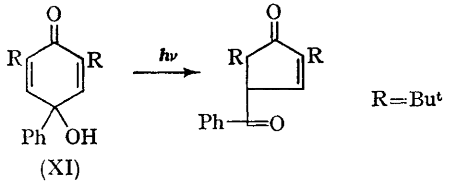


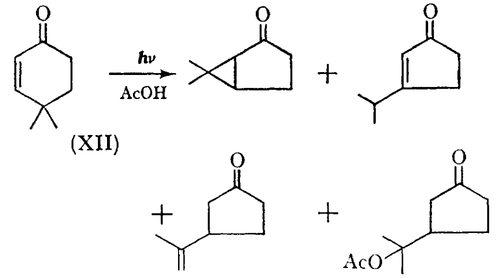
These structures conform to the custom that no atom of the first short period can be associated with more than eight electrons in the outer shell, but this is not necessarily true where antibonding orbitals are occupied, as in this case. The clear distinction between electrons in the bonding framework of the molecule and electrons in delocalised antibonding orbitals is considered to be an advantage of structure (IV), and we would represent the $n\pi^*$ state of the dienone as:



Using this representation, the dienone rearrangement would be formulated:







In the pathway proposed by Zimmerman[2], rearrangement must be preceded by demotion, since this generates the ionic species (VIII) which is subsequently isomerised to (X) by a concerted or stepwise rearrangement. In the scheme above there is the possibility of rearrangement occuring partly or wholly in the excited state, with three alternative stages at which demotion may occur. The conversion of (V) into (VI) might be explained by the extension of the conjugated system with a corresponding decrease in the energy of the bonding and antibonding π-orbitals. The formation of carbonium ions like (VI) and (IX) is consistent with the observed photoreactions of (XI)[3] and (XII)[4].

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[1] O. L. Chapman, *Adv. Photochem.*, 1963, **1**, 323.

[2] H. E. Zimmerman, ref. 1, p. 183.

[3] E. R. Altwicker and C. D. Cook, *J. Org. Chem.*, 1964, **29**, 3087.

[4] O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 1963, 2049.