

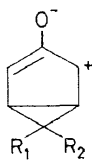
REPORT ON RECENT PHOTOCHEMICAL INVESTIGATIONS

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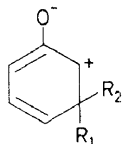
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A mechanistic treatment of organic photochemical reactions was proposed by us earlier¹ wherein the electronic details of molecular transformations occurring may be considered in detail. The portion of this hypothesis dealing with unsaturated ketones is the subject of the present talk.

In our earlier publications we proposed that mesoionic species of types (I) and (II), and their conjugate acids, are intermediates in many of the photochemical reactions of cross-conjugated cyclohexadienones. This portion of



(I)

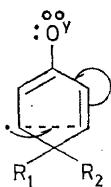


(II)

our suggestions seems to have gained acceptance and will not now be considered. Rather, we will direct attention to more controversial aspect of our proposals, namely how these species are engendered.

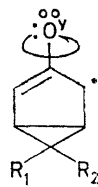
To begin with, our suggestion that it is an $n-\pi^*$ state which leads to these species by the processes in equations (1) and (2) has lacked firm support. If it were invariably the singlet excited states of the cyclohexadienones and

$n-\pi^*$
excited state of a
cyclohexadienone



(III)

β,β -bonding



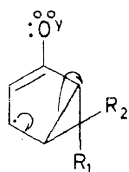
(IV)

Electron
demotion

(1)

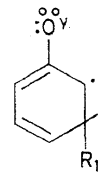
(1)

$n-\pi^*$
excited state of
a bicyclo-
(3,1,0) hex-3-en-2-one



(V)

Bond
fission



(VI)

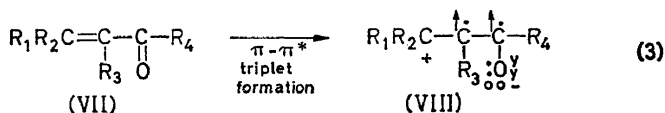
Electron
demotion

(II)

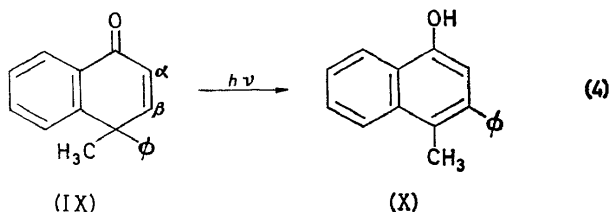
(2)

unsaturated ketones which undergo molecular change, then our hypothesis might pose a less formidable challenge to substantiate. Thus it is known that in these systems the $n-\pi^*$ singlet is of considerably lower energy than the $\pi-\pi^*$ singlet, internal conversion is generally very rapid, and the reactions in question do proceed nicely when only the lower energy $n-\pi^*$ singlet is generated.

However, intersystem crossing of excited ketone singlets to give triplets is known to be fast. In the case of 4,4-diphenylcyclohexadienone we have shown² the triplet to be the excited species rearranging. In contrast to the singlet state situation, for triplets there has remained the possibility that the $\pi-\pi^*$ species might be of lower energy than the $n-\pi^*$ state of the dienones and enones. It is likely but not totally certain that the lowest energy triplet would also be the reacting triplet. The above possibility has been suggested in the literature. To the extent that the $\pi-\pi^*$ triplet has an electron distribution approaching that of the singlet $\pi-\pi^*$ species, the β -carbon of the triplet might be electron deficient as suggested frequently in the literature:

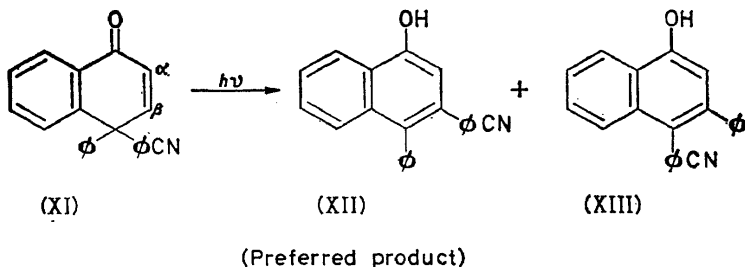


One photochemical rearrangement we now report³, that of γ to β aryl migration of 4,4-diaryl-1(4*H*)-naphthalenones, has proven of value in



probing the β -carbon valency in the excited state. That a simple aryl migration occurs without skeletal rearrangement is shown by the example in equation (4) in which the methyl group is an effective label.

The photolysis of 4-phenyl-4-*p*-cyanophenyl-1(4*H*)-naphthalenone (XI) was found to afford products of both cyanophenyl and phenyl migration. However, *p*-cyanophenyl migration was preferred by ratios of 3 : 2 to 2.2 : 1 depending on conditions³.



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Further, the reaction has been shown by benzophenone sensitization experiments³ to proceed *via* a triplet state. The preferential migration of a cyanophenyl group clearly shows that the β -carbon (*i.e.* C-3) of the excited triplet enone moiety is not primarily electron deficient in character. In contrast, the non-photochemical, acid-catalysed rearrangement of enone (XI), where the β -carbon does become electron-deficient, gives exclusively the product of phenyl migration (*i.e.* XIII). Whether in the photochemical reaction the triplet excited state β -carbon reactivity is better described as odd electron or two electron in capability is undecided by this experiment. The $n-\pi^*$ triplet species would be expected to have odd electron capabilities at the β -carbon and this site would also have a π system electron rich relative to the ground state reactant. Thus the reaction is depicted as in *Figure 1*.

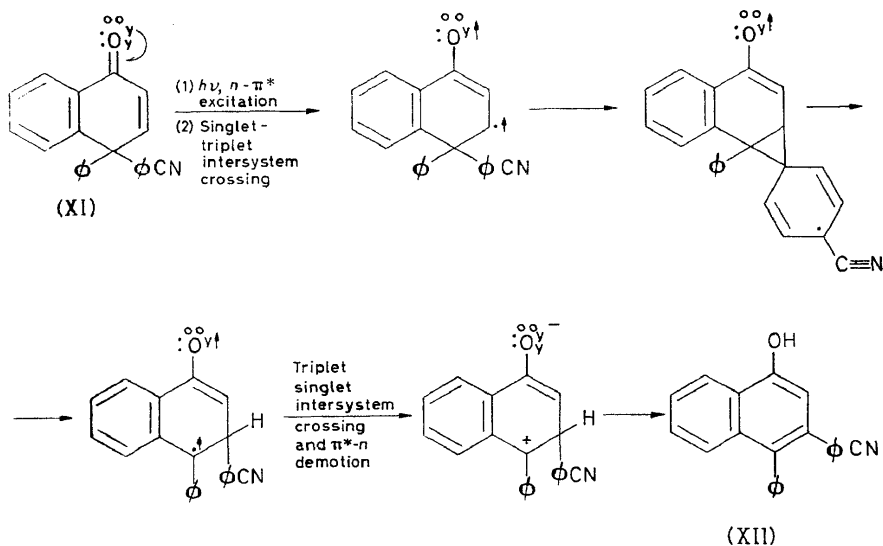


Figure 1

The experiments just described depend on the reactivity of the triplet which can be taken as deriving from the electronic makeup of the triplet. Nevertheless, it is desirable to obtain evidence directly on the electron distribution in the triplet state before molecular change. The four substituted 2,5-cyclohexadienones in *Figure 2* were studied⁴. It was found that

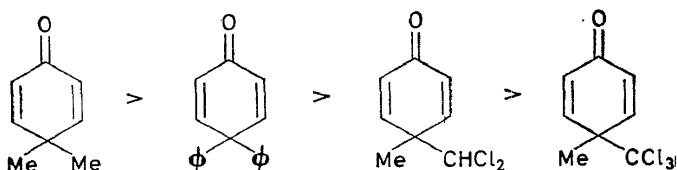


Figure 2

the triplet energies varied in a pattern paralleling the order of the $n-\pi^*$ singlet species but not the $\pi-\pi^*$ singlet states. The decrease in energy as

more electronegative groups are placed near the β -carbon is expected for states in which the β -carbon is more electron-rich than the ground state. This has, in fact, been observed previously for singlet $n-\pi^*$ states by Kosower⁵.

Simple molecular orbital calculations, not differentiating between singlet and triplet states, do predict an enhancement of π electron density at the β -carbon atom of the 2,5-cyclohexadienone system in accord with both the singlet and triplet observations. Also, interestingly, these calculations² predict an enhancement of the β, β - (i.e. 3,5-) bond order (note Figure 3).

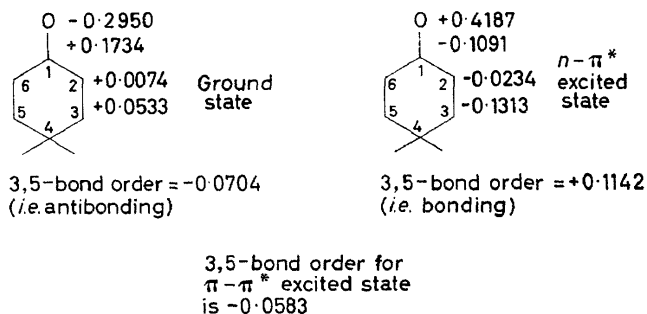
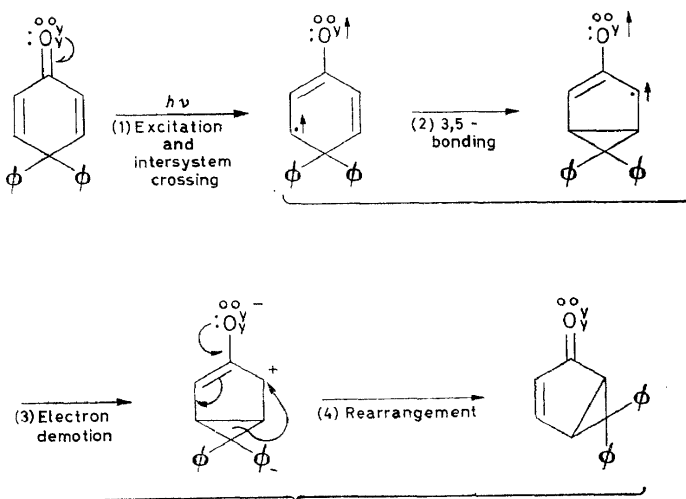


Figure 3. Formal charges and bond orders for cyclohexadienones

This enhancement is in accord with the β, β -bonding suggested¹ as the first step following formation of the $n-\pi^*$ triplet² of cyclohexadienones. The remaining steps leading to zwitterion (I), namely intersystem crossing, electron demotion and cyclopropylcarbinyl rearrangement need little discussion. However, it is worthwhile to note that such rearrangements of triplet excited states may be so rapid as to compete with diffusion controlled



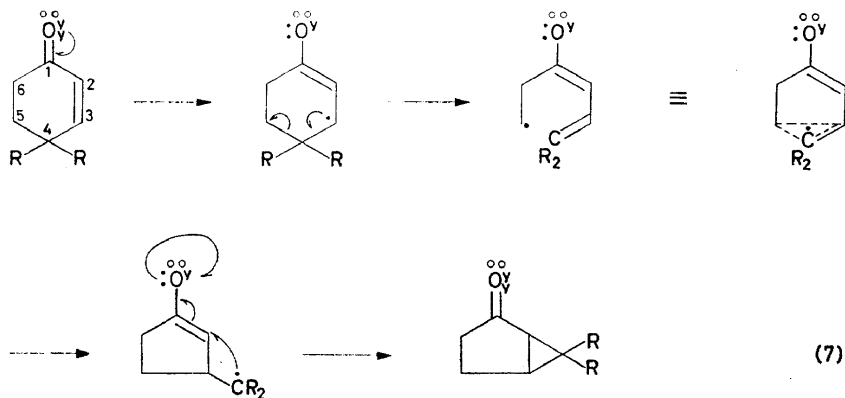
Rapid relative to rate of diffusion and triplet destruction by quencher

Figure 4

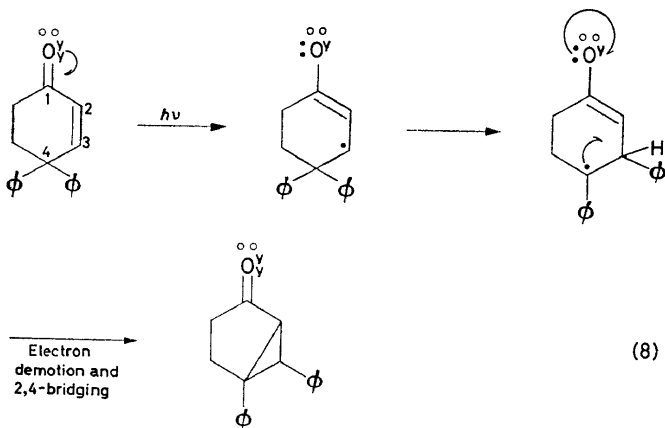
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quenching. This is the case in the photochemical rearrangement of 4,4-diphenylcyclohexadienone². In such instances lack of quenching does not suffice to prove absence of a triplet mechanism.

Relevant to the mechanism proposed for the dienone reactions is the situation with cyclohexenones. It has been found by Gardner⁶ and Chapman⁷ that the monoenones rearrange in a formally similar manner. Here there is certainly no possibility for operation of the mechanism proposed by us for the dienones. For the monoenones we have suggested a mechanism involving homolytic fission of bond 4-5 of the $n-\pi^*$ excited state. Bonding of C-5 to C-3 and π^*-n electron demotion is seen to rationalize the observed^{6, 7} rearrangements.

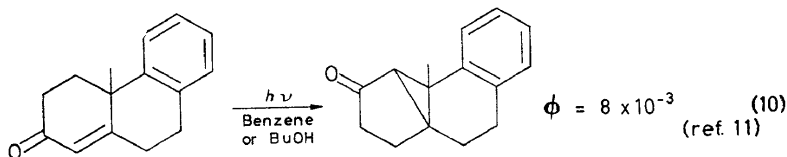
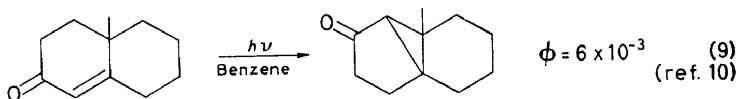


We have studied the related 4,4-diphenylcyclohexenone rearrangement. Here phenyl migration occurs with subsequent 2,4-bridging.



Since the same 4 to 3 phenyl migration was an *a priori* possibility in the case of 4,4-diphenylcyclohexadienone but did not occur, we can conclude that β , β -participation of the second double bond is preferred over phenyl

migration. Similarly, since the ring contractive rearrangement of the alkyl substituted cyclohexenones was a non-occurring possibility for the 4,4-diaryl analogue, we can conclude that the rearrangement of 4,4-dialkylcyclohexenones is the least efficient of all of the rearrangements. This is reasonable considering the required homolytic fission of a σ bond (*vide supra*). Support for this view is found in the low quantum efficiency encountered in such rearrangements; for example^{10, 11}:



That these reactions are also triplet rearrangements is shown by acetophenone sensitization. Most interesting is the observation that reaction (9) is heavily quenched by $10^{-5}M$ ferric dipivaloylmethide. Similarly, literature evidence¹² shows that the photolysis of such enones affords four-ring dimer and pinacolic product, the latter resulting from hydrogen abstraction from solvent. It is clear that triplet rearrangement in the present instance of enones is sufficiently slow to allow quenching and reaction with the environment. Hydrogen abstraction is characteristic of $n-\pi^*$ excited triplets.

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