

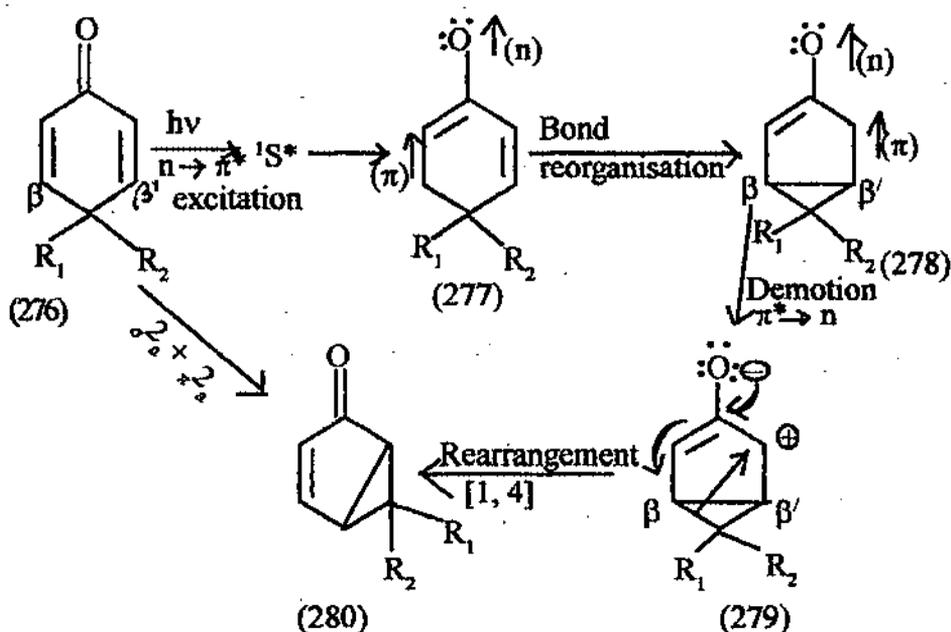
CHAPTER - II

(A short review on Mechanistic Aspect of Cyclohexadienone Photochemistry)

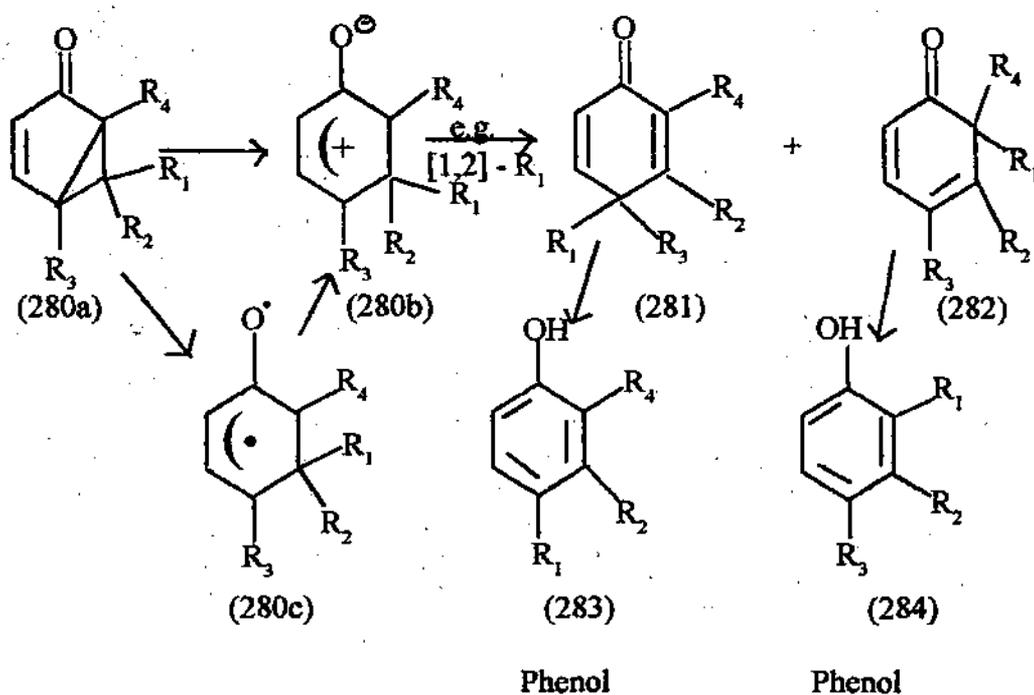
Introduction :

Because of facile, fascinating but complicated nature of deep-seated molecular rearrangements of cross-conjugated cyclohexadienones initiated by UV-irradiation between 250 to 360 nm their mechanisms have attracted a good deal of work over last three decades. Eventually, a deep-insight into the various aspects of the mechanisms^{16,17} has been achieved. A unifying concept has been arrived at encompassing the polar state proposition put forward by Chapman¹² and non polar radical type species developed during initial stages of electron excitation and demotion as postulated by Zimmerman and Schuster.⁷⁸

Scheme - III



Formation of bicyclo [3, 1, 0] hexenone(230) from photo-reaction of a model 2,5-cyclohexadienone (276) has been considered to proceed through a series of steps involving n, π^* singlet excited state (276), inter system crossing to the triplet n, π^* state (277), β, β' bridging (rebonding) to furnish (278) which is still an electronically excited molecule of the n, π^* type and results in ground state zwitterion (279) which rearranges finally to the lumiketone (280). The cyclohexadienone \rightarrow bicyclohexenone transformation can be viewed in a formal manner as a concerted $\sigma^2_a + \pi^2_a$ cyclo addition in terms of conservation of orbital symmetry principles formulated by Woodward-Hoffman. The process can also be dissected into the initial formation of a new bond between β, β' carbon atom (279) followed by [1, 4] - sigmatropic shift across 2-oxybutenyl frame with inversion of configuration at the migrating carbon atom. In



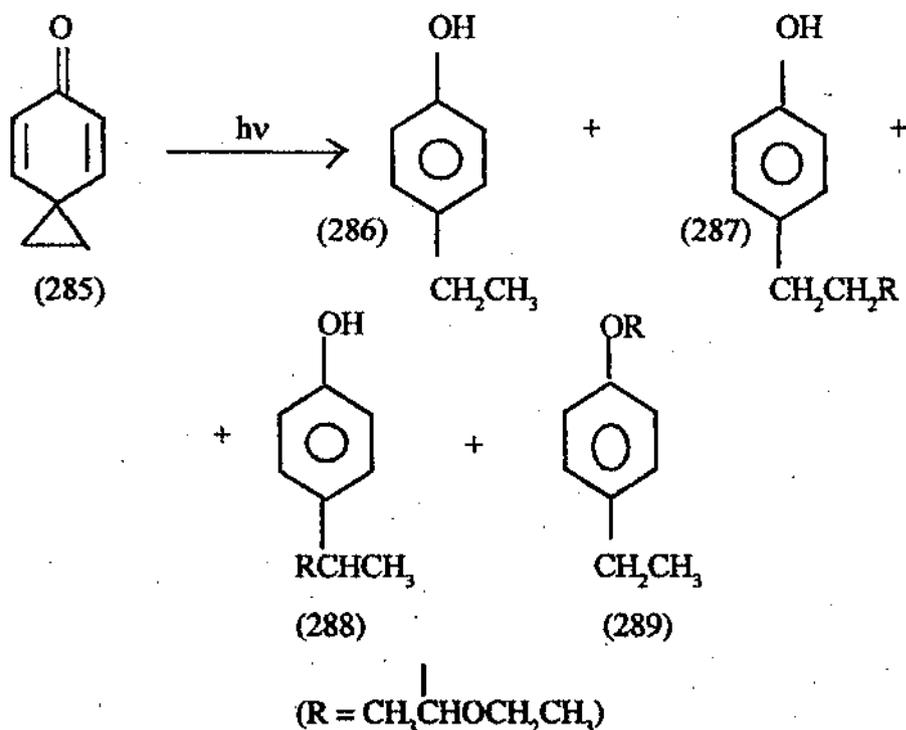
lumiprotect (280a) prolonged irradiation eventually gives rise to secondary photoproducts e.g. phenols (283) and (284) and ketones (281) and (282) as indicated above depending upon the nature of substitution. In the beginning we shall consider evidence in support of radical species generated during initial electron excitation

(SECTION-A) and subsequently involvement of Zwitterionic polar species following electron demotion (SECTION - B). Finally, we shall discuss on the spin multiplicity of excitation i.e. singlet vs. triplet (SECTION - C) and evidence on the electronic configuration i.e. n, π^* vs. π, π^* of the reactive excited state (SECTION-D).

SECTION - A

(Involvement of Free Radical Intermediates)

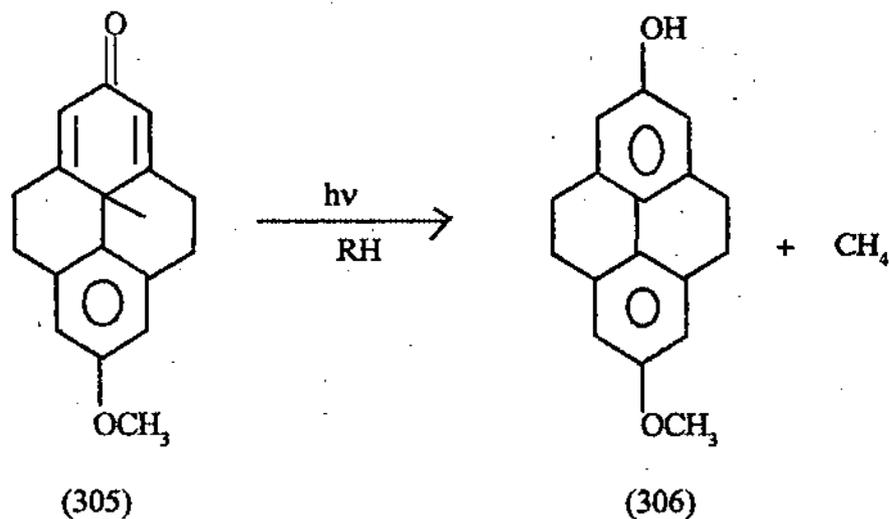
Convincing evidence was sought by Schuster group^{107,115} for involvement of free-radical intermediate using spiro-dienone (285). Photolysis of (285) in ether yielded four principal products (286), (287), (288) and (289). Formation of these products clearly demonstrated the involvement of free - radical intermediates and hence strongly disfavours the idea of polar state description of the excited state.



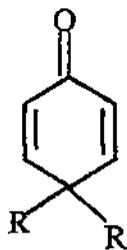
Further in-depth study was carried on better model compound trichloromethyl dienone (290) which is practically strainless as compared to highly strained spiro dienone (285) and contains a trichloromethyl substituent at C_4 which is easily expellable as radical. On irradiation (290) afforded chloroform, hexachloroethane and p-cresol as depicted in the scheme below. This reaction has been found to occur efficiently in solvents e.g. 2-propanol, diethyl ether and cyclohexane which are known as good hydrogen donors toward free radicals. A ketyl radical (291) is first generated by

abstraction of hydrogen by triplet excited dienone(290) and then elimination of the substituent as radical occurs from the radical (291). This reaction could be quenched by triplet quenchers and sensitized by triplet sensitizers¹⁸. Rate constant for H-abstraction derived from Stern - Volmer plot was $3.9 \times 10^8 \text{ M}^{-1} \text{ S}^{-1}$. This value is considerably higher than H-abstraction by standard n, π^* triplet such as benzophenone ($K_{\text{obs}} \sim 10^6 \text{ M}^{-1} \text{ S}^{-1}$) but close to value derived for intramolecular H abstraction in the Norrish type II reaction ($K_{\text{obs}} \sim 10^8 \text{ M}^{-1} \text{ S}^{-1}$). When flash photolysis was carried out on (290) in degassed isopropyl ether, ethyl ether or cyclohexane, but not in benzene, CCl_4 or t-BuOH, a long-lived transient which decayed by first order kinetics with a lifetime of $\sim 200 \mu\text{s}$ was observed.¹¹⁷ This transient exhibited maxima at 540 and 580 nm were assigned to ketyl radical (291) by comparison with the spectrum of the parent cyclohexadienyl radical (291) and precursors (presumably the dienone triplet) were intercepted by oxygen and ditertiary - butyl nitroxide but 1,5-cyclohexadiene only intercepts the precursor. P-cresol and CHCl_3 were also obtained in good yield when (290) was thermolyzed at 80° in presence of benzoyl peroxide in isopropyl alcohol. This affords a technique to generate Me_2COH radical from isopropanol by a non-photochemical path, which can initiate the radical chain reaction.

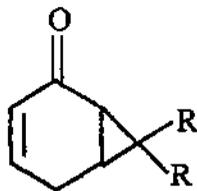
These studies unequivocally prove the free radical nature of the lowest dienone triplet state. In 2-propanol, hydrogen abstraction which leads to (293) competes with the ionic route to (301). The addition of lithium chloride selectively reduced the yield of only the later product. This demonstrates the sequential formation of dienone triplet state (291) and zwitterion (295) in accordance with the Zimmerman-Schuster mechanism. When irradiated in hydrogen-donating solvent cyclohexadienone (305) afforded phenol (306) and methane following the same mechanistic route as (290) \longrightarrow (293). The compound does not react in benzene and all attempts to trap a Zwitterion intermediate with nucleophile or 1,3-dipolarophiles was unsuccessful.⁶⁷



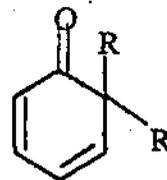
In order to examine the possibility of formation of bicyclohexenones at the bridged biradical state after $\beta - \beta'$ bonding, Swenton *et.al.*⁸³ conducted the photochemistry of 2,5-cyclohexadienones both in solution state and gas phase. At the photoenergies used in the ϵ excitation of the dienones (< 4 ev) in isolated molecules, it is unlikely that polar structures in which unit charges are separated by the distance of one C-C bond are attainable. In polar solvents, on the other hand, with high dielectric constant of medium as well as solvation can lower the energy with respect to the ground state of these structures to a point where they may be accessible to the electronically excited dienone molecules. Thus, involvement of the intermediacy of ionic species may be examined by the comparison of the photochemistry of a given compound in the gas phase at low pressure and in solution in a polar solvent. Irradiation of (276a) and (276b) in solution in cyclohexane at 300-370 nm gave two isomeric ketones (280c) and (280d) and (282a) and (282b). Irradiation of (276a) at the same wavelength in aqueous dioxane gave in addition to (280c) two phenols characterised as (283a) and (283b).



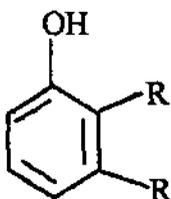
(276a) $R = CH_3$
 (276b) $R = C_6H_5$



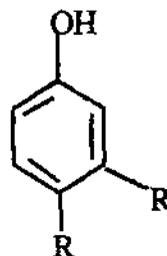
(280c) $R = CH_3$
 (280d) $R = C_6H_5$



(282a) $R = CH_3$
 (282b) $R = C_6H_5$

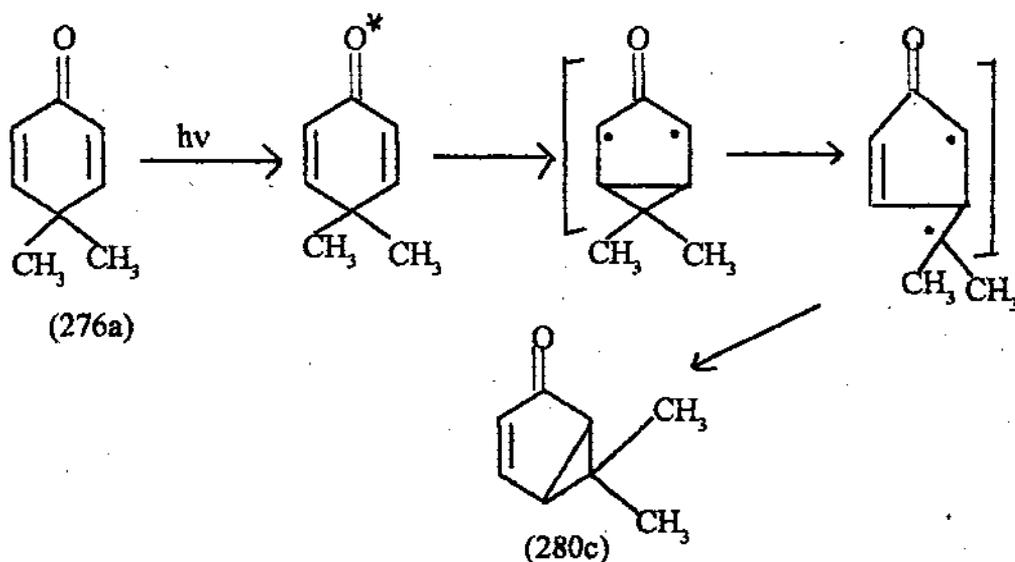


(283a)

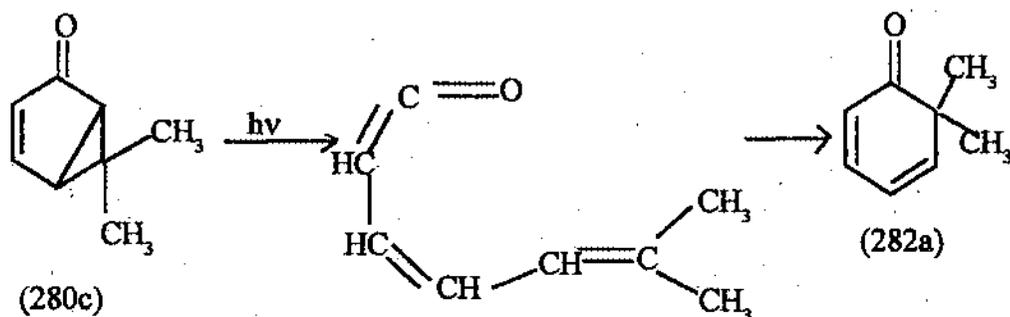


(283b)

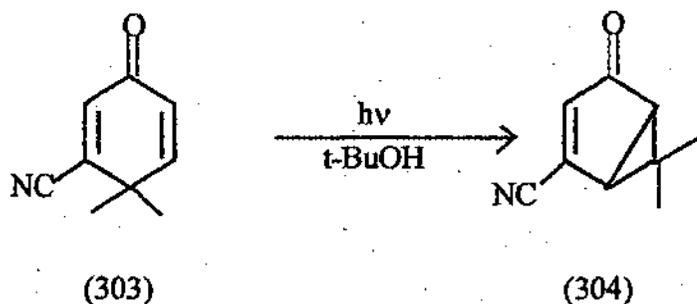
The gas phase irradiation of (276a) at 366 nm at 85°C and at pressure of 6 torr. gave at first (280c) but as soon as about 6% of (280c) had built up in the reaction system, (282a) began to appear. The mass balance was excellent upto about 15% conversion of (276a). There is no doubt that (276a) leads to (280c) which in turn gives (282a). In contrast to irradiation of aqueous dioxane where involvement of mesoionic intermediates has been proposed¹¹⁸ at least in this instance (276a) can be transformed to (280c) via nonionic intermediate. This conversion may be viewed as a specific example of the vinyl methane to vinyl cyclopropane rearrangement which is known to be a general photochemical process¹¹⁹. Based on this idea, the following mechanism has been advanced.



In the vapour phase the transformation of (280c) and (282a) should also involve a nonionic pathway, whereas the formation of the phenols (283a) and (283b) from (280c) probably involves zwitterionic intermediates since it is only observed in a polar medium. The formation of (282a) is reduced by the presence of methanol which supports the intermediacy of a ketone which ultimately can cyclize to yield (282a) as shown below :



The assumption that unit charge separation necessary for zwitterion formation is not possible in vapour state and hence the reaction proceeds from excited bridged biradical species, has been challenged by Schuster¹⁸ who argued that the available excited state energy of ca. 100 Kcal/mole might still be sufficient to accommodate the energy requirement for charge separation in the vapour state. The regioselective transformation (303) to (304) in *t*-butyl alcohol serves a better case in favour of rearrangement in the biradical stage¹²⁰. In a zwitterionic intermediate, [1,4] shift would have been expected to give the 5-cyano isomer rather than the product (304).

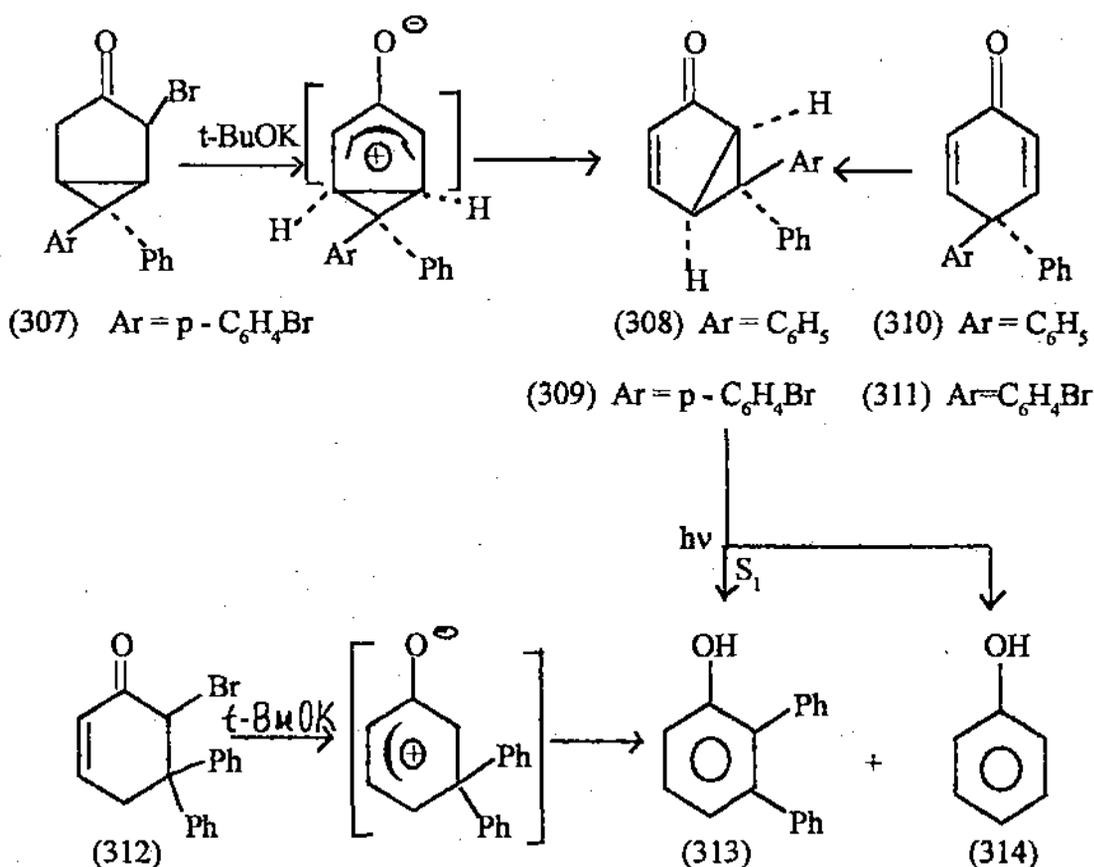


All the physicochemical studies described above supposes a description of the primary photochemical intermediate as a radical like species.

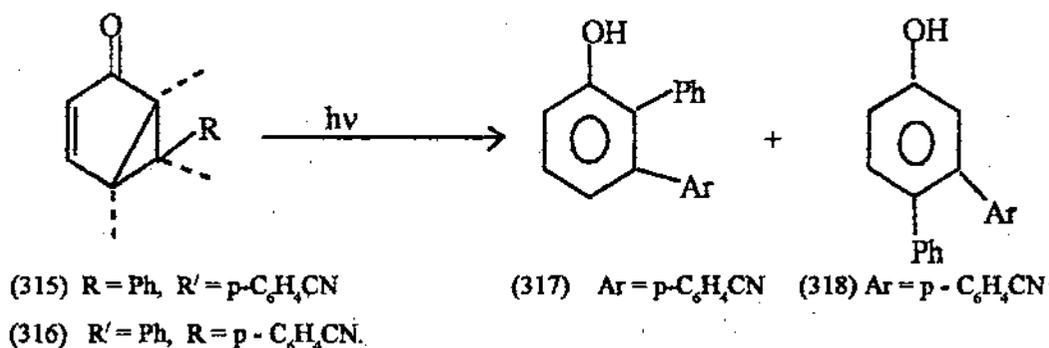
SECTION - B

(Involvement of Zwitterion Intermediates)

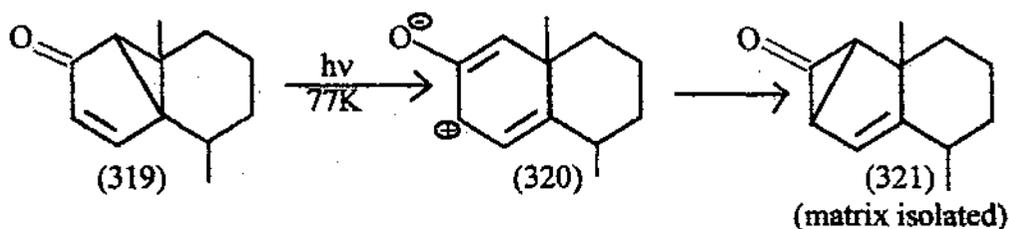
Formation of a vast multitude of products on photoexcitation of cyclohexadienones and bicyclohexenones has got strong resemblance to the products obtained from ground state electron deficient species, although the rearrangements do not completely rule out involvement of biradical species (278) and (280a). Nonetheless some type of products, for instance, formation of hydroxy ketone in acidic medium is really difficult to explain without participation of zwitterion intermediates (279) and (280b).



Zimmerman developed experiments¹²¹⁻¹²⁴ to generate zwitterion in ground state process of the type (279) and (280b) which undergo rearrangement to bicyclohexenones and phenols respectively. Favorskii-type rearrangement, as described above, of the bromoketone (307) furnished in high yield (309), one of the stereoisomeric photoketone of the corresponding dienone(311). The bromoketone (312) yielded the phenols (313) and (314) on treatment with *t*-BuOK in the same ratio as is obtained from the photolysis of (308). This result supports the proposition that generation of phenol from irradiation of bicyclohexenone proceeds through the intermediacy of zwitterion. Under both direct irradiation²⁹ and triplet-sensitized condition the stereo isomeric ketones (315) and (316) in aqueous *t*-butanol rearranges to similar ratios of phenols (317) and (318). No cyanophenyl migrated product was formed. Therefore, phenyl migration occurred to a positive centre rather than to a radical one and hence gave support that demotion to zwitterion must have preceded the rearrangement.

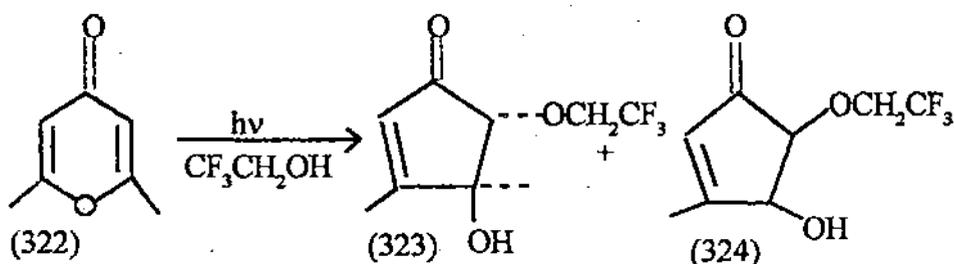


Formation of (321), a close form of zwitterion (320), which can be matrix isolated from the irradiation of (319) leads further support^{93,94} for zwitterion hypothesis.

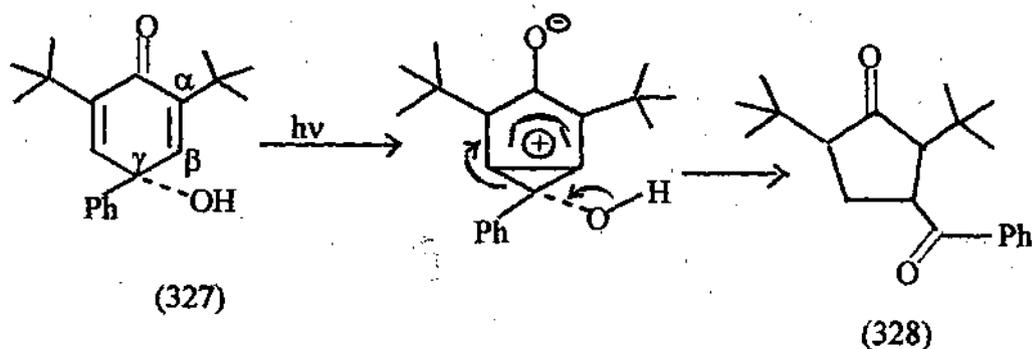
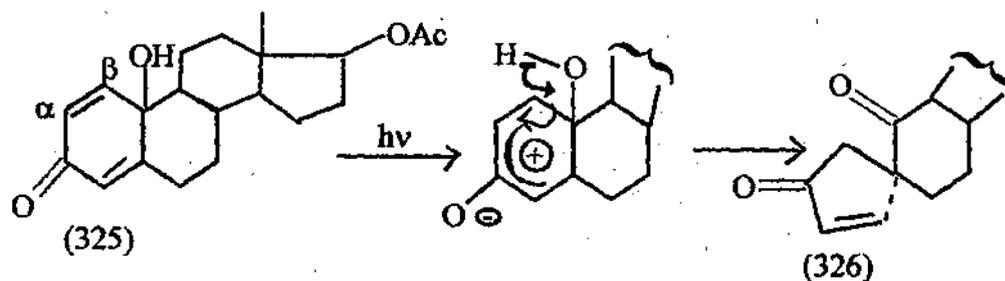


A direct evidence that leads to the definitive involvement of zwitterions in these types of photorearrangement in solution would require their capture, when formed photochemically from dienones by nucleophiles before further conversion occurs. The dienone (290) and related compounds have been found to be very suitable for this purpose and subjected to extensive studies¹⁸⁻²¹. The build up of positive charge at C-4 in (290) has greatly enhanced owing to the attachment of electron-withdrawing trichloromethyl substituent and hence making [1,4] rearrangement and cyclopropane cleavage in (279) less favourable. This also improved the susceptibility of these intermediates to capture by nucleophile and rendered the zwitterion (295) accessible for trapping and kinetic study. The species (332) has been found to be the common precursor of products (296), (298), (301) and (302). In alcohols (methanol, ethanol, propan-2-ol) acidified with hydrogen chloride protonation of (295) gives (297) which by capture of solvent affords (334). It is unique in the sense that these are examples of dienone photoproducts in which the skeleton of the proposed zwitterion is preserved. In absence of the appropriate electrophile (332) was captured by nucleophiles such as alcohol solvent and added halide ions to yield (299) and (300) respectively, which then undergo fragmentation in an anionic Grob-type process giving (301) and (302). In 2,2,2-trifluoro ethanol and methanol, the ratios (302)/(296) and (302)/(301) has been noted to increase linearly as the LiCl concentration in the solutions was increased and the quantum efficiency of formation of zwitterion (295) was nearly unity.

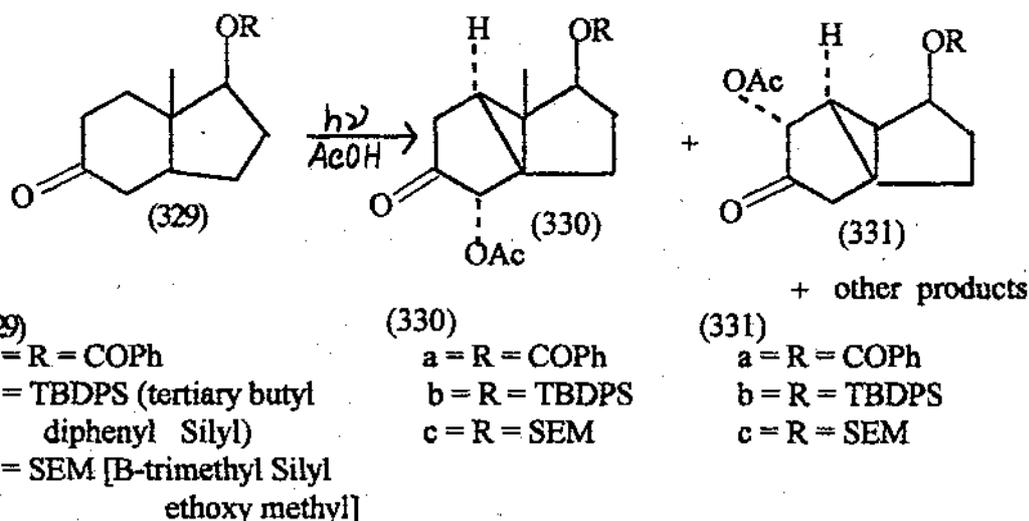
Just as the trichloromethyl compound (290) discussed above, zwitterion derived from 4H-pyran-4-ones e.g. (322) should also be susceptible to nucleophilic trapping and fragmentation. This expectation was borne out when it was recorded^{23,24} that irradiation of (322) in 2,2,2-trifluoro ethanol afforded the stereoisomer (323) (major isomer) and (324) (minor one) clearly resulting from trapping of zwitterion intermediate.



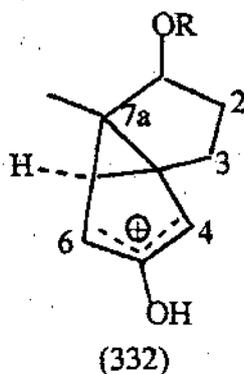
A few examples can be cited to demonstrate that nature of the photoproducts formed is explained by proposition of zwitterion intermediates.



4-hydroxycyclohexadienones (γ -substituted with respect to carbonyl group) (325) and (327) furnished ring contracted photoisomerised enediones, (326)¹¹² and (328)¹¹³ respectively on photolysis in anhydrous and aqueous dioxene. Many more cases¹²⁵⁻¹²⁸ of similar photoisomerization have since been reported. Recently Caine et al.¹²⁹ have demonstrated the formation of, amongst other products, tricyclic ketones of the type (330), (331) in polar solvent (acetic acid) on irradiation of bicyclic cross conjugated cyclohexadienones having 8-oxy substituents, (329a-c).



The tricyclic acetoxo-ketones (330a-c) and (331a-c) were derived from trapping of Zimmerman-Schuster cyclopropyl carbocation intermediate (332) by acetic acid. These products provided the first examples of solvent trapping of Zimmerman-Schuster intermediates during photolysis of fused-ring cross-conjugated cyclohexadienones.



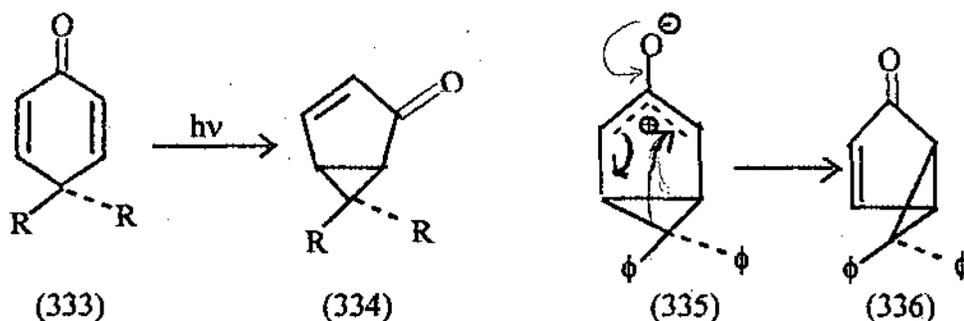
This type of reaction was reported by Schuster and coworkers¹¹⁷ in monocyclic dienone (290) discussed earlier. Interestingly product of the type (330) or (331) was not formed¹³⁰⁻¹³¹ when irradiation was carried out on the substrates 6/5 fused dienones without containing 8-oxygen substituents. Therefore, in dienones such as (329) it appears that the C-1 oxysubstituents reduce the rate of cleavage of the cyclopropane ring of the Zimmerman-Schuster intermediate (332) sufficiently to permit the trapping process occur. This effect may_A^{be} steric and/or electronic in origin.

Schuster and Liu²¹ observed that addition of LiCl had absolutely no effect on the efficiency of lumiketone formation on photolysis of santonin or dienone(310) in 2,2,2-trifluoro-ethanol and no new products were obtained. This shows that either (a) zwitterions are not reaction intermediates in these systems or (b) zwitterions are actually involved but their lifetimes are much shorter than that of (279). The authors favoured the explanation (b). Since lumiketone formation is the only primary reaction occurring on photolysis of santonin and (310), zwitterions in these cases have only two options, (i) decay to the ground state dienone and, (ii) [1,4] sigmatropic rearrangement. Since the lumiketone formation has high quantum efficiencies (~ 0.85), it is evident that lifetime of zwitterion is determined principally by rate of lumiketone formation.

Fisch and Richards^{132,133} observed the formation of a blue transient intermediates from the irradiation of santonin, lumisantoinin and some α -haloderivatives in glasses or polystyrene at 77°K. These intermediates are not paramagnetic and considered to be corresponding zwitterions. This assignment must be considered tentative as these species could not be trapped.

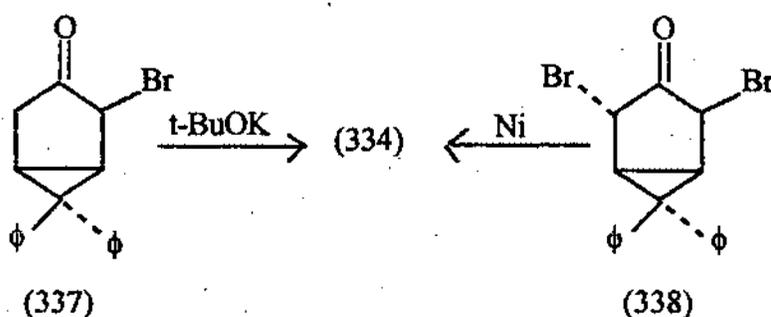
In summary, the discussion so far made clearly points to the involvement of diradical species during electronic excitation and demotion followed by zwitterion generation in the cross - conjugated cyclohexadienone and bicyclohexenone photorearrangement at ambient temperature as postulated in Zimmerman-Schuster mechanism.

Much work has been done to elucidate the mechanism¹³⁴ of the photochemical rearrangement of 4,4-disubstituted cyclohexadienones (333) to form 6,6-disubstituted bicyclo [3.1.0] hex-3-ene-2-ones (334), products which themselves suffer subsequently further rearrangements, ring opening and so on.



It was proposed at early stage⁷⁸ (e.g. when R = phenyl) that the initial cold product was a Zwitterion (335) which subsequently rearranged to (336).

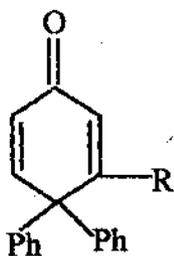
Strong evidence^{124,135} for such an intermediate is the fact that both the dehydrobromination of (337) with base and the debromination of (338) with sodium produce (334).



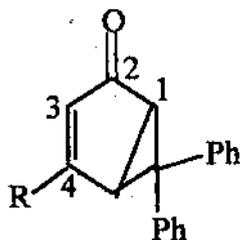
With a view to understanding regioselectivity in cyclohexadienone photochemistry, Zimmerman and Pasteris¹⁴⁵ studied the photochemistry of 3-cyano-4,4-diphenyl-2,5-cyclohexadienone (303a) and also the dark generation of the 1-cyano-6,6-diphenylbicyclo [3.1.0] type A zwitterion (351). Despite the possibility of the formation of both 4-cyano-6,6-diphenyl bicyclo [3.1.0] hex-3-en-2-one (304a) and its 5-cyano isomer (340) only the 4-cyano regioisomer was formed both in direct and methoxyacetophenone sensitized irradiations. The independent generation of the ground-state type A zwitterion was achieved by base treatment of 1-cyano-2-bromo-6,6-diphenyl bicyclo [3.1.0] hexan-3-one (347) and its 4-bromo isomer (348). Both

reactions led to the regioselective formation of the 4-cyano bicyclic photoproduct. In addition, the reaction of diiron nonacarbonyl with 1-cyano 2,4-dibromo-6,6-diphenyl bicyclo [3.1.0] hexan-3-one (349) led to the same bicyclic product. Hence, the type A zwitterion leads to complete regioselectivity to that isomer of bicyclic product (350) having the cyano group on the residual double bond and the photochemistry is consistent with a zwitterion pathway. It has also been observed that the regioselectivity did not depend on solvent polarity.

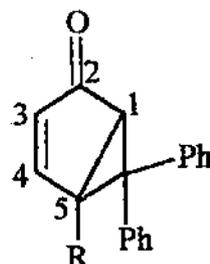
Zimmerman and Pasteris¹⁴⁶ also carried out the irradiation of 3-methoxy-4,4-diphenyl-2,5-cyclohexadienone (303b). Here, too, the product is regioselective with a preference for formation of 4-methoxy-6,6-diphenyl bicyclo [3.1.0] hex-3-en-2-one (304b) relative to 5-methoxy isomer (346a) formed (1.4:1) in benzene.



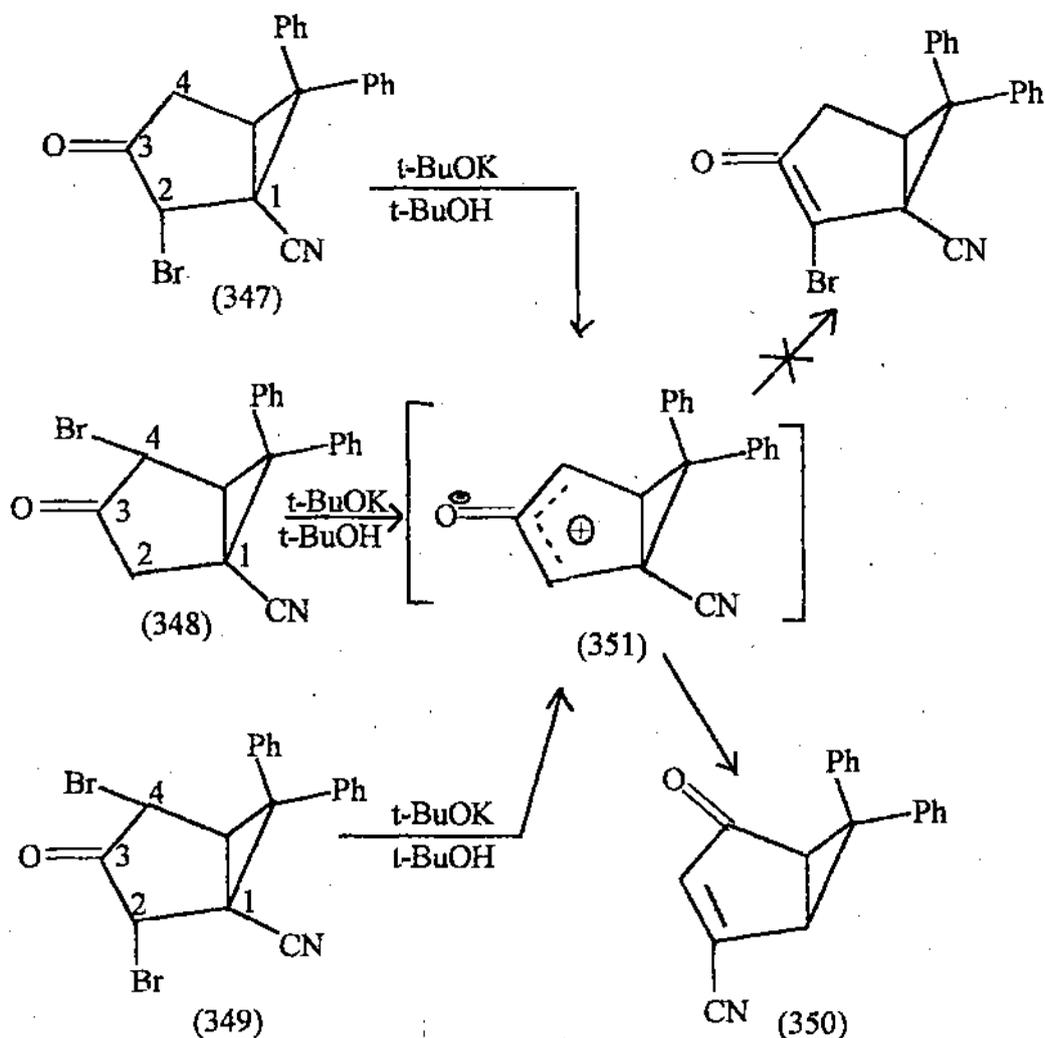
(303a), R = -CN
(303b), R = -OCH₃



(304a), R = -CN
(304b), R = -OCH₃



(346), R = -CN
(346a), R = -OCH₃



(Zwitterion Mechanism for the Dark type A Rearrangement)

Schuster and Liu¹⁴⁷ presented a detailed kinetic study which showed that a zwitterionic species is an obligatory intermediate in the photochemical conversion of 2,5-cyclohexadienone to lumiprodukt. Lithium chloride present in the reaction mixture successfully intercepts the zwitterionic intermediate. Their studies on the temperature dependence of the zwitterion-derived photoreactions also reveal that the main source of inefficiency in the system appears to be electrocyclic reversion of zwitterion to the cyclohexadienone by an orbital symmetry forbidden pathway that becomes increasingly important as the temperature is raised.

SECTION - C

(Multiplicity and Energy of the Reactive Excited State)

A good deal of efforts has been directed to study the nature of multiplicity, energy and electronic configuration of reactive excited state of cross conjugated cyclohexadienone photochemistry. Numerous mechanistic proposals that have piled up over last three decades, will now be considered in the light of available data.

Photoconversion of santonin and dienones (310) and (311) to lumiketone on direct irradiation has been favoured to be very efficient and the quantum yield almost approaches to unity. Same quantum efficiency has been recorded on sensitised reaction from triplet sensitizer such as benzophenone ($E_T = 68.5$ KCal/mole) or acetophenone ($E_T = 73.6$ KCal/mole). This gives some idea that the photoreaction occurs from triplet state and $S \rightarrow T$ intersystem crossing efficiency is nearly unity. This was further strengthened by the observation that the photoconversion is completely quenched if irradiation of α -santonin at 3660Å or (290) under a pyrex filter¹⁴⁸ is carried out in piperylene as a solvent, a triplet state quencher. Similar results were obtained with another triplet state quencher 1,3-cyclohexadiene.

Schaffner et al. made an interesting observation that γ -irradiation of toluene or benzene solutions of 1-dehydrotestosterone acetate induced isomerisation to the corresponding lumiprodut with a G-value of 1.9 to 3.0, which on further irradiation afforded the same mixture of ketonic and phenolic products as obtained by photolysis at $\lambda > 280$ nm. Since isomerization could not be induced in the absence of an aromatic sensitizer, triplet sensitization by aromatic solvents have been proposed¹³⁶.

Although the sensitization studies with triplet sensitizers and quenching studies with piperlin (1,3-pentadiene) and 1,3-cyclohexadiene indicate the involvement of a triplet path, the result from another triplet quencher naphthalene renders the quenching studies inconclusive as regards the precise nature, energy and identity of quenchable triplet. Low temperature phosphorescence measurements of α -santonin, (290) and (310) led to the determination of the lowest spectroscopic triplet state energy to be $E_i = 68$ KCal/mole. This values indicates that triplet energy transfer to naphthalene ($E_i = 61$ KCal/mole), 1,3-pentadiene ($E_i = 57 - 59$ KCal/mole) and 1,3-cyclohexadiene

($E_1 = 53$ KCal/mole) should take place at the same diffusion-controlled rate. Contrary to the expectation, naphthalene failed completely to quench (310) and the quenching ability of 1,3-pentadiene has been found to be considerably lower than 1,3-cyclohexadiene in case of santonin, (290) and (310). Two possible explanations have been advanced¹⁶. Firstly a triplet exiplex $^3(\text{DA})^*$ formation between the donar (D) and acceptor (A) has been proposed. It might diminish the rate constants for energy transfer by factors other than the difference in donor (D) and acceptor (A) triplet energies and it is different for different acceptors. Secondly, the quenching of the spectroscopic dienone triplet might not occur, since the relaxation to a lower-energy geometry might be sufficiently fast. Furthermore, this relaxed quenchable triplet was considered to adopt a geometry, interposed between (277) and (278), which has an out-of-plane twist of the dienyl radical moiety and possesses an energy about or lower than 60 KCal/mole.

SECTION - D

(Electronic Configuration of Reactive Excited State [n, π^* vs. π, π^*])

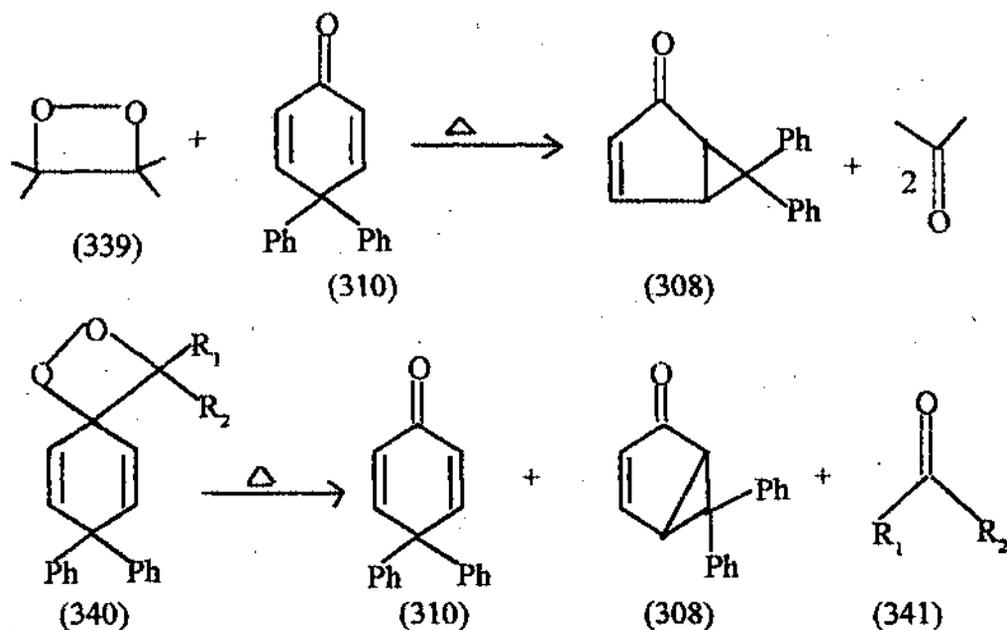
Cross-conjugated cyclohexadienones show an intense absorption band centred around 240 nm and another less intense band around 300 nm. The former band is associated with $\pi-\pi^*$ and the later to $n-\pi^*$ electronic transitions. All the usual photochemical rearrangements undergone by dienone systems can be effected by photolysis at either wavelength. Of course, the quantum efficiency and chemical yields of various products vary substantially. As because the initiation of the photoreaction can occur at wavelengths corresponding to low energy n, π^* transition, it is often assumed that reactive excited state is of n, π^* character. This has been the basis of Zimmerman-Schuster⁷⁸ mechanism of cyclohexadienone photorearrangement.

Since the photoreaction occurs from a triplet state, as discussed earlier, this could be $^3n, \pi^*$. This contention has been supported^{137,138} by low temperature phosphorescence measurements of (290) and some other monocyclic dienones in glasses. On the basis of short emission life time (about 0.5 msec.), direction of emission polarization, effect of solvent polarity on emission wavelength and the similarity of the vibrational pattern of the phosphorescence emission spectrum with that characteristic of n, π^* emission, support the $^3n, \pi^*$ configuration.

Phosphorescence was thought to originate from $^3n, \pi^*$ state. However, phosphorescence excitation measurement at 4.2 K and investigation of heavy atom effects on santonin and some analogues¹³⁹ led to the proposition that phosphorescence in later cases stems from $^3\pi, \pi^*$ state lying below the $^3n, \pi^*$ state. There is also strong vibronic interaction between the two states. Interestingly, Schuster has observed that (292a), 3-methyl analogue of (292) possesses a lowest $^3\pi, \pi^*$ state though (292) a $^3n, \pi^*$ state. It shows that slight change in geometry by introducing a substituent or conformational flexibility may switch over from one energy state to the other. The T_2 state can be thermally populated from an unreactive T_1 state, particularly when the two triplets are energetically proximate, at ambient temperature as observed¹⁴⁰ in case of certain aryl ketones. Therefore, reaction of the type e.g. β, β' bonding [(278) \rightarrow (279) Scheme -III] from an $^3n, \pi^*$ state (T_1 or T_2) is still a distinct possibility. To adduce further evidence in support of involvement of $^3n, \pi^*$ excited state, Zimmerman et al.¹⁴¹ generated triplet acetone

from thermolysis of dioxitane (339), which by triplet excitation converted (310) to (308). Then, an idea of effecting intramolecular electronic excitation by internal incorporation of a dioxitane moiety was envisaged by him in order to effect unimolecular rearrangement in excited state. These are examples of photochemistry without light, since in these cases excitation energy is not derived from irradiation but derived from thermolysis.

The lumiketone (308) was formed in considerable yield ($16.6 \pm 3.2\%$) on thermolysis of five different dioxitances (340a - e). In four cases, the alternative (341a-d) have higher triplet energies than (310), but in the fifth case (340c) the reaction course was not altered despite the product (341e) acetone has lower energy π, π^* triplet ($E_T = 59$ KCal/mole) than the n, π^* triplet of (310) ($E_T = 68.5$ KCal/mole). The argument has been advocated that the higher energy n, π^* triplet of (310) is formed preferentially to the lower energy π, π^* triplet of (341). This also supports the view that the n, π^* triplet of (310) is kinetically formed and rearranges prior to any equilibration with the π, π^* excited state.

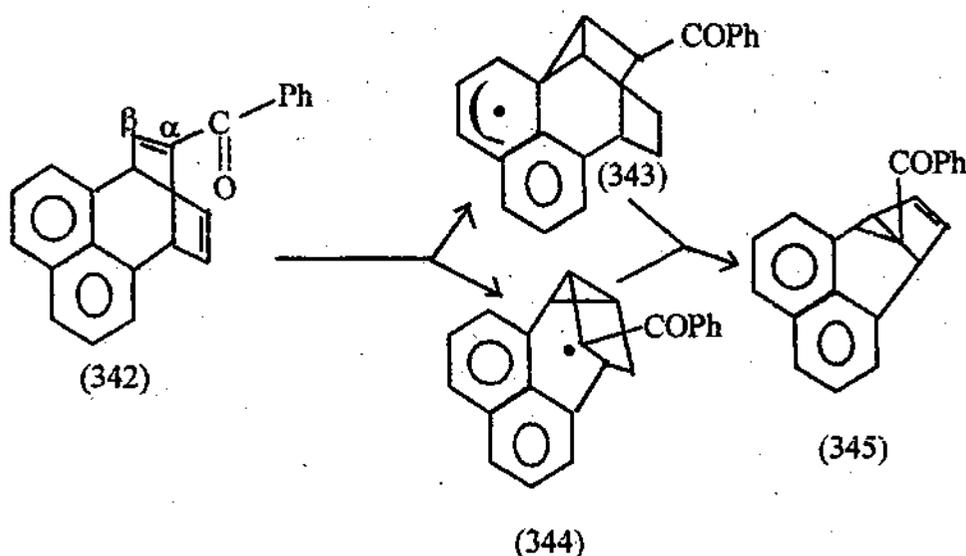


(340)

a= R_1 =Me, R_2 =Ph; b= R_1 =Me, R=*n*-MeOPh;c= R_1 =Bu, R_2 =Ph, d= R_1 = R_2 =Me;e = R_1 =Me, R_2 =2-naph.

Although this strengthens support for the involvement of the n, π^* excited state, proposed long ago, cannot rule out yet the possibility that n, π^* triplet of (310) is not reactive but thermally populates the higher-lying $^3\pi, \pi^*$ state after which the rearrangement occurs.

Schaffner and coworkers^{142,143} have carried out an interesting photoreaction of (342) giving further insight into this mechanistic aspect. This reaction is structurally related to the β, β' bonding process in (278) \longrightarrow (279) and afforded the photo product (345) which is formed via two competing rearrangement paths initiated by bridging from the olefinic β -carbon of the cross-conjugated ketone in (342) as depicted below



The phosphorescence spectrum of (342) is that of a 1,8-bridged naphthalene and possesses $E_p = 58.2$ KCal/mole. The quantum yield of the photorearrangement has been determined at different wave length as well as on sensitization with donors of different triplet energies between 61.9 to 68.9 KCal/mole. It has also been observed that all of these occurred at similar rates close to diffusion-limited in benzene $[(2.8-4.2) \times 10^9 \text{M}^{-1}\text{Sec}^{-1}]$. A nanosecond transient intermediate at room temperature has been demonstrated in laser flash experiments and *e s r* at 77K and IR spectroscopy in 77-294 K range exhibited two biradical intermediates (343) and (344). They have envisaged that the initial excitation leads to an upper singlet (S_2) π, π^* state which is followed by a highly efficient intersystem crossing to populate T_2 ($60 < E_p < 63$ KCal/mole) or by direct formation of biradicals with an efficiency similar to that from t_2 or

by both reaction pathways. Irradiation with 435 nm generates lowest-lying naphthalene triplet state. Reaction from this state or energy transfer from phenanthrene ($E_T=61.9$ KCal/mole) occurs with via thermal population of T_2 or separate inefficiency path. They also adduced evidence¹⁴⁴ to show that the rearrangement (342) \rightarrow (345) occurs also from ground state thermal process reversibly through competing stepwise and thermally allowed concerted processes.
