

TRANSIENT SPECIES IN THE PHOTOCHEMICAL VALENCE TAUTOMERIZATION OF 2,3-DIPHENYLINDENONE OXIDE

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Summary

A variable temperature flash photolysis study of 2,3-diphenylindenone oxide, 2,3-diphenyl-4,7-dimethylindenone oxide and tetraphenyl-2,3-diphenylindenone oxide in various solvents shows, in each case, the existence of two transients having wavelength maxima at about 510 and 530 nm and energies of activation for the thermal back reaction of 1 and 6 kcal mol⁻¹. Combination of the flash data with fluorescence measurements indicates that both transients contribute to the photochemical valence tautomerization of these compounds.

1. Introduction

Ullman and coworkers [1 - 7] have examined the photochromism of 2,3-diphenylindenone oxide (I) in detail in order to study the geometric and energetic changes which occur during photochemical primary processes and have shown that (I) (white) and its valence tautomer (II) (red) can be photochemically interconverted (Fig. 1). A quantitative analysis of the fate of each of the excited states of (I), combined with other evidence that tends to exclude interconversions between any of the electronically excited states of (I) and electronically excited states of (II), has allowed Ullman to suggest that, in a condensed phase at room temperature, both the forward and reverse reactions proceed via vibrationally excited ground states of the two tautomers. However, it is often argued that such states cannot be important intermediates in solution photochemistry and therefore a conclusive demonstration of their involvement in a condensed phase at room temperature would be quite significant [8 - 10]. Bertelson [11], when reviewing the work of Ullman, has expressed the opinion that Ullman has not conclusively proven his case; Calvert and Pitts [12] and Wagner and Hammond [13] have suggested that triplet intermediates may in fact be involved in this photoisomerization. Actually, one of the basic arguments with which Ullman sup-



Fig. 1. The photochemical interconversion between (I) and (II).

Fig. 2. The structures of (III) and (V).

ports his interpretation, the fact that photostationary states are established either under direct irradiation or by use of sensitizers having triplet energies higher than 68 kcal while sensitizers with lower excitation energies result in no appreciable conversion of (I) to (II), is viewed by Wagner and Hammond as an indication for a triplet mechanism. Wagner and Hammond have noted that high energy sensitizers may transfer energy to both (I) and (II) while those having low energies may be quenched selectively by (II). We therefore carried out a re-examination of the mechanism of the photochemical interconversion between the epoxy ketone (I) and the benzopyrylium oxide (II), using mainly the flash photolysis technique, in the hope of finding short-lived intermediates between (I) and (II) and thus of clarifying the sequence of events that occur after the absorption of light energy. Two new derivatives of (I), namely 2,3-diphenyl-4,7-dimethylindenone oxide (III) and tetraphenyl-2,3-diphenylindenone oxide (V), were prepared for reasons of comparison (an increase in the size of the molecule) (Fig. 2).

2. Experimental

2.1. Materials

Spectrograde ethanol, heptane, benzene, methylcyclohexane and ether-isopentane-ethanol (EPA) from Merck were used without further purification.

2,3-Diphenylindenone oxide (I) was prepared according to the literature [14] and was recrystallized from ethanol-water to a constant melting point of 142 - 143 °C. 2,3-Diphenyl-4,7-dimethylindenone oxide (III) and tetraphenyl-2,3-diphenylindenone oxide (V) were also prepared by this method and had melting points of 98 - 100 °C and 198 - 200 °C respectively. The analysis results were as follows: calculated for (III), C, 84.66%; H, 5.52%; found, C, 84.80%; H, 5.62%; calculated for (V), C, 89.70%; H, 4.98%; found, C, 89.50%; H, 4.90%.

3,4-Diphenylisocoumarin (IX) and the dimer (X) of 2,3-diphenylindenone oxide were prepared according to literature processes [6, 15].

2.2. Light sources and filters

A U-shaped 100 W Hanovia medium-pressure mercury lamp was used with a Corning 9863 filter. For flash photolysis of the photoproducts (II),

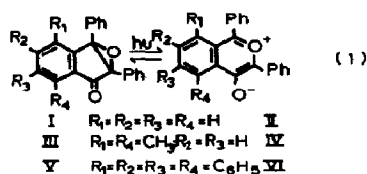


Fig. 3. The photochemically reversible isomerization reaction (1).

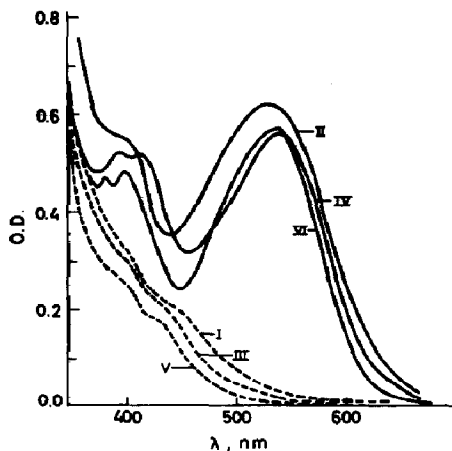


Fig. 4. Absorption spectra of 1×10^{-4} M 2,3-diphenylindenone oxide (I), 2,3-diphenyl-4,7-dimethylindenone oxide (III) and tetraphenyl-2,3-diphenylindenone oxide (V) in EPA at 77 K before (---) and after (—) illumination with light of wavelength 365 nm for 15 min when the photoproducts (II), (IV) and (VI) are produced.

(IV) and (VI) in the visible region, the flashlamps were covered with a blue (gelatine) Kodak filter; this filter absorbs all the light at wavelengths less than 350 nm, has a transmission of about 60% at 450 nm and has a transmission of 30% at 500 nm.

2.3. Spectra

Conventional spectroscopic methods were used, except for the determination of the spectra of the transients (XI) and (XII) for which the point-by-point method in 20 cm optical cells of the flash apparatus was used.

2.4. Fluorescence lifetime

A model PS-3 pulse-sampling fluorimeter (Applied Photophysics Ltd.) was employed.

2.5. Flash photolysis

The flash photolysis apparatus had a 100 W quartz-iodine lamp as the analysing source; it was focused by means of quartz lenses through the long axis of the flash photolysis cells onto the entrance slit of a Hilger-Watts grating monochromator. The output of an EMI 9660 B photomultiplier tube was fed via a cathode follower to a Tektronix 545 B oscilloscope equipped with a 1A5 plug-in unit and a C-12 Tektronix camera. The photolytic flash had a width at half-height of about 30 μ s at full power. The sample was placed between two krypton flashlamps. Concentrations were generally 5×10^{-5} M and all samples were vacuum degassed by repeated freezing and thawing in quartz glass UV 20 cm cells which then were flame sealed under a

vacuum of 10^{-4} Torr. For variable temperature studies the flash cell was mounted in an optical quartz Dewar and was cooled by a flow of heated liquid nitrogen. The temperature inside the Dewar was monitored by an iron-constantan thermocouple, the voltage of which regulated a relay to control a heating coil which boiled the liquid nitrogen. A fresh solution was used after each flash except in cases where the effect of successive flashes was examined.

Reaction rate constants were determined by a least-squares approximation of first and second order reactions using a computer.

3. Results and discussion

The photochemically reversible isomerization (1) (Fig. 3) of (I) (white) to its red valence tautomer, benzopyrylium oxide (II), and the parallel thermal or under illumination interconversions between (I) and (II) have been studied by Ullman and coworkers [1, 3, 6]. We prepared two new derivatives (III) and (V), which were increased molecular size derivatives of (I), for reasons of comparison.

As with the indenone oxide (I) [6], when (III) and (V) are irradiated in degassed methylcyclohexane, benzene or ethanol solutions with 365 nm light, the red pyrylium oxides (IV) and (VI) are formed but the solutions are exceptionally unstable. The colour does not become as intense in these solvents and continuous irradiation leads to destruction of the starting material. However, in EPA solutions at liquid nitrogen temperatures the colour becomes intense and remains stable as long as the rigidity of the solution is maintained. In Fig. 4 are shown the absorption spectra of solutions of (I), (III) and (V) in EPA before and after illumination with 365 nm light at 77 K when the photoproducts (II), (IV) and (VI) are formed. The photoproducts disappear on thawing the rigid glass to room temperature. The absorption spectrum of (II) is similar to that obtained by Ullman and Henderson [6] indirectly using the tritium-recoil-labelled indenone oxide (I) in hexane, benzene and ethanol. Satisfactorily stable photoproducts are also formed in the crystalline state. Thus polycrystalline films of (I), (III) and (V) on irradiation with light of wavelength 365 nm turn red and present similar absorption spectra to those obtained in solution. The colour disappears on standing in the dark and we found that the decay follows first order kinetics. The situation for compound (I) is shown in Fig. 5; in this case the first order decay has a rate constant $k = 1.0 \times 10^3 \text{ min}^{-1}$ at 25 °C.

In general the behaviour of (III) and (V) is similar to that of (I). However, the stability of the red photoproducts is found to decrease in the order (II) > (IV) > (VI), probably because the methyl and phenyl groups attached to (IV) and (VI) facilitate the thermal back reaction.

The identification of the photoproducts (IV) and (VI) was elucidated as in the case of (II) [1] by their reaction with bicyclo[2.2.1]heptadiene. This reagent is known to be very reactive towards dipolar ions, yielding the

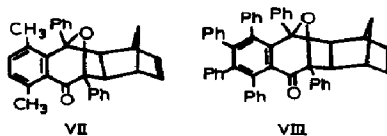
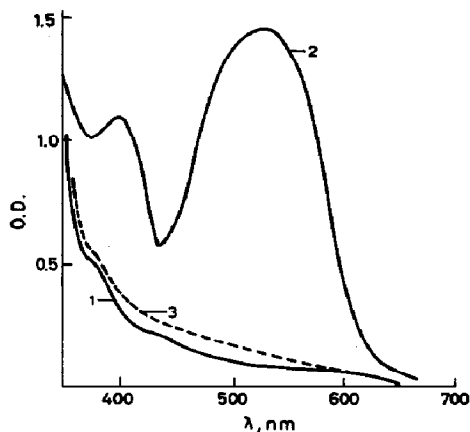


Fig. 5. Absorption spectra of a thin crystalline film of 2,3-diphenylindenone oxide (I): 1, before illumination; 2, after illumination for 3 h with light of wavelength 365 nm (photoequilibrium); 3, after standing in the dark for 12 h.

Fig. 6. The structures of the 1:1 adducts (VII) and (VIII).

1:1 adducts (VII) and (VIII) (Fig. 6) with satisfactory carbon and hydrogen analyses. The structures of these adducts are also supported by the shifts in the IR carbonyl peaks (KBr) of (VII) ($5.89 \mu\text{m}$) and (VIII) ($5.90 \mu\text{m}$) with respect to those of (III) ($5.80 \mu\text{m}$) and (V) ($5.82 \mu\text{m}$).

On exposing 10^{-4} M oxygen-free solutions of (I), (III) or (V) in ethanol, methylcyclohexane, heptane and benzene to a high intensity pulse of UV light, two new absorption bands with maxima at about 510 and 530 nm are observed. The situation for compound (I) in methylcyclohexane is shown in Fig. 7. The two transient species disappear in the millisecond region. In all cases a residual and long-lived absorption is also observed, indicating the formation of the photoproducts (II), (IV) and (VI). If after flashing the disappearance of (II) with time is followed at room temperature, it is found to follow a first order decay with $k = 6.6 \times 10^{-5} \text{ s}^{-1}$, in good agreement with the findings of Ullman and Henderson [6] by another method. The thermal decay of the photoproducts (IV) and (VI) at room temperature also follows first order kinetics with $k = 3.4 \times 10^{-4} \text{ s}^{-1}$ and $k = 1.1 \times 10^{-4} \text{ s}^{-1}$ respectively. The kinetics of the fading of the two transient species in each case, followed at various temperatures, are also first order. The energies of activation for the thermal back reaction and the half-lifetimes of the transients monitored in ethanol solutions are summarized in Table 1.

The results of Table 1 do not change markedly for the other solvents. However, a clear oxygen effect is observed when non-degassed solutions of (I), (III) and (V) are used; the absorbances of the transients are depressed to approximately one-third; the depression of the photoproducts (II), (IV) and (VI) is analogous when compared with the absorbances of the degassed solutions.

TABLE 1

Energies of activation and half-lifetimes of the transients of the compounds (I), (III) and (V) in 5×10^{-5} M ethanol solution

Compound	E_a (kcal mol $^{-1}$)		$t_{1/2}$ (ms) at 25 °C	
	Transient maximum 510 nm	Transient maximum 530 nm	Transient maximum 510 nm	Transient maximum 530 nm
(I)	1.0	6.0	0.7	0.2
(III)	1.2	6.2	0.9	0.3
(V)	1.0	6.1	1.0	1.7

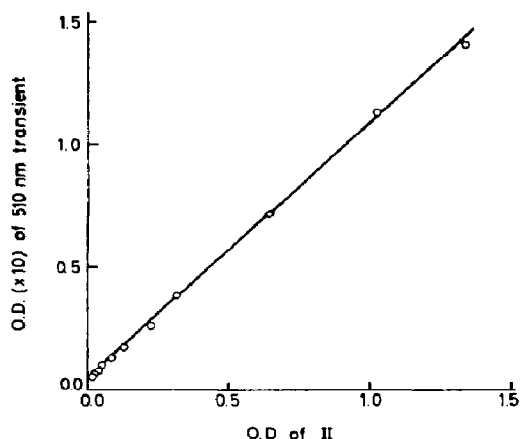
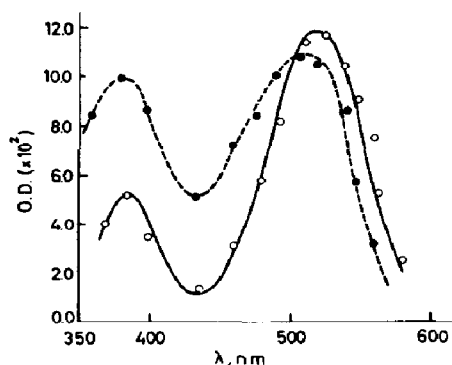


Fig. 7. Transient absorption spectra after flash photolysis of degassed 5×10^{-5} M 2,3-diphenylindenone oxide (I) in methylcyclohexane: ●, the transient with a wavelength maximum at 510 nm; ○, the transient with a wavelength maximum at 530 nm. The optical density (OD) was read 500 μ s after the start of the flash.

Fig. 8. The relationship between the optical density (OD) of the 510 nm transient and that of the photoproduct (II) at 544 nm after repeated flashes of degassed 1.5×10^{-5} M 2,3-diphenylindenone oxide (I) in heptane.

The following cases can be considered for the nature of the two short-lived transients. They may originate from the activation of (1) one of the photoproducts (II), (IV) or (VI), (2) a stable photoproduct, since side products of this reaction have been identified [6, 7], (3) the starting material leading to some stable product or (4) the starting material leading to the red photoproduct (II), (IV) or (VI).

An examination of our results combined with literature data excludes the first three possibilities, leaving the fourth as the operating situation. The first possibility is excluded since photolysis of concentrated solutions of (II) with light absorbed only by this species presents no intermediates. Similarly

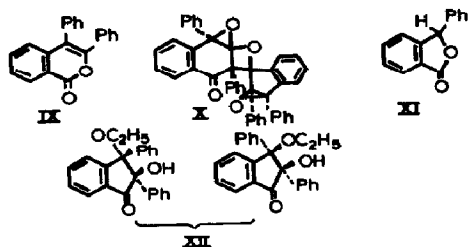


Fig. 9. The structures of (IX), (X), (XI) and (XII).

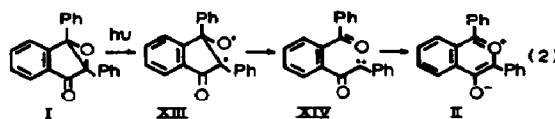


Fig. 10. Scheme (2).

flash photolysis of the photoproducts (IV) and (VI) in ethanol or benzene produces no transients at all. The experiment is performed by first turning red the solution of (I), (III) or (V) with UV light and then flashing after covering the solutions with a special Kodak filter which allows passage of light absorbed only by (II), (IV) or (VI). The only effect which is observed with this "visible flash" is the back conversion of (II), (IV) and (VI) partly (approximately 6%) to (I), (III) and (V).

The second possibility is excluded mainly for two reasons: (a) the two intermediates are observed when fresh solutions of (I), (III) or (V) are used and (b) repeated flashing of (I), (III) and (V) results in a decrease in the absorbances of the transients and of the photoproducts (II), (IV) and (VI), while in all cases a linear relationship exists between the absorbances at λ_{\max} for the transients and for the photoproducts. This relationship between the shortest lived transient ($\lambda_{\max} = 510 \text{ nm}$) and the photoproduct (II) ($\lambda_{\max} = 544 \text{ nm}$) is shown in Fig. 8 for a series of repeated flashes of a $1.5 \times 10^{-5} \text{ M}$ degassed solution of (I) in heptane, indicating the transformation of this transient into (II).

The third possibility is excluded on the basis of the results of Ullman and Henderson [7] from which it has been shown that photolysis of (I) in benzene (or hexane) produces 3,4-diphenylisocoumarin (IX), the dimer (X) and 3-phenylphthalide (XI), whereas photolysis of (I) in ethanol produces the hydroxy ethers (XII) (Fig. 9); the isocoumarin (IX) is also formed in solutions of (I) in ethanol, but in this case from the photoproduct (II) [6].

However, since the behaviour of the transients in all cases is the same in the two solvents, they might be placed as intermediates between (I) and (II) (between (III) and (IV) and (V) and (VI) in the other cases). Thus, for (I), the photochemical reaction (1) is transformed to scheme (2) (Fig. 10) which includes the intermediates (XIII) and (XIV).

The assignment of the structures (XIII) and (XIV) to the two transients is based on the following experimental and literature data. Becker *et al.* [16] as well as Trozzolo *et al.* [17] have shown that photolysis of various solutions of phenyloxiranes (XV) leads to phenylcarbenes (XVII) and ketones (XVIII). The available data concerning the fragmentations of oxiranes are summarized in scheme (3) (Fig. 11).

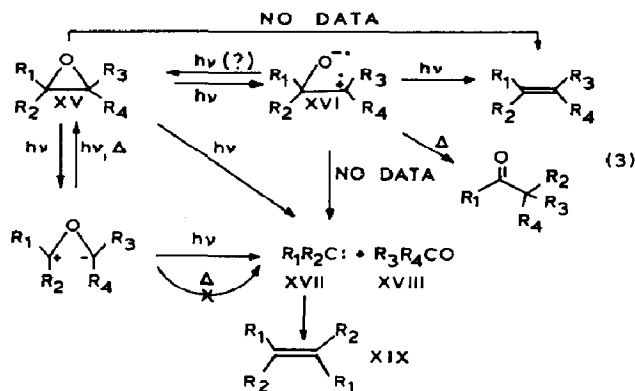


Fig. 11. Scheme (3).

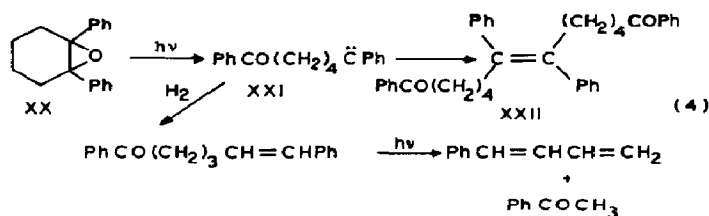


Fig. 12. Scheme (4).

Trozzolo and Leslie [18] have recently demonstrated using double irradiation experiments that this process is wavelength dependent and that (XVII) is also formed directly from (XV). A nitrogen laser ($\lambda = 337.1$ nm) flash of 5 ns duration shows that the ylide forms immediately with the flash which means that its lifetime is of the same order. In contrast, if an excimer laser ($\lambda = 248$ nm) is used the carbene (XVII) is observed.

In scheme (3) (Fig. 11), although there are no data available showing that (XVII) is also formed from (XVI), this has not been excluded. In addition to optical and electron paramagnetic resonance data, evidence for the formation of phenylcarbenes (XVII) is based on the observation that dimers such as tetraphenylethylene (XIX) are formed upon thawing photolysed rigid solutions of (XV) [16, 17, 19] and cyclopropanes are produced on irradiating (XV) with alkenes.

In the case of bridged cyclic oxiranes such as (XX) it is proposed that photolysis leads to ketocarbene formation, *i.e.* to (XXI), in accordance with scheme (4) (Fig. 12); (XXI) dimerizes to (XXII) in a manner similar to that just reported.

This proposal is based on the observation that a phosphorescence similar to that of acetophenone is observed among the photoproducts of (XX) and, on warming that matrix and recooling, an emission similar to that for *trans*-stilbene appears [16]. Although this explanation is consistent with the data, Griffin and coworkers [20, 21] have recently shown that prolonged

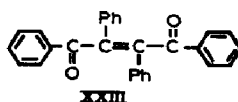
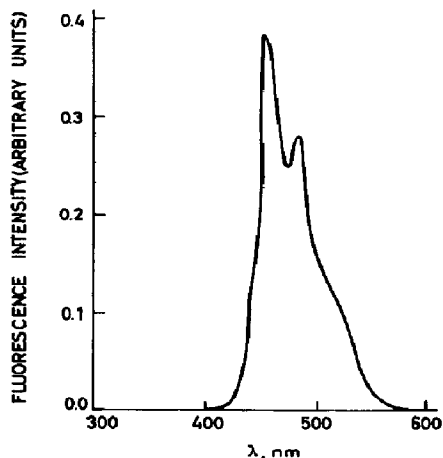


Fig. 13. The emission spectrum of 2,3-diphenylindenone oxide (I) under the conditions described in the text.

Fig. 14. The structure of (XXIII).

irradiation of the observed ketoalkene photoproduct may proceed by 1,2 hydrogen migration followed by Norrish-type cleavage to acetophenone and butadiene (lower part of scheme (4)). However, further evidence of keto-carbene intermediacy comes from double irradiation experiments (simultaneous irradiation with UV and visible light) of (XX) which show acceleration in its conversion to the ketoalkene, a result which supports the contention that this conversion may occur, at least in part, according to the keto-carbene mechanism depicted in scheme (4) [21].

In our experiments, when a solution of the indenone oxide (I) in methylcyclohexane is first illuminated at room temperature with 365 nm light and is subsequently left to equilibrate, it shows detectable fluorescence with an emission maximum at 455 nm when 416 nm exciting light is used. Solutions of the indenone oxides (III) and (V) in methylcyclohexane show, under the same conditions, similar fluorescence displaced to lower energy by about 80 nm. The intensity of this fluorescence has a fourfold increase in degassed solution. The emission spectrum of compound (I) under these conditions is shown in Fig. 13. The fluorescence lifetime of this fluorescent species was found to be 8 ns.

When a solution of (I) in methylcyclohexane is illuminated at -196°C with UV light (turns red) and subsequently with white light (decoloration) and then brought to room temperature, it no longer shows fluorescence at 455 nm. The fluorescence is not produced by (I) since no emission was observed initially on illuminating a colourless glass (only (I) present). It is also not produced by (II), since it is known [6] that this compound fluoresces with an emission maximum at around 630 nm. We found analogous fluorescence with compounds (IV) and (VI). From an examination of authentic samples, 3,4-diphenylisocoumarin (IX) and the dimer (X), which

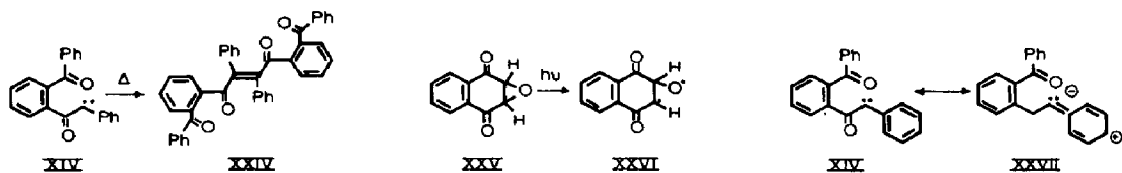


Fig. 15. The structures of (XIV) and (XXIV), (XXV) and (XXVI), and (XIV) and (XXVII).

are formed during the photochemically reversible isomerization of (I) to its red valence tautomer (II) [6], show no detectable fluorescence in methylcyclohexane in this spectral region.

The fluorescence observed for (I) with $\lambda_{\text{max}} = 455 \text{ nm}$ is similar to that of *trans*-dibenzoylstilbene (XXIII) (Fig. 14) (maximum at 400 nm), while the fluorescence lifetime of (I) (8 ns) compares well with that of *trans*-stilbene (about 3 - 5 ns) [22]. The appearance of this fluorescence possibly verifies the existence of the diphenylcarbene (XIV) which dimerizes to the fluorescent *trans*-dibenzoylstilbene (XXIV) (Fig. 15). In addition, fluorescence is not observed when (I) is illuminated (with visible light) at liquid nitrogen temperatures, a fact which may show that dimerization is not taking place, because of the high viscosity of the rigid glass.

The form of the biradical (XIII) may be justified from the corresponding biradical (XXVI) (Fig. 15) which is produced on photolysis of the epoxyquinone (XXV) [23].

In addition, Salem [24] has suggested that a biradical is not likely to be in an energetic minimum and therefore will not have an activation energy higher than about 1 kcal mol^{-1} , in good agreement with the activation energy found for the shortest lived transient. For the activation energy found for the other transient, carbenes like (XIV) are considered to be quite stable intermediates, and the phenyl ring is an additional stabilizing factor [25] since it introduces resonance forms such as those shown in Fig. 15. Therefore, the value of 6 kcal mol^{-1} observed is considered to be satisfactory for the arylcarbene (XIV). Finally the absorption spectra of the transients (XIII) and (XIV), calculated from plots of $\log \log(I_{\infty}/I)$ against time at various wavelengths (given in Fig. 7), are in agreement with the absorption maxima which have been observed [16] in *cis*- and *trans*-diphenyl-oxirane at 501 nm and 506 nm respectively.

The tentative mechanism proposed (scheme (2) (Fig. 10)) for the basic rearrangement of the indenone oxide after absorption of light energy indicates a triplet state mechanism, as Wagner and Hammond [13] have already suggested and as Ullman and Henderson [6] have accepted to be true at least for a small fraction of the reaction.

Acknowledgments

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