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EXPERIMENTAL PROOF FOR THE INTERMEDIACY OF ZWITTERIONS IN THE PATHWAY LEADING TO LUMIKETONES UPON IRRADIATION OF 2,5-CYCLOHEXADIENONES[†]

DAVID I. SCHUSTER[*] and KOU-CHANG LIU
Department of Chemistry, New York University, New York, NY 10003, U.S.A.

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Abstract—Details are presented of kinetic studies which demonstrate that a zwitterionic species is an obligatory intermediate in the photochemical rearrangement of a model 2,5-cyclohexadienone to its isomeric bicyclo(3.1.0)hex-3-en-2-one (lumiketone). In these studies, the zwitterionic intermediate has been successfully intercepted by lithium chloride present in the mixture. In addition, studies of the temperature dependence of zwitterion-derived processes suggest that cycloreversion of the zwitterion to the starting dienone by a symmetry-forbidden process is the main source of energy wastage in this system, and that this reversion becomes increasingly efficient as the temperature is raised.

In 1961 and 1962, Zimmerman and this author presented [2,3] a mechanism to account for the photorearrangements of 2,5-cyclohexadienones to bicyclo(3.1.0)hex-2-en-1-ones (lumiketones) and a variety of other products which had previously eluded rational mechanistic analysis. The proposed mechanism was notable in that it provided a step by step description of these complex photorearrangements, which was one of the first attempts of its kind in the history of organic photochemistry. Indeed, many people at that time felt that it was foolhardy to expect that reactions occurring on absorption of light energy in excess of 80 kcal/mole would follow the same sort of rules which seemed to govern ground state behavior of organic molecules. However, the Zimmerman–Schuster mechanism still serves to rationalize the behavior of the large number of 2,5-cyclohexadienones and related molecules which have been subjected to photochemical investigation.[4]

One of the key postulates of the original mechanism[2,3] was the suggestion that ground state zwitterions are transient intermediates which are derived from the triplet n,π^* electronic state of the cyclohexadienone, and that these zwitterions subsequently undergo a ground state rearrangement to the lumiketones by a mechanism which was found to have analogy in the rearrangements of cyclopropylcarbinyl carbocations,[5] a process which was subsequently recognized[6] as a classic example of a (1,4)-sigmatropic shift. One of us has previously summarized the case for zwitterion intermediates in these photochemical rearrangements,[7] and noted that although such zwitterions served well to rationalize the course of these photorearrangements, direct evidence for their intermediacy was lacking. Support for zwitterions in the photochemical system was obtained from the observation that products identical to those observed in the photorearrangements can be produced when zwitterion-like intermediates are generated thermally by Favorskii-type reactions;[8] however, this does not unequivocally rule out alternative mechanisms for the photochemical system which bypass zwitterion intermediates.[9] Ideally, one would like to be able to directly observe zwitterions in the photoreactions using flash techniques, and unsuccessful efforts have been made in that direction.[10]

An alternative way to demonstrate the intermediacy of zwitterions on the pathway to lumiketones would be to divert the course of reaction utilizing an external reagent and to demonstrate by kinetic criteria that the zwitterion must be a common intermediate along both pathways. We set out to accomplish this some years ago using the model cyclohexadienone 1 which had served us so well in delineating many features of cyclohexadienone photochemistry,[7] and where evidence had been obtained that the intermediate zwitterions might be subject to trapping by reactive nucleophiles.[11] Indeed, as reported in a preliminary communication,[12] we were able to demonstrate that an intermediate which was subject to capture by lithium chloride was also an obligatory intermediate on the pathway to lumiketone. This is, in fact, the *only* evidence of its kind to be presented in the literature of cyclohexadienone photochemistry, to the best of our knowledge.[4,7]

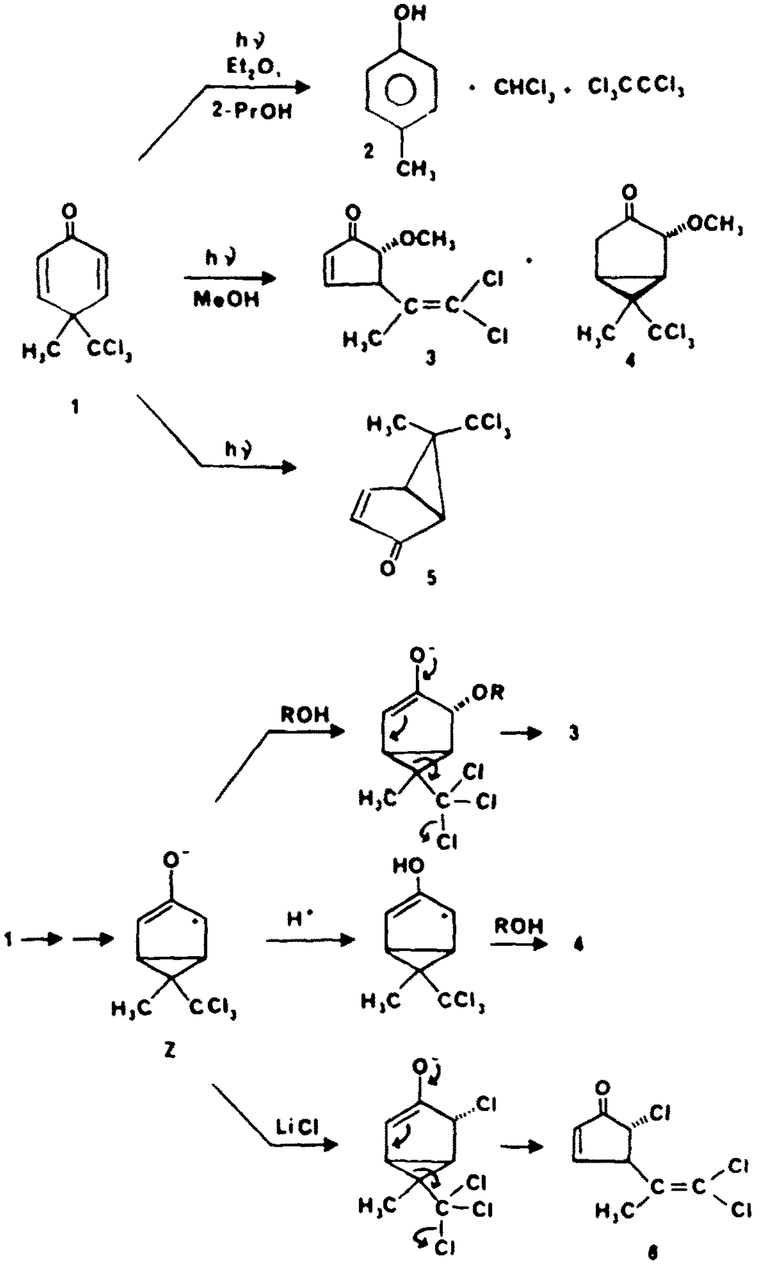
Other zwitterion-trapping reactions have been reported. In a prototypical reaction, the zwitterion derived from α-santonin can be diverted in aqueous acid to give isophotosantonic lactone, rather than proceeding on to lumisantonin, by a reaction involving protonation of the zwitterion followed by attack of aqueous acid, according to a mechanism first proposed by Zimmerman.[3] Similar behavior is shown by analogous steroid dienones.[4] More recently, trapping by dienes of the zwitterion derived from 1 has been reported.[13] However, in none of these studies was evidence reported to define the kinetic relationship between the trapping reaction and lumiketone formation, that is, evidence which would *require* postulation of a zwitterion as a common intermediate in these competitive reaction pathways. Because of renewed interest in zwitterions[9,13,14] and the unique aspects of our zwitterion-trapping kinetic studies, we are prompted to publish at this time our full data on this subject as part of this Symposium-in-Print in Organic Photochemistry.

[†] Work done at the University Heights Center of New York University, Bronx, NY 10453, U.S.A.

RESULTS

Earlier work by Patel had established that when dienone 1 was irradiated in media containing a good H-donor toward free radicals, 1 was converted into *p*-cresol (2) accompanied by $CHCl_3$ and Cl_3CCCl_3.[11,15] Later studies by Liu and Barile[16-18] established that this was a free-radical reaction, which in certain media such as secondary alcohols (e.g. 2-propanol) occurred by a radical chain mechanism. Patel also established that irradiation of 1 in methanol gave the methyl ethers 3 and 4, where the former is the exclusive product in neutral or basic media and the latter is the main product in acidic media.[11] Analogues of 3 and 4 were formed when other alcohols were used as solvents.[11] These reactions can be readily rationalized on the basis of a mechanism involving zwitterion intermediates (Scheme 1), as discussed previously. In addition to these transformations, the lumiketone 5 is formed on irradiation of 1 in virtually all media examined to date.[7] The stereochemistry of the transformation, a matter of some interest, is discussed in detail elsewhere.[19]

When dienone 1 was irradiated in methanol, t-butyl alcohol, isopropyl alcohol or 2,2,2-trifluoroethanol in the presence of lithium or tetramethylammonium chloride, a new product was formed at the expense of the ethers of type 3 and 4,[14] whose structure was assigned as 6 on the basis of spectral data, which were very similar to those of compound 3.[11] Compound 6 was not formed when 1 was irradiated in alcoholic solutions containing lithium or tetramethylammonium bromide or the corresponding iodides. Analysis by glpc showed new products were



Scheme 1.

present, presumably the bromo and iodo analogs of **6**, but attempts to isolate and characterize these thermally labile materials were unsuccessful.[16] No reaction of **1** could be detected when solution of **1** in these alcohols in the presence or the absence of lithium chloride were kept in the dark for periods of time equivalent to those used in the irradiations.[16]

When α-santonin or 4,4-diphenyl-2,5-cyclohexadienone was irradiated in trifluoroethanol saturated with lithium chloride, under conditions which led to the formation of **6** from **1**, no products of chloride trapping were observed according to GLPC and spectral data, and no quenching by LiCl of the phototransformations of these dienones was noted.[16]

Kinetic studies. The high dielectic constant of 2,2,2-trifluoroethanol (TFE) coupled with its low nucleophilicity makes it an ideal solvent for study of the competition between formation of lumiketone **5** and the chloroadduct **6**. Thus, the solubility of the inorganic salts needed for these trapping experiments should be relatively high in TFE, while its relatively poor nucleophilicity should inhibit trapping by solvent of the proposed zwitterion intermediate, which itself may be stabilized to some extent by interaction with the solvent.

The yields of lumiketone **5** and chloroadduct **6** in TFE as a function of the concentration of added LiCl under two different sets of experimental conditions were measured by glpc using internal standards. The results summarized in Tables 1 and 2 show that addition of LiCl to the reaction system results in a steady decrease in the yield of **5** concomitant with an increase in the yield of **6**.

A similar experiment was carried out in 2-propanol. In addition to *p*-cresol, which arises via the H-abstraction pathway,[18] irradiation of **1** in 2-propanol gives the ether **7**, whose structure was assigned on the basis of spectral data (Experimental), including an UV maximum at 266 nm, ε 9,400. The data are inconsistent with those anticipated for ether **8**, the expected photoproduct analogous to **3**. However, thermal rearrangement of **8** to **7**, particularly with acid catalysis, is precedented in the behavior of **3** as well as the hydroxy analog **9**.[11,20] Therefore, we believe that **8** is probably formed initially during the irradiation, but rapidly rearranges to **7** under the reaction conditions, although we have no direct experimental evidence to support this hypothesis. Since in this reaction system we have products which arise by both a free-radical and an ionic pathway, it was possible to determine the effect of added lithium chloride on both of these pathways in the same reaction system. The results are given in Table 3. Once again, addition of LiCl results in a steady increase in the yield of **6** and a decrease in the yield of **7**, while there is no change within experimental error in the yield of *p*-cresol. This proves that LiCl intercepts a reaction intermediate in the pathway leading to **7** that is not on the pathway leading to *p*-cresol.

Dienes such as piperylene and 1,3-cyclohexadiene quench the conversion of **1** to ether **3** in methanol and to lumiketone **5** in a variety of solvents,[11,21] as the result of energy transfer of triplet excitation from the dienone to the diene. Data for quenching of the formation of *p*-cresol and ether **7** from **1** in 2-propanol by 1,3-cyclohexadiene is given in Table 4, while Table 5 gives similar date for quenching by CHD of the formation of *p*-cresol, **6** and **7** in 2-propanol saturated with LiCl. The data are presented in the form of Stern-Volmer quenching plots in Figs. 1 and 2. It can be seen in both figures that diene concentrations up to 0.1 M produce a large reduction in

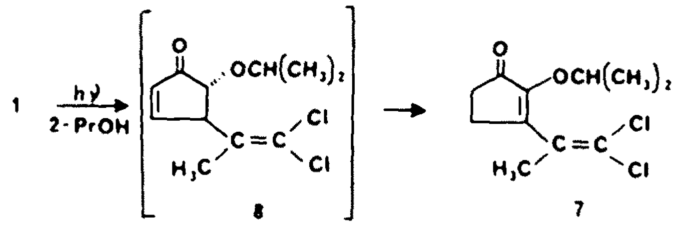
Competition between formation of lumiketone **5** and chloroadduct **6** on irradiation of dienone **1** in 2,2,2-trifluoroethanol. Run 1

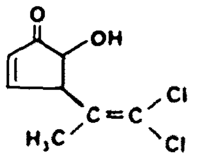
LiCl, M	Ratio to Internal Standard (GLPC)		Relative Yield		Φ_6	$(\Phi_0/\Phi)_5$	$\Phi_6/(1-\Phi_6)$
	5	6	5	6			
1.20	0.17	1.75	0.40	3.37	0.80	9.18	4.00
0.60	0.26	1.69	0.62	3.25	0.76	5.92	3.17
0.30	0.55	1.63	1.31	3.14	0.74	2.80	2.85
0.23	0.66	1.36	1.57	2.62	0.62	2.34	1.63
0.15	0.75	1.15	1.78	2.21	0.52	2.06	1.08
0.075	0.97	0.80	2.31	1.54	0.36	1.59	0.56
0.038	1.16	0.40	2.76	0.77	0.18	1.33	0.22
0.000	1.54	0.00	3.67	0.00	0.00	1.00	0.00

[a] Samples irradiated using a 550-W high pressure Hanovia lamp through Corning 5860 and 7380 filters in a rotating turntable in a water bath. The reaction temperature was recorded as 22-27^0 during the run. The dienone concentration was 0.222 M.

[b] Gas-liquidChromatography on a 1/8 in. x 6 ft. 10% OV-225 on chromosorb Q column. The internal standard, acenaphthene, was added following irradiation. The glpc response factors were determined to be 0.42 for lumiketone 5 and 0.52 for chloroadduct 6 relative to acenaphthene = 1.00 under these conditions.

[c] Calculated from these data using the absolute quantum yield of 0.52 for formation of 6 at 366 nm in the presence of 0.15 M LiCl as determined on an optical bench.





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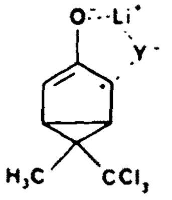

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Table 2. Competition between formation of lumiketone 5 and chloroadduct 6 on irradiation of dienone 1 in 2,2,2-trifluoroethanol. Run 2

z.

LiCl, M	Ratio to Internal Standard (GLPC)		Relative Yield		Φ_6	$(\Phi_0/\Phi)_5$	$\Phi_6/(1-\Phi_6)$
	5	6	5	6			
0.126	0.27	0.88	0.64	1.69	0.602	3.70	1.51
0.075	0.40	0.69	0.95	1.33	0.474	2.38	0.90
0.050	0.55	0.64	1.31	1.23	0.438	1.92	0.78
0.025	0.72	0.35	1.72	0.67	0.238	1.39	0.31
0.000	0.87	0.00	2.07	0.00	0.000	1.00	0.00

[a] Samples irradiated using a 450-W high pressure Hanovia lamp through a corning 0-52 filter in a rotating turntable for 68 min. No bath was used, and the reaction temperature was found to be 40-50° C. The dienone concentration was 0.042 M.

[b] Gas-liquid chromatography on a 1/8 in. x 6 ft. 10% QF-1 on chromosorb P column. The internal standard, acenaphthene, was added following irradiation. The glpc response factors were determined to be 0.42 for lumiketone 5 and 0.52 for chloroadduct 6 relative to acenaphthene = 1.00.

[c] See footnote c in Table I.

the yield of p-cresol, and a moderate increase in the yield of both 6 and 7. All three products are quenched by CHD concentrations greater than 0.1 M with slopes that are indistinguishable within the limits of the experimental uncertainty.

Temperature effects. The temperature dependence of the yield of 3 on irradiation of dienone 1 in methanol is summarized in Table 6. In both runs, an increase in temperature resulted in a decrease in the relative quantum yield for formation of 3. Absolute quantum yields for formation of p-cresol and ether 7 on irradiation of 1 in 2-propanol were measured as a function of temperature, and the data are given in Table 7. Once again, the yield of the ether product decreased as the temperature was raised, but in contrast the yield of p-cresol shows a considerable increase over the same range. Finally, relative quantum yields for the formation of lumiketone 5 and chloroadduct 6 in TFE at two different temperatures are given in Table 8. It is obvious that the yield of 6 in TFE containing 1.21 M LiCl is higher than the yield of lumiketone at the same temperature in TFE without added LiCl, and that the discrepancy in yields is greater at 38° than at 0°. The importance of this result will become clear in the following Discussion.

Attempted zwitterion trapping by cycloaddition. Several attempts were made to trap the proposed zwitterion intermediate by cycloaddition reactions. Trapping with dimethylacetylene dicarboxylate or N-methylpyrrole at room temperature was completely unsuccessful. A new major product was formed on irradiation of dienone 1 in furan or in an ethyl ether solution of furan, both at room temperature and at Dry Ice temperatures, according to glpc analysis. All attempts to isolate the new product were unsuccessful. Recently, Samuel[13] has succeeded in isolating and characterizing products which can be attributed to trapping by furan and cyclo-

Table 3. Competition between formation of *p*-cresol, ether 7 and chloroadduct 6 on irradiation of dienone 1 in 2-propanol[a]

LiCl, M	Ratio to Internal Standard p-cresol	6	7	Relative Yields p-cresol	6	7
1.25	0.85	0.46	0.40	1.67	0.89	0.57
1.10	0.83	0.46	0.56	1.63	0.89	0.80
0.94	0.85	0.44	0.60	1.67	0.85	0.86
0.79	0.97	0.34	0.67	1.90	0.65	0.96
0.63	0.97	0.30	0.73	1.90	0.58	1.04
0.31	0.96	0.21	1.05	1.88	0.40	1.50
0.16	0.95	0.12	1.33	1.86	0.23	1.90
0.08	0.85	0.034	1.38	1.67	0.06	1.97
0.00	1.01	0.00	1.55	1.98	0.00	2.22

[a] Solutions containing 0.044 M dienone in a rotating turntable were irradiated at room temperature for 1 hr. with a 450-W high pressure Hanovia lamp through Corning 0-52 filters. A duplicate run gave essentially identical results.

[b] Gas-liquid chromatographic analysis on a 1/8 in. x 6 ft. 5% OV-225 on chromosorb G column using an oven temperature of 140-165°C. The internal standard, acenaphthene, was added following irradiation. The glpc response factors were determined to be 0.51 for p-cresol, 0.70 for ether 7 and 0.52 for chloroadduct 6 relative to acenaphthene = 1.00.

Table 4. Quenching by 1,3-cyclohexadiene of the formation of *p*-cresol and ether 7 on irradiation of dienone 1 in 2-propanol[a]

CHD Concn, M	Ratio to Internal Standard p-cresol	7	Φ_0/Φ p-cresol	7
0.000	1.26	1.00	1.00	1.00
0.012	0.76	1.49	1.58	0.67
0.024	0.67	1.45	1.79	0.69
0.036	0.65	1.43	1.85	0.70
0.060	0.61	1.42	1.97	0.71
0.12	0.52	1.03	2.31	0.97
0.24	0.50	0.96	2.40	1.04
0.95	0.38	0.37	3.16	2.70

[a] Irradiation of samples in a rotating turntable at 55°C using a 550-W Hanovia high pressure mercury lamp and Corning #5860 and 7380 filters. The dienone concentration was 0.16 M. Solvent and CHD were freshly distilled. Samples were not degassed.

[b] Gas-liquid chromatographic analysis on a 1/8 in. x 8 ft. 5% SE-30 on chromosorb G column. The internal standard benzophenone, was added following irradiation.

Table 5. Quenching by 1,3-cyclohexadiene of the formation of *p*-cresol, ether 7 and chloroadduct 6 on irradiation of dienone 1 in 2-propanol saturated with lithium chloride[a]

CHD Concn, M	GLPC Ratio to Internal Std. cresol	7	6	Φ_0/Φ cresol	7	6
0.000	1.85	0.60	0.49	1.00	1.00	1.00
0.013	0.93	0.83	1.09	1.99	0.72	0.45
0.025	0.92	0.96	1.22	2.01	0.63	0.40
0.050	0.87	0.85	1.10	2.13	0.71	0.45
0.075	0.86	0.85	1.10	2.18	0.71	0.45
0.125	0.72	0.73	0.99	2.57	0.82	0.50
0.250	0.57	0.63	0.81	3.25	0.95	0.60
0.500	0.43	0.47	0.64	4.30	1.27	0.72
0.952	0.33	0.32	0.46	5.61	1.87	1.06

[a] Conditions the same as in Table IV, except that the reaction temperature during irradiation was maintained at 22-27°C. Dienone concentration = 0.17 M.

[b] GLPC analysis conditions as in Table IV.

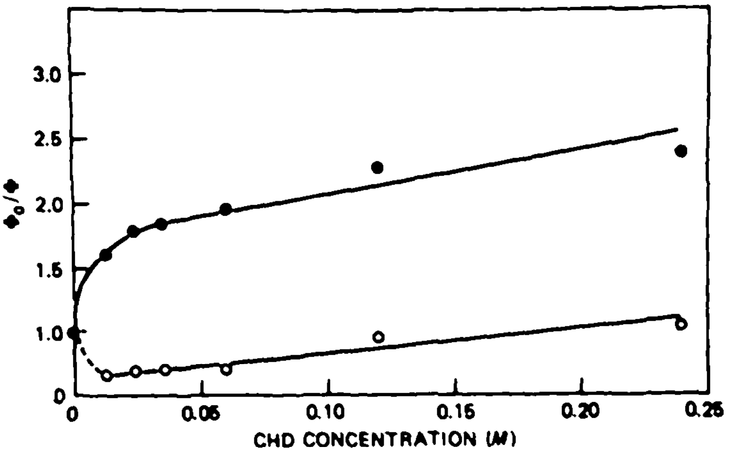


Fig. 1. Stern–Volmer plot of quenching data from Table 4. Solid dots are data points for *p*-cresol, and open circles for ether 7.

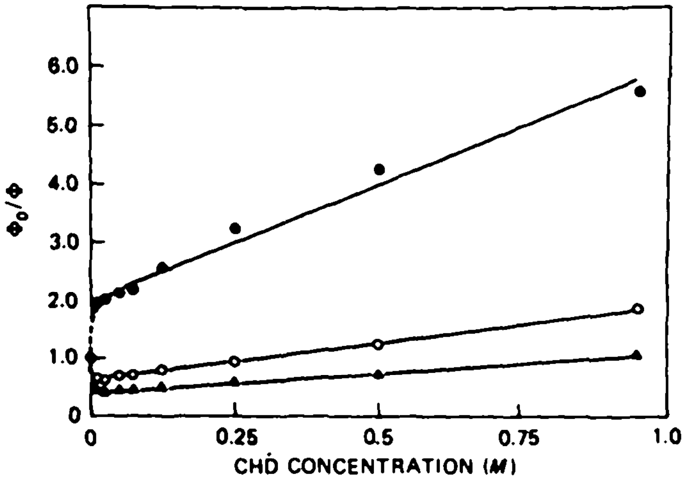


Fig. 2. Stern–Volmer plot of quenching data from Table 5. Solid dots are data points for *p*-cresol, open circles for ether 7 and solid triangles for chloroadduct 6.

Table 6. Temperature dependence of formation of ether 3 on Irradiation of Dienone 1 in methanol[a]

Temperature, °C		Ratio of 3 to Internal Standard	Relative Yield of 3
Run I	0	0.85	1.00
	15	0.65	0.92
	42	0.53	0.62
	62	0.18	0.21
Run II	0	1.78	1.00
	34	1.42	0.80
	64	0.56	0.32

[a] Irradiation of samples in a rotating turntable within a constant temperature bath for 1 hr. using a 100-W high pressure Hanovia lamp and a Pyrex filter. Most determinations done in duplicate. Dienone concentration = 0.055 M.

[b] GLC analysis on a 1/8 in. x 10 ft. 20% GEXE-60 on chromosorb W column using acenaphthene as internal standard, added following irradiation.

Table 7. Temperature dependence of absolute quantum yields for formation of *p*-cresol and ether 7 on irradiation of dienone 1 in 2-propanol[a]

Temperature, °C	Quantum Yields[b] p-Cresol	Ether 7
24	0.23	0.87
41	0.34	0.57
61	0.59	0.40

[a] Samples in quartz cells irradiated at 366 nm using a 200-W high pressure mercury lamp coupled with a Bausch and Lomb Grating Monochromator, in a water bath with a quartz window. Temperature maintained to ± 1°C. Dienone concentration 0.089 M.

[b] Potassium ferrioxalate actinometry was used. By means of a split beam technique (sample: reference 13.0·1) the light on the reference actinometer solution was monitored throughout the reaction. GLC analysis done on 1/8 in. x 6 ft. 10% carbowax on chromosorb Q and 20% GEXE-60 on chromosorb W columns using acenaphthene as internal standard, added following irradiation. GLC response factors as in Table III.

Table 8. Temperature effect on formation of lumiketone 5 and chloroadduct 6 on irradiation of dienone 1 in 2,2,2-trifluoroethanol.[a]

Temp, o C	LiCl, M	Ratio to GLC Internal Standard[b] 5	5a	6	Corrected Yield 5	6	Total Yield
38	0.00	0.62	0.03	0.00	1.67	0.00	1.67
38	1.21	0.02	0.00	1.65	0.048	3.18	3.23
0	0.00	0.86	0.07	0.00	2.50	0.00	2.50
0	1.21	0.03	0.00	1.88	0.07	3.62	3.69

[a] Irradiation for 1 hr. of samples in a rotating turntable set in a constant temperature bath using a 550-W Hanovia high pressure mercury lamp and Corning #5860 and 7380 filters. Dienone concentration 0.222 M.

[b] GLC analysis on a 1/8 in. x 6 ft. 10% OV-225 on Chromosorb Q column with acenaphthene as internal standard, added following irradiation.

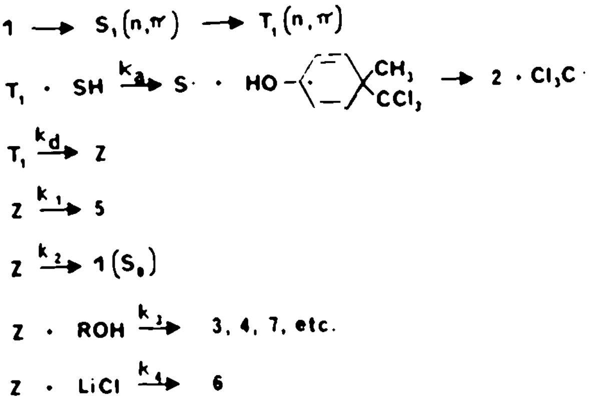
[c] Lumiketone 5a is a known secondary photolysis product of lumiketone 5, formed from 5 with a quantum efficiency of 0.36.

[d] Yield of lumiketone 5 taken to be the sum of 5 + 5a/0.36, corrected for the glc response factor of 0.42 relative to the internal standard. The response factor for 6 is 0.52.

pentadiene of the proposed zwitterion intermediate derived from 1, lending further support to our postulated mechanism. However, the kinetic relationship between the formation of such cycloadducts and the normal dienone photolysis products has not been reported.

DISCUSSION

The results presented above, together with those reported previously,[7,11] allow specification of the sequence of events occurring upon electronic excitation of dienone 1, and these are summarized in Scheme 2. The diene quenching studies indicate that all photoproducts of 1 are derived ultimately from a single electronically excited triplet state of 1, presumably the n,π^* triplet. (The latter assignment has been discussed in detail elsewhere).[4,7,9] The curved quenching plots observed in 2-propanol but not in benzene, methanol or diethyl ether can be rationalized in terms of the radical chain mechanism proposed for the pathway leading to *p*-cresol in 2-propanol following the initiation step (eqn ii in Scheme 2)[17,18]. The increase in quantum yield for formation of products 6 and 7 has been attributed [17,18] to scavenging by CHD of radicals which are capable of reacting with and consuming 6 and 7. Experimental support for this hypothesis derives from studies in which the radical chain process leading from 1 to *p*-cresol was initiated by thermal decomposition of benzoyl peroxide in 2-propanol and resulted in consumption of quantities of 7 added to the reaction system. The quenching data at >0.1 M CHD is therefore considered to represent the triplet quenching process uncontaminated for the most part by radical quenching. The slopes of these plots for the



Scheme 2.

various transformations of 1 under a given set of conditions are the same, within experimental error, pointing to one and only one reactive triplet excited state precursor for all these reactions.

Since added LiCl has no effect, as expected, on the free radical pathway leading to *p*-cresol, the marked effect of LiCl on the formation of lumiketone 5 and ether 7 must be attributed to interception of an ionic intermediate which itself is derived from the triplet excited state precursor. The fact that this quenching process is accompanied by the formation of chloroadduct 6 identifies this intermediate as zwitterion Z. The mechanism of formation of 6 on reaction between Z and LiCl as depicted in Scheme 1 is totally analogous to that proposed some time ago for the formation of 3 and 1 in methanol.[11] This involves nucleophilic attack on carbon *α* to the CO from the side of the zwitterion opposite to the cyclopropane bridge followed by Grob-like anionic fragmentation to give 6 and another chloride ion. Coordination of the lithium ion with the carbonyl oxygen of Z as in structure 10 appears to enhance the formation of chloroadduct 6, since the yield of 6 in TFE saturated with LiCl was 7.5 times greater than the yield in TFE saturated with KCl, and 5 times greater than the yield of 6 even when a trace of 18-crown-6 was added to the TFE/KCl solution.[22] Also, both LiBr and Li_2SO_4 greatly enhanced the yield of 6 on irradiation of TFE/KCl solutions.[22]

Based on the mechanism outlined in Scheme 2, the lifetime of the zwitterion Z in the absence of added nucleophile is given by eqn (1), while the quantum yield for formation of lumiketone 5 is given by eqn 2, where Φ_z is the quantum efficiency of formation of the zwitterion.

$$1/\tau_z = k_1 + k_2 + k_3[ROH] \qquad (1)$$

$$\Phi^{0}_{\mathrm{lumi}} = \frac{\Phi_z k_1}{k_1 + k_2 + k_3[ROH]} = \Phi_z k_1 \tau_z \qquad (2)$$

In the presence of chloride ion, the quantum efficiency for formation of lumiketone 5 should be given by eqn (3) if chloride is intercepting an intermediate (i.e. Z) which is on the pathway to lumiketone.

$$\Phi^{Q}_{\mathrm{lumi}} = \frac{\Phi_z k_1}{k_1 + k_2 + k_3[\mathrm{ROH}] + k_4[\mathrm{Cl}^-]} \qquad (3)$$

From eqns (2) and (3), one can readily derive the Stern-Volmer expression given in eqn (4) for the effect of chloride on the yield of lumiketone. The same expression should hold for quenching

$$(\Phi^0/\Phi^Q)_{\mathrm{lumi}} = (\Phi^0/\Phi^Q)_{\mathrm{ethers}} = 1 + k_4\tau_z[\mathrm{Cl}^-] \qquad (4)$$

of the formation of other products such as ethers 3 and 7 which arise from zwitterion Z according to the kinetic scheme.

The quantum efficiency for formation of chloroadduct 6 is given by eqn (5), which can be manipulated to give eqns (6) and (7). Comparing eqns (4) and (7), it can be seen that the slopes of plots of Φ_0/Φ_q for formation of lumiketone 5 or ethers 3 and 7 and of plots of $\Phi_6/(1 - \Phi_6)$ vs chloride concentration should be identical if, and only if, there is a common intermediate in

$$\Phi_6 = \Phi_z \frac{k_4[\mathrm{Cl}^-]}{k_1 + k_2 + k_3[\mathrm{ROH}] + k_4[\mathrm{Cl}^-]} \qquad (5)$$

$$\begin{aligned}\Phi_z/\Phi_6 &= 1 + \frac{k_1 + k_2 + k_3[\mathrm{ROH}]}{k_4[\mathrm{Cl}^-]}\\ &= 1 + \frac{1}{k_4\tau_z[\mathrm{Cl}^-]}\end{aligned} \qquad (6)$$

$$\frac{\Phi_6}{\Phi_z - \Phi_6} = k_4\tau_z[\mathrm{Cl}\ ] \qquad (7)$$

these reactions which is being intercepted by chloride ion. In TFE, where the formation of *p*-cresol is not detectable, $\Phi_6 = 0.52$ and $\Phi_5 = 0.43$ at 366 nm in the presence of 0.15 M LiCl. Thus, it is reasonable to assume that $\Phi_z \sim 1.0$ in TFE and that any inefficiency in formation of photoproducts is due to radiationless decay to ground state dienone from the zwitterion (see below). In both Figs. 3 and 4 where the data from Tables 1 and 2 are plotted according to eqns (4) and (7), the data points for lumiketone 5 and chloroadduct 6 fall on a common straight line[†] up to ~0.6 M LiCl. The deviation at high LiCl concentration is unexplained, but could be the result of experimental uncertainty since small differences in Φ_6 lead to large changes in $\Phi_6/(1 - \Phi_6)$. The differing values of $k_4\tau_z$ (slopes) reflect differences in reaction conditions given in Tables 1 and 2, most importantly differences in reaction temperature. Since we can not assign values to either k_4 or τ_z independently, rate constants for any of the individual reactions of zwitterion *Z* can not be derived from these experiments.

[†] Within experimental uncertainty.

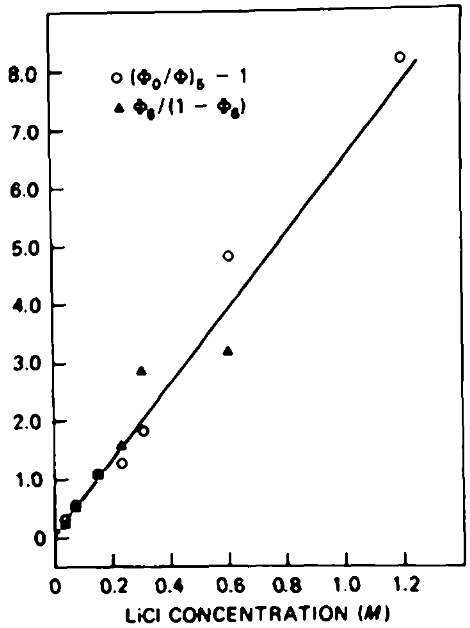


Fig. 3. Plot of data from Table 1 for formation of lumiketone 5 and chloroadduct 6 in TFE as a function of the concentration of LiCl.

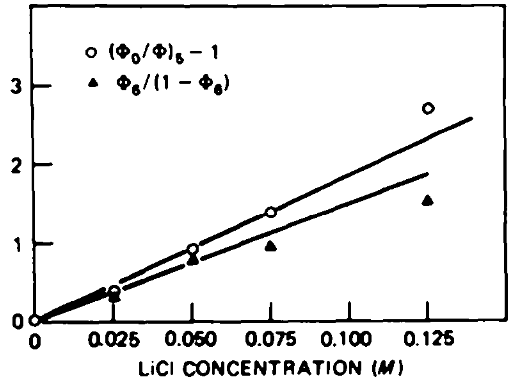


Fig. 4. Plot of data from Table 2 for formation of lumiketone 5 and chloroadduct 6 in TFE as a function of the concentration of LiCl.

In 2-propanol, where the H-abstraction pathway leading to p-cresol is an important primary process, there is considerable uncertainty in the efficiency of zwitterion formation (Φ_z), unlike the situation in TFE. The data in Table 7 also indicate that quantum efficiencies in 2-propanol are very sensitive to slight variations in reaction temperature. At the present time, there is insufficient reliable quantitative product data in 2-propanol to permit construction of plots analogous to those in Figs. 3 and 4. However, the data in Table 3 and in other runs in 2-propanol[16] demonstrate an inverse relationship between the yields of 6 and 7 as a function of LiCl concentration, consistent with the view that the intermediate trapped by LiCl is on the pathway leading to 7, but is not an intermediate in cresol formation. We see no logical alternative to zwitterion Z as the species which would logically serve as a precursor to both 6 and 7 and to lumiketone 5 as well.

The fact that LiCl has no effect on the phototransformations of α-santonin and of 4,4-diphenyl-2,5-cyclohexadienone, and that chloroadducts are not formed in these systems, has been explained[7] in terms of differences in zwitterion lifetimes. In non-nucleophilic solvents the quantum efficiencies of the lumiketone rearrangement are usually very large, often approaching unity.[4,7,14] In the transition state for the (1,4)-sigmatropic rearrangement of the zwitterion, positive charge is concentrated on the migrating carbon, originally C_4 of the dienone.[6] Therefore, electron withdrawing groups such as CCl_3 should retard the rearrangement rate and increase the steady-state zwitterion lifetime, while alkyl and aryl groups should enhance the rate of the rearrangement and reduce the zwitterion lifetime. The presence of the CCl_3 group at C_4 of the dienone results in a sufficient lengthening of the zwitterion lifetime to permit trapping by nucleophiles as well as by dienes.[13] Other cyclohexadienones with electron-withdrawing groups at C_4 ought to show similar behavior, but no such data have been reported to date, to the best of our knowledge. Trapping of highly reactive zwitterions may be possible at low temperatures, and experiments along those lines are in progress.

The observation that the quantum yield for formation of p-cresol increases as the temperature is raised is consistent with observations in other systems that a small energy of activation is associated with rates of H-abstraction from appropriate donors by n,π^* triplet excited states.[21] What is more unusual is the finding that the quantum yields for formation of ethers 3 and 7 are dramatically reduced upon moderate increases in the temperature of the reaction system. There seems no reasonable alternative but to ascribe this to deactivation of the zwitterion Z by a pathway which becomes increasingly competitive with progress to products 3 (in MeOH) and 7 (in 2-PrOH) as the temperature is raised. Since vapor chromatograms gave no evidence for the formation of a new product, we are forced to conclude that this alternative pathway is electrocyclic ring opening of zwitterion Z to ground state dienone. This process is formally forbidden on the basis of orbital symmetry considerations,[6] and indeed Zimmerman and Swenton have shown that these zwitterions correlate with a doubly excited state of the cyclohexadienone.[24] Therefore, a high activation barrier should be associated with the reversion, so that the rate of the reversion should increase sharply as the temperature is raised, at the expense of other zwitterionic reactions with more moderate energy requirements.

Further support for this hypothesis comes from the temperature dependence of chloride quenching in TFE. It can be seen that 1.21 M LiCl results in nearly complete quenching of the formation of lumiketone 5 at both 0° and 38°. However, the yield of chloroadduct 6 resulting from zwitterion capture is considerably greater than the yield of lumiketone at both temperatures, to the extent of (3.23–1.67)/3.23 = 48% at 38° and (3.69–2.50)/3.69 = 32% at 0°. Since the TFE analogy of 3 is formed in only very small amounts, the conclusion seems inescapable that there must be an additional zwitterion reaction path in TFE which is increasingly competitive with formation of lumiketone 5 as the temperature is raised. These observations are nicely rationalized by the proposed temperature-dependent reversion of zwitterion to ground state cyclohexadienone.

As a result of the differing responses to temperature of the various processes resulting from electronic excitation of **1**, we find that the product ratios in this system are very sensitive to temperature.[16] This has important consequences with respect to optimizing yields of a particular product for preparative purposes. We are currently doing further work to more fully characterize the temperature dependence of the various primary processes in the photochemistry of dienone **1** and related compounds, including the elucidation of the low temperature phototransformations of these dienones in fluid as well as rigid media.

CONCLUSIONS

The most important result of the present study is the kinetic demonstration of a common intermediate in the photochemical rearrangement of cyclohexadieneone **1** to lumiketone **5** and in the pathways leading to ethers **3** and **7** and chloroadduct **6**. The ionic nature of the processes which lead to **3**, **6** and **7** identify this intermediate as the zwitterion Z, the species proposed twenty years ago[2] as the key intermediate in 2,5-cyclohexadienone photochemistry. Studies of the temperature dependence of the zwitterion-derived photoreactions reveal that the main source of inefficiency in this system appears to be electrocylic reversion of zwitterion Z to cyclohexadienone **1** by an orbital symmetry-forbidden pathway that becomes increasingly important as the temperature is raised.

EXPERIMENTAL

4 - *Trichloromethyl* - 4 - *methyl* - 2,5 - *cyclohexadienone* (**1**) was prepared as described previously.[11] Conditions for the various kinetic experiments are given in Tables 1–8. All glpc analyses were made using a Hewlett-Packard F and M Model 5750 Chromatograph equipped with dual column flame ionization detectors and an HP model 7172A strip chart recorder and a disc integrator. All chemicals and solvents were purified by recrystallization or distillation prior to each kinetic experiment.

5 - *Chloro* - 4 - (1 - *methyl* - 2,2 - *dichloroethenyl*) - *cyclopent* - 2 - *en* - 1 - *one* (**6**). Upon irradiation of 18 g (0.08 mol) of **1** in 300 mL MeOH containing 50 g (1.18 mol) LiCl in a Pyrex immersion well with a 450-W Hanovia lamp for 2.75 hr., 90% of the dienone had been converted into a mixture containing ether **3** and the chloroadduct **6** and other products. After being concentrated, the photolysate was chromatographed on silica gel using $CHCl_3$ as the eluent. Compound **6** was isolated and recrystallized from hexane to give white crystals, m.p. 52–53°. Spectral data: Mass (*m/e*) 224 (3 Cl), 189 (2 Cl), 161 (2 Cl), 153 (1 Cl), 125 (1 Cl), 91 (1 Cl); IR (CCl_4) 2925, 1735, 1610, 1578, 903, 854 cm^{-1}; PMR (CCl_4) δ 7.60 (dd 1H), 6.43 (dd 1H), 4.47 (m 1H), 4.14 (d 1H), 1.86 (3 3H).

2 - *Isopropoxy* - 3 - (1 - *methyl* - 2,2 - *dichloroethenyl*) - *cyclopent* - 2 - *en* - 1 - *one* (**7**). Irradiation of 20 g (0.089 mol) of **1** in 500 mL 2-PrOH in a Pyrex immersion well with a 550-W Hanovia high pressure mercury lamp gave **7** in addition to *p*-cresol and other products (glpc analysis). The solvent was removed under reduced pressure and the resultant thick slurry was dissolved in ethyl ether. The ethereal soln was washed twice with 5% NaOH and twice with water to remove *p*-cresol. After being dried over $MgSO_4$, the solution was concentrated on a Rotovap and the residue was chromatographed on silica gel twice using hexane–ether mixtures as eluent. Material was obtained which showed only one peak on glpc analysis. Spectral data: Mass (*m/e*) 250 (2 Cl), 215 (1 Cl), 187 (1 Cl), 179, 151, 127; IR (CCl_4) 3000, 2945, 1715, 1625, 1600, 1380, 1140, 1080, 915 cm^{-1}; UV (EtOH) λ_{max} 266 nm (ϵ 9,400); PMR (CCl_4) δ 4.96 (sept 1 H, J 5.8 Hz), 2.54 (m 2H), 2.36 (m 2H), 1.98 (s 3H), 1.10 (d 6H), J 5.8 Hz).

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