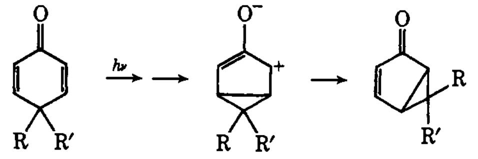
# Nucleophilic Trapping of Photochemically Generated Zwitterions. Evidence for the Intermediacy of Zwitterions in the Photochemical Rearrangement of Cyclohexadienones[1]

*Sir:*

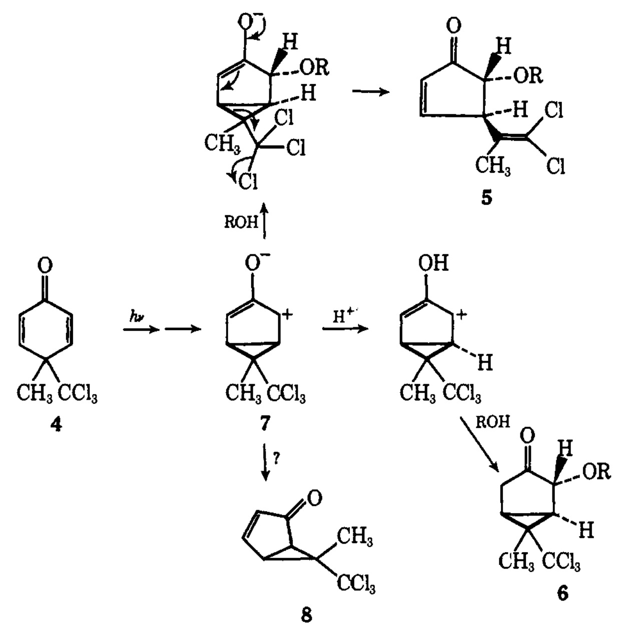
It was postulated a decade ago that bicyclic zwitterions **2** were intermediates in the photorearrangement of 2,5-cyclohexadienones **1** to bicyclo[3.1.0]hex-3-en-2-ones (**3**) (lumiketones).[2] This postulate has been generally accepted,[3] although direct experimental evidence *requiring* the intermediacy of zwitterions in this photochemical rearrangement has been lacking, as pointed out previously.[4] We now report some experimental evidence which demonstrates that zwitterions which can be trapped by nucleophilic reagents are intermediates in the photochemical lumirearrangement in at least one case.[5–8]

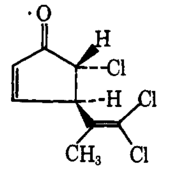


1 2 3

The variety of reactions which ensue on irradiation of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone (**4**) provides a handle to the elucidation of reaction mechanism because of the sensitivity of the system to changes in reaction medium.[4,9] It was shown that irradiation of **4** in methanol gives ethers **5** and (in acidic solution) **6**, products that most reasonably arise as shown below from an intermediate zwitterion **7**.[4,9b,10] However experimental proof of the intermediacy of **7** in the rearrangement of **4** to lumiketone **8** has been lacking until now.

If **4** is irradiated in methanol, *tert*-butyl alcohol, 2-propanol, or $CF_3CH_2OH$ in the presence of lithium or tetramethylammonium chloride, a new product **9** is formed at the expense of ethers of type **5**. The product, mp 52–53°, has the formula $C_8H_7Cl_3O$, from its elemental analysis and parent mass spectral peaks at *m/e* 224, 226, and 228. The carbonyl band in the infrared at 1735 cm$^{-1}$ is consistent with an α-chloro-2-cyclopenten-1-one system. The nmr spectrum of **9** is very similar to that of ethers **5**[4,9b] with a methyl singlet at δ 1.86 ppm, two olefinic protons (doublets of doublets) at 6.43 and 7.60, a proton, $H_4$, at 4.47 coupled to $H_2$ and $H_3$, and a proton $H_5$ at 4.14 (d) coupled to $H_4$. Only structure **9** is consistent with these data.





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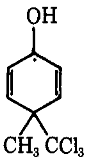

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Compound **9** is not formed from dienone **4** and LiCl in the dark. Irradiation of **4** in solutions containing lithium or tetramethylammonium iodide and bromide gave products other than **9**, according to glpc analysis, presumably the 5-bromo and 5-iodo analogs of **9**. Thus, **9** arises as does **5** from intermolecular nucleophilic attack on zwitterion **4**, and not by an intramolecular rearrangement.

Varying the concentration of LiCl in methanol, it was shown that **9** and **5** (R = Me) are formed competitively from a common intermediate. In *tert*-BuOH and $CF_3CH_2OH$, where lumiketone **8** is a major product of irradiation of **4**, addition of LiCl diminished the yields of lumiketone **8** as well as ethers **5**, with concomitant formation of chloro adduct **9**.[11]

If zwitterion **7** is an intermediate in the formation of **5**, **8**, and **9**, but not in the formation of *p*-cresol,[4,9] the following scheme applies (eq 1–9). The deactivation of **7**

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(1) Photochemistry of Ketones in Solution. XXXIII. Part XXXII: D. I. Schuster and D. Widman, *Tetrahedron Lett.*, 3571 (1971).

(2) H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **83**, 4486 (1961); **84**, 4527 (1962); H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963).

(3) For recent reviews of cyclohexadienone photochemistry, see P. J. Kropp in "Organic Photochemistry," O. L. Chapman, Ed., Vol. 1, Marcel Dekker, New York, N. Y., 1967; K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966); N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, p 162 ff; see also M. H. Fisch, *Chem. Commun.*, 1472 (1969).

(4) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968).

(5) It has been demonstrated that zwitterions 2 (or species closely related to 2) generated thermally by Favorskii reactions isomerize to lumiketones 3.[6] These results support, but do not *require*, the intermediacy of 2 in the photochemical isomerization.

(6) H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **90**, 5612 (1968); T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5614 (1968); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

(7) The present results seem most readily interpretable on the basis of zwitterion rather than cyclopropanone or allene oxide intermediates. The structural relationships of such species will be discussed in the full report.

(8) The formation of zwitterion (step 2, below) represents the radiationless intersystem crossing step on the route from triplet excited state to ground-state product.

(9) (a) D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **87**, 2515 (1965); **88**, 1825 (1966); (b) D. J. Patel and D. I. Schuster, *ibid.*, **89**, 184 (1967); **90**, 5137 (1968).

(10) D. I. Schuster and V. Y. Abraitys, *Chem. Commun.*, 419 (1969).

(11) Analysis was by glpc on 5% VO-225 on Chromosorb G at 150–170°, with acenaphthene as internal standard added after irradiation on a merry-go-round apparatus, with a 450-W Hanovia high-pressure lamp, Corning 0–52 filters, room temperature.

$$\mathbf{4} \xrightarrow{h\nu} {}^1\mathbf{4}^* \xrightarrow{k_{st}} {}^3\mathbf{4}^* \quad (1)$$

$$^3\mathbf{4}^* \xrightarrow{k_r} \mathbf{7} \quad (2)$$

$$^3\mathbf{4}^* + \mathrm{R'H} \xrightarrow{k_a} \mathbf{10} + \mathrm{R'}\cdot \quad (3)$$

$$\mathbf{10} \longrightarrow p\text{-cresol} + \cdot\mathrm{CCl_3} \quad (4)$$

$$^3\mathbf{4}^* + \mathrm{Q} \xrightarrow{k_q} \mathbf{4} + {}^3\mathrm{Q}^* \quad (5)$$

$$\mathbf{7} \xrightarrow{k_1} \mathbf{8} \quad (6)$$

$$\mathbf{7} \xrightarrow{k_2} \mathbf{4} \quad (7)$$

$$\mathbf{7} + \mathrm{ROH} \xrightarrow{k_3} \mathbf{5} + \mathrm{Cl^-} + \mathrm{H^+} \quad (8)$$

$$\mathbf{7} + \mathrm{Cl^-} \xrightarrow{k_4} \mathbf{9} + \mathrm{Cl^-} \quad (9)$$

to ground-state dienone, although a symmetry-forbidden reaction, is included because of some evidence that this may be the pathway for the residual inefficiency (usually 15–25%) observed in these rearrangements.[12,13] From this scheme, the lifetime of zwitterion **7** in the absence of added chloride is

$$1/\tau_z = k_1 + k_2 + k_3[\mathrm{ROH}] \quad (10)$$

and the following relationships for product yields as a function of chloride concentration can be derived, where $\Phi_z$ (the yield of zwitterion **7**) = $k_r\tau_T$.

$$(\Phi_0/\Phi)_5 = (\Phi_0/\Phi)_8 = 1 + k_4\tau_z[\mathrm{Cl^-}] \quad (11)$$

$$\frac{\Phi_9}{\Phi_z - \Phi_9} = k_4\tau_z[\mathrm{Cl^-}] \quad (12)$$

The quantitative data for competitive formation of **8** and **9** in $CF_3CH_2OH$ as a function of LiCl concentration, plotted according to the expressions on the left side of eq 11 and 12, respectively, give excellent straight lines of common slope, 7.8 ± 0.4 $M^{-1}$, as required by the kinetic scheme. The slope $k_4\tau_z$ cannot be broken down to give values of $k_1$, $k_2$, and $k_3$ because of the current lack of information about the magnitude of $k_4$. Similarly, the data for formation of ethers **5** (R = isopropyl) and **9** in 2-propanol as a function of [LiCl], plotted as above, also give straight lines of common slope = 2.03 ± 0.15 $M^{-1}$. In this solvent *p*-cresol is a major product, and addition of LiCl up to 1 *M* reduced its yield by at most 10%,[14] much less than the effect on the yield of **5**. This is consistent with the scheme and the earlier postulate[4,9] that *p*-cresol is derived directly from the dienone triplet by a hydrogen abstraction–radical fragmentation pathway,[9a] and that the zwitterion is a later intermediate along the reaction pathway. Quenching experiments show that all photoproducts of **4** are derived from a common triplet excited state intermediate.[15]

Addition of LiCl was found to have no effect on the efficiency of formation of lumiketone from 4,4-diphenylcyclohexadienone[1] (**11**) and α-santonin (**12**),[16] suggesting that the zwitterions from these two dienones have much shorter lifetimes $\tau_z$ than for **7**. This is reasonable if $\tau_z$ in nonnucleophilic solvents is determined mainly by the rate constant $k_1$ for [1,4] sigmatropic rearrangement to lumiketone. In the intermediate stage of this rearrangement, positive charge should be localized to some extent on $C_6$. Thus, the rearrangement rate should be decreased in the case of **7** → **8** because of the electron-withdrawing $CCl_3$ group, in contrast to the stabilization offered by phenyl and alkyl substituents, increasing $k_1$ in the cases of **11** and **12**.

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[12] K. Liu, unpublished results from these laboratories.

[13] H. E. Zimmerman and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 2753 (1970); D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

[14] This is probably due to a salt effect on reaction 2, increasing $\Phi_z$.

[15] S. Denver and K. Liu, unpublished results.

[16] D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968); M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **85**, 3029 (1963), and earlier references cited in these papers.

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# *Book Reviews**

**The Interpretation of Vibrational Spectra.** By D. Steele (University of London). Barnes and Noble, Inc., New York, N. Y. 1971. 67 pp. $4.00.

This softbound volume is a workbook for teaching interpretation of infrared spectra of organic molecules. There is an 11-page introduction to vibrational spectroscopy, and the rest of the book consists of the spectra of 26 compounds, each of which is analyzed on the following page for the structural information that can be deduced from it. An unusual feature of the book is a "Flow Chart," reproduced on an inside fold-out of the front and back covers. It is a systematized key to infrared spectra, wherein to look up a given band frequency and find out, firstly, the possible origins of it, and, secondly, other bands to look for that will confirm, extend, or modify the interpretation. It is all very handy, but the book is such a wee thing!

**Crystal Structures. Second Edition Volume 6 Part 2** By R. W. G. Wyckoff (University of Arizona). Wiley-Interscience, New York, N. Y. 1971. viii + 615 pp. $37.50.

This latest volume in this standard work attests to the steadily mounting rate at which crystal structures of organic compounds are being determined. In order to keep the large amount of mate-

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* Unsigned book reviews are by the Book Reviews Editor.