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Photoinduced Reactions. XLI.[1] Stereochemical Course in the Photochemistry of a 2,5-Cyclohexadienone

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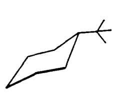
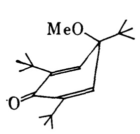
Mechanism for the photochemical transformation of a 2,5-cyclohexadienone into a bicyclo[3.1.0]hex-3-en-2-one (so-called lumiketone) was discussed. Photolysis of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (VII) gave only one stereoisomer (VIIIa) of the corresponding lumiketones. This fact and the prediction by the Woodward-Hoffmann rule indicate that a biradical-like excited state XI with 3,5-bonding gives rise to a direct rearrangement to lumiketone VIIIa as shown in Path B (Scheme II).

The transformation of 2,5-cyclohexadienone into bicyclo[3.1.0]hex-3-en-2-one, the so-called lumiketone, is a most intriguing photochemical reaction. It was originally postulated[2] that the course of this transformation involves the sequence of events shown in Scheme I (Path A), namely, rebonding of the triplet excited state II to give the bridged excited state III, followed by electron demotion to the ground-state zwitterion IV which finally undergoes rearrangement to the product V. That the immediate precursor to the lumiketone is the zwitterion is generally accepted in recent discussions.[3] However, Schuster and Patel[4] suggested that an alternative pathway, by which rearrangement and electron demotion occur simultaneously without involvement of the zwitterion intermediate (Path B in Scheme I), is favorable in the photochemical transformation of 4-trichloromethyl-4-methyl-2,5-cyclohexadienone (VI) into the corresponding lumiketone (XVII). The latter possibility (Path B) was also supported by Swenton *et al.*[5] We now wish to discuss these possibilities from the stereochemical viewpoint of this photochemical reaction.

In a previous paper,[6] we reported that photolysis of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (VII) underwent the same transformation as mentioned above to yield a lumiketone (VIII), which on further irradiation gave photoketone(IX) and photophenol(X). For the transformation of VII into VIII, two routes, Path A and Path B shown in Scheme II, are also possible. It can be expected that intermediates of steric formulas, XIa for a biradical-like species and XIIa for a zwitterion species, are preferred to the isomeric forms, XIb and XIIb, respectively. It is well known that the preferred conformation of *t*-butylcyclohexane is i. The methoxyl of VII showed its NMR signal at τ 6.88. This value is relatively large compared with that of dimethyl ether (τ 6.76), and may indicate that this methoxyl is located on a shielding area of π-clouds. Therefore, it is reasonable that the preferred conformation of VII is depicted as ii, and that XIa is more easily formed from VII than XIb is formed.



i



ii

Zimmerman and Crumrine,[7] and Brennan and Hill[8] have shown that the isomerization of the zwitterions, which were produced by treatment of XIIIa and XIIIb with potassium *t*-butoxide and of XIIIc with zinc, to the corresponding lumiketones follows the "slither" mechanism, involving two 1,2-shifts with C-6 migrating from C-5 to C-4 and then from C-1 to C-5 (Scheme III). There-

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[1] Photoinduced Reactions. XL. I. Saito, S. Kato and T. Matsuura, *Tetrahedron Letters*, 239 (1970).

[2] H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, **84**, 4527 (1962).

[3] a) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y. (1965). b) K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966). c) P. J. Kropp in "Organic Photochemistry," O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y. (1967), p. 1ff. d) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); O. L. Chapman, *ibid.*, **1**, 323 (1963).

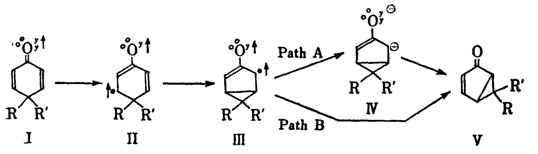
[4] D. I. Schuster and D. J. Patel, *J. Amer. Chem. Soc.*, **90**, 5145 (1968).

[5] J. S. Swenton, E. Saurborn, R. Srinivasan and F. I. Sonntag, *ibid.*, **90**, 2990 (1968).

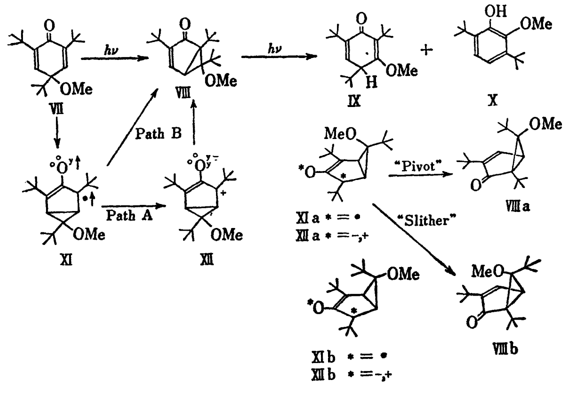
[6] T. Matsuura and K. Ogura, *ibid.*, **89**, 3846 (1967).

[7] H. E. Zimmerman and D. S. Crumrine, *ibid.*, **90**, 5612 (1968); *ibid.*, **91**, 434 (1969).

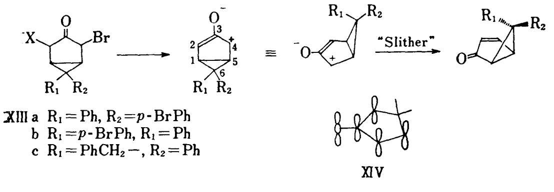
[8] T. M. Brennan and R. K. Hill, *ibid.*, **90**, 5615 (1968).



Scheme I



Scheme II



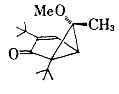
Scheme III

ψ_3 of XIV and p-orbital

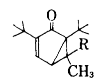
ψ_4 of XIV and sp^3-orbital

Scheme IV

fore, if the zwitterion XI is involved in the photochemical reaction of VII, VIIIb should be the preferred structure for the lumiketone. The conjugated system, over which 1,4-sigmatropic migration occurs, may be considered as a 2-oxobutadiene skeleton. Calculation of the symmetry properties of the Hückel molecular orbitals of XIV shows that the highest occupied molecular orbital (ψ_2 of butadiene or ψ_3 of 2-oxobutadiene) is antisymmetric irrespective of the effect of the oxygen. Thus it is supported that the transformation of IV to V follows the slither mechanism.[7,8] However, the lowest vacant molecular orbital (ψ_3 of butadiene or ψ_4 of 2-oxobutadiene) is symmetric, and consequently a concerted suprafacial rearrangement in an excited state requires inversion of configuration of the migrating group (the "pivot" mechanism, the orbital at C-6 detaching itself from C-1, then bonding to C-4 as shown in Scheme IV).[9] If the photochemical isomerization of VII to VIII follows Path B (Scheme II), the lumiketone with structure VIIIa should be formed predominantly.

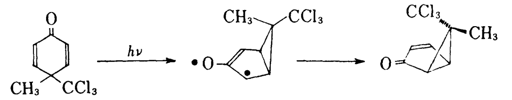


XV



R=Allyl or n-Pr

XVI



VI XVII

Photolysis of VII in petroleum ether with a visible light gave only an isomer of VIII. Furthermore, careful chromatographic analyses of the reaction mixture at various stages of irradiation showed that only one isomer of VIII was formed in addition to recovered VII. The configuration of this lumiketone was deduced by comparing its NMR spectrum with that of 1,3-di-t-butyl-6-methyl-6-methoxybicyclo[3.1.0]hex-3-en-2-one (XV), which was formed on photolysis of 2,6-di-t-butyl-4-methyl-4-methoxy-2,5-cyclohexadienone.[10),*1] The resonance of the methoxyl of VIII appeared at τ 6.73, similar to that of dimethyl ether (τ 6.76), while the methoxyl singlet of XV was observed at an unusually high field (τ 6.97). The high-field shift should result from diamagnetic shielding by the enone system of XV. The analogous unusual shifts were also observed in a methoxyl of α-lumicolchicine[11] and C-6 methyl of 1,3-di-t-butyl-6-allyl (or n-propyl)-6-methylbicyclo[3.1.0]-hex-3-en-2-one (XVI),[12] and it was suggested that the shifts were ascribed to the location of these groups over the π-electron clouds. In the NMR spectra of VII and XV measured in benzene, the methoxyl signal of VIII appeared at a field (τ 6.70) similar to that in $CDCl_3$, while the methoxyl of XV was shifted to a higher field (τ 7.17). This might indicate that the methoxyl group of XV is located over the cyclopentenone ring but not that of VIII.[13]

Both of the t-butyl groups of XV at C-1 and C-3 positions were shifted to lower fields by using benzene as a solvent instead of $CDCl_3$. Although two t-butyl signals of VIII appeared at lower fields

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[9] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.* **87**, 2511 (1965).

[10] T. Matsuura, This Bulletin, **37**, 564 (1964).

[*1] VPC and TLC analyses showed that only one isomer of XV was not necessarily formed.

[11] O. L. Chapman and H. G. Smith, *J. Amer. Chem. Soc.*, **83**, 3915 (1967).

[12] B. Miller and H. Margulies, *ibid.*, **89**, 1678 (1967).

[13] a) J. Ronayne and D. H. Williams, *Chem. Commun.*, **1966**, 712. b) C. J. Timmons, *ibid.*, **1965**, 576.

in benzene than in $CDCl_3$, other *t*-butyl signal shifted to a higher field. This suggests that the *t*-butyl of VIII at C-6 position may have an endo-configuration. The aliphatic methyl signal of XV appears at τ 8.45, characteristic of an exo-geometry.*2.

Accordingly, formulas VIIIa and XV were given as the stereochemical structures of the "lumi" compounds VIII and XV, respectively. It seems reasonable from the stereochemical structure of VIIIa and the above prediction by the Woodward-Hoffmann rule that Path B (Scheme II) is favorable in the photochemical reaction of VII. It should be also noted that the same stereochemistry is held in the photochemical transformation of VI into its lumiketone XVII.*3 Of course, our conclusion does not necessarily deny the zwitterion intermediate (Path A) in the photochemical transformation of 2,5-cyclohexadienones. It can be expected that the formation of lumiketones predominantly follows Path A (the "slither" mechanism), if electron demotion occurs faster than direct isomerization of III to V (Path B) or if Path B (the "pivot" mechanism) is stereochemically excluded (for example, the photochemical formation of lumisantonine from santonin[2]).

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*2 Miller and Margulies[12] reported that an exo-methyl at C-6 position of XVI shows its NMR signal at a lowet field (τ 8.60 or 8.65) than an endo-methyl (τ 9.05 or 9.08).

*3 Schuster and Patel[14] reported that this transformation is stereospecific and formula XVII is assigned as the stereochemical structure of this lumiketone. This stereochemical assignment is supported by the fact that the methyl of XVII shows its NMR signal at a field analogous to that of XV.

14) D. J. Patel and D. I. Schuster, *J. Amer. Chem. Soc.*, **90**, 5137 (1968).