normal enthalpy (eq 13). The corresponding expression for Γ_1 in this case is

$$\Gamma_1 = -RT\left(\frac{\partial y_1}{\partial A_1}\right)_{T,P,y_2} = \left\{\frac{1/\tau_2 - 1/\tau_1}{a_{21}{}^2}\right\}\times$$

$$\left\{\left[\frac{1}{(\mathrm{AU})(1/\tau_2 + a_{11})} + \frac{1}{(\mathrm{A})(1/\tau_2 + a_{11})} + \frac{(1/\tau_2 + a_{11} + a_{21})(2/\tau_2 + 2a_{11} + a_{21})}{(\mathrm{U})a_{21}{}^2(1/\tau_2 + a_{11})} + \frac{(1/\tau_2 + a_{11}}{(\mathrm{U_2})a_{21}{}^2}\right]^{-1} - \left[\frac{1}{(\mathrm{AU})(1/\tau_1 + a_{11})} + \frac{1}{(\mathrm{A})(1/\tau_1 + a_{11})} + \frac{(1/\tau_2 + a_{11} + a_{21})(2/\tau_2 + 2a_{11} + a_{21})}{(\mathrm{U})a_{21}{}^2(1/\tau_1 + a_{11})} + \frac{(1/\tau_2 + a_{11})^2}{(\mathrm{U_2})a_{21}{}^2(1/\tau_1 + a_{11})}\right]^{-1}\right\} \quad \text{(A-7)}$$

where A_1 is the normal chemical affinity associated with y_1.

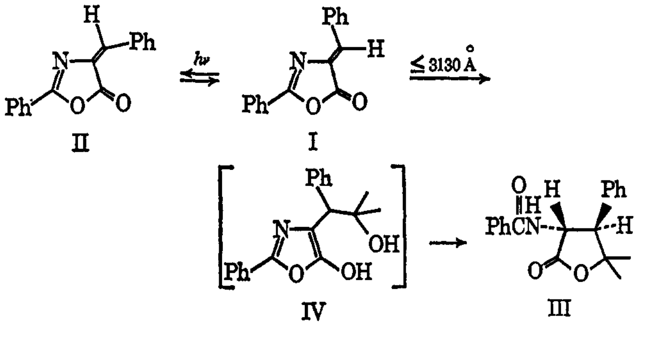
Communications to the Editor

Wavelength-Dependent Photochemical Reactions of Lactones

Sir:

During a study of potential photochemical ring atom transposition reactions in heterocycles, the photochemical behavior of 3-benzal-5-phenylazlactone (I) was found to display a marked wavelength dependence. As there are relatively few authentic examples of wavelength-dependent reactions in solution involving excitation of only one species,[1] the photochemistry of this compound and simpler related esters has been examined.

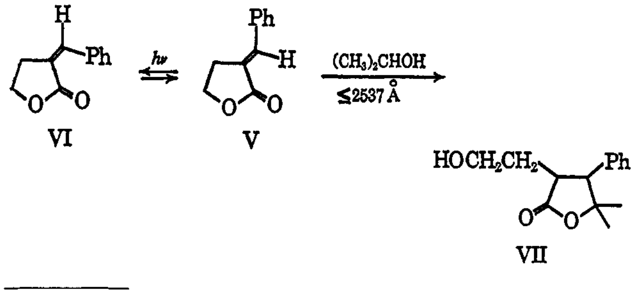
Irradiation of I [$\lambda_{\max}^{i\text{-PrOH}}$ 259 (ϵ 26,500), 346 (32,000), 361 (42,000), and 381 mμ (30,000)] in degassed isopropyl alcohol with 3650-Å light led to diminution of the long-wavelength maximum with the appearance of isosbestic points at λ 345, 355, 364, and 377 mμ. After the rapid initial spectral changes no further changes were observed on prolonged irradiation. The only components of the reaction mixture were I and a previously known geometrical isomer II.[2] Irradiation of II with 3650-Å light gave the same photostationary mixture.



Irradiation of the azlactone I in isopropyl alcohol with 2537-Å light led to spectroscopic changes characteristic of the above geometric isomerization plus a gradual disappearance of absorption throughout the ultraviolet region. A similar result was observed with 3130-Å light although the rate of azlactone disappearance was reduced relative to the isomerization reaction. The major product, isolated in 17% yield, was the adduct III: ν_{NH} 3430, ν_{COO} 1757, and ν_{CON} 1667 cm^{-1}; nmr (CDCl$_3$) τ 8.48 and 8.92 (2CH$_3$), 6.2 (PhCH, d, J = 13 Hz), 4.5 (O=CCH, 2d, J = 13 Hz, J' = 8 Hz), and 1.06 (NH, d, J' = 8 Hz); m/e 309 (M), 265 (M − CO$_2$), and 223 (M − CO − (CH$_3$)$_2$CO).

A plausible pathway for the formation of III is through hydrogen abstraction from solvent by the excited azlactone I (or II) followed by combination of the resulting radical pair to give IV which subsequently lactonizes. This interpretation is supported by the finding that the rate of disappearance of the azlactones using 2537-Å light was related to the availability of solvent hydrogen, *i.e.*, isopropyl alcohol > ether > cyclohexane ≫ acetonitrile. Moreover, the reaction was inhibited by trace amounts of oxygen and yielded numerous side products and polymeric products characteristic of a free-radical mechanism.

The photochemistry of α-benzal-γ-butyrolactone (V) [$\lambda_{\max}^{i\text{-PrOH}}$ 218 (ϵ 12,400), 224 (10,700), and 281 mμ (24,000)] was analogous to that of the azlactone I. On irradiation of V in isopropyl alcohol with 3130-Å light, only geometrical isomerization was observed (isosbestic points at 226, 244, and 300 mμ). Thermal (160°) re-formation of V from the isomer VI and deshielding of the olefinic hydrogen of V (τ 2.45) relative to VI (τ 3.01)[3] confirm the assigned stereochemistry.



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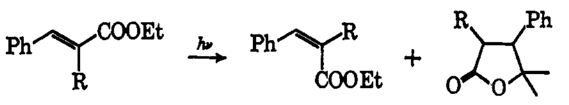
[1] Reports of reactions yielding qualitatively different products with different wavelengths include: (a) N. C. Yang, N. Nussim, M. J. Jorgenson, and S. Murov, *Tetrahedron Letters*, 3657 (1964); (b) R. C. Helgeson and D. J. Cram, *J. Am. Chem. Soc.*, **88**, 509 (1966); (c) E. F. Ullman and B. Singh, *ibid.*, **88**, 1844 (1966); **89**, 6911 (1967); (d) J. Streith and J. Cassal, *Comp. Rend. Ser. C*, **264**, 1307 (1967).

[2] Speculative stereochemical assignments for I and II based on melting point comparisons (R. E. Buckles, R. Filler, and L. Hilfram, *J. Org. Chem.*, **17**, 233 (1952)) are contrary to the present tentative assignments based on near-quantitative thermal conversion (150°) of II to I.

[3] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p 124.

On irradiation of V with 2537-Å light, diminution of all the ultraviolet bands again occurred, and a hydrogen abstraction process again appeared to be involved. In addition to polymer and pinacol, a mixture of four lactones was isolated in about 30% yield. One of these, VII, crystallized after chromatography and distillation: $\nu_{C=O}$ 1760 cm^{-1}; nmr τ 6.30 (CH_2O, quartet sharpened by D_2O), 6.71 (2CH, m), 7.49 (OH), 8.16 (CH_2, m), and 8.50 and 8.91 ($2CH_3$); *m/e* 234 (M), 176 (M − $(CH_3)_2CO$), and 148 (M − CO − $(CH_3)_2CO$). The remaining products appeared to be closely related structural and geometrical isomers.

Like the above esters, ethyl *trans*-cinnamate (VIII) and ethyl *trans*-α-methylcinnamate (IX) on irradiation in isopropyl alcohol with 2537-Å light yielded their geometrical isomers together with a multiplicity of products, including low yields (3 and 8%) of the respective lactones X [$\nu_{C=O}$ 1755 cm^{-1}; τ 2.73 (5ArH), 6.48 (1CH, t, J = 9 Hz), 7.10 (CH_2, d, J = 9 Hz), 8.49 (CH_3), and 9.00 (CH_3); *m/e* 190 (M), 162 (M − CO), 104 (M − CO − $(CH_3)_2CO$)] and XI [stereoisomeric mixture, $\nu_{C=O}$ 1750 cm^{-1}; *m/e* 204 (M), 176 (M − CO), and 118 (M − CO − $(CH_3)_2CO$)]. However, VIII and IX failed to show wavelength dependence, and both the isomerization and hydrogen abstraction reactions were induced with the longest wavelengths of light (3103 Å) that could be absorbed.



VIII, R = H
IX, R = CH_3

X, R = H
XI, R = CH_3

Although products derived from hydrogen abstraction by several photochemically excited α,β-unsaturated esters have been reported, wavelength dependence of these reactions remains largely unstudied.[4,5] The present examples of hydrogen abstraction by the unsaturated lactones with only short wavelengths suggest that a reactive upper excited state is populated which has sufficient lifetime to undergo a bimolecular reaction. Based on analogy with the photochemistry of ketones, this behaves like an n,π^* state. On the other hand the wavelength-insensitive geometrical isomerization reactions probably proceed through π,π^* states since both reactive states of I and V probably have triplet character, and their reactivity difference most likely rests, therefore, in factors other than multiplicity.[6]

A particularly interesting aspect of the present data is the failure of the reactions of the acyclic esters to display similar wavelength dependence. Although the acyclic esters may exist predominately in their *s-trans* conformations as opposed to the enforced *s-cis* conformations of the lactones, it seems unlikely that differences between the very closely related *s-cis* and *s-trans* chromophores could alone be responsible for the observed behavior. On the other hand, molecular orbital calculations imply that a significant lowering of n,π^* relative to π,π^* levels results from a 90° twisting about the carbonyl-to-oxygen single bond of the acyclic esters. Provided the n,π^* triplets of these compounds are of higher energy than the π,π^* triplets (as implied in the above discussion), internal conversion of an initially formed planar n,π^* triplet of an acyclic ester will be facilitated by the mixing of states resulting from rotation about the carbonyl-to-oxygen single bond. Reactions characteristic of both excited states might therefore be expected with all wavelengths of light, as is, in fact, observed.

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[4] (a) M. J. Jorgenson, *Chem. Commun.*, 137 (1965); (b) M. Pereyre, G. Colin, and J. Valade, *Tetrahedron Letters*, 4805 (1967).

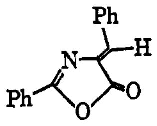
[5] A report that diethyl maleate reacts with dioxane only with <300-mμ light is of uncertain significance since wavelength dependence was not found with tetrahydrofuran: I. Rosenthal and D. Elad, *Tetrahedron*, 23, 3193 (1967).

[6] Although proof of a triplet intermediate for the direct light-induced isomerization is lacking, sensitization studies show that the reaction can proceed through a triplet state. Since hydrogen abstraction resulting from direct or sensitized irradiation occurs through a triplet state which differs from that leading to isomerization, these excited-state symmetry assignments appear to be reasonable at least in the sensitized reactions: E. F. Ullman and N. Baumann, *J. Am. Chem. Soc.*, 90, 4158 (1968).

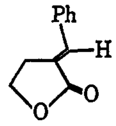
Photosensitization of Wavelength-Dependent Lactones. Influence of Orbital Symmetries on Triplet Energy Transfer

Sir:

The preceding communication[1] describes two lactones, I and II, that were shown to undergo wavelength-dependent photochemical reactions. Although both compounds were found to undergo geometrical isomerization with all absorbed wavelengths, hydrogen abstraction from solvent was found to proceed only at relatively short wavelengths. We report here evidence concerning the multiplicity of the reactive excited states involved in these reactions which may provide some insight into the general problem of energy-transfer mechanisms.



I



II

During the investigation of the above lactones, the photoefficiency of the hydrogen abstraction process was found to be exceptionally sensitive to the lactone concentration. Increasing the concentration of I from 10^{-5} to 10^{-4} *M* in isopropyl alcohol resulted in a sharply reduced rate of lactone disappearance (hydrogen abstraction) while leaving the geometrical isomerization rate nearly unaffected. The lactone II displayed similar behavior, and quantitative measurements yielded a linear Stern–Volmer relationship if the lactone was assumed to act as a self-quencher.[2] A quantum efficiency for hydrogen abstraction at infinite dilution of 0.4–1.0 and a lifetime of the reactive species of τ = $(4 \pm 2) \times 10^{-4}$ sec (assuming $k_{dif} = 2.7 \times 10^9$ sec^{-1}) were estimated. This long lifetime is clearly consistent with a triplet rather than a singlet excited state. If the excited state is in fact a triplet, the existence of the self-quenching process then raises the question of how

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[1] N. Baumann, M. Sung, and E. F. Ullman, *J. Am. Chem. Soc.*, 90, 4157 (1968).

[2] Probable traces of a radical scavenger (oxygen?) interfered with quantitative studies of the direct photolyses of I.