References and Notes

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(3) Unpublished work of H. T. Hall, R. A. Volkmann, and W. S. Johnson. See the Ph.D. dissertation of H. T. Hall, Stanford University, 1973.

(4) A number of variants can be envisaged, including the "forbidden" concerted intramolecular cycloaddition of the acetylene residue to the cyclopentenyl cation to produce **3** or **4**.

(5) Cf. W. S. Johnson, M. B. Gravestock, R. J. Parry, and D. A. Okorie, *J. Am. Chem. Soc.*, **94**, 8604 (1972).

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(13) The NMR and ir spectra were entirely consistent with the assigned structure, and satisfactory C, H analyses were obtained.

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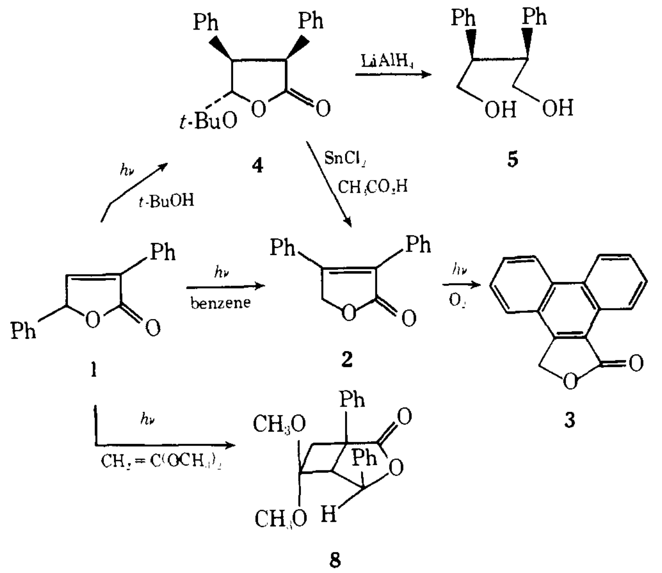
Photochemical Rearrangement in the 2(5*H*)-Furanone System[1]

Sir:

Light-induced transformations of five-membered enol lactones have been the subject of recent intensive study.[2-6] These compounds undergo a facile decarbonylation when subjected to ultraviolet excitation and produce α,β-unsaturated ketones as primary photoproducts. Chapman and McIntosh have previously noted that a critical requirement for clean photochemical cleavage of the acyl-oxygen bond is the presence of a double bond adjacent to the ether oxygen.[3] Stabilization of the incipient oxy radical was considered to be a determining factor in the photocleavage of this bond. In sharp contrast to the extensive studies concerned with the photochemistry of enol lactones, only scattered reports have appeared concerning the photochemical behavior of the related α,β-unsaturated-γ-lactone system.[7-9] We now wish to report a novel rearrangement which occurs on irradiation of an α,β-unsaturated-γ-lactone and to describe some of the salient features of this reaction.

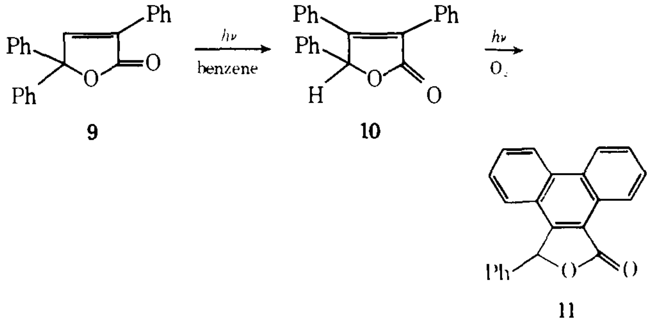
Irradiation of 3,5-diphenyl-2(5*H*)-furanone[10] (**1**) in benzene under an argon atmosphere with Corex-filtered light for 1.5 hr gave 3,4-diphenyl-2(5*H*)-furanone[11] (**2**) in quantitative yield. If molecular oxygen is present, **2** reacts further by the well-known stilbene-phenanthrene cyclization route to produce phenanthro[9,10-*c*]furanone (**3**), mp 253-254°.[12] Studies on the photochemical behavior of **1** were also carried out using *tert*-butyl alcohol as the solvent (Scheme I). In this case, the only product isolated (87%) was *cis*-3,4-diphenyl-*trans*-5-*tert*-butoxy-γ-lactone (**4**), mp 113-114°. Elemental analysis, the infrared spectrum ($CHCl_3$, 1776 cm^{-1}), the mass spectrum (*m/e*, 286 ($M^+ - CO_2$)), and the NMR spectrum (100 MHz, δ 1.30 (s, 9 H), 3.68 (dd, 1 H, J = 9.0 and 2.0 Hz), 4.48 (d, 1 H, J = 9.0 Hz), 5.85 (d, 1 H, J = 2.0 Hz), 6.70-7.10 (m, 10 H)) suggest **4** as the structure of the photoadduct.[13] An alternative structure in which *tert*-butyl alcohol had added across the C-C double bond in a Michael fashion was ruled out on the basis of chemical degradation studies. Treatment of **4** with stannous chloride in refluxing acetic acid gave **2**, while reduction of **4** with lithium aluminum hydride gave the known *meso*-2,3-diphenyl-1,4-butanediol (**5**).[14] Further evidence which supports the stereochemical assignment was obtained by the observation that **4** was cleanly epimerized to *trans*-3,4-diphenyl-*trans*-5-*tert*-butoxy-γ-lactone (**6**), mp 86-87°, on treatment with lithium diisopropylamide in tetrahydrofuran. Subsequent reduction of **6** with lithium aluminum hydride produced *d,l*-2,3-diphenyl-1,4-butanediol (**7**) which was identical with an authentic sample prepared by the lithium aluminum hydride reduction of *trans*-2,3-diphenylsuccinic anhydride.

Scheme I



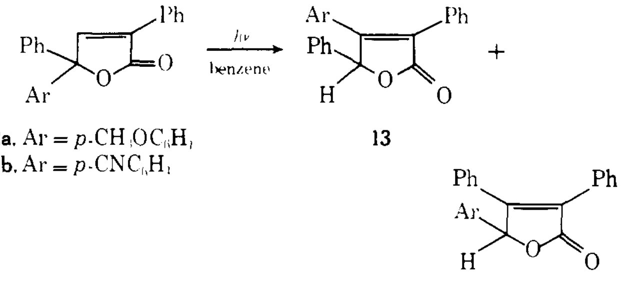
The photochemical reaction of **1** with an excess of 1,1-dimethoxyethylene in benzene was also studied. Irradiation of the mixture for 1 hr gave a single photoadduct (**8**), mp 181-182°, in nearly quantitative yield whose structure was assigned on the basis of the following spectral properties: ir (KBr) 1760 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 2.30 (dd, 1 H, J = 12.0 and 1.5 Hz), 2.50 (d, 1 H, J = 12.0 Hz), 2.78 (s, 3 H), 3.30 (s, 3 H), 4.20 (s, 1 H), 4.80 benzylic proton (d, 1 H, J = 1.5 Hz long range W-coupling), and 7.0-7.8 (m 10 H). Under these conditions the photochemical rearrangement of **1** $\rightarrow$ **2** was completely suppressed.

Similar irradiation of 3,5,5-triphenyl-2(5*H*)-furanone (**9**) gave 3,4,5-triphenyl-2(5*H*)-furanone[12] (**10**) as the initial photoproduct (78%); longer irradiation led to the formation of phenylphenanthro[9,10-*c*]furanone[12] (**11**) in high



yield. The photochemical rearrangement of **9** in benzene was remarkably efficient, with a quantum yield $\Phi = 0.47$. Photosensitization of **9** in benzene with acetophenone or *m*-methoxyacetophenone gave $\Phi = 0.47$. The equivalence of direct and sensitized quantum yields provides strong evidence for a triplet excited state. That the rearrangement is quenched by piperylene furnishes additional confirmation for the triplet state assignment.

In order to gain insight into the nature of the rearranging excited state, the photolysis of the 5-(4′-anisyl)- (**12a**) and 5-(4′-cyanophenyl)-3,5-diphenyl-2(5*H*)-furanone (**12b**) systems[15,16] were investigated with the view that migratory aptitudes could be used as a probe for excited-state electronic make up and reactivity.[17] The initial study explored the competition in migratory aptitudes of *p*-anisyl vs. phenyl, and of *p*-cyanophenyl vs. phenyl. When benzene was used as the solvent, it was observed that *p*-anisyl migrated in strong preference to phenyl (ratio **13**/**14** = 16/1) in the first case and that *p*-cyanophenyl migrated in preference to phenyl (ratio **13**/**14** = 3.5/1) in the second case. The photoproducts were identified by comparison with authentic samples prepared by independent syntheses.[15,16] The rearrangements were efficiently sensitized by propiophenone and were quenched by piperylene thereby indicating the involvement of a triplet state in the direct irradiations.



12a, Ar = p-$CH_3OC_6H_4$
b, Ar = p-CNC_6H_4

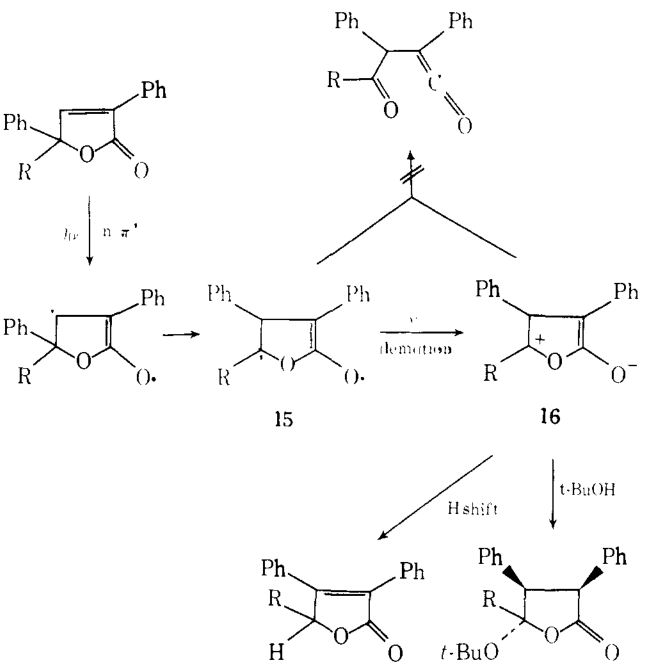
13

14

The preferential migration of *p*-cyanophenyl over phenyl clearly indicates that the β-carbon atom of the 2(5*H*)-furanone system does not exhibit electron-deficient reactivity. Similarly, the fact that *p*-anisyl migrated in preference to phenyl by a factor of 16 indicates that $^{-}CC{=}CO^{+}$ is not a useful representation of the excited state of the 2(5*H*)-furanone system in nonpolar solvents. The present results can best by explained by invoking a low-lying n-π^* triplet as the reactive electronic state involved in these rearrangements. The electronic configuration associated with the n-π^* triplet possesses substantial odd electron character at the β-carbon atom of the unsaturated lactone and nicely accommodates the observed migratory aptitudes.[18,19] It should be pointed out that the migratory aptitudes encountered in this work are closely analogous to those obtained by Zimmerman and coworkers in the diarylcyclohexenone system.[17]

The mechanism involved in these reactions can be pictured as shown in Scheme II. Here excitation is followed by an extremely efficient intersystem crossing to afford the n-π^* triplet state. The bridging step and the subsequent cleavage leading to **15** are simply the first two formal steps of a di-π-methane rearrangement.[20] Electron demotion through the divalent oxygen atom proceeds to give a zwitterion (**16**) which is trapped by the alcoholic solvent. In the absence of a hydroxylic solvent the zwitterion undergoes a hydride shift to give the observed product. A ketene intermediate could not be detected by low temperature infrared studies, thus ruling out a fragmentation of **15** or **16**. Agosta[21] and Zimmerman[22] had previously reported that irradiation of the closely related 4,4-diarylcyclopentenone system proceeds by a mechanism which involves ring opening to a transient ketene. This process and the photochemical ring openings reported for the β,γ-unsaturated lactones[2-6] do not appear to occur in the 2(5*H*)-furanone system. The contrast in behavior with the 4,4-diarylcyclopentenone system probably results from the ability of the oxygen to stabilize the adjacent positive charge in the zwitterion **16**.

Scheme II



We are continuing to examine the mechanistic aspects of the aryl migration process as well as the [2 + 2]cycloaddition reaction and will report additional findings at a later date.

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(18) The assumption is made that the migratory behavior of *p*-anisyl and *p*-

cyanophenyl serves as a useful probe of excited-state electron distribution in the same way as in ground-state systems.
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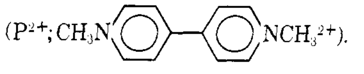
Kinetic Relaxation Measurement of Rapid Electron Transfer Reactions by Flash Photolysis. The Conversion of Light Energy into Chemical Energy Using the $Ru(bpy)_3{}^{3+}$–$Ru(bpy)_3{}^{2+*}$ Couple

Sir:

There is growing evidence that the excited states of certain transition metal complexes can be quenched by electron transfer. Electron transfer quenching is potentially of importance in energy conversion, especially for metal complexes since they often absorb strongly in spectral regions of maximum solar insolation.

Quenching processes involving the excited states of tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3{}^{2+*}$, have been particularly well studied.[1-6] It has been found, for example, that net electron transfer occurs from $Ru(bpy)_3{}^{2+*}$ to such oxidants as $Fe(H_2O)_6{}^{3+}$,[3] Tl(III),[5] $Ru(NH_3)_6{}^{3+}$,[3,4] and paraquat[3]



Flash photolysis and emission quenching studies have shown that $Ru(bpy)_3{}^{2+*}$ can be quenched at, or near, the diffusion-controlled limit (eq 2), and that the quenching step is followed by a rapid thermal electron transfer reaction (eq 3).[3]

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} Ru(bpy)_3{}^{2+*} \qquad (1)$$

$$Ru(bpy)_3{}^{2+*} + P^{2+} \longrightarrow Ru(bpy)_3{}^{3+} + P^{+} \qquad (2)$$

$(k = 2.4 \times 10^9\ M^{-1}\ \text{sec}^{-1})$[3]

$$Ru(bpy)_3{}^{3+} + P^{+} \longrightarrow Ru(bpy)_3{}^{2+} + P^{2+} \qquad (3)$$

$(k = 8.3 \times 10^9\ M^{-1}\ \text{sec}^{-1})$[3]

By combining eq 1, 2, and 3 under conditions where (3) becomes rate determining, the flash photolysis experiment can be used as a relaxation technique for measuring the rates of very rapid electron transfer reactions.[3]

A more general relaxation scheme can be devised if two *different* redox couples can be made to participate in reactions like 2 and 3. The thermodynamic limitations on such a scheme can be estimated from available reduction potential data (Table I). Estimates for the excited state couple, $Ru(bpy)_3{}^{3+}$–$Ru(bpy)_3{}^{2+*}$, are available from spectroscopic data[4] and from a recent quenching study using a series of neutral quenchers.[6]

From the data in Table I, it can be predicted that if a solution initially containing $Ru(bpy)_3{}^{2+}$, NPh_3, and P^{2+} is subjected to flash photolysis, the sequence of reactions outlined in Scheme I will occur. If reaction 4 can be made more rapid than reaction 3, the combination of reactions 1, 2, and 4 gives reaction 6 in which a chemical reaction has been driven in the nonspontaneous direction using light energy.

Table I. Reduction Potential Data in Acetonitrile Solution

Couple	E, V[a]
$Ru(bpy)_3{}^{3+} + e \rightarrow Ru(bpy)_3{}^{2+}$	1.29[b]
$NPh_3{}^{+} + e \rightarrow NPh_3$	1.00[c]
$P^{2+} + e \rightarrow P^{+}$	−0.45[d]
$Ru(bpy)_3{}^{3+} + e \rightarrow Ru(bpy)_3{}^{2+*}$	−0.81[6]

[a] At 25 ± 2°; in 0.1 M $Et_4N^+ClO_4^-$, or $(n\text{-}Bu)_4N^+ClO_4^-$, or $(n\text{-}Bu)_4N^+PF_6^-$–acetonitrile solutions. [b] G. M. Brown, Ph.D. Thesis, University of North Carolina, Chapel Hill, N.C., 1974. [c] S. C. Creason, J. Wheeler, and R. F. Nelson, *J. Org. Chem.*, 37, 4440 (1972). [d] A. Ledwith, *Acc. Chem. Res.*, 5, 133 (1972).

Scheme I

$$Ru(bpy)_3{}^{2+} \xrightarrow{h\nu} Ru(bpy)_3{}^{2+*} \qquad (1)$$

$$Ru(bpy)_3{}^{2+*} + P^{2+} \longrightarrow Ru(bpy)_3{}^{3+} + P^{+} \qquad (2)$$

$$Ru(bpy)_3{}^{3+} + NPh_3 \longrightarrow Ru(bpy)_3{}^{2+} + NPh_3{}^{+} \qquad (4)$$

$$NPh_3{}^{+} + P^{+} \longrightarrow NPh_3 + P^{2+} \qquad (5)$$

$$NPh_3 + P^{2+} \xrightarrow{h\nu} NPh_3{}^{+} + P^{+} \qquad (6)$$

In an actual experiment, a 0.1 M $(n\text{-}Bu)_4N^+ClO_4^-$–acetonitrile solution which contained $Ru(bpy)_3{}^{2+}$ ($\sim 2 \times 10^{-5}$ M), P^{2+} (2.0×10^{-3} M), and NPh_3 (2.0×10^{-3} M) was flashed at 410 nm $< \lambda <$ 500 nm. The resulting spectral changes were monitored at a series of wavelengths from 380 to 700 nm. Absorption maxima for P^+ (395 and 603 nm) appeared rapidly, and their disappearance followed second-order, equal-concentration kinetics for two–three half-lives. In a similar experiment using NPh_2H as reductant, direct spectral evidence was obtained for the presence of both P^+ and NPh_2H^+ (λ_{max} 680 nm).[7] After the flash, no spectral changes were observed at 450 nm (λ_{max} for $Ru(bpy)_3{}^{2+}$). The reaction observed with NPh_3 present must be eq 5 and with NPh_2H present, eq 7.

There were no permanent spectral changes in the solutions after a series of flash photolysis experiments.

$$NPh_2H^{+} + P^{+} \longrightarrow NPh_2H + P^{2+} \qquad (7)$$

The combination of flash photolysis and the series of reactions in Scheme I leads to a kinetic relaxation technique for measuring the rates of rapid, thermodynamically highly allowed, reactions. Rate constants for reactions 5 and 7 were 4.5×10^9 M^{-1} sec^{-1} (NPh_3) and 5.3×10^9 M^{-1} sec^{-1} (NPh_2H) at room temperature. The technique is potentially a general one with regard to the excited states and redox couples used, however, the potentials for the redox couples must fall between the ground and excited state potentials for the absorbing species. In practice, the technique is limited by several factors including: (1) efficient energy transfer quenching by either oxidant (P^{2+} in the scheme) or reductant (NPh_3), (2) numerically small rate constants for reactions like 2 and 4 when compared to 5, or much faster rates for reactions like 3 compared to 5, (3) instability of the components in the system, (4) overly competitive light absorption by either quencher or reductant, (5) an inability to observe redox products in the quenching step.[6]

The set of reactions in Scheme I is remarkable in that light energy is used to drive a highly favored redox reaction in the nonspontaneous direction, even though neither reac-