the use of gas phase data to explain electrochemical phenomena must be done prudently, it is often successful,[2b,7] and in this case the pe results demand that the electronic states of the electrochemical intermediates be considered.

The present results nicely compliment those of Gooden and Brauman, although they do reveal complications concerning the nature of the electronic state and structure of the parent ion which is initially formed by electron impact on butyrophenone. The electrochemical results suggest that the observed 3-eV band in the kinetic spectrum of butyrophenone radical cation might arise from a transition originating from the γ radical cation analogous to $n_O\gamma$ of Scheme I.

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(3) The ketones discussed here have no symmetry elements. However, we use the "Π_S" designation to refer to the ionic wave function which would be symmetric to a plane perpendicular to that of the aryl group, i.e., ignoring the absence of this symmetry element for the acyl substituent. The "Π_A" designation refers to the ionic wave function which would be antisymmetric with respect to σ_v with the same exception. The n_O symbol refers to the ion with a vacancy localized on oxygen in what would be the σ plane, ignoring the absence of this element for the alkyl group.

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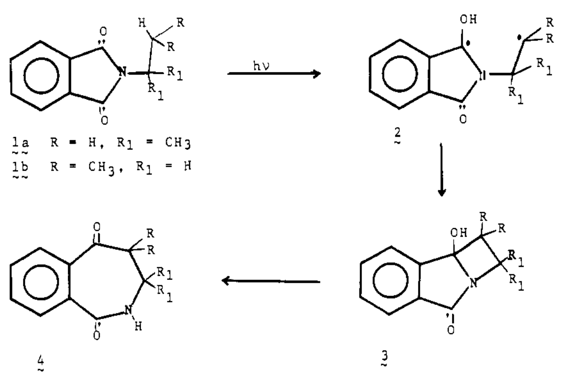
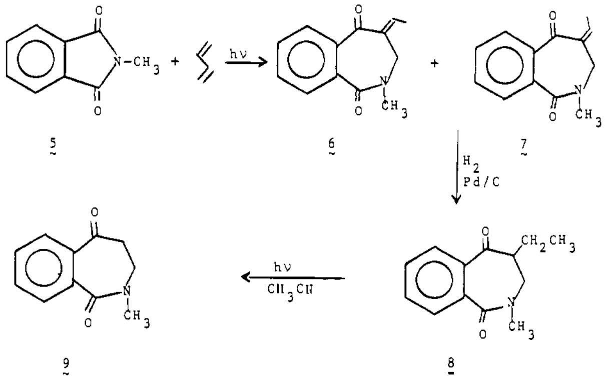
Photochemical Addition of Dienes to N-Alkylphthalimides

Sir:

The photochemical rearrangement of *N*-alkylphthalimides to benzazepinediones **1** → **4** via a type II process has been the subject of numerous recent studies.[1-14] The reaction has been shown to be quite general, occurring with O,[3,4] S,[5,6] N,[7,15] and aromatic moieties[2,10,11] incorporated in the *N*-alkyl substituent. Despite the large amount of work on the scope of these reactions there is little mechanistic information available with the exception of reports[1,5,13,14] that some of the reactions occur via the triplet state since they are quenched by dienes.

When we conducted quenching studies on phthalimides **1a**, our results indicated that normal photochemical quenching was not occurring but that the phthalimides were efficiently reacting with the *cis*-piperylene quencher. We investigated this reaction using *N*-methylphthalimide (**5**) and butadiene in order to avoid unnecessary complications from competition with type II processes (i.e., **1** → **4**) and isomer formation. A 1% solution of **5** (3 g) in 2:1 butadiene-acetonitrile was irradiated for 6.5 h with a Hanovia 450-W medium-pressure lamp through quartz. NMR analysis of the semisolid residue from solvent evaporation indicated that 69% of **5** had been converted to product. Silica gel chromatography afforded a 93% yield of product[16] which was shown to consist of a mixture of *anti*-(**6**) and *syn*-3,4-benzo-6,7-dihydro-6-ethylidene-1-methylazepine-2,5-dione (**7**). The structure of the major product follows from chemical and spectroscopic evidence. The ^{1}H NMR spectrum ($CDCl_3$) of the major product (**6**, mp 109-111 °C), after purification by preparative TLC and recrystallization, showed δ 2.05 (d, 3 H, *J* = 7 Hz), 3.15 (s, 3 H), 4.25 (s, 2 H), 7.1 (q, 1 H, *J* = 7 Hz), 7.40-8.00 (m, 4 H); IR (CCl_4) 1680, 1650 cm^{-1}; *m/e* 215 (10). The ^{1}H NMR of the minor product **7** showed δ 2.3 (d, 3 H, *J* = 7 Hz), 3.20 (s, 3 H), 4.05 (s, 2 H), 6.5 (q, 1 H, *J* = 7 Hz), 7.4-8.0 (m, 4 H).

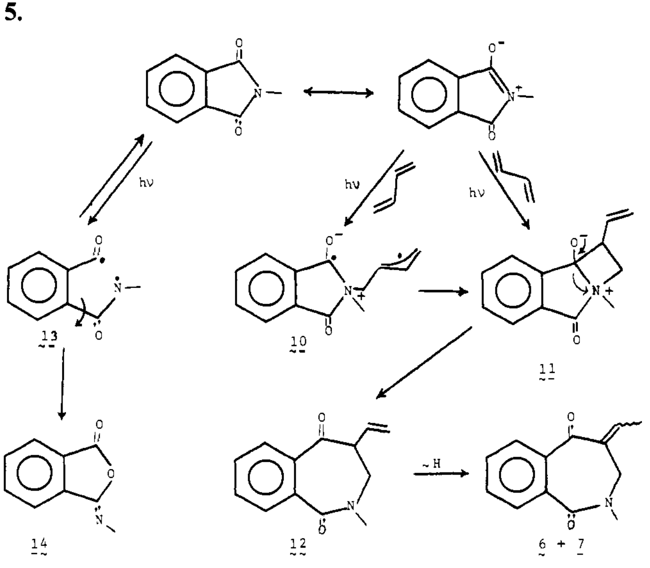




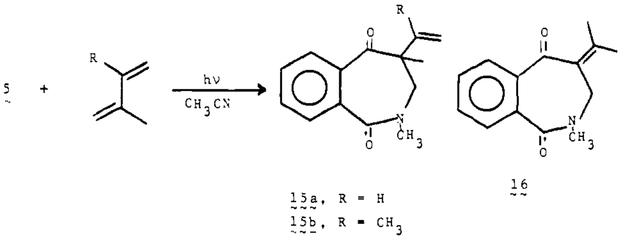
The anti orientation of the vinyl methyl group in **6** follows from its chemical shift (δ 2.05) when compared with that of the vinyl methyl group in the syn isomer (δ 2.30) which is shifted downfield by the *cis*-carbonyl group. A complementary shift is seen with the vinyl proton in **6** which is shifted downfield by 0.6 ppm from its position in **7**.[17]

Confirmatory evidence for the structure of **6** and **7** was obtained by hydrogenation of the product mixture at atmospheric pressure in ethanol over 5% Pd/C to give the ethyl derivative **8**: NMR ($CDCl_3$) δ 1.0 (t, 3 H, *J* = 7 Hz), 1.3-1.8 (m, 2 H), 2.7-3.1 (m, 1 H), 3.2 (s, 3 H), 3.5-3.8 (m, 2 H), 7.3 -7.9 (m, 4 H); IR (CCl_4) 1690, 1650 cm^{-1}; *m/e* 217 (26). Irradiation of this material in acetonitrile cleanly converted it to the parent 3,4-benzo-6,7-dehydro-1-methylazepine-2,5-dione (**9**): NMR ($CDCl_3$) δ 2.8-3.1 (m, 2 H), 3.20 (s, 3 H), 3.6-3.8 (m, 2 H), 7.4-7.9 (m, 4 H); IR (CCl_4) 1695, 1655 cm^{-1}; *m/e* 189 (1954). The type II cleavage of the ethyl group[6] clearly establishes the position of the substituent as α to the carbonyl. No evidence for any 7-substituted products was obtained.

Possible mechanisms for this novel reaction,[18] formally a $[_\pi 2 + {}_\sigma 2]$ photochemical cycloaddition, must explain the observed regiospecificity; i.e., the diene always adds with its terminal carbon attached to nitrogen. We suggest the sequence shown, which meets these general criteria, involving diene addition to give dipolar biradical **10**, subsequent closure to azetedine **11**, and opening to **12**. An alternative mechanism would involve α cleavage to biradical **13** which could add diene to afford **12** directly. However, if rotation around the C-C(O) bond in **13** is competitive with reclosure to **5**, a reasonable expectation in view of the fact that diene addition must compete with reclosure, we would expect to see the formation of the isomeric imine **14** in the absence of diene. Irradiation of **5** in pure acetonitrile or *tert*-butyl alcohol gave only unreacted **5**.



The addition reaction occurs with several other dienes with comparable efficiency. Thus, irradiation of **5** in the presence of isoprene affords a 45:55 mixture of **15a** and **16** in 49% isolated yield. The ^{1}H NMR spectrum of **15a** showed δ 1.45 (s, 3 H), 3.2 (s, 3 H), 3.30 and 3.83 (AB pattern, J = 14 Hz), 5.0–5.6 (m, 3 H), 7.3–7.9 (m, 4 H); IR (CCl_4) 1698, 1655 cm^{-1}; *m/e* 229 (9). The spectra of **16** showed δ 2.15 (s, 3 H), 2.35 (s, 3 H), 3.25 (s, 3 H), 4.30 (s, 2 H), 7.5–8.0 (m, 4 H); IR (CCl_4) 1670, 1655 cm^{-1}; *m/e* 229 (100). Similarly, 2,3-dimethylbutadiene gave a 50% isolated yield of **15b**:[20] δ 1.4 (s, 3 H), 1.7 (s, 3 H), 3.18 (s, 3 H), 3.3 and 4.0 (AB pattern, J = 15 Hz), 4.7–4.9 (m, 2 H), 7.2–7.7 (m, 4 H); IR (CCl_4) 1695, 1655 cm^{-1}; *m/e* 243 (9). The photoaddition occurs with 1,3-pentadiene to give the expected products from initial addition of the N atom in **5** to the 1 and 4 positions in the diene.[21] However, we were unable to detect any product formation when **5** was irradiated in the presence of either cyclopentadiene or 2,5-dimethyl-2,4-hexadiene.[22] Experiments with isoprene and phthalimide and *N*-phenylphthalimide also afforded no product suggesting that the reaction is sensitive to electronic effects. Research on the scope and mechanism of these reactions is continuing.



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(21) The structures of these products were determined by ^{1}H NMR on isomer mixtures. At present we are unable to separate the isomeric products and pure samples were not available.
(22) This observation is important in that it appears that the reaction is least efficient with those dienes having the lowest ionization potentials. Phthalimides have been shown to form weak charge-transfer complexes with amines and aromatic compounds.[10,23] If either a charge-transfer complex or an exciplex was an intermediate in this reaction, we would expect those dienes with the lowest ionization potentials to form the ground- or excited-state complex and react most efficiently. These points are being investigated presently.
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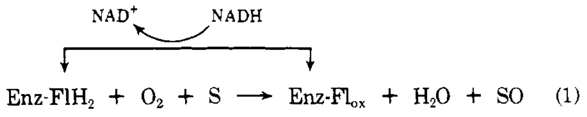
Chemiluminescence Accompanying the Decomposition of 4a-Flavin Alkyl Peroxide. Model Studies of Bacterial Luciferase

Sir:

Flavoenzyme external monooxygenases, in the reduced state (Enz-FlH$_2$), combine with molecular oxygen and substrate (S) to yield enzyme-bound oxidized flavin (Enz-Fl$_{ox}$), water, and oxygenated substrate (eq 1).[1] The oxidation of S involves the



$$\text{Enz-FlH}_2 + O_2 + S \longrightarrow \text{Enz-Fl}_{ox} + H_2O + SO \qquad (1)$$

stepwise processes of combination of enzyme-bound dihydroflavin (Enz-FlH$_2$) with oxygen to provide an oxygenated flavin species (Enz-FlH$_2$O$_2$) which then reacts with the bound substrate.[1] It has been suggested that the FlH$_2$O$_2$ moiety possesses a 4a-hydroperoxylfavin structure (4a-FlHOOH).[1,2] We have recently reported the synthesis and characterization of 4a-FlC$_2$H$_5$OOH and established that its spectrum is almost superimposable upon that of Enz-FlH$_2$O$_2$ prepared from *Beneckea harveyi* luciferase.[3] Further, we have established that