

***Ab initio* Theoretical Investigation
of a Formal Alkene-Enedione Intramolecular [2 + 2]
Photocyclization**

Alan P. Marchand,^{a,*} Trevor D. Power,^a and Hendrik G. Kruger^{b,*}

^aDepartment of Chemistry, University of North Texas,
Denton, Texas 76203-5070, USA

^bSchool of Pure & Applied Chemistry, University of Natal,
Durban 4001, South Africa

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Irradiation of **1** with visible light results in intramolecular [2 + 2] photocyclization to afford the corresponding pentacyclic cage diketone, *i.e.*, pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**2**). The mechanism of this reaction has been scrutinized by using *ab initio* theoretical methods. The results of these calculations provide new evidence which supports earlier suggestions that alkene-enedione photocyclizations may actually proceed *via* a diradical stepwise mechanism through the triplet excited state rather than as concerted [2 + 2] cycloadditions.

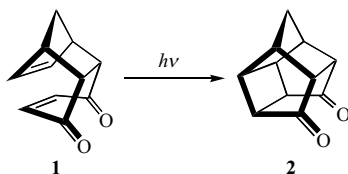
Key words: photocyclization, intramolecular photocyclization, diketone, *ab initio*.

INTRODUCTION

Intramolecular photocyclization of 1 α ,4 α ,4 α ,8 α -tetrahydro-1,4-methanonaphthalene-5,8-dione (*i.e.*, **1**, Scheme 1) was first studied experimentally by Cookson and coworkers.¹ Subsequently, the photocyclization product, **2**, and related functionalized pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes have received considerable attention.²

Some aspects of the photophysics of several polycyclic enediones have been reported recently.³ A growing body of experimental evidence has appeared

* Author to whom correspondence should be addressed.



Scheme 1

which suggests that photocyclization reactions of the type **1**→**2** proceed as stepwise processes *via* diradical triplet intermediates^{3,4} rather than as concerted [2 + 2] cycloadditions that proceed in accordance with the principle of conservation of orbital symmetry.⁵ In addition, cyclobutanes formed *via* photocyclization of alkenes to a C=C bond in quinones and haloquinones have been shown to result *via* triplet diradical intermediates without involvement of single electron transfer between the alkene and enedione C=C double bonds.⁶

In an effort to foster an improved understanding of the various contributing electronic and/or steric factors that control the course of photocyclization of **1** to **2**, we have undertaken an *ab initio* theoretical study of this reaction. The results of our efforts, which indeed provide new insight into the detailed mechanism of reactions of this type, are reported herein.

COMPUTATIONAL METHODS

Intramolecular alkene-enedione photocyclization of dienedione **1** was examined with basis set 6-31+G at the restricted open shell Hartree-Fock (ROHF) and CI-Singles⁷ levels of theory by using Gaussian 98.⁸ The inclusion of diffuse functions to heavy atoms (»+«) is necessary in order to obtain accurate results for calculations that involve excited state species.⁹ Transition states were characterized *via* second derivative vibrational frequency calculations. Restricted configuration interaction singles (RCIS) was employed to approximate the first excited singlet and triplet energies of **1**. Restricted open shell Hartree-Fock (ROHF) calculations were used to locate triplet transition states and intermediates and to locate singlet dienedione **1** and its corresponding intramolecular photocyclization product, **2**.

THEORETICAL RESULTS OBTAINED FOR INTRAMOLECULAR PHOTOCYCLIZATION **1**→**2**

In Figure 1, the progress of reaction diagram and relative energies obtained for photocyclization of **1** to **2** are presented. The information contained therein results from calculations performed at the ROHF level of theory by using basis set 6-31+G. The first singlet and triplet excited states of **1** were

found to be *ca.* 99 kcal mol⁻¹ and 64 kcal mol⁻¹, respectively. These energies correspond to photons of *ca.* 286 nm and 447 nm, respectively. It should be noted that the first excited singlet and triplet states of dienedione **1** are estimated values (RCIS calculation) and do not reflect stationary points.

In all likelihood, these RCIS calculations overestimate the first singlet and triplet excited state energies by at least 5 kcal mol⁻¹ since the photocyclization reaction was performed in acetone solution either by using sunlight ($\lambda > 300$ nm, which corresponds to $E = 95$ kcal mol⁻¹) or by using Pyrex-filtered UV light ($\lambda > 300$ – 330 nm, which corresponds to $E = 86$ – 95 kcal mol⁻¹) as the photon source. Acetone requires *ca.* 336 nm photons ($E = ca.$ 85 kcal mol⁻¹) in order to reach its first singlet excited state.¹⁰ The first triplet state of acetone requires excitation energy of *ca.* 78 kcal mol⁻¹ (which corresponds to $\lambda = 367$ nm).¹⁰ Thus, although the possibility that acetone might function as a photosensitizer in this reaction should not be ruled out, it should be noted that photocyclization of **1** to **2** has been performed successfully in other solvents (*e.g.*, EtOAc).¹¹

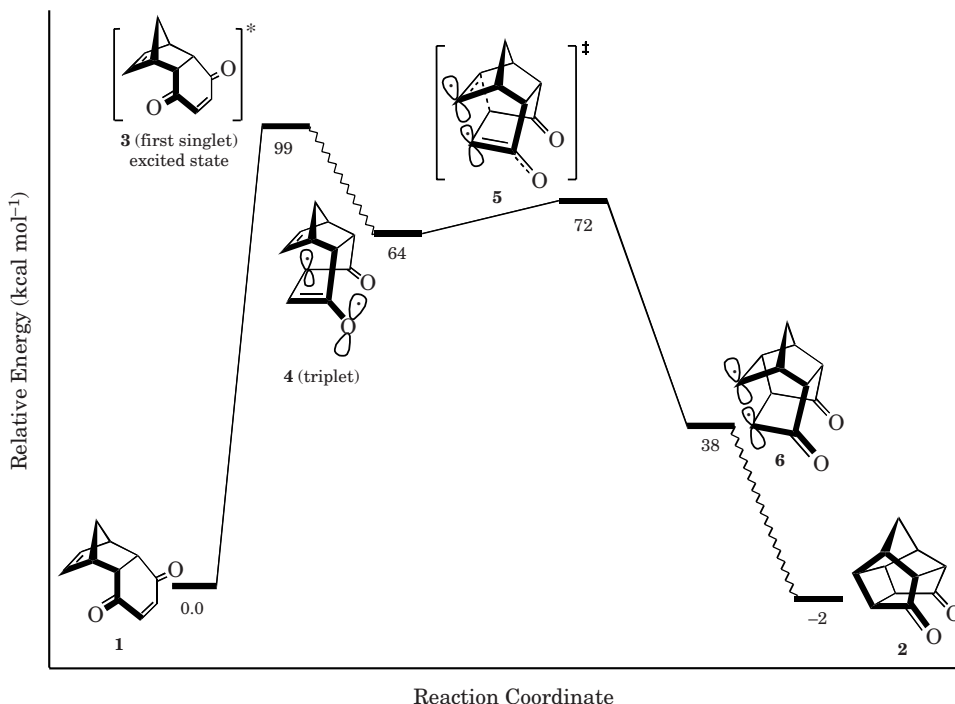


Figure 1. Calculated (ROHF/6-31+G) energy profile for photocyclization of **1** to **2**. Relative energies are given in kcal mol⁻¹.

Cookson and co-workers^{1a} reported the UV spectrum of **1** in cyclohexane. Subsequently, they assigned the various spectral transitions as follows: $S_0 \rightarrow S_3$ at 226 nm (127 kcal mol⁻¹, due to a $\pi \rightarrow \pi^*$ transition), $S_0 \rightarrow S_2$ at 278 nm (103 kcal mol⁻¹, due to charge transfer between the norbornene C=C double bond and the enedione moiety) and $S_0 \rightarrow S_1$ at 385 nm (74 kcal mol⁻¹, due to an $n \rightarrow \pi^*$ transition). The first singlet excited state occurs within the enedione chromophore, wherein one of the oxygen nonbonded (*i.e.*, lone-pair) electrons is promoted into an empty π -orbital. Hence, the calculated value for the first singlet excited state (*i.e.*, *ca.* 99 kcal mol⁻¹) is *ca.* 25 kcal mol⁻¹ higher than the experimental value determined by Cookson *et al.*^{1a}

The reaction depicted in Figure 1 suggests that the overall photocyclization reaction of **1** to **2** is virtually thermoneutral. Nevertheless, photochemical excitation of **1** to its first singlet excited state requires input of a relatively large amount of energy, *i.e.*, *ca.* 100 kcal mol⁻¹. Most likely, the final step of this reaction (*i.e.*, **6**→**2**) is slow, as is the case with most T_1 to S_0 transitions. However, as Catalani and coworkers³ point out, Mehta *et al.*^{4c} found only one transient; the enedione triplet prior to the formation of Dilling's^{4a} biradical intermediate **6**. Therefore the rate-determining step of this reaction must be the decomposition of triplet enedione **4** to the corresponding triplet ring-closed product **6** rather than the conversion of **6** to **2**.

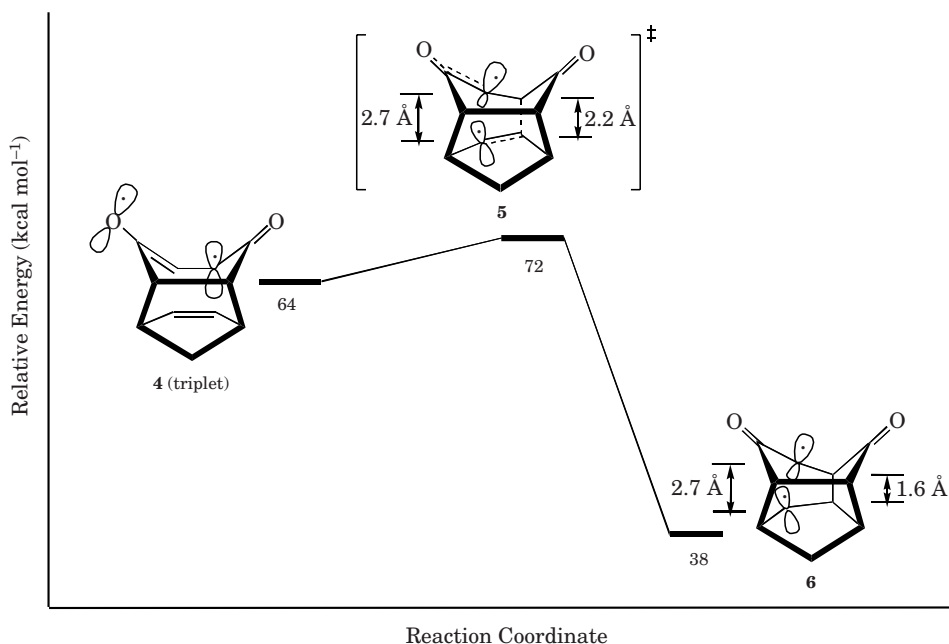


Figure 2. Calculated (ROHF/6-31+G) partial energy profile for photocyclization of **1** to **2** (detail of a portion of Figure 1). Relative energies are given in kcal mol⁻¹.

In Figure 2, the first and last steps have been removed from the progress of reaction diagram depicted in Figure 1. Here, upon inspection of transition state **5**, the nonsynchronous nature of the photocyclization reaction becomes evident.

The experimentally determined^{1a} first excited singlet state of **1** requires *ca.* 74 kcal mol⁻¹ of activation energy. The computational results suggest that the rate determining step of the overall reaction proceeds *via* transition state **5** which lies *ca.* 72 kcal mol⁻¹ above the ground state of enedione **1**. After this point on the energy diagram has been reached, the succeeding cyclization reaction is clearly exothermic. Intermediate triplet **4** is expected to be highly reactive; thus, the energy barrier required for conversion of **4** to **6** (*ca.* 8 kcal mol⁻¹) does not appear to be excessive. Intermediate **6** is a diradical which must undergo spin-inversion, prior to closure to **2**.

SUMMARY AND CONCLUSIONS

Theoretical investigation into the intramolecular photocyclization of 1 α , 4 α , 4 $\alpha\alpha$, 8 $\alpha\alpha$ -tetrahydro-1,4-methanonaphthalene-5,8-dione (**1**) to form the corresponding cage diketone (*i.e.*, pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (**2**), Scheme 1) clearly reveals the stepwise nature of this alkene-enedione photocyclization reaction. This virtually thermoneutral reaction proceeds in stepwise fashion *via* diradical intermediates, as indicated by the reaction profile shown in Figure 1. The fact that this reaction proceeds *via* the triplet state rules out a concerted mechanism for photocyclization of **1** to **2** due to spin incompatibility between electrons in the π -orbitals that ultimately result in final σ -bond formation to afford **2**.

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SAŽETAK

Teorijsko istraživanje formalne intramolekularne [2+2] alken-endion fotociklizacije s pomoću proračuna *ab initio*

Alan P. Marchand, Trevor D. Power i Hendrik G. Kruger

Ozračivanjem $1\alpha,4\alpha,4a\alpha,8a\alpha$ -tetrahidro-1,4-metano-naftalen-5,8-diona (**1**) vidljivom svetlošću došlo je do intramolekulske [2+2] fotociklizacije kojom je nastao odgovarajući pentaciklički kavezni diketon, tj. pentaciklo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undekan-8,11-dion (**2**). Mehanizam te reakcije pomno je istražen teorijskim proračunima *ab initio*. Izračunani podaci dali su nove dokaze koji su potkrijepili prijašnje pretpostavke da se fotociklizacija alken-endion odvija putem biradikalnog stupnjevitog mehanizma preko tripletnog pobuđenog stanja, a ne kao sukladna [2+2] cikloadicija.