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PHOTOCHEMICALLY INDUCED REACTIONS OF CIS,CIS-CYCLOOCTADIENONE

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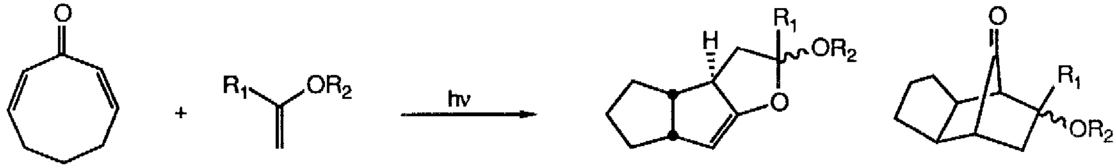
Abstract: Irradiation of 2,7-cyclooctadienone **1** produces cis,trans-2,7-cyclooctadienone **5** which has been characterized by low temperature ^{13}C NMR. Dienone **5** is in equilibrium with a zwitterionic oxyallyl species **6** via B, B' bond formation. Zwitterion **6** forms cycloadducts with ethyl vinyl ether and 2-methoxypropene.

The photochemistry of cross conjugated dienones has been intensely studied over the past 25 years.[1] A typical reaction pathway for these systems involves bond formation across the β,β' carbons to produce a putative zwitterionic intermediate. In 1968 Haseltine and Crandall,[2] and Noyori and Kato[3] reported that the irradiation of cis,cis-cyclooctadienone **1** in the presence of methanol or furan gave rise to the formation of 1:1 adducts which contained a cis-bicyclo[3.3.0]octanone ring system. Both groups suggested that a zwitterionic oxyallyl system **6** was a plausible intermediate. In addition, Haseltine and Crandall demonstrated that a reactive ground state species, which is stable at -78° C, intervenes between the excited state of **1** and the formation of adducts. Following our interest in the electronic structure and reactivity of non-Kekule systems,[4] we recently reinvestigated the photochemistry of **1** as a potential entry onto an oxyallyl energy surface. Here we report the spectroscopic observation of cis,trans-cyclooctadienone **5** and the trapping of a reactive intermediate in a new way with electron-rich olefins.



1 **2** **3**

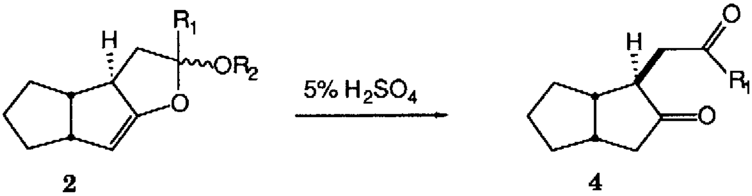
a: $R_1 = H, R_2 = CH_2CH_3$
b: $R_1 = R_2 = CH_3$

Table 1.
Irradiation of 2,7-cyclooctadienone in the presence of hexanes/vinyl ether (4/1) solutions.

Vinyl Ether	Products	Yield[a]
Ethyl Vinyl Ether	**2a** (73%), **3a** (27%)	54
2-Methoxypropene	**2b** (53%), **3b** (47%)	62

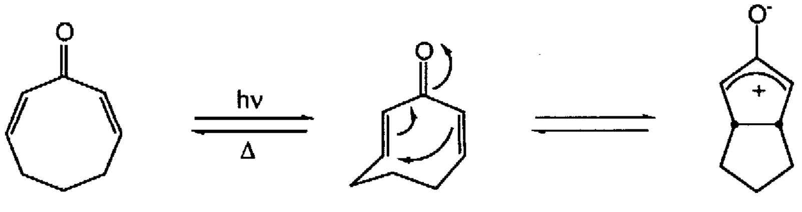
a. Combined isolated yield after flash chromatography.

Irradiation of dienone **1** (.05M in hexanes) in the presence of ethyl vinyl ether (EVE) or 2-methoxypropene (0° C, Rayonet Photochemical Reactor- 3500A lamps, 9 hours) gives rise to two families of 1:1 adducts. The adducts were isolated by flash chromatography and identified as the vinyl ether-ketals **2** and ketones **3** (Table 1).[5] Upon treatment with 5% H_2SO_4 the diastereomeric mixtures **2a** and **2b** converge, respectively, to a single aldehyde **4a**, or ketone **4b**.[5]



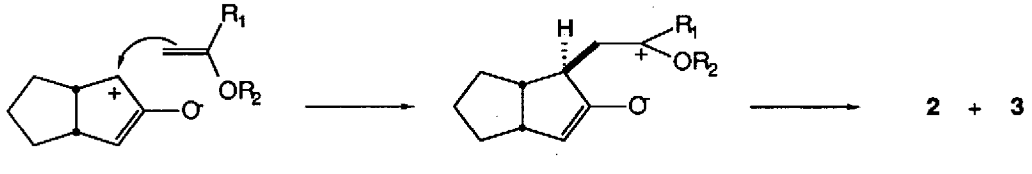
2 **4**

Following the studies of Crandall and Haseltine, **1** was irradiated at -78° C in CH_2Cl_2 for one hour and then EVE or 2-methoxypropene was added in the dark. The reaction mixture was warmed to room temperature and analyzed. Adducts **2** and **3** were formed in about the same ratio as seen in the photochemical studies carried out in the presence of trap. These experiments indicate that a storeable ground state species is on the reaction pathway. When **1** is irradiated at -78 C (CD_2Cl_2) and then examined at -78° C by ^{13}C NMR, eight new signals appear at δ 196.5, 160.6, 152.0, 140.4, 127.9, 38.8, 33.1, 32.2. The new signals are about 1/10 as strong as 3 of the 5 signals (δ 193.7, 142.8, 135.2, 27.2, 24.8) displayed by dienone **1** suggesting that the photoproduct is formed in about 20% under these conditions. The NMR data requires that **1** is isomerized to a compound of lower symmetry and that this compound contains 4 olefinic carbons, 3 alkyl carbons, and 1 carbonyl group. These data are in accord with the photochemical conversion of **1** to the cis,trans isomer **5**. In the absence of trapping agent the cis,trans isomer **5** is stable for several hours at 0° C.



1 5 6

Strained trans cyclic enones typically suffer nucleophilic attack at the β position and give [2+2] adducts with olefins. For example, irradiation of cis-2-cyclooctenone generates the trans isomer which reacts in the dark with methanol to give "Michael" addition products[6] and affords head-to-head [2+2] cycloadducts with 1,1-dimethoxyethylene.[7] In the photo-induced reactions of **1** we have not observed any [2+2] adducts even when EVE or methoxypropene was used as the solvent.[8] In the present system, the observed products require that bond formation occur at the α-carbon of the enone skeleton. Therefore the trans isomer **5** while on the reaction pathway does not appear to be the intermediate that reacts with the olefin. Trans dienone **5** may be in equilibrium with the oxyallyl species via a thermal conrotatory ring closure/opening process.[9]



6 7

The formation of adducts **2** and **3** can be conceived as being derived from the capture of the oxyallyl intermediate in a step-wise fashion. The nucleophilic olefin attacks the oxyallyl species preferentially from the convex face, followed by intramolecular C and O-alkylation of the resultant enolate. Oxyallyl zwitterions are typically captured in concerted [4+2] cycloadditions by dienes (*vide supra*).[10] Trapping of simple oxyallyl intermediates with electron-rich olefins presents a novel and intriguing new reaction pathway.[11,12]

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Notes and References

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5. All new compounds have been characterized by ^{1}H and ^{13}C (DEPT) NMR, IR and MS.

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7. E. J. Corey, J. D. Bass, R. LeMahiev, R. B. Mitra, *J. Am. Chem. Soc.*, **1964**, 86, 5570.

8. When dienone **1** was irradiated in neat EVE the product ratio changed to 88% **2a** and 12% **3a**. No shift in the product composition is observed in the reaction of **1** with neat 2-methoxypropene.

9. The transformation of **1** to **5** to **6** was originally proposed by Haseltine; see R. P. Haseltine, Ph. D. Thesis, University of Indiana, **1970**; University Microfilms # 70-19,095, Ann Arbor, Michigan.

10. a) N. J. Turro, *Pure and Appl. Chem.*, **1971**, 27, 679; b) N. J. Turro, S. S. Edelson, S. S. Williams, T. R. Darling, W. B. Hammond, *J. Am. Chem. Soc.*, **1969**, 91, 2283.

11. Haseltine did not observe any 1:1 adducts when dienone **1** was irradiated in the presence of 1,2-dichloroethylene, vinyl acetate or dimethyl acetylenedicarboxylate. See reference 9.

12. Noyori has reported that formal (3+2) oxyallyl-olefin cycloadditions can be effected using α,α'-dibromoketone-$Fe_2(CO)_9$ systems. See R. Noyori, *Acc. Chem. Res.*, **1979**, 12, 61.

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