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PHOTOLYSIS OF 4-SUBSTITUTED-4-HYDROXY-3-CYCLOBUTEN-1-ONES: A NEW ROUTE TO BUTENOLIDES FROM 4-HYDROXYCYCLOBUTENONES

Steven T. Perri, Lafayette D. Foland and Harold W. Moore
Department of Chemistry, University of California, Irvine
Irvine, California 92717

Abstract: Photolysis of 4-substituted-4-hydroxy-3-cyclobuten-1-ones undergo electrocyclic ring opening followed by ring closure to provide butenolide products. This transformation is envisaged to involve a stereoselective disrotatory electrocyclic ring opening to the corresponding conjugated ketene in which the C_4 hydroxyl group rotates inward towards the ketene moiety. Intramolecular trapping of the ketene moiety with the proximal hydroxyl group results in the corresponding butenolide products.

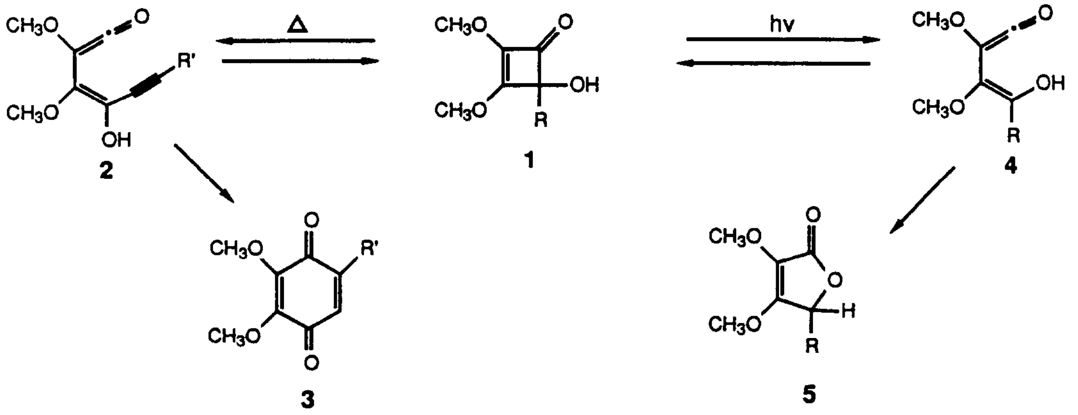
Reported in this Letter is the photochemical ring expansion of 4-hydroxycyclobutenones **1** to the butenolides **5**, a transformation involving the proposed ketene intermediate **4**. In addition to its synthetic utility, the selectivity of this rearrangement is also of mechanistic interest since thermolyses of cyclobutenones in this series, (4-alkynyl- and 4-aryl-4-hydroxycyclobutenones **1a-g**) have previously been shown to undergo electrocyclic ring opening to the conjugated ketene **2** followed by ring closure to quinone or hydroquinone products **3**.[1-5] These results along with the data presented here show that 1 can be employed to selectively give products arising from ketene **2** or **4** by respectively thermal or photolytic conditions.

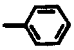
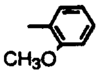
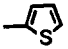
The starting cyclobutenones **1a-i** were obtained in 61-92% yield upon treatment of dimethyl squarate (dimethoxycyclobutenedione) with the respective organo lithium reagent in THF at -78° C.[6] Photolyses of cyclobutenones **1a-i** were carried out on THF solutions at 0° C using a quartz immersion well and a medium-pressure photochemical lamp (Hanovia 400W). The reactions were monitored by TLC, and the photolysis ceased when the starting cyclobutenones had been consumed. Under these conditions the yields of the butenolides were not maximized since control experiments showed the butenolide products to be photolytically unstable. The butenolides **5** all show spectral (IR, NMR, MS) and analytical properties which are in accord with their proposed structures. Significant data include the absorption in the IR spectra in the range 1750-1760 cm^{-1} which is characteristic of a conjugated enone and the absorption of the methine proton in the ^{1}HNMR spectra at 4.5-5.0 ppm.

For the examples studied, the major products isolated were the 1(5H)-furanones **5a-h**. One exception to this was observed from the photolysis of **1i**. Here, the major products isolated were the unsaturated lactone **6** and the hydroxyfuran **7**. These products are viewed as arising from the initially formed 1(5H)-furanone which then undergoes proton shifts to give the observed products **6** and **7**. Characteristic properties of these compounds follow: **6**: IR ($CHCl_3$) 2950, 1770, 1642 cm^{-1}; ^{1}HNMR ($CDCl_3$) 1.91 (s, 3H), 2.00 (s, 3H), 3.89 (s, 3H), 4.16 (s, 3H); ^{13}CNMR ($CDCl_3$) 17.9, 19.7, 59.4, 60.7, 122.3, 125.4, 136.0, 151.6, 164.8; exact mass calcd. for $C_9H_{12}O_4$: 184.0735; Found: 184.0741. **7**: IR ($CHCl_3$) 3550, 2940, 1602 cm^{-1}; ^{1}HNMR ($CDCl_3$) 2.17 (s, 3H), 3.88 (s, 3H), 3.91 (s, 3H), 5.26 (s, 1H), 5.38 (s, 1H), 6.48

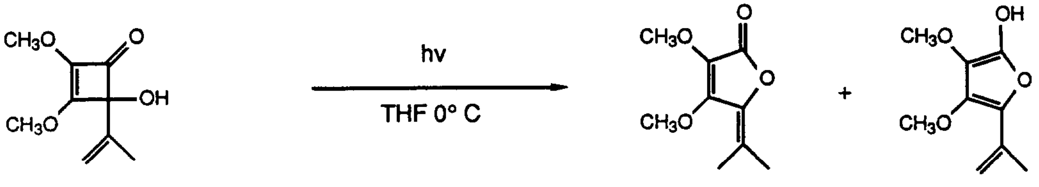
(s, 1H); ^{13}CNMR ($CDCl_3$) 15.6, 61.0, 61.1, 111.5, 119.6, 137.4, 139.2, 140.6, 141.8; exact mass calcd. for $C_9H_{12}O_4$: 184.0735; Found: 184.0742.

Scheme 1



Cyclobutenones			Products		
Compd	R	% Yield	Compd	Time (h)	% Yield
1a		79	**5a**	4	28
1b		89	**5b**	2.5	50
1c		82	**5c**	2	52
1d		77	**5d**	4	27
1e	 CH3O	56	**5e**	2.5	51
1f	 O	66	**5f**	4	60
1g	 S	80	**5g**	1.5	37
1h		92	**5h**	5.5	39
1i		61	**6 + 7**	2.5	33, 22

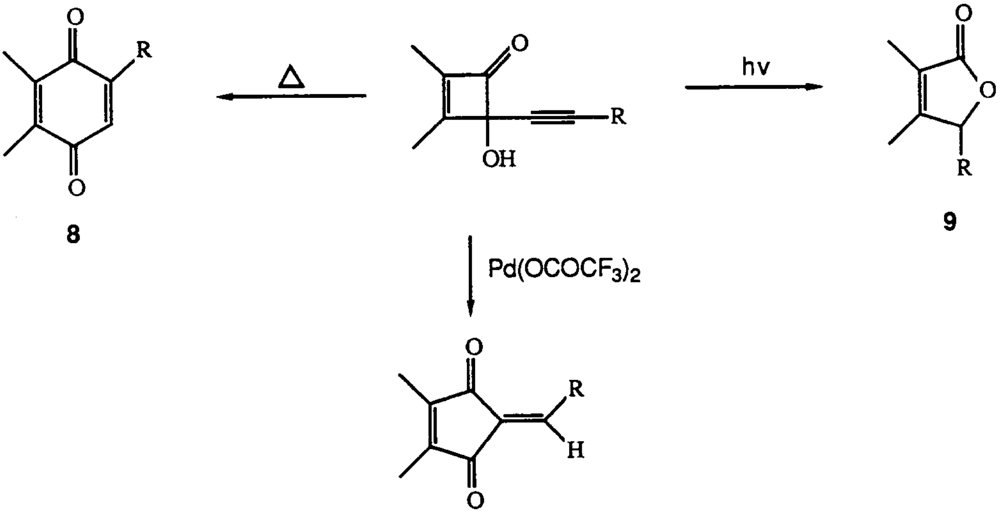
Scheme 2



1i 6 33% 7 22%

Several investigations have appeared which are relevant to the conversion of 1 to 5.[7-10] These include computational studies concerning the *thermal* electrocyclic ring opening of cyclobutenes to butadienes which conclude that the observed outward rotation of electron donating groups at C_3 and C_4 of cyclobutenes can be rationalized on the basis of electronic effects.[11] Furthermore, the tendency of outward rotation of electron donor groups was noted to increase as the donor ability of the substituent increases. Although little has appeared regarding the analogous ring opening of cyclobutenones similar electronic effects are assumed to control the selectivity of the ring opening. In this regard, Baldwin and McDaniel reported the valence isomerization of 2,4-dichloro-3-phenyl-3-cyclobutenone and observed products having different stereochemistries as a function of the reaction conditions.[12] Specifically, thermolysis of a methanolic solution of the cyclobutenone afforded the (E)-ester while photolysis gave the (Z)-ester. The results given in this Letter are complimentary and show generality and synthetic utility to this selective photo-induced rearrangement.

Scheme 3



8 9 10

In conclusion, the following significant points are noted: 1) 4-substituted-4-hydroxy-3-cyclobuten-1-ones can be thermolyzed to provide quinone products or photolyzed to provide butenolides; 2) this transformation must involve a stereoselective ring opening of the cyclobutenone in which the C_4 hydroxyl group rotates outward under thermal conditions and inward under photochemical conditions; 3) the electronic effects which govern the stereoselective ring opening of these rearrangements find direct analogies in the stereoselective ring opening of cyclobutenes. Finally, it is noted that the results presented here add to the arsenal of useful transformations of 4-alkynyl-4-hydroxycyclobutenones (Scheme 3); as mentioned earlier, benzoquinones **8** are formed when theses compounds are subjected to thermolysis, butenolides **9** arise from their photolysis and methylenecyclopentene-1,3-diones **10** have been shown to result when they are treated with palladium trifluoroacetate.[13]

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