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COMPARATIVE PHOTOLYSIS OF TETRAMETHYLCYCLOBUTANE-1,3-DIONE AND 2,2,4-TRIMETHYL-3-HYDROXY-3-PENTENOIC ACID, β-LACTONE IN METHANOL[1]

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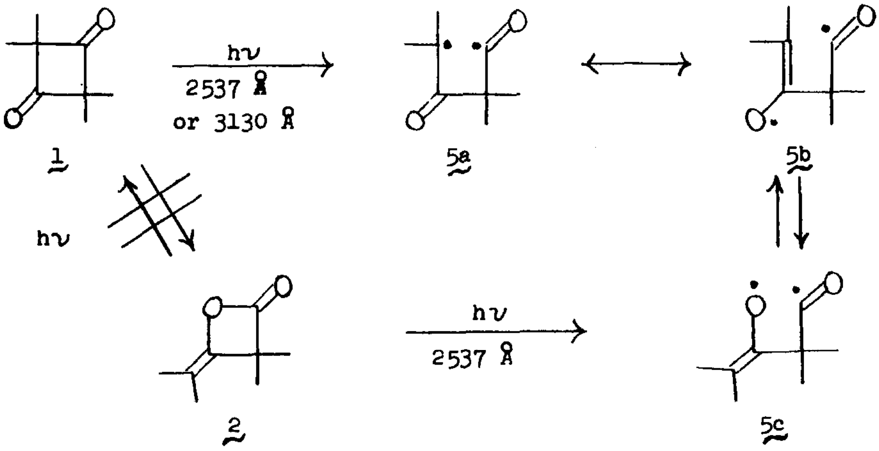
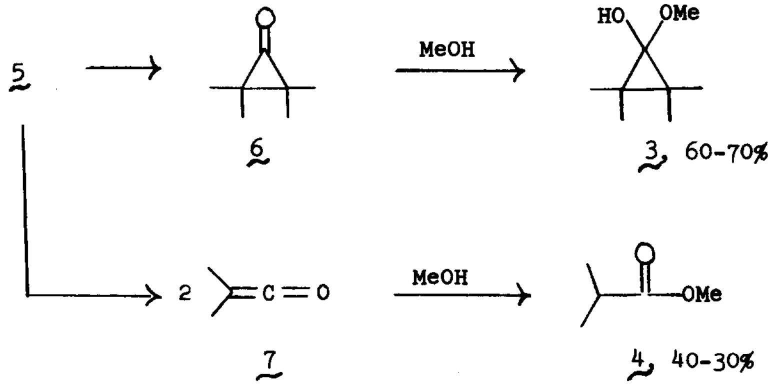
The photochemistry of alkyl enol esters and enol lactones has received considerable study over the last several years.[2-10] The products are generally consistent with a primary photochemical homolytic cleavage of the carbonyl-alkoxyl bond to yield a solvent caged acyl and enolic radical pair.[11] The fates of the caged radical pair include (a) recombination to form starting material; (b) decarbonylation of the acyl radical followed by combination of the resulting alkyl radical and the enol radical; (c) coupling of the acyl radical to the enolic radical to form a 1,3-dione. Interestingly, the photochemistry of cyclic non-enolic 1,3-diones[8-10] sometimes results in (partially photoreversible) formation of enol lactones. Although a common intermediate can be considered for the latter interconversion, no mechanistic study is available which correlates the rearrangement of an enol ester (or enol lactone) to a 1,3-dione with a common intermediate. Cases are known in which the related photo-Fries rearrangement[11] possibly proceeds not via an intermediate at all but via a concerted mechanism from an excited state which can also simultaneously fragment; thus, qualitative product studies may be a poor guide to mechanism unless proper controls are run. We report here a study of the photochemistry of methanolic solutions of tetramethylcyclobutane-1,3-dione (1) and its enol lactone isomer (2) which strongly implicate the occurrence of a common biradical intermediate preceding product formation.

The salient features of our results may be summarized as follows: (a) under the conditions studied, only the hemiketal (3) and methyl isobutyrate (**4**) are observed as products, with **3** invariably being produced as the major product; (b) the ratio of **3**/**4** is relatively insensitive to solvent (neat methanol, CH_3CN or C_6H_6) and temperature (-60° to $+70^\circ C$); (c) **1** and **2** are not measurably interconverted under our irradiation conditions;[10b] (d) photolysis of **1** or **2** cannot be sensitized by xanthone[12] ($E_3 \sim 74$ kcal/mole); (e) neither **1** nor **2** quenches the Type II photoelimination of butyrophenone[13] ($E_3 \sim 74$ kcal/mole) in methanol; and (f) the photolysis of **1** in methanol is not quenched by 1 M 1,3-pentadiene.

Our results are consistent with the intermediacy of the biradical **5** in the photolysis of **1** and **2** in MeOH. **5** can either lose CO to yield the cyclopropanone **6** or fragment to the ketene **7**. The similar product distribution (a) at a variety of temperatures and (b) in polar (CH_3CN) and non-polar (C_6H_6) solvents makes unlikely alternate mechanisms involving concerted cycloelimination from excited **1** or **2** to yield **6** and **7** respectively which competes with cleavage of excited **1** or **2** to yield **5** by an independent path. It is interesting to note that the mass spectrum[14] of **2** shows fragments expected from decomposition of **1**, a result which suggests partial interconversion of the molecular ions of **1** and **2** to a common intermediate.





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