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PHOTOCHEMICAL REACTION OF 3-HEXENE-2,5-DIONE WITH TETRAMETHYLETHYLENE: STEREOSPECIFIC SYNTHESIS OF TRANS-1,2-DIACETYL-3,3,4,4-TETRAMETHYLCYCLOBUTANE

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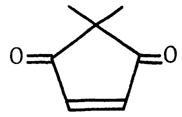
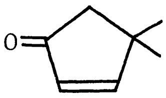
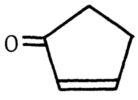
Photochemical reaction of 3-hexene-2,5-dione (**1**) with tetramethylethylene has been found to lead to stereospecific formation of trans-1,2-diacetyl-3,3,4,4-tetramethylcyclobutane. No evidence for oxetane formation has been obtained.

In preceding papers,1,2) we reported that the photochemical reactions of 4-cyclopentene-1,3-diones (A) with olefins including tetramethylethylene (TME) gave exclusively the oxetanes, and those of 4,4-disubstituted 2-cyclopentenones (B, synthetic equivalent to A) with TME both the oxetanes and the cyclobutanes, in contrast with exclusive formation of the cyclobutane in the photochemical reaction of cyclopentenone (C) with TME. Such marked difference in photoreaction behavior among A, B and C led us to investigate the photochemical behavior of enedione (D) possessing open-chain structure. We wish to report here that photocycloaddition of 3-hexene-2,5-dione (**1**) with TME results in the stereospecific formation of diacetylcyclobutane.


A


B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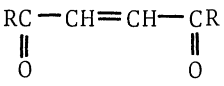
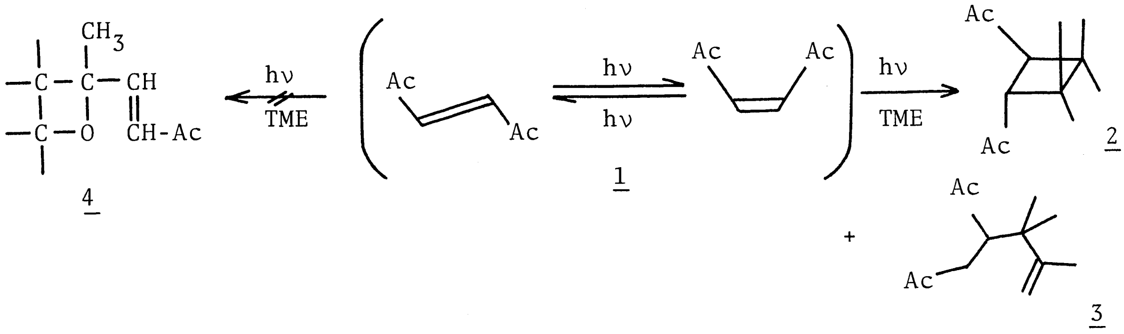
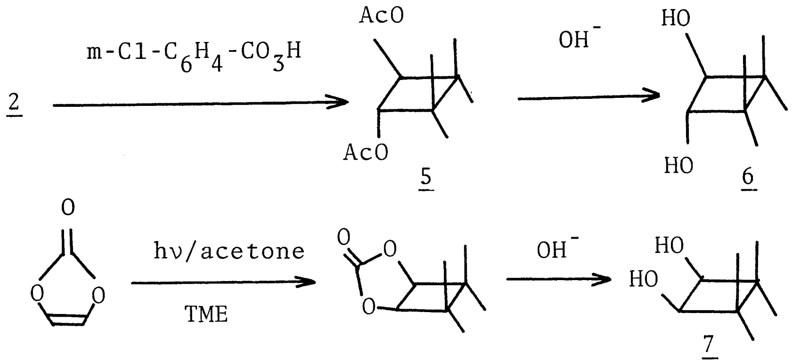

$$\underset{\overset{\|}{O}}{RC}-CH=CH-\underset{\overset{\|}{O}}{CR}$$
D

Irradiation to a solution of trans-**1**3) and large excess of TME in carbon tetrachloride with light of $\lambda > 330$ nm gave a photostationary state mixture of cis-**1** and trans-**1**. The solution was found by nmr analysis to contain more than 95% of cis-**1**. Photoaddition of TME to **1** was observed to proceed very sluggishly.

Vacuum distillation at 100-105°/6 mm of the reaction mixture gave the 1:1 adduct in 60% yield. This adduct was found to consist of two isomers in the ratio of 5:1 on the basis of the vpc. The major product was identified as trans-1,2-diacetyl-3,3,4,4-tetramethylcyclobutane 2 from spectroscopic and chemical data: 2 ir; 1715 cm^{-1} ($\nu_{C=O}$); nmr (CCl_4), τ 6.84 (s, 2H), 7.99 (s, 6H), 8.87 (s, 6H), 9.09 (s, 6H). The minor adduct was assigned to be acyclic adduct 3, the ir spectrum of which showed characteristic terminal-methylene group absorption at 895 cm^{-1}. Vpc analysis indicated no formation of oxetane (4) but the formation of a small amount of hexane-2,5-dione. Also no spectroscopic evidence for oxetane (4) formation was obtained. That is, the reaction mixture after removal of the solvent showed neither nmr signals expectable for α,β-unsaturated ketone structure, nor any significant ir absorptions near 1000 cm^{-1} which are characteristic ν_s and ν_{as} bands of oxetanes.



In order to determine the configuration of two acetyl groups of 2, a chemical derivation was carried out. Diketone 2 was oxidized with m-chloroperbenzoic acid (Bayer-Villiger oxidation) to give the diacetate (5). Subsequent hydrolysis of 5 with dilute alkali afforded a diol 6, which was subjected to ir examination in highly dilute solutions (0.05 M in carbon tetrachloride) and assigned as trans-diol on the basis of the observation of only one O-H absorption band at 3610 cm^{-1} due to free O-H, because the cis-isomer of 6 is expected to show two O-H absorptions due to free and intramolecular hydrogen-bonded OH. Actually, cis-diol (7) prepared by the photocycloaddition of vinylene carbonate with TME followed by alkaline hydrolysis[4)] exhibited two O-H absorption bands at 3620 cm^{-1} (free) and 3570 cm^{-1} (intramolecular hydrogen bond). Since it is established that the Baeyer-Villiger oxidation proceeds with retention of configuration during its rearrangement process,[5)] the above derivation from 2 to 6 must have occurred with no inversion of the initial geometry. Thus, the cyclobutane 2 was determined to be trans-1,2-diacetyl-3,3,4,4-tetramethyl-



cyclobutane. It is noteworthy that 1 gives specifically trans-diacetylcyclobutane, in spite of its dominant existence as cis-form at the photostationary state. And this reaction is considered to be useful as stereospecific synthesis of trans-1,2-diacetyl cyclobutanes from which monomers (such as trans-diols and trans-dicarboxylic acids) for new type polyester possessing cyclobutane ring[6)] in the main chain could be prepared. The ketone-sensitized photoreaction of 1 have also been attempted: By irradiations carried out in the presence of sensitizers under the conditions where most of light was absorbed by sensitizer, it was found that acetophenone (E_T 74 kcal/mole),[8)] p-methoxy acetophenone (72), benzophenone (69), 2-acetonaphthone (59) and biacetyl (55) could sensitize the reaction. This fact suggests that the photoaddition should proceed via triplet state of 1 and that E_T of 1 is lower than 55 kcal/mole.

Summarizingly photochemical behavior of the acyclic enedione 1 is of quite contrast to that of cyclic enedione (A) and further progress involving mechanistic problems is now under way.

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