Tetrahedron Letters No. 12, pp 1001 - 1004, 1975. Pergamon Press. Printed in Great Britain.

PHOTOCHEMICAL OXETANE FORMATION FROM 4-SUBSTITUTED 2-CYCLOPENTENONES

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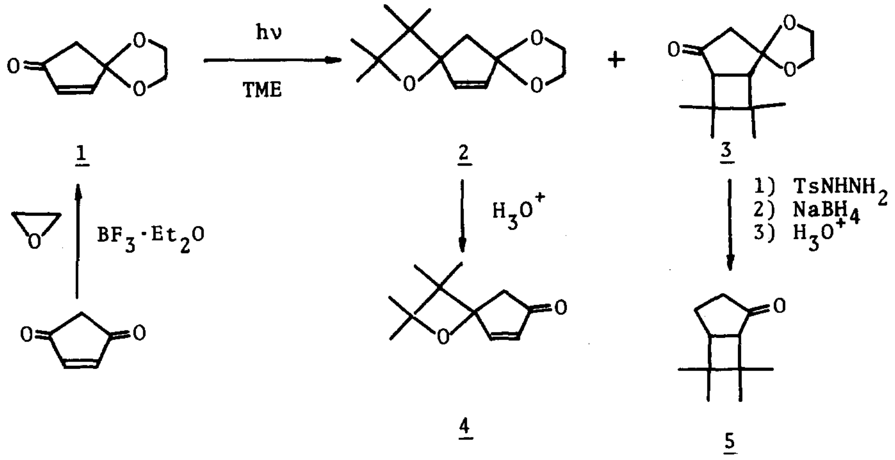
(Received in Japan 18 January 1975; received in UK for publication 11 February 1975)

Photochemical reactions of 2-cyclopentenones are well known to result in dimerizations at their carbon-carbon double bond or cyclobutane formations with olefins.[1] In contrast, we have recently reported the photochemical cycloaddition of 4-cyclopentene-1,3-diones with olefins to give exclusively corresponding oxetanes.[2] This remarkably different behavior between 2-cyclopentenones and 4-cyclopentene-1,3-dione involved us to investigate photochemical behavior of some 4-substituted 2-cyclopentenones, since substituents should affect the energy levels of π, π^* and n, π^* triplets, which have been postulated to lie close each other.[1c] We wish to report, in this communication, new finding that 4-substituted 2-cyclopentenones photochemically undergo both oxetane formation and cyclobutane formation. The reactions have promised considerable potential in organic synthesis.

A 4-substituted 2-cyclopentenone 1 was newly synthesized by adding large excess of ethylene oxide to a solution of 2-cyclopentene-1,3-dione in carbon tetrachloride in the presence of boron trifluoride etherate. This cyclopentenone exhibited the following spectral characteristics: ir (CCl_4) 1725 cm^{-1} ($\nu_{C=O}$), 1600 ($\nu_{C=C}$) and 1010; pmr ($CDCl_3$) τ 2.77 (d, β-olefinic, J=6.0 Hz), 3.80 (d, α-olefinic, J=6.0 Hz), 5.92 (s, 4H) and 7.40 (s, 2H); uv (EtOH) 212 (ε 8,400) and 321 (ε 34).

Irradiation to a mixture of 1 and tetramethylethylene (TME) through a Pyrex filter (λ > 300 nm) was found to afford two isomeric mixture of 1 : 1 adducts in high yields. One of the adducts, which showed no carbonyl absorption in the ir spectrum, was identified as a spirooxetane 2 by its derivation with dilute acid to known compound 4.[2] Another was assigned to be cyclobutane 3, in which the carbonyl absorption was observed at 1754 cm^{-1}, but no olefinic protons in the pmr spectrum. The compound 3 was converted

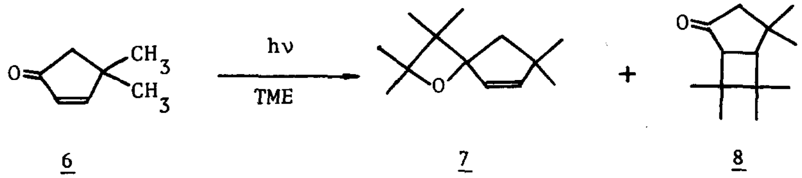
Scheme I.



by way of its tosylhydrazone to the ketone 5, prepared from relevant reaction,[3] as illustrated in Scheme I.

Interestingly irradiation to a mixture of 4,4-dimethyl-2-cyclopentenone 6 and TME under similar condition yielded a oxetane 7 as well as cyclobutane 8 (Scheme II), although the enone 6 was reported to form dimerized cyclobutane like parent 2-cyclopentenone.[4] This result is consonant to six-membered analogue, 4,4-dimethyl 2-cyclohexenone,[5] which is known to an unique case for oxetane formation among a large number of cyclic enones.

Scheme II.



In order to investigate the solvent effect on the photochemical cycloaddition of <u>1</u> and <u>6</u> with TME, the reactions were carried out in several polar and nonpolar solvents. The results were summalized in Table I. It was found that in both the enones the extent of oxetane formation tends to decrease as solvent polarity increases. The fact that both type of photocycloadditions depend upon external circumstance clearly indicates the existence of two reactive species, namely, n,π^* triplet responsible for oxetane formation and π, π^* triplet for cyclobutane formation. Furthermore, these two tripletes should lie within a few kilocalories in energy levels each other, because both oxetane and cyclobutane were obtained through changing solvent polarity. In photochemical cycloaddition of 2-cyclopentenone with olefin, triplet energy is estimated to be ∿74 kcal/mole.[3] Thus it could be concluded that both of n, π^* and π, π^* triplets of the 4-substituted 2-cyclopentenone lie very closely in the region near 70 kcal. In this sense, cyclopentenedione employed in our previous work[2] could be considered as the 2-cyclopentenone substituted by carbonyl group at the 4-position, suggesting that 4-substitution of 2-cyclopentenone has an important relation with the oxetane formation via n, π^* triplet.

Table I. The Formation Ratios of Oxetane to Cyclobutane

Solvent	Enone 1 (0.5 M)	Enone 2 (0.5 M)
Cyclohexane	76:24	53:47
Chloroform	63:37	———
Acetonitrile	62:38	29:71

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