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PHOTOCHEMICAL CYCLOADDITION OF 4-CYCLOPENTENE-1,3-DIONES WITH OLEFINS. SELECTIVE OXETANE FORMATION

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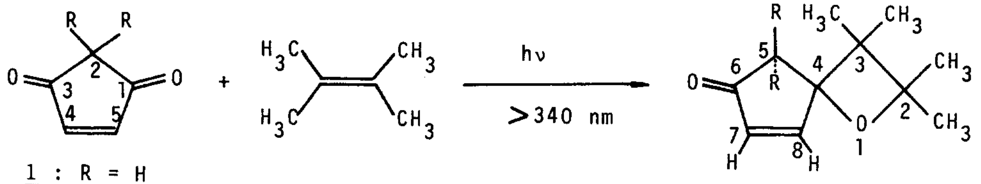
Although photochemical cycloaddition of unsaturated cyclic ketones has been extensively studied from synthetic and mechanistic viewpoints,[1] photoreaction of 2-ene-1,4-dione in which the second carbonyl chromophore is conjugated with the enone double bond has not been encountered so far except the following reactions. That is, Diels-Alder adducts of p-benzoquinone to cyclic dienes are known to isomerize cage-cyclobutane derivatives,[2] while those to non-cyclic dienes have been reported to give rearranged products.[3] We wish to report photochemical cycloaddition of 4-cyclopentene-1,3-dione (1) and its 2,2-dimethyl derivative (2) with olefins leading exclusive oxetane formation.

On irradiation at room temperature of a carbon tetrachloride solution of 1[4] and large excess of tetramethylethylene (TME) with light of wave-lengths above 340 nm,[5] 1 was observed to be rapidly consumed. By removing the unreacted 1 by treatment of the reaction mixture with dilute aq. alkali and subsequent distillation under reduced pressure, the product was obtained as a colorless liquid (bp 86 ∿ 88°/1.0 mm), which was assigned to be 2,2,3,3-tetramethyl-1-oxaspiro[3.4]oct-7-ene-6-one (3): m/e 180 (M^+, weak); ir (neat) 1715 cm^{-1} ($\nu_{C=O}$), 1600 ($\nu_{C=C}$); pmr ($CDCl_3$) δ 7.74 (d, J = 6.0 Hz, 1H, H_8), 6.16 (d, J = 6.0 Hz, 1H, H_7), 2.30 centered (AB_q, J = 18.8 Hz, 2H, H_5), 1.46, 1.38, 1.23, 1.12 (all s, 3H, methyl). Exclusive oxetane formation was found out by pmr measurement of the reaction mixture in the pmr sample tube at intervals of irradiation. Singlet of the olefinic protons of 1 at δ 7.2

was replaced linearly to irradiation time by a pair of doublets at δ 7.74 and 6.16 and the sum of the intensities due to all the olefinic protons of 1 and 3 was observed to be kept constant up to around 90 % conversion. The same type of adduct 4 was obtained from the photoreaction of 2[6] with TME. 4: m/e 208 (M^+); ir (neat) 1715 cm^{-1} ($\nu_{C=O}$), 1600 ($\nu_{C=C}$); pmr ($CDCl_3$) δ 7.89 (d, J = 6.0 Hz, 1H, H_8), 6.11 (d, J = 6.0 Hz, 1H, H_7), 1.45, 1.32, 1.27, 1.25, 1.17, 1.15 (all s, 3H, methyl). In these reactions no spectroscopic evidences for the formation of cyclobutane derivatives (5 and 6) were obtained.

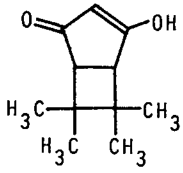


1 : R = H

2 : R = CH_3

3 : R = H

4 : R = CH_3



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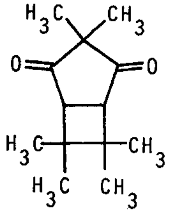

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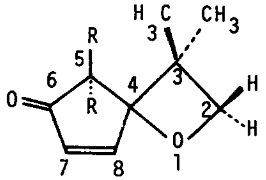
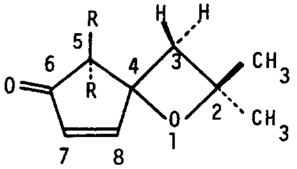
In order to inspect the regioselectivity in the cycloaddition, photochemical reaction of 1 or 2 with isobutylene were carried out under similar condition to the above reactions with TME. Both 1 and 2 were found to afford the corresponding spirooxetanes, as mixtures of stereochemical isomers (7 and 8). Attempt to separate these isomers by vpc was failed, because these oxetanes were thermally unstable over ca. 130°. However, distributions of the isomers could be readily determined by pmr analysis. For instance, distribution of 7a of the isomers was determined on the basis of the following pmr data; a) the relative intensity of the H_8 proton signal of 7a to that of 7b, and b) the percent ratio of the intensity due to the two methylene protons at

2-position in 7a (absent in 7b) to the total intensity due to the H_7 and H_8 protons in both 7a and 7b.[7] It was found that adduct of 1 and isobutylene is composed of 81 ± 3 % of 7a and 19 ± 3 % of 7b, being indicative of Markownikoff-type addition.[8] This type of orientation of olefins was further illustrated in the case of 2. Adduct of 2 and isobutylene was composed of 78 ± 3 % of 8a and 22 ± 3% of 8b. Though the methyl groups are much crowded in 8a, 8a is still predominant over 8b.



7a : R = H

8a : R = CH_3



7b : R = H

8b : R = CH_3

By using cis- and trans-2-butene, it was examined whether the oxetane formation lose the configuration of the olefins or not. The photochemical reaction of 1 and seven-fold of olefin was found to give all of four possible oxetanes, whether started with cis- or trans-olefin, in the ratio of 5.5:2.1:0.7:1.7 or 4.1:1.5:0.9:3.5.[9] There was no significant isomerization of 2-butene prior to addition, which was ascertained by vpc analysis of the reaction mixture.[10] Accordingly, stereochemical scrambling of 2-butene must have occured during the course of the addition reaction.

The result that this oxetane formation undergoes Markownikoff type addition and stereochemical scrambling is consistent with stereochemical aspects of the well-established mechanism of oxetane formation via $n\pi^*$ triplet which involves more stable triplet diradical and its spin-inversion to singlet diradical.[8, 11]

Conclusively, it has been elucidated that the photochemical reaction behavior of 4-cyclopentene-1,3-dione with olefins is different from that of

2-cyclopentenone, the reaction of which results in cyclobutane ring-formation associated with π-π^* triplet, but rather resembles that of p-quinone.[12] Further studies are in progress.

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5) The light of high-pressure mercury lamp was filtered through a 1.0 M naphthalene-benzene solution of 1 cm cell-path and pyrex filter.

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7) Chemical shifts used for this analysis are as follows: 7a, 7.80 ppm (H_8), 6.15 (H_7) and 4.30 (ABq center, Hz); 7b; 7.54 (H_8), 6.01 (H_7); 8a, 7.92 (H_8), 6.14 (H_7) and 4.40 (ABq center, Hz); 8b, 7.54 (H_8), 6.04 (H_7).

8) For terminology see J. C. Dalton, P. A. Wride, and N. J. Turro, J. Am. Chem. Soc., 92, 1318 (1970).

9) The ratio was determined according to available difference in chemical shifts of H_8 protons and is lined with upper field of their protons.

10) Surely small extent of isomerization of olefin could be detected, but such a large excess of olefin was used that influence to the addition is negligible.

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12) D. Bryce-Smith and A. Gilbert, Proc. Chem. Soc., 87 (1964); D. Bryce-Smith, A. Gilbert, and M. G. Johnson, J. Chem. Soc. (C), 383 (1967).