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THE NORRISH TYPE II PHOTOREACTION OF BENZOYLVALERATES. STEREOCHEMICAL CONTROL IN 1,4-BIRADICAL CYCLIZATION

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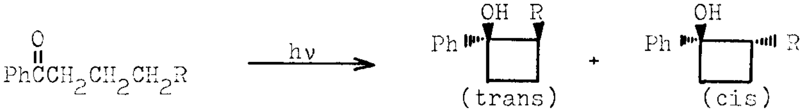
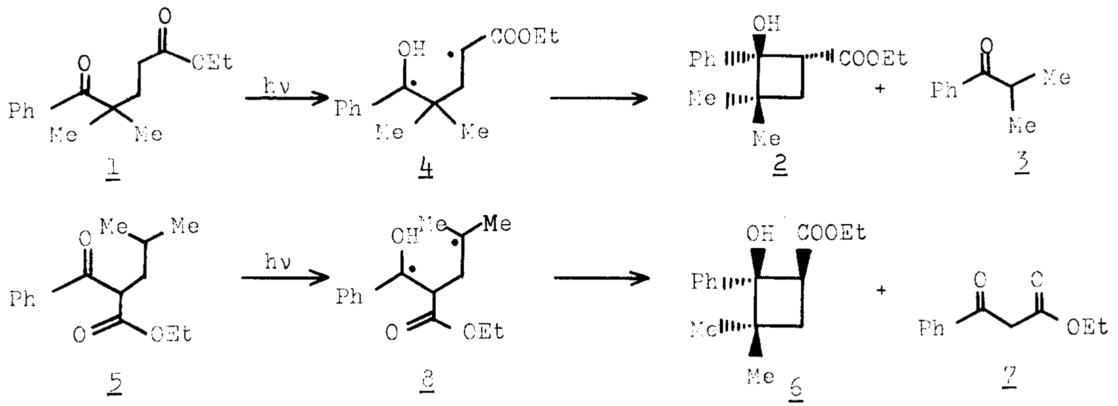
The δ- and β-oxoester 1 and 5 underwent the Type II photoreaction to give the stereoisomeric cyclobutanol 2 and 6, respectively; the ethoxycarbonyl group in the esters determines the stereochemistry of 1,4-biradical cyclization.

The Type II photoprocesses of phenyl ketones have been the subject of intense investigation. The intermediacy of a 1,4-biradical is now well established.1) The steric repulsive interaction between the phenyl group and the γ-substituent in the transition state of 1,4-biradical cyclization enhances the formation of the trans-cyclobutanol.2),3) A little is known about the neighboring group effects other than the steric interaction in the 1,4-biradical intermediate.3),4) We report here that the ethoxycarbonyl group in benzoylvalerate 1 and 5 determines the mode of the 1,4-biradical cyclization; the 4-benzoylvalerate 1 undergoes the Type II cyclization to give the cis-cyclobutanol 2, whereas the 2-benzoylvalerate 5 yields the trans-cyclobutanol 6.



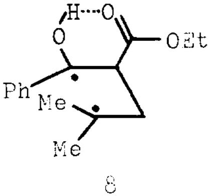
Irradiation of ethyl 4-benzoyl-4-methylvalerate (1) in benzene under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter gave cis-2-ethoxycarbonyl-4,4-dimethyl-1-phenylcyclobutanol (2) and iso-butyrophenone (3) in 26 and 35% yield, respectively. The ir spectrum of 2 showed the characteristic hydroxy and carbonyl absorption at 3475 and 1735 cm^{-1}, respectively. On the other hand, irradiation of ethyl 2-benzoyl-4-methylvalerate (5) under the same conditions gave the isomeric trans-cyclobutanol 6 and ethyl benzoylacetate (7) in 9 and 87% yield, respectively. The ir spectrum of 6 also showed the characteristic hydroxy and carbonyl absorption at 3480 and 1720 cm^{-1}, respectively.

The stereochemistry of the isomeric cyclobutanol 2 and 6 was determined by nmr spectroscopy. The nmr spectrum of 2 showed two singlets at δ 0.58 and 1.34 attributable to the cis- and the trans-methyl group, respectively. The peak of the alkyl group cis to the phenyl group on cyclobutanols showes the upfield shift.2) The cis- and the trans-methyl signal in the cyclobutanol 6 appeared at δ 0.74 and 1.26, respectively. The cis-methyl group of 2 and the



trans-methyl group of $\underline{6}$ are found slightly further upfield than the corresponding methyl group of the isomers. The upfield shift can be explained in terms of diamagnetic anisotropy by the carbonyl group. Therefore, the stereochemistry of $\underline{2}$ and $\underline{6}$ was determined to be cis and trans, respectively. The ir absorption of carbonyl group ($\underline{6}$, 1720 intramolecular hydrogen-bonded and $\underline{2}$, 1735) strongly supports the stereochemistry. The following chemical evidences also support the structure of the cyclobutanol $\underline{2}$ and $\underline{6}$. The cyclobutanol $\underline{6}$ was easily and quantitatively converted to the δ-oxoester $\underline{1}$ by heating in benzene ($k = 7 \times 10^{-6}$ sec^{-1}; E_A = 25 kcal/mole). On the other hand, the cyclobutanol $\underline{2}$ was hardly converted to the δ-oxoester under the same conditions. The cyclobutanol $\underline{2}$ rearranged quantitatively to the δ-oxoester $\underline{1}$ by refluxing in benzene containing acetic acid. These results indicate that the hydroxy group participates in the reaction of $\underline{6}$, so that the hydroxy group is cis to the ethoxycarbonyl group.

Formation of the cis-cyclobutanol $\underline{2}$ from the Type II photocyclization of the δ-oxoester $\underline{1}$ can be explained in terms of repulsive interaction between the lone-pair electrons on hydroxy oxygen and carbonyl π-electrons in the transition state of 1,4-biradical cyclization. Production of the trans-cyclobutanol $\underline{6}$ from the β-oxoester $\underline{5}$ can be explained in terms of intramolecular hydrogen bonding between the hydroxy group and the ethoxycarbonyl group in the process of the 1,4-biradical cyclization.



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The Type II photoreaction of the benzoylvalerate $\underline{1}$ and $\underline{5}$ was efficiently quenched with 1,3-pentadiene, so that the reaction takes place from the n,π* triplet state.

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