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ON THE MECHANISM OF THE PHOTOCHEMICAL REACTION OF CONJUGATED ESTERS. THE IMPORTANCE OF GEOMETRICALLY ISOMERIC EXCITED STATES.[1]

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In a previous publication (2) we have reported that acyclic α,β-unsaturated esters undergo a smooth photochemical transformation to β,γ-unsaturated esters or cyclopropylacetic esters, in a hydrogen abstraction reaction which is remarkably general (3) and less dependent on the type of hydrogen involved than in the case of corresponding ketones (4). A peculiar and yet unexplained feature of the photochemical reactions of ester I is that of the two competitive pathways possible, the cyclopropane product II is produced with apparent greater facility than the β,γ-isomer III (2), giving rise to a hydrogen abstractability sequence which favors a primary non-allylic to a primary allylic hydrogen, in discord with the expected order (5). In an orthogonal intermediate the non-allylic hydrogens, whose abstraction is also favored statistically, approach the carbonyl oxygen at much closer range than the allylic hydrogens; the observed preference could be accounted for by the intervention of such a common species in the formation of II and III. We wish to report here some experimental findings which provide insight into the mechanism of the photochemical reactions of α,β-unsaturated esters.

Irradiation of Ia (3.5 g.) in methanol (150 ml.) with a Hanovia 450 watt lamp and vycor filter led to results which are plotted in Fig. 1. This reaction profile corresponds to that of a typical run, the crucial feature being the induction period which precedes the attainment of a constant rate for II and which extends over part of the photoequilibration interval. These results conclusively show that II originates from Ib and that a common intermediate cannot be involved in the product determining step leading to II and III. When the cis isomer, Ib, was employed as starting material, II was formed immediately, while formation of III was delayed.

Generation of III commenced immediately when the trans isomer, Ia, was employed as starting material, but the rate of formation of III was erratic. Typical plots of the amount of III formed as a function of time revealed a fast rate at the early stages of the reaction, as shown in Fig. 1, followed by substantial or complete quenching. The quenching occurred at irregular intervals and to different degrees in runs conducted under identical conditions. Consequently, the amounts of III formed varied from as little as 2% to as much as 30-40% of product. (6)

The reaction profile in Fig. 1 demonstrates that the initial rate of formation of III is much faster, by about a factor of ten, than the ultimate rate of formation of II.

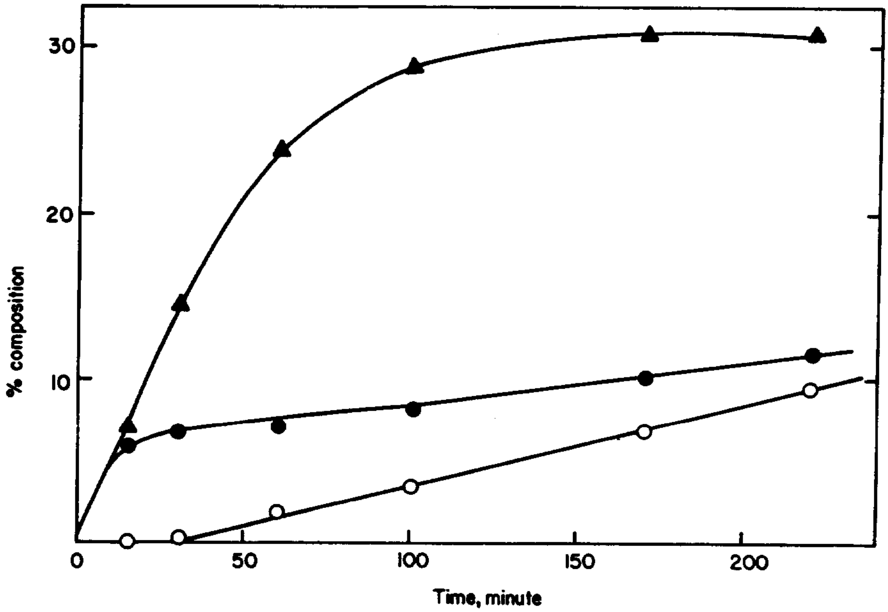

Fig. I. Photolysis of Ia
○ appearance of II, ● appearance of III ▲ photoequilibration
(% of I present as Ib)

Clearly, the loss of allylic hydrogens in Ia occurs more rapidly than that of the non-allylic hydrogens in Ib. Because of the occurrence of quenching, the final product composition is misleading as a measure of relative rates.

Photolysis of Ia in methanol-O-D gave rise to II and III which contained one deuterium of the α-carbon. This clearly establishes the intervention of the enol intermediates IV and V (Chart I) in the reaction course. Together with the demonstration of the stereospecific photochemical origins of II and III, these results conclusively define the operation of a cyclic hydrogen transfer mechanism in the photochemical reactions of I (7,8) and eliminate allylic (1,3 sigmatropic) hydrogen shifts for the formation of III and homoallylic hydrogen shifts for the origin of II from consideration. Experimental proof for a cyclic pathway in the β,γ-isomerization and cyclopropane formation reaction of α,β-unsaturated carbonyl compound has been lacking.

Attempts to photosensitize the formation of II and III with acetonaphthone, phenanthrene, benzophenone, acetophenone and acetone failed, but photointerconversion of Ia and Ib took place with the last three sensitizers, which have the highest triplet levels (9). These experiments suggest that II and III are formed from the singlet excited states of Ia and Ib, respectively. The strong sensitivity of the formation of

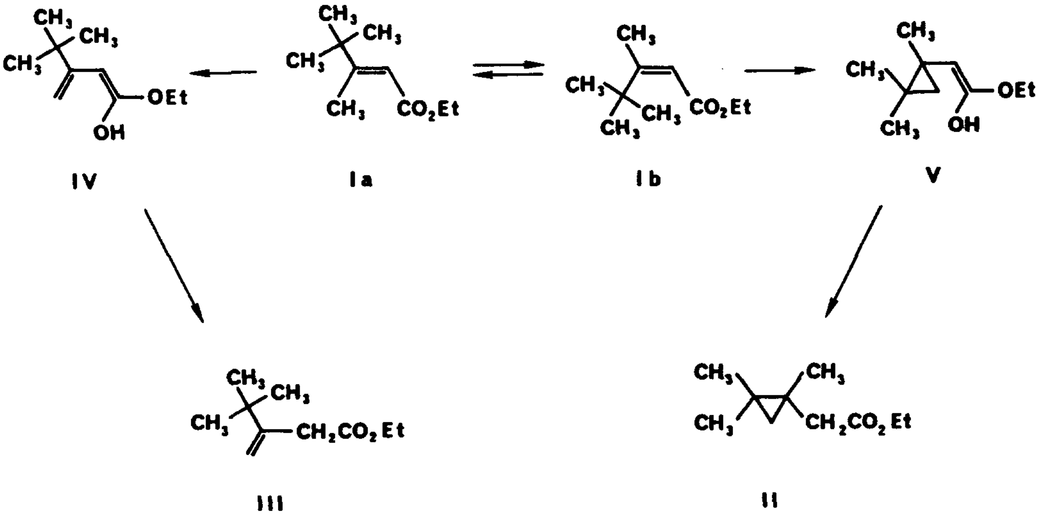

CHART I

III to solvent media (2) contrast with the unperturbed rate at which II is formed, suggesting that two different mechanisms are operative in the formation of II and III.

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References

1. Photochemistry of Unsaturated Esters V. Paper IV, M.J.Jorgenson and T.Leung, J. Am. Chem. Soc., 90, 0000 (1968).
2. M.J.Jorgenson, Chem. Comm., 7, 137 (1965).
3. Isomerizations which involve the abstraction of vinyl or cyclopropyl hydrogens in the γ-position have also been shown to occur. (Unpublished results from these laboratories.)
4. N.C.Yang and M.J.Jorgenson, Tetrahedron Letters, 19, 1203 (1964).
5. C.Walling and M.J.Gibian, J. Am. Chem. Soc., 86, 3902 (1964); A.Padwa, Tetrahedron Letters, 3465 (1964).
6. Control experiments established that quenching was not due to the presence of oxygen, Ib, II and III and that it was not eliminated by a change in reaction scale, concentration or the intensity of the light source. The causes of this phenomenon remain obscure and further studies are required for their elucidation.
7. The question of a diradical intermediate vs a concerted pathway is not debated here but will receive attention in a full publication.
8. Barltrop and Wills in independent studies have demonstrated the intervention of such a mechanism in the photochemical isomerization of ethyl crotonate to its β,γ isomer (J.A.Barltrop and J.Wills, accompanying communication).
9. The cis-trans ratios of I were strongly dependent on E_T of the sensitizer.