THE MECHANISM OF THE PHOTOISOMERISATION OF α,β-UNSATURATED ESTERS

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The photoisomerisation of α,β-unsaturated esters and acids to their β,γ-unsaturated

isomers is an efficient process which has recently become well-documented (1,2,3,4).   This

communication reports data bearing on the mechanism of the crotonate/isocrotonate/buten-3-oate

transformation:-
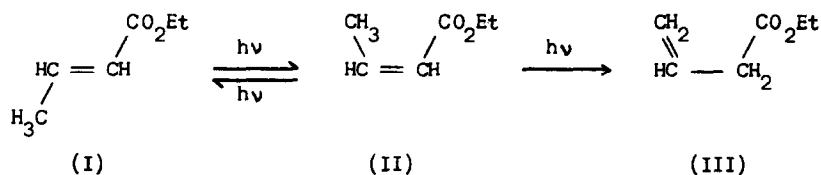
The irradiation of deoxygenated solutions of (I) in acetonitrile with u.v. ($\lambda > 210$ mμ)

led firstly to a rapid interconversion of (I) and (II) and then, after an induction period, to

a steady production of (III).   An irradiation of (II) gave similar results except that no

induction period was observable.   The initial stages of these reactions (analysed by g.l.c.)

are shown in Figs. 1 and 2.   Control experiments showed that (I) is thermally stable and (III)

is photostable under the conditions used.

These results show that it is the cis-isomer (II) which is the immediate precursor of

(III), as was proposed by Kropp & Krauss (3).

Irradiations of (I) and (II) performed in the presence of benzophenone, acetophenone

and acetone as sensitisers, under conditions where the sensitisers absorbed 95% of the light,

gave no (III) although rapid photoequilibration of (I) and (II) occurred to give photostationary

states characteristic of the sensitiser.   (Jorgenson (5) has obtained similar results with

ethyl 3,4,4-trimethylpent-2-enoate).   Rigorously deoxygenated 0.1 molar solutions of (I) in

acetonitrile, when irradiated through a pyrex filter, slowly gave (II) but no detectable
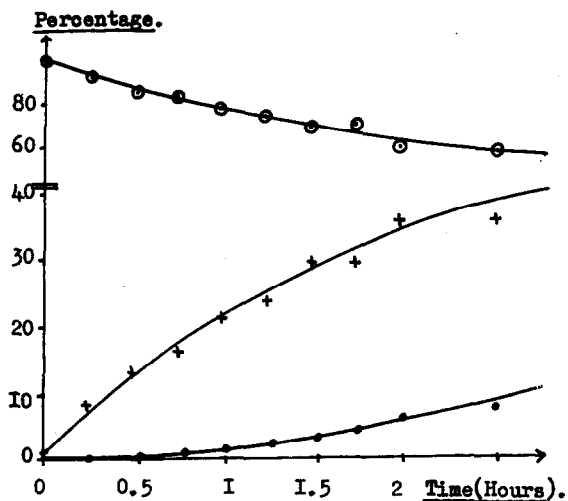
FIG.1

Photolysis of (I).

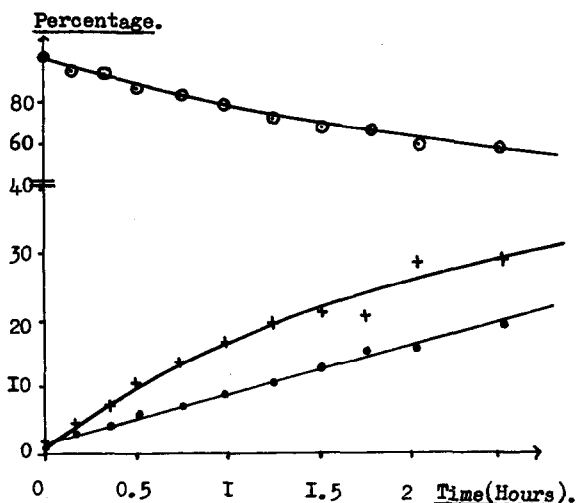⊙ Disappearance of (I).
+ Appearance of (II).
● Appearance of (III).

FIG.2

Photolysis of (II).

⊙ Disappearance of (II).
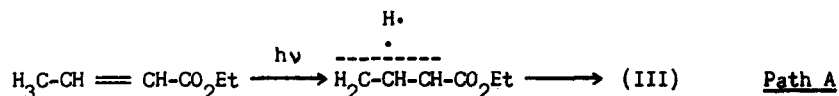+ Appearance of (I).
● Appearance of (III).

amount of (III). This interconversion was strongly inhibited by 0.002 molar piperylene. Complete quenching of the reaction failed to occur even with piperylene concentrations as high as 0.1 molar. In all these experiments > 90% of the light was absorbed by (I).

It seems then that the interconversion of (I) and (II) is chiefly a triplet state reaction and that (III) is probably derived from an excited singlet state of (II), although the possibility of reaction through a triplet state other than T_1 cannot be entirely excluded.

The u.v. absorption spectra of ethyl crotonate and isocrotonate in cyclohexane exhibit, on the long wavelength side of the intense $\pi\pi^*$-band, a shoulder ($\lambda \simeq 240$ mμ, $\varepsilon \simeq 50$-100) which is ascribed (cf 6) to a lower energy $n \rightarrow \pi^*$ transition because of its low intensity and because it is displaced to the blue by polar solvents and becomes submerged beneath the much more intense $\pi \rightarrow \pi^*$-band. The bottom excited singlet thus seems to be a $n\pi^*$ excited state and this is therefore almost certainly the entity involved in the double bond migration.

Cyclic and acyclic mechanisms for the production of the β,γ-unsaturated ester require discussion. The acyclic mechanism, exemplified by the (1,3)-sigmatropic hydrogen migration

(Path A) fails to explain the observation that it is isocrotonate and not crotonate which is the precursor.

$$H_3C-CH \equiv\!\!= CH-CO_2Et \xrightarrow[\quad]{h\nu} \overset{\overset{\text{H·}}{\overset{\bullet}{\text{---------}}}}{H_2C-CH-CH-CO_2Et} \longrightarrow (III) \qquad \underline{\text{Path A}}$$

This geometric requirement similarly eliminates acyclic <u>inter</u>molecular mechanisms involving H-migration (either as H^+, $H^{\bullet}$ or H^-).

Logic requires a cyclic mechanism and we propose Path B (7) for the following reasons:-

(IV)
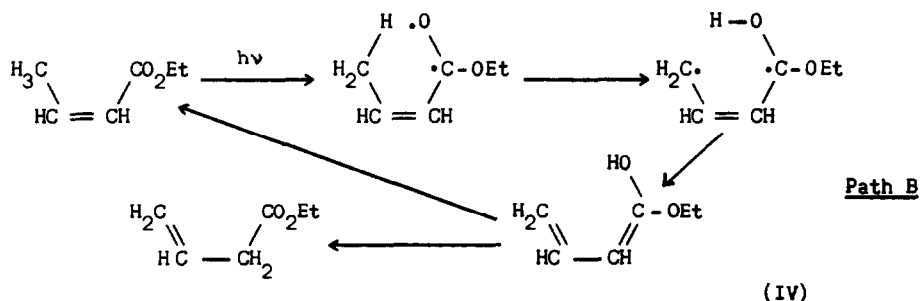
(i) It explains the geometric requirement that the ester group must be <u>cis</u> with respect to the γ-carbon atom (methyl cyclohex-1-enecarboxylate and ethyl <u>trans</u>-crotonate fail to isomerise).   (ii) Ethyl crotonate, irradiated in MeOD, gives rise to (III) containing at least 97% of one deuterium atom on the carbon atom adjacent to the ester group, an observation consistent with the participation of an enol (IV).   In this context it was observed that the rate of photoisomerisation in alcoholic solvents is about twice that in benzene, ether, or acetonitrile.   This may reflect a solvent effect <u>either</u> on the quantum efficiency of the intramolecular hydrogen-abstraction leading to (IV) <u>or</u> on the ease of ketonisation of (IV) to (III).   These points will be discussed in the full paper.

REFERENCES

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