

PHOTOCHEMISTRY OF BICYCLO[9.3.1]PENTADEC-14-ENE-13-ONE

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Recently several photochemical reactions of conjugated cyclopentenones and cyclohexenones,<sup>(1-3)</sup> in which a key step is intramolecular transfer of hydrogen to the  $\beta$ -carbon atom of the enone system, have been described.

The results described stress the controlling effect of the ring size on photochemical behaviour: both intermolecular<sup>(1)</sup> and intramolecular<sup>(2)</sup> abstractions are much less successful with cyclohexenones than with cyclopentenones.

We describe here the photochemical isomerisation of bicyclo[9.3.1]penta-14-ene-13-one (I)<sup>(4)</sup> and point out that for this cyclohexenone the photochemical process is highly specific and that the transformation observed strongly suggests that a mechanism of hydrogen transfer to the  $\beta$ -carbon of the enone system may be operative.

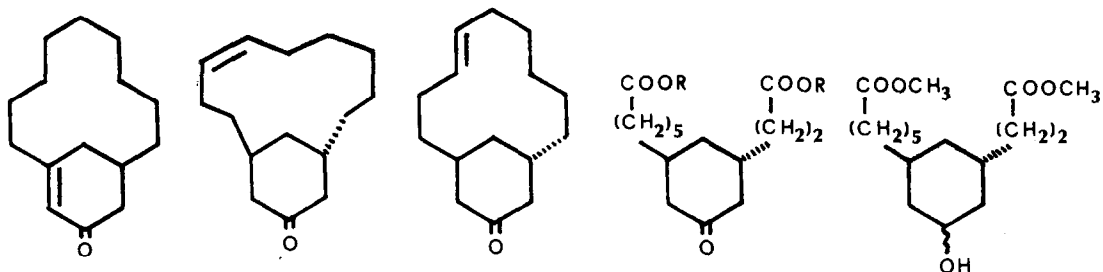
The title compound (I) (2mg/ml, benzene) was irradiated (internally, pyrex apparatus thermostated at 20°) with a 125 watt high-pressure Hg lamp, after flushing with dry nitrogen for 15 min.

The progress of the photochemical reaction was monitored by periodically withdrawing the aliquots and examining them by analytical g.c.<sup>(5)</sup>; the internal standard technique was used for quantitative experiments.

After six hours irradiation, 94% of the starting material appears to have reacted and the total amount of volatile products is 63%.<sup>(6)</sup> G.c. analysis<sup>(5)</sup> shows that the volatile fraction consists of 7% of an equimolecular mixture of three by-products, 84% of a (II) and (III) mixture (2:1 ratio) and 9% of unreacted material. Column chromatography (SiO<sub>2</sub>, n-pentane/Et<sub>2</sub>O 4:1) and fractional crystallisations from n-pentane yielded (II) and (III) in a pure state.<sup>(7)</sup> [(II), m.p. 76° from n-pentane; IR(nujol):  $\nu_{CO}$  at 1700 cm<sup>-1</sup>; PMR(CDCl<sub>3</sub>): 5.4 $\sigma$  (2H, m, olefinic protons)], [(III), b.p. 0.1 115-120°; IR(film):  $\nu_{CO}$  at 1700 cm<sup>-1</sup>,  $\nu_{-CH=CH-}$  at 980 cm<sup>-1</sup>; PMR(CDCl<sub>3</sub>): 5.45 $\sigma$  (2H, m, olefinic protons)].

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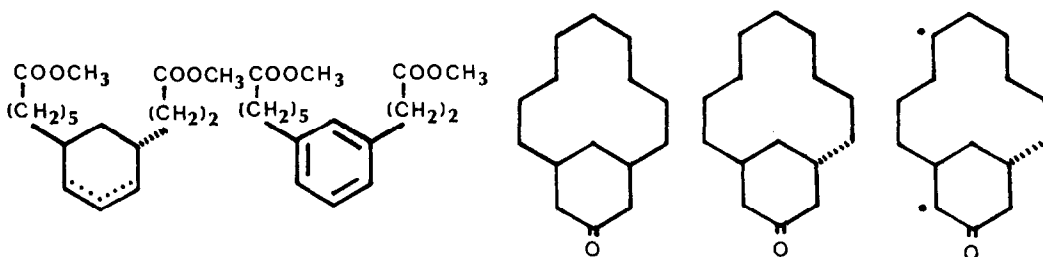
(I)

(II)

(III)

(IV) R=H

(VI)

(V) R=CH<sub>3</sub>

(VII)

(VIII)

(IX)

(X)

(XI)

Analytical and spectroscopic data indicate that both (II) and (III) arise from a transfer of unsaturation to the polymethylene chain.

The unsaturation position is the same in the two compounds: this was proved by separate ozonization of (II) and (III), reduction of the ozonide by Zn dust in AcOH and chromic-acid oxidation of the resulting dialdehyde; the same dicarboxylic acid [(IV), m.p. 111° from Et<sub>2</sub>O; IR (nujol):  $\nu_{OH}$  at 3300–2500 cm<sup>-1</sup>,  $\nu_{CO}$  at 1700 cm<sup>-1</sup>; PMR(CDCl<sub>3</sub>): 8.4 $\sigma$ (2H, bs, -COOH), 2.4 $\sigma$ (8H, m), 1.8 $\sigma$ (6H, m), 1.4 $\sigma$ (8H, m)] arises from both (II) and (III). The presence of a strong band at 980 cm<sup>-1</sup> in the IR spectrum of (III) is indicative of a trans double bond; therefore (II) is the cis isomer.

The double bond position was determined by reduction of the ketodiester [(V), o.p. 0.1 155–160°; IR(film):  $\nu_{CO}$  at 1710 and 1740 cm<sup>-1</sup>; PMR(CDCl<sub>3</sub>): 3.65 $\sigma$ (6H, s, -COOCH<sub>3</sub>), 2.3 $\sigma$ (8H, m), 1.7 $\sigma$ (6H, m), 1.3 $\sigma$ (8H, m), [from the acid (IV) with CH<sub>2</sub>N<sub>2</sub> ethereal solution] with NaBH<sub>4</sub> in THF-H<sub>2</sub>O to the corresponding alcohol [(VI), undistillable oil; IR(film):  $\nu_{OH}$  at 3410 cm<sup>-1</sup>,  $\nu_{CO}$  at 1735 cm<sup>-1</sup>; PMR(CDCl<sub>3</sub>): 3.6 $\sigma$ (6H, s, -COOCH<sub>3</sub>), 3.6 $\sigma$ (1H, m, -CHOH), 2.8 $\sigma$ (1H, s, -OH), 2.2 $\sigma$ (4H, dt, -CH<sub>2</sub>-COOCH<sub>3</sub>)]. The

cyclohexene [(VII), b.p.<sub>0.1</sub> 140-145°; IR(film):  $\nu_{\text{CO}}$  at 1735  $\text{cm}^{-1}$ ; PMR( $\text{CDCl}_3$ ) : 5.7 $\sigma$ (2H, bs, olefinic protons), 3.7 $\sigma$ (6H, s,  $-\text{COOCH}_3$ )] was obtained from (VI) by  $\text{SOCl}_2$  in pyridine. The aromatic derivative [(VIII), b.p.<sub>0.1</sub> 155-160°; IR(film):  $\nu_{\text{CO}}$  at 1730  $\text{cm}^{-1}$ , bands at 1610, 1590, 870, 795 and 705  $\text{cm}^{-1}$ ; PMR( $\text{CDCl}_3$ , 100 MHz): 7 $\sigma$ (4H, m, aromatics protons), 3.65 $\sigma$ (6H, s,  $-\text{COOCH}_3$ ), 2.93 $\sigma$ (2H, m,  $-\text{Ph}-\text{CH}_2-\text{CH}_2-\text{COOCH}_3$ ), 2.6 $\sigma$ (4H, m), 2.3 $\sigma$ (2H, m,  $-\text{Ph}-(\text{CH}_2)_4-\text{CH}_2-\text{COOCH}_3$ )] was prepared by treating (VIII) with Se at 270-300° (overall yield: 30%).

The structure of (VIII) was rigorously defined by IR, Mass and PMR data. Decoupling experiments indicate the presence of the  $-\text{Ph}-\text{CH}_2-\text{CH}_2-\text{COOCH}_3$  grouping.

The stereochemistry of the ring junction in (II) and (III) proved to be trans. Catalytic hydrogenation ( $\text{AcOCH}_3$ -Pd/C 10%) of the starting material (I) gave a mixture of the two isomers (IX) and (X) (6:4 ratio) which were separated by column chromatography ( $\text{SiO}_2$ , n-hexane/ $\text{Et}_2\text{O}$  9:1). [(IX), m.p. 79° from n-hexane; IR(nujol):  $\nu_{\text{CO}}$  at 1700  $\text{cm}^{-1}$ ], [(X), m.p. 77° from n-hexane; IR(nujol):  $\nu_{\text{CO}}$  at 1700  $\text{cm}^{-1}$ ]. Catalytic hydrogenation of both (II) and (III) led to the same dihydroderivative, identical with (X) (glc, IR and PMR spectra).

The isolation of optically active (X) by means of l-menthylazide<sup>(8)</sup>, demonstrate that the stereochemistry of the rings fusion is trans.

The results suggest that hydrogen abstraction by the  $\beta$ -carbon atom to form (XI), from which (II) and (III) arose by a second hydrogen transfer, can also play a significant role in the photochemistry of cyclonexenones.<sup>(9)</sup>

Irradiation for 10 hours of (II) (2mg/ml, benzene) in the conditions previously described for (I), gave a mixture of (II) and (III) (2:1 ratio) together with 20% of an uninvestigated non-volatile fraction; it is therefore possible that (III) is derived mainly from (II) by photochemical isomerisation.

The particular behaviour of this cyclonexenone is due to the bridged polymethylene chain which may give rise to lower ring flexibility and/or conformation control of the reaction.

The nature of the by-products is under investigation; one of these has the same glc retention time as (IX) and its percentage increase to 10% of the volatile fraction when irradiation is carried out in cyclohexane.

In a forthcoming full paper we shall describe related transformation of other types of cyclonexen-2-ones.

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