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ON THE MECHANISM OF THE PHOTOLYSIS OF STRAINED CYCLOALKANONES

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Recent review[1] on the photolysis of cycloalkanones (I) has demonstrated the formation of the photolysis products, III or IV via the intramolecular hydrogen shift of the diradical II, which arises from the α-cleavage (ring cleavage) on the side of the more highly substituted α-C-atom with respect to the carbonyl group of the cycloalkanones.

Migration of a hydrogen atom of the diradical from the position adjacent to the acyl radical to the alkyl radical-site leads to the formation of the isomeric ketene (III), and the hydrogen migration from the position adjacent to the alkyl radical to the acyl radical-site gives rise to the unsaturated aldehyde (IV) (path A).

On the other hand, the other possible mechanism on the formation of the unsaturated aldehyde has been suggested by Srinivasan[2] to be a transfer of the hydrogen atom from the β-position to the carbonyl carbon before or at the same time as the ring is broken (path B).

In this communication, we provide some interesting photolyses of strained cycloalkanones.

The relationship between the structures of the starting cycloalkanones and the resulting photolysis products are summarized in TABLE 1.

The photolyses products* have the following properties.

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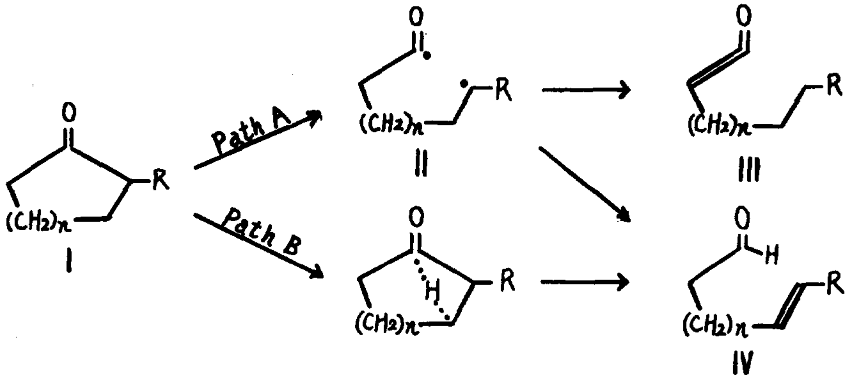
* all the new compounds described herein have the satisfactory elemental analyses.



Compound VI --- semicarbazone of VI, m.p. 179 - 180°. IR spectrum of VI, 2618, 1701 cm^{-1} (formyl group), 1639,907 cm^{-1} (disubstituted terminal methylene). Compound VIII --- IR spectrum, 1754 cm^{-1} (ester group). Compound X --- semicarbazone of X, m.p. 172 - 173°. IR spectrum of X, 2762, 1733 cm^{-1} (formyl group), 731 cm^{-1} (*cis*-disubstituted double bond). Nmr spectra of these compounds shows in TABLE 2.

Table 1 indicates that there were two different types on the rate of the photolysis of these cycloalkanones. Compounds V and IX belong to the same type and afford the unsaturated aldehyde as the main product, in which the rates of the formations of the photolysis products are faster than those of the other type, to which compounds VII and XI belong.

These differences on the rate of photolysis are illustrated with the concept of the overlapping of the 2 p_x orbital of the carbonyl group and the sp^3 orbital of the β-hydrogen located almost perpendicularly to the plane of the carbonyl group, as illustrated in FIG.1.

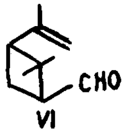
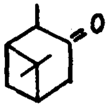
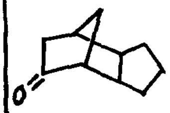
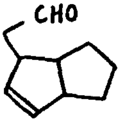
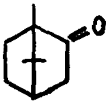
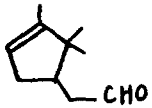
FIG. 1.

V

IX

TABLE 1

Photochemical Conversion[a] of cycloalkanones

cycloalkanone	irradiation product	irradiation time (min.)	composition[b] after irradiation (%)	
			starting ketone	irradiation product
 V[c,d]	 VI	30 60 120	56 29 7	42 68 89
 VII	 VIII	60 120 240	65 41 8	35 59 92
 IX	 X	30 60 120	52 22 0	48 78 100
 XI[c]	 XII	70 120 230	69 49 17	26 43 68

a: a solution of cycloalkanone (4 g) in methanol (600 ml) was irradiated with a 250-W high pressure mercury lamp (Taika Ind. Co.) in a quartz immersion vessel under nitrogen atmosphere.

b: Compositions of each run were estimated by gas-liquid chromatography technique.

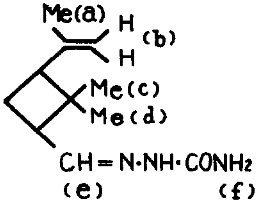
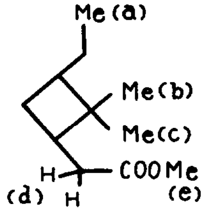
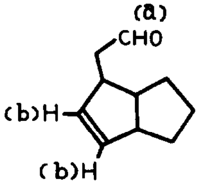
c: In the cases of Isoverbanone (V) and Camphor (XI), some unknown products were formed with relatively low yield.

d: prepared on the catalytic reduction of Verbenone.

e: UV spectrum of V, VII, IX, XI in methanol shows λ_{max} 280 mμ (ε 40.1), 288(19.6), 287(43.9), 287(35.2), respectively.

TABLE 2

Chemical Shifts* of Photolysis Products

	a	1.65	broad singlet	3H
	b	6.65	broad quartet	2H
	c	1.27	singlet	3H
	d	0.89	singlet	3H
	e	4.38	broad singlet	1H
	f	9.02	broad singlet	2H
	a	1.00	triplet	3H
	b	1.00	singlet	3H
	c	0.82	singlet	3H
	d	2.14	multiplet	2H
	e	3.58	singlet	3H
	a	9.94	triplet	1H
	b	5.65	singlet	2H

* Nmr spectra were taken in CCl_4 on a Varian A-60 spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane standard at 0 ppm.

This overlapping of the orbitals between the carbonyl and the hydrogen might accelerate the rate of the formation of the photolysis products.

From the basis of the above discussion it is reasonably expected that the intramolecular migration of the hydrogen atom from the β-position to the carbonyl occurs before or at the same time as the ring cleavage (path B) in the cases of compounds V and IX, leading to the formation of the unsaturated aldehydes.

On the other hand, the photolyses of the compounds VII and XI might proceed through the path A mechanism involving the formation of the diradical (II). The choise between (III) and (IV) as the hydrogen-transfer product depends on the steric requirements for hydrogen abstraction in the transition state. [1,3]

These observations on the photolyses products and the rates of their formation have shown the existences of at least two different pathways (A and B) on the formation of the unsaturated aldehyde by the intramolecular migration of the hydrogen.

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