

MOLECULAR PHOTOCHEMISTRY. XV. PHOTOCHEMISTRY OF
2-ISOPROPYLIDENECYCLOBUTANONES.

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Introduction

Research on the photochemistry of small ring compounds should provide a valuable probe for understanding the effects of "ring strain" on the properties of electronically excited states.⁴ We report here our results on the photochemistry of 2-isopropylidenecyclobutanones. These compounds were of considerable interest because of the generality of the unexpected photo ring expansion discovered for cyclobutanone and its derivatives.

Results

Irradiation of non-conjugated cyclobutanones^{5,6} in solution generally results in three types of reactions: (a) photodecarbonylation; (b) photocyclo-elimination and (c) photo ring expansion.

Irradiation of 1 in MeOH (or MeOD) yields 2 in 95% yield. 2 was characterized by its spectral properties (Table 1) and by its ozonolysis to 3 and hydrogenation to 5. Irradiation of 1 in pentane saturated with oxygen yields 6. Irradiation of 1 in pentane (1% soln) followed by addition of MeOH in the dark also affords 2, thus requiring the formation of an intermediate, 4.

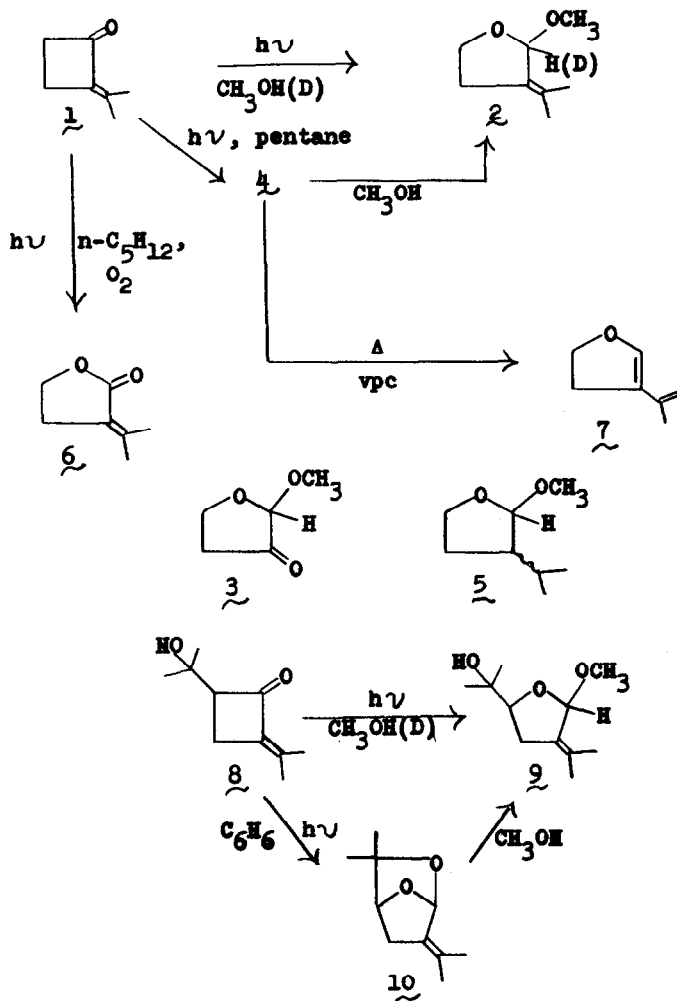
Attempts to isolate 4 by vpc lead to isolation of 7. Irradiation⁷ of 8 in MeOH (or MeOD) results in formation of 2 (95%), which was characterized by its spectral properties (Table 1). Irradiation of 8 in C₆H₆ followed by addition of MeOH in the dark results in formation of 2 (60%). Rapid work up of

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Table 1
Spectral Data for Products Derived
from the Photolyses of 1 and 8

Compound		2	9	10	6
NMR*	<p>R' = $(\text{CH}_3)_2\text{COH}$</p>	4.92 (s)	4.78 (s)	4.16 (s)	-----
		8.33 (broad s)	8.33 (broad s)	8.30, 8.39 (s)	7.82, 8.14 (s)
*TMS internal standard, τ units	R = OCH_3	7.80, 7.30 (m)	7.8 (m)	7.53 (m)	7.16 (m)
		6.10 (m)	6.05 (t)	5.90 (t)	5.81 (t)
IR*	* CCl_4 soln., cm^{-1} units	-----	8.80, 8.90 (s)	8.78, 8.91 (s)	-----
		6.78 (s)	7.02 (s)	-----	-----
Mass Spectra	* CCl_4 soln., cm^{-1} units	1635 (C=C)	3310 (OH)	1470 (CH ₃)	1748 (C=O)
		1460, 1380 (CH ₃)	1645 (C=C)	1355 (CH ₃) ³	1672 (C=C)
		1085, 1030, 975 (C-O-C)	1050 (C-O-C)	1200, 1055, 1040, 960 (C-O-C)	1439, 1366 (CH ₃) 1182, 1042, 1026 (C-O-C)
		142 (M ⁺ , 1%)	168 (M ⁺ -CH ₃ OH)	168 (M ⁺)	126 (M ⁺ , 100%)
		110 (M ⁺ -CH ₃ OH)	110 (M ⁺ -CH ₃ OH- (CH ₃) ₂ CO)	140 (M ⁺ -H ₂ O)	111 (M ⁺ -CH ₃)
				110 (M ⁺ -(CH ₃) ₂ CO)	68 (M ⁺ -C ₂ H ₂ O ₂)

the C_6H_6 photosate before methanol addition affords 10 (40%) which is quantitatively converted to 9 by addition of methanol.



Discussion

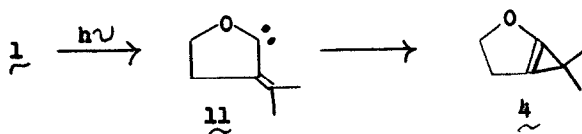
A carbene intermediate has been proposed for the photo ring expansion reaction of cyclobutanones.^{5,6} To date, external carbene traps, except for alcohols, have not been successful scavengers of this hypothetical intermediate. The results reported here appear to be the first example of an intramolecular trapping of a carbene intermediate by an OH group.

Photoprocesses (a) and (b) mentioned above apparently cannot compete ef-

ficiently with the ring expansion reaction of 2-isopropylidenecyclobutanones, in contrast to the situation for non-conjugated cyclobutanones.^{5,6}

Since a path analogous to $\underline{8} \rightarrow \underline{10} \rightarrow \underline{9}$ is unavailable for the conversion of $\underline{1} \rightarrow \underline{2}$, we were surprised to find that the irradiation of $\underline{1}$ in pentane followed by addition of MeOH in the dark results in formation of $\underline{2}$.

The structure of the intermediate $\underline{4}$ (which has proven to be too unstable to isolate to date) seems best described as an intramolecular carbene insertion product. The NMR of the crude photolysis solutions of $\underline{1}$ is also consistent with this structure.



It thus appears that the carbene intermediates of type $\underline{11}$ can be trapped with oxygen or methanol, and can also undergo intramolecular insertion reactions to yield reactive intermediates.

References

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7. Compound $\underline{8}$ is formed by treatment of $\underline{1}$ with acetone and base. $\underline{8}$ was fully characterized by its spectral properties and elemental analysis.