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MOLECULAR PHOTOCHEMISTRY. IV. SOLUTION PHOTOCHEMISTRY OF CYCLOBUTANONE AND SOME DERIVATIVES*

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Introduction

Irradiation of cyclobutanone (1) in the vapor phase results in formation of ethylene ($\Phi = 0.35$), and (presumably) ketene, carbon monoxide ($\Phi = 0.51$), cyclopropane and propylene (1,2,3,4). A minor amount ($\Phi < 0.004$) of material isomeric with cyclobutanone has been detected but not identified (3). Although available evidence is not compelling, these results may adequately be explained in terms of one primary photochemical process, i.e., an α-cleavage from the n,π* state of 1 (singlet or triplet) to yield a biradical 2 which is stabilized by decarbonylation (Eq. 1) or cycloelimination (Eq. 2).

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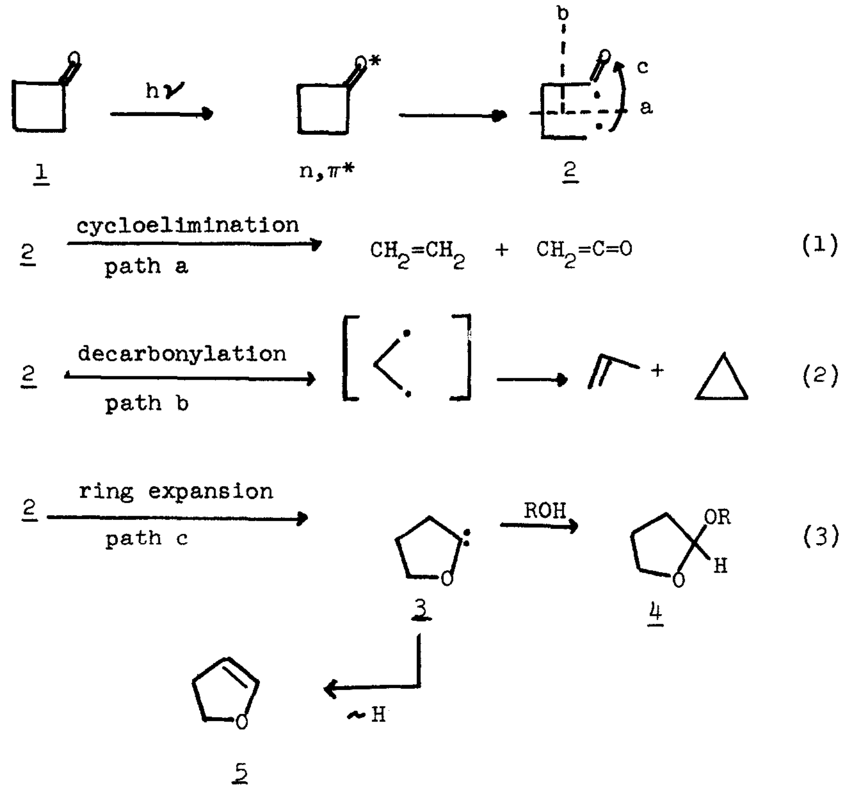
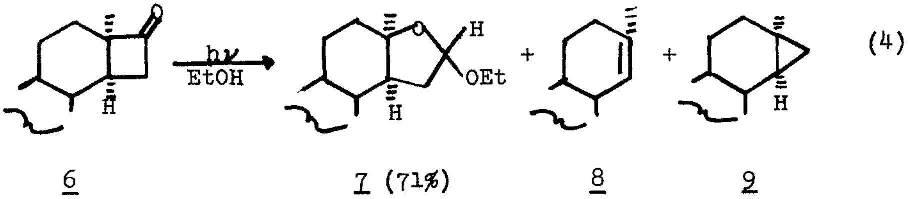
* For paper III, see N.J. Turro, et. al., J. Am. Chem. Soc., 87, 2613 (1965).

** Fellow of the Alfred P. Sloan Foundation



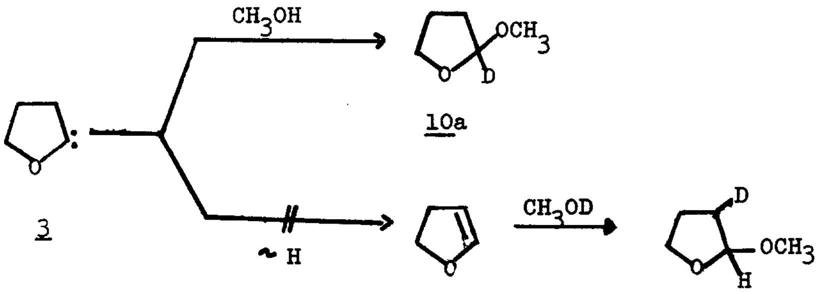
Recent reports on the photochemistry of polycyclic cis-fused cyclobutanones (5,6,7) indicate that in addition to cycloelimination and decarbonylation, a third fate of the hypothetical biradical 2 is possible, e.g., path c shown in Eq. 3. Thus, an α-ethoxy tetrahydrofuran derivative 7 is formed by a photo-ring expansion of a steroidal cyclobutanone 6, in addition to the cycloelimination and decarbonylation products 8 and 9, respectively (6).



Results

A quantitative study of the solution photochemistry of cyclobutanone and some of its derivatives is reported in Table 1. Structures of the compounds listed in Table 1 are based on comparison of NMR, IR and mass spectra with authentic samples, where possible. Some significant spectral properties of new compounds are reported in Table 2.

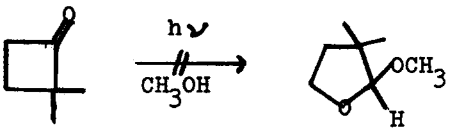
Irradiation of 1 in CH_3OD leads to nearly exclusive formation of 10a. This result indicates that an O-D insertion reaction (Eq. 5) of the presumed carbene intermediate 3 occurs, rather than a potential alternative path (Eq. 6) involving a hydrogen shift and addition of CH_3OH across a double bond.



10a (5)

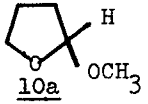
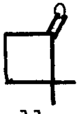
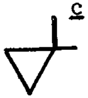
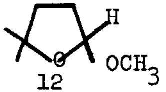
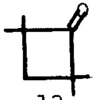
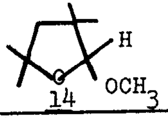
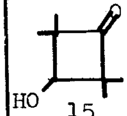
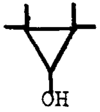
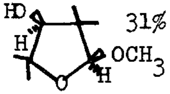
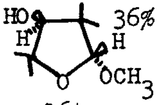
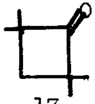
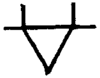
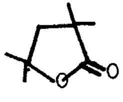
3 5 10b, NOT FORMED (6)

Irradiation of 2,2-dimethylcyclobutanone, 11, in methanol, results in the product given in Table 1 and only traces of methyl isobutyrate. The carbene derived product 12, which would result from cleavage of the less substituted bond α to the carbonyl group, could not be detected.



11 12 (7)

TABLE 1. PHOTOLYSIS OF CYCLOBUTANONES IN SOLUTION [a]

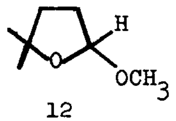
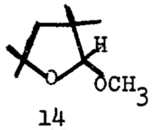
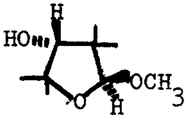
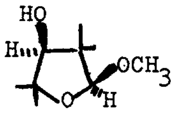
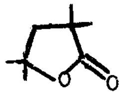
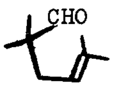
		cycloelimination	decarbonylation	ring expansion
 1	$\xrightarrow[CH_3OH]{h\nu}$	CH_2=C=O [b] 48%	 [c] -	 10a 8%
 11	$\xrightarrow[CH_3OH]{h\nu}$	CH_2=C=O [b] 32% $(CH_3)_2C=CH_2$ -	 [c] ~7%	 12 41%
 13	$\xrightarrow[CH_3OH]{h\nu}$	$(CH_3)_2C=C=O$ [b] 13% $(CH_3)_2C=CH_2$ -	 [c] 11%	 14 68%
 15	$\xrightarrow[CH_3OH]{h\nu}$	$(CH_3)_2C=C=O$ [b] 16% $(CH_3)_2CHCHO$ ~14%	 ~17%	 16c 31%  16t 36%
 17	$\xrightarrow[C_6H_6,(O_2)]{h\nu}$	$(CH_3)_2C=CH_2$ 20%	 12%	 17

(a) Hanovia 450 watt medium pressure lamp, quartz or silica equipment, 0.8M solution of Ketone

(b) Trapped and analyzed as methyl ester (vpc)

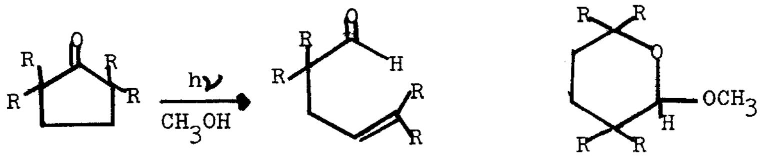
(c) Detected by vpc and analyzed by nmr

TABLE 2. SPECTRA OF NEW COMPOUNDS*

 12	NMR:	5.10τ (t.,1); 6.73τ (s.,3); 8.0τ (m.,2) 8.17τ (m.,2); 8.65τ (s.,3); 8.77τ (s.,3)
	IR:	1380-1365cm^{-1} (gem dimethyl), 1098cm^{-1}-1040cm^{-1} (C-O)
	MS:	130 (M^+, V.W.), 115 (M^+ - CH_3), 99 (M^+- CH_3O) 98 (M+- CH_3OH).
 14	NMR:	5.50τ (s.,1), 6.49τ (s.,3), 7.98τ, 8.22τ (AB, J= 12cps); 8.48τ (s.,6); 8.68τ (s.,3); 8.74τ (s.,3).
	IR:	1382cm^{-1} 1377cm^{-1}, 1364cm^{-1}, 1359cm^{-1} (gem-dimethyls) 1094cm^{-1}, 1032cm^{-1} (C-O).
	MS:	158 (M^+, V.W.), 143 (M^+ - CH_3), 127 (M^+ - CH_3O).
 16t	NMR:	5.59τ (s.,1); 6.09τ (s.,1); 6.60τ (s.,3), 7.68τ (s.,1) 8.59τ, 8.71τ, 8.83τ, 8.89τ (each a 3 proton singlet)
	IR:	3638cm^{-1}, 3465cm^{-1} (polymeric OH)
	MS:	174 (M+, V.W.); 159 (M+ - CH_3); 143 (M+ - OCH_3)
 16c	NMR:	5.48τ (s.,1), 6.50τ(overlapping 1 and 3 proton singlets); 7.64τ (s.,1); 8.45τ, 8.68τ, 8.76τ (each a 3 proton singlet).
	IR:	3572cm^{-1} (intramolecular OH)
	MS:	174 (M+, V.W.); 143 (M+ - OCH_3); 144 (M+ - CH_3OH)
 17	NMR:	7.78τ (s.,2); 8.31τ (s.,6); 8.46τ(s.,6)
	IR:	1770cm^{-1} - 1762cm^{-1} (lactone), 1382cm^{-1} - 1370cm^{-1} (gem dimethyl), 1095cm^{-1} (C-O)
	MS:	142 (M^+, V.W.), 127 (M^+- CH_3), 98 (M^+ - CO_2)
 22	NMR:	0.53τ (s.,1); 4.89τ (t.J=9cps of sps.J=1 cps,1) 7.82τ (d.,J=9 cps,2), 8.25τ (m.,3); 8.35 (m.,3); 8.95τ (s.,6).
	IR:	2700 cm^{-1}, 2800cm^{-1} (HCO) 1720cm^{-1} (C=O)

* t.=triplet; s.=singlet; m.=multiplet; v.w.=very weak; sp.=septet
NMR taken on Varian A-60 or A-60 A Spectrometer (CCl_4 solution, TMS external std)
IR on Perkin-Elmer Grating 421
MS on Hitachi -Perkin Elmer RMU-6D Mass Spectrometer

Cyclopentanone 18 and 2,2,5,5-tetramethyl cyclopentanone 21 were irradiated in methanol to determine if a ring expansion analogous to that observed for cyclobutanones occurs. In both cases, however, α-cleavage followed by intramolecular disproportionation to the unsaturated aldehydes 19 and 22 was observed. No evidence for the formation of the carbene derived products 20 (or 23) could be obtained by vapor chromatographic analysis ($<$ 1% of 20 could have been detected).



(8)

18, R=H
21, R=CH$_3$

19, R=H
22, R=CH$_3$

20, R=H
23, R=CH$_3$
NOT FORMED

Discussion

From our results and those of previous workers (5,6,7), it appears that ring expansion to produce an oxocarbene intermediate is a general primary process of cyclobutanones. This latter process and cycloelimination appears to be structurally specific, i.e., the more electron rich α bond (most highly alkyl substituted) cleaves and migrates preferentially. In addition, there is no indication that the ring expansion reaction occurs for simple cyclopentanones, although an analogous reaction of a tricyclic cyclopentanone is known (8). The results of Quinkert et. al., (6) indicate the reaction may be stereospecific. Alkyl substitution α-to the carbonyl also enhances the yield of ring expansion products relative to decarbonylation and cycloelimination (9,10).

It remains to be established whether the n,π* singlet or triplet (or both) is involved in these photoreactions and whether the effect of alkyl substitution on the product distribution is a result of different rate constants for a primary α-cleavage or different possibilities for stabilization of a biradical intermediate.

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