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PHOTOCHEMISTRY OF β,γ-UNSATURATED CARBONYL COMPOUNDS.

2,3,3-TRIMETHYL-1-PENTEN-4-ONE*

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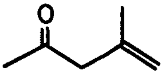
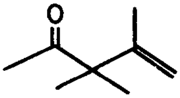
A recent report by Yang and Thap[1] on the photochemistry of isomesityl oxide [1] prompts us to communicate in preliminary form the results of photolysis of a similar compound, 2,3,3-trimethyl-1-penten-4-one [2].



[1]



[2]

The principal interest in compounds of this type derives from the possibility of activation of both the allylic C-C bond (leading to α-cleavage) and γ-C-H bonds (leading to type II fragmentation and/or cyclobutanol formation), relative to the corresponding saturated ketones:

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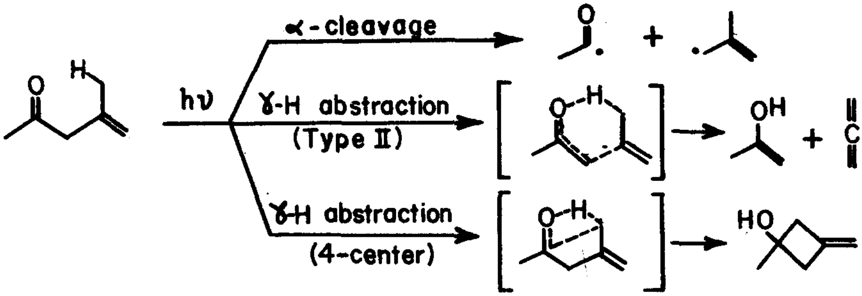
*Abstracted from the M.S. Thesis of D. A. Carlson, University of Hawaii, 1965.



We have independently investigated the photolysis of [1], but since our qualitative results merely confirm those of Yang and Thap, it seems appropriate to draw on the background provided by those authors[1] and highlight only the differences in photochemical behavior which might be expected from the introduction of a gem-dimethyl group at the 3-position. Enhancement of either type II fragmentation (whether based on increased stability of intermediates or products) or cyclization (via the Thorpe-Ingold effect) should be relatively unimportant compared to the expected acceleration of α-cleavage, in which the radical-stabilizing ability of the methyl groups is made immediately available to the excited state ketone. In fact, the marked activating influence of α-substituents in liquid-phase photodecarbonylation noted by Starr and Eastman[2] might lead one to predict that free radical α-cleavage would be the dominant, if not exclusive, photolytic pathway of compound [2].

A more interesting point of difference between ketones [1] and [2] concerns the relative symmetry of the allylic fragment formed from each by α-cleavage. Whereas the dominant process arising from such cleavage--radical recombination within the solvent cage--escapes detection in [1] because it can produce no structural change, the corresponding process in [2] should give rise to a new ketone:*

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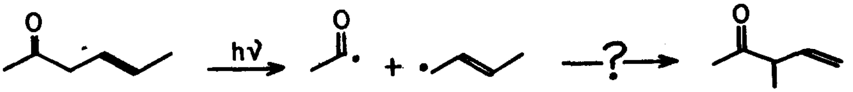
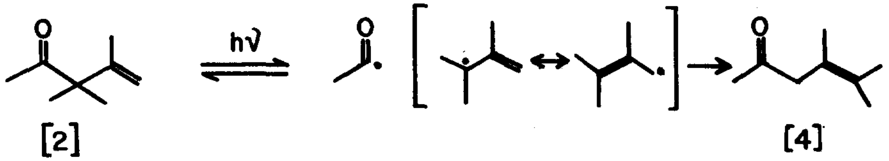
*It is interesting that Morrison[3] did not report the analogous photoisomer [i] among the photolysis products from 4-hexen-2-one:



[i]



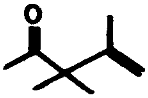
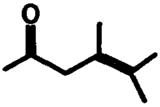
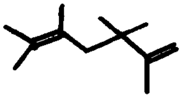
[2] [4]

Compound [2], b.p. 70° (27 mm) was prepared in 63% yield by acetylation of tetramethylethylene with acetic anhydride in the presence of zinc chloride, and was characterized by its analysis (found: C, 76.43; H, 11.22) and infrared ($\bar{\nu}_{max}$ 1707, 1660 cm^{-1}) and n.m.r. spectra: $\tau_{max}^{CCl_4}$ 8.82 (6H, singlet), 8.36 (3H, triplet), 8.05 (3H, singlet), and 5.1 (2H, multiplet). Photolysis was carried out under a wide variety of conditions, including adsorption of the ketone on silica gel during irradiation in an effort to prohibit undesired bimolecular reactions.[4] Although the reaction was considerably slower with pyrex-filtered light than in quartz vessels, no novel variations in product composition were noted over the range of liquid-phase conditions studied. Typically, a 10% solution of [2] in heptane was irradiated with a Hanovia 200-watt mercury lamp until no further significant increase in products was noted in the vapor-phase chromatogram. (About 30 minutes was required per gram of [2].) After removal of the solvent _in vacuo_, seven products were separated by preparative v.p.c. (see Table I.) The major product [3] collected as fine white needles, m.p. 26-29°, Mol. Wt. (mass spec.) 126, which had IR bands at 3340 (O-H), 1675 (C=C) and 870 cm^{-1} (C=CH$_2$). The n.m.r. spectrum permits an unequivocal structural assignment as 1,2,2-trimethyl-3-methylenecyclobutanol: $\tau_{max}^{CCl_4}$ 9.02 (3H, singlet, 8.87 (3H, singlet), 8.78 (3H, singlet), 7.56 and 7.24 (2H, AB part of an ABXY spectrum; $J_{AB} = \pm 15$ c.p.s., $J_{AX(AY)} = \pm 2.2$ c.p.s., $J_{BX(BY)} = \pm 3.0$ c.p.s.), 6.4 (variable, 1H, singlet), 5.32 and 5.23 (2H, XY part of ABXY; $J_{AX(AY)} = \pm 2.2$ Hz., $J_{BX(BY)} = \pm 3.0$ Hz., $J_{XY} \sim 0$). The assigned structure is supported by the appearance of strong mass spectral peaks at m/e 82 (P-C$_2$H$_4$O), 43 (C$_2$H$_3$O$^+$) and 111 (P-CH$_3$).

Compound [4] was similarly shown to be 2,3-dimethyl-2-hexen-5-one by its analysis (found: C, 75.79%; H, 11.09%) and IR ($\bar{\nu}_{max}$ 1707 cm^{-1}; no olefinic or hydroxyl bands) and n.m.r. spectra: $\tau_{max}^{CCl_4}$ 8.34 (6H, broadened singlet), 8.27 (3H, broadened singlet), 7.95 (3H, singlet), and 6.93 (2H, tight unresolved multiplet). Further structure proof was provided by the fact that photolysis of [4] regenerates compound [2], along with [3].

TABLE I

Products Isolated from Photolysis of 2,3,3-Trimethyl-1-penten-4-one.

Product	Retention Time[a]		Compound	% Yield[b]
	Sil.	TCEP		
[2]	8	8.0		--
[3]	7.5	11.3		55
[4]	9.5	17.2		32
[5]	9.5	18.5		8
[6]	14.5			1
[7]	16		ketone	3
[8]	19		diketone	1

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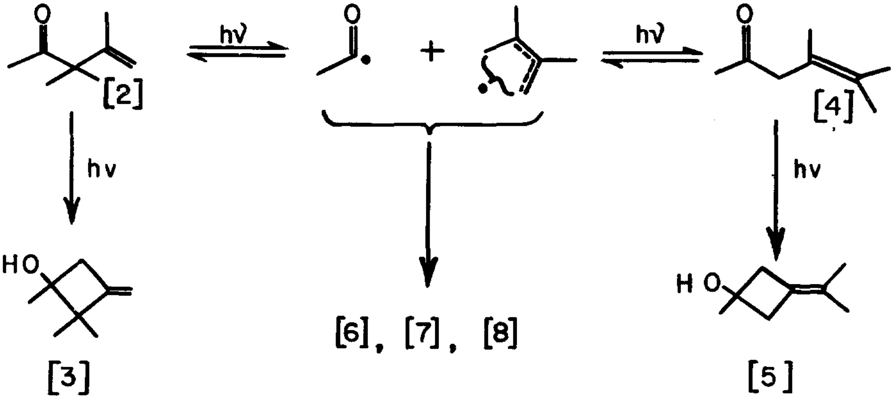
a) V.p.c. retention times in minutes. Sil. = 20' x 3/8" SE-30 silicone oil column at 150°; TCEP = 10' x 1/4" tris-cyanoethoxypropane column at 130°.

b) Based on 55% conversion to volatile products.

Compound [5] showed a hydroxyl band in the infrared ($\bar{\nu}_{max}$ 3350 cm^{-1}) and n.m.r. ($\tau^{CCl_4}_{max}$ 6.2, variable), and additional n.m.r. lines at τ 8.68 (3H, singlet), 8.47 (6H, quintet, $J_{AX} = 1$ Hz.), 7.43 (4H, A_2B_2 multiplet with additional splitting by the methyl protons), and was assigned the structure 1-methyl-3-isopropylidenecyclobutanol. As additional evidence for this assignment, [5] was found to be the major photolysis product of ketone [4]. Compounds [6], [7], and [8] were not obtained in sufficient analytical purity for conclusive identification; spectroscopic examination indicated that they are most probably bimolecular free radical products analogous to those reported by Morrison[3] and Yang.[1] Compounds with the same v.p.c. retention times are produced in similar quantities in the photolysis of [4].

In view of the results previously outlined[1] for isomesityl oxide [1], the constitutions of the above products present no major surprises, and can be most simply accounted for by the following scheme:



Supporting evidence for a solvent-cage free radical mechanism for the $[2] \longrightarrow [4]$ rearrangement was obtained from experiments in the vapor phase, in which the formation of [4] was almost entirely suppressed, and that of [3] somewhat diminished, in favor of low-boiling cleavage products. (The decreased yield of [3] follows from the reduced probability of regeneration of [2] by radical recombination.) Irradiation of [2] in cyclohexene or in the presence of radical scavengers such as iodine resulted in only a slight decrease in the [4] : [3] ratio obtained.

Perhaps the major novelty of our results lies in the unexpectedly high efficiency of cyclobutanol formation from [2]; the yields of [3] are virtually identical to that reported[1] for the corresponding cyclobutanol from [1]. Since the relative efficiency of the solvent-cage cleavage--recombination path of [1] is unknown, there is no way to determine at present whether the apparent invariance of cyclobutanol yield has theoretical significance or is the result of a fortuitous combination of conformational and electronic factors. In any case, this result is consistent with the supposition of Yang[1] that the photolysis of this class of compounds proceeds via a very short-lived-possibly singlet--excited state. Considerably more mechanistic information bearing on this point[5,6] can be obtained by examining the photochemistry of ketone [4] and another isomer, 2-isopropyl-1-penten-4-one (both of which can also give rise to cyclobutanols [3] and [5]), the results of which are still in progress.

Finally, the results reported herein also demonstrate the generality of the photoreaction of α-isopropenylketones as a proposed[1] synthetic route to methylenecyclobutanols.

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4. We thank Dr. Peter A. Leermakers for suggesting this technique prior to publication of his results. Cf. P.A. Leermakers, L.D. Weis, and H.T. Thomas, J. Am. Chem. Soc., **87**, 1620, 4403 (1965).
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