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PHOTO-INDUCED POLAR ADDITION OF PROTIC SOLVENTS TO 2-CYCLOHEPTENONE

H. Nozaki, M. Kurita and R. Noyori

Department of Industrial Chemistry, Kyôto University, Kyôto, Japan

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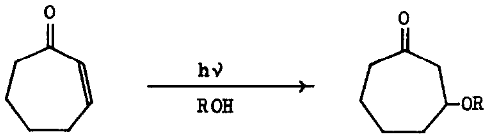
Recent publications on the detailed photochemistry of 2-cyclopentenone (1) and -hexenone (2) have prompted us to record preliminary findings on the photochemical behaviours of the next higher homologue, 2-cycloheptenone (I) in various solvents.

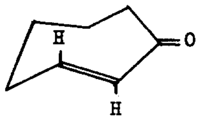
Irradiation of I in hydrocarbon solvents induces photochemical isomerization to highly strained trans-2-cycloheptenone (II) which is followed by thermal dimerization (3). Use of protic solvents has now been found to favour polar addition of the solvents at the expense of the dimerization. Preparative photoreaction was effected on 0.05 ~ 0.2 M solution of I (4) placed in a sealed quartz tube by means of 200W high-pressure mercury arc at room temperature. Products were isolated by vacuum distillation of the photolysate and subsequent GLC purification. Structural determination was made on the basis of elemental analyses and spectrometric data (Table 1). Reaction in alcoholic solvents afforded 3-alkoxycycloheptanones (III-VI). The observed fission of polar O-H bond of alcohols indicates that the reaction is ionic in nature (5). As summarized in Table 2, an increase in polarity of the alcohol enhances the formation of the addition products. This type of reaction proceeded in acetic acid as well and yielded 3-acetoxycycloheptanone (VII). Irradiation of I in aqueous acetonitrile solution gave 3-hydroxycycloheptanone (VIII), the structure being confirmed by converting to the acetate VII.

The selective introduction of oxygen functions into the β-position of the unsaturated ketone characterizes the addition reaction mentioned here, and provides synthetic utility. Similar photo-induced addition of protic solvents has been reported for certain unsaturated ketones such as 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrone (6), Pummerer's ketone (7) or 1-acetylcyclohexene (8), whereas such simpler cyclic enones as 2-cyclopentenone and 2-cyclohexenone have been reported to show no evidence of polar addition (1, 2). The reactive species involved in the polar addition might be an electronically excited enone I (8) or alternatively a strained ground molecule II (5).



I

III, R = Me VI, R = *t*-Bu
IV, R = Et VII, R = Ac
V, R = *i*-Pr VIII, R = H



II

TABLE 1

Physical Properties of Polar Addition Products

Adduct	B.p., °C/mm	IR, cm^{-1} [a] (assignment)	NMR, δ ppm from TMS [b]				
			$C(2)H_2$	C(3)H	$C(4\text{-}6)H_2$	$C(7)H_2$	Others
III	67-70/6	1700 (C=O) 1090 (COC)	2.70*m*[c]	3.45*m*	1.9-1.6*m*	2.38*m*	3.30*s* (CH_3)
IV	65-69/3	1700 (C=O) 1085 (COC)	2.65*m*[c]	3.65*m*	2.0-1.5*m*	2.40*m*	3.47*q* ($C\underline{H}_2CH_3$)[d] 1.15*t* ($CH_2C\underline{H}_3$)[d]
V	70-74/3	1700 (C=O) 1060 (COC)	2.70*m*[c]	3.85*m*	2.0-1.5*m*	2.46*m*	3.65*m* ($C\underline{H}(CH_3)_2$)[e] 1.15*d* ($CH(C\underline{H}_3)_2$)[e]
VI	105-110/10	1700 (C=O) 1050 (COC)	2.55*m*[c]	3.80*m*	1.9-1.6*m*	2.32*m*	1.16*s* ($C(CH_3)_3$)
VII	80-90/3	1740 (OC=O) 1700 (C=O) 1240 (OAc)	2.68*d*[e]	5.00*m*	1.9-1.6*m*	2.38*m*	1.97*s* (CH_3)
VIII	107-110/3	3450 (OH) 1695 (C=O) 1040 (COH)	2.70*d*[f]	4.00*m*	2.0-1.6*m*	2.45*m*	4.05*s* (OH)

[a] Neat liquid film. [b] Taken in 5-10% CCl_4 solutions. An abbreviation *s* stands for singlet, *d* for doublet, *t* for triplet, *q* for quartet, and *m* for multiplet. [c] AB part of ABX system. [d] J = 7 cps. [e] J = 6 cps. [f] J = 5 cps.

TABLE 2

Irradiation of 2-Cycloheptenone in Various Solvents [a]

Solvent	Conversion, % [b]	Yield of Product, % [c] Polar Adduct	 Dimers
Cyclohexane	77	—	88
Methyl alcohol	68	86	0
Ethyl alcohol	66	73	0
Isopropyl alcohol	54	50	18
t-Butyl alcohol	40	3	56
Acetic acid	34	23	31
Water-Acetonitrile (1:5)	61	27	18

[a] Irradiation was effected on 0.07 *M* solutions in quartz tubes (1 x 8 cm) with an external 200W high-pressure Hg arc at a distance of 1.5 cm at 26° for 10 min.

[b] Determined by GLC (Apiezon L 30% (2 m)). [c] Determined by GLC (Apiezon L 30% (2 m) or SE-30 5% (0.75 m)), and based on the consumed enone.

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