

226. Photochemical Reduction of 2-Bromo-4,4-dimethyl-2-cyclohexenone

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(16. IX, 82)

Summary

The photochemical behaviour of 2-Bromo-4,4-dimethyl-2-cyclohexenone (**1**) was studied in 2-propanol and cyclohexane. In both solvents ($n-\pi^*$)-excitation followed by intersystem crossing leads to population of a low-lying triplet (T_1) state, which can be quenched by 1,3-cyclohexadiene but does not undergo chemical transformation efficiently. ($\pi-\pi^*$)-Excitation affords 4,4-dimethyl-2-cyclohexenone (**2**) as the only product. While in 2-propanol **2** is formed in 60% from the S_2 -state and in 40% from the T_2 -state, in cyclohexane reduction occurs exclusively from this upper triplet state. The T_2 -state can also be populated *via* energy transfer using acetone or benzene as sensitizer. The mechanistic dissimilarities for the reduction of excited **1** in either 2-propanol or cyclohexane are discussed.

The photoreduction of 5-bromouracil in 2-propanol affording uracil has been investigated in some detail [1] [2], as DNA with enhanced photosensitivity is obtained when substituting thymine by 5-bromouracil in the nucleic acid. We now report results on the photoreduction of 2-bromo-4,4-dimethyl-2-cyclohexenone (**1**) in 2-propanol and cyclohexane. Compound **1** seemed us to be better suitable for clarifying mechanistic aspects of the photochemical behaviour of α -bromocycloalkenones in oxidizable solvents, as the energy gap between S_1 and S_2 for **1** is much larger than for 5-bromouracil (28 vs. 10 kcal/mol) thus facilitating selective irradiations into the ($n-\pi^*$)- or the ($\pi-\pi^*$)-absorption band. Furthermore we had already gathered mechanistic evidence on the electrochemical reduction of **1** [3] [4].

Direct irradiations of **1** were performed in 2-propanol or cyclohexane using light of $\lambda = 313$ nm ($(n-\pi^*)$ -excitation) or 254 nm ($(\pi-\pi^*)$ -excitation). Sensitized irradiations were run in a 1:2 mixture of either of the solvents and acetone ($\lambda = 313$ nm) or benzene ($\lambda = 254$ nm). In both solvents **1** is converted exclusively to 4,4-dimethyl-2-cyclohexenone (**2**), as determined by GC./MS. analysis and coinjection with an authentic sample [5]. All experiments were run in the presence of solid NaHCO_3 to trap the HBr formed. The quantum yields for these reactions are summarized in the *Table*.

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Table. *Quantum yields for the irradiation of 1* (10^{-2}M)

$\lambda_{(\text{nm})}$	Solvent	Φ_{-1}
313	2-propanol	$3 \cdot 10^{-3}$
313	C_6H_{12}	$3 \cdot 10^{-3}$
254	2-propanol	$7 \cdot 10^{-2}$
254	C_6H_{12}	$19 \cdot 10^{-2}$
313	2-propanol/acetone 1:2	$8 \cdot 10^{-2}$
313	cyclohexane/acetone 1:2	$4 \cdot 10^{-2}$
254	2-propanol/benzene 1:2	$3 \cdot 10^{-2}$
254	cyclohexane/benzene 1:2	$3 \cdot 10^{-2}$

Quenching experiments were run using 2,5-dimethyl-2,4-hexadiene as quencher for irradiations at 254 nm and 1,3-cyclohexadiene for irradiations at 313 nm. The amount of diene dimers formed in the latter reaction was compared to the one formed in a sample where **1** was replaced by acetophenone. The results of these experiments are given in *Figures 1* and *2*.

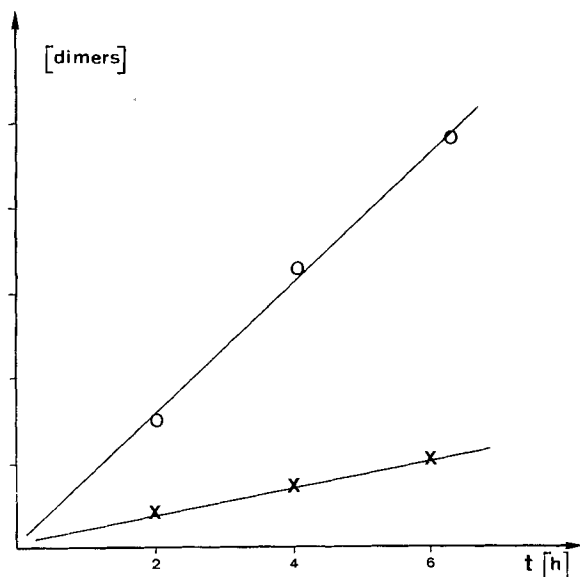


Fig. 1. Rate of formation of cyclohexadiene dimers in the irradiation (313 nm) of **1** (x) or acetophenone (o) (10^{-1}M) in benzene containing 1M 1,3-cyclohexadiene

From the UV. absorption data of **1** (*cf. Exper. Part*) and the results described above a state-energy diagram for the photoreduction of **1** (*Figure 3*) was established.

Important differences in the efficiency of photoreduction as a function of the excitation wavelength have already been noted for 2-chloro-4,4-dimethyl-2-cyclohexenone [6] and for 5-bromouracil [2]. In the latter case it was concluded that population of the S_2 -state was necessary for singlet reactivity and intersystem crossing (ISC.) to the triplet state. For **1** it is immediately apparent that ($n-\pi^*$)-

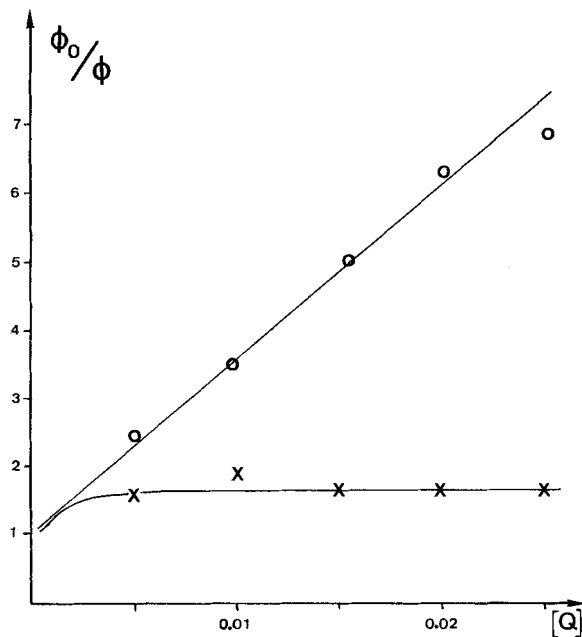


Fig. 2. Irradiation (254 nm) of **1** ($10^{-2}M$) in 2-propanol (x) and cyclohexane (o) in the presence of 2,5-dimethyl-2,4-hexadiene (Q)

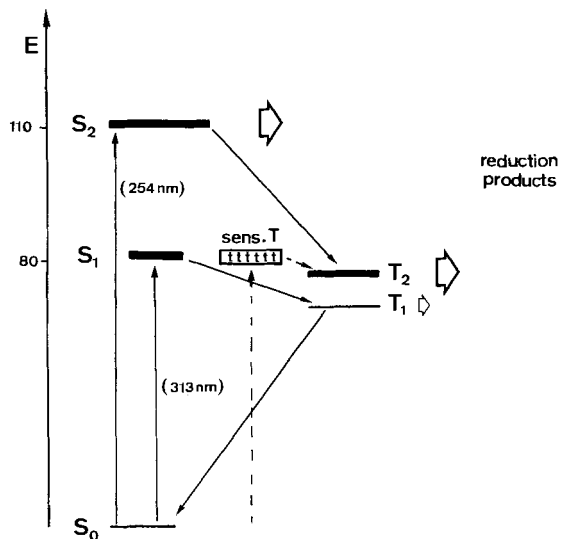


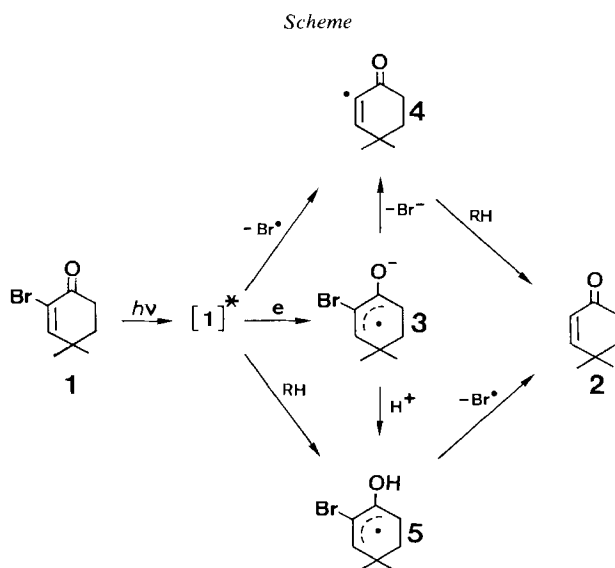
Fig. 3. State-energy diagram for the photoreduction of **1** (energies in kcal/mol)

excitation is followed by ISC. to the T_1 -state with a minimum efficiency of 20% as compared to acetophenone. Most probably this efficiency is even higher, the slower energy transfer to 1,3-cyclohexadiene from **1** being due to a lowering of k_q on steric reasons. In fact the introduction of *gem*-dimethyl groups can reduce the rate of collisional energy transfer by a factor of 3–4 [7]. The reason for the inefficient photo-reduction of **1** from this T_1 -state is very likely an effective heavy-atom accelerated ISC. back to the ground state.

The results of the sensitized irradiations demonstrate the presence of a second (higher) triplet state, from which photoreduction occurs with more than tenfold efficiency as compared to T_1 . The energy of this T_2 -state must be lower than E_T of the sensitizers (≈ 80 kcal/mol for acetone) and is probably not much lower than that of S_1 (≈ 82 kcal/mol) as it is not populated *via* ISC. from this state. Efficient population of this T_2 -state occurs *via* ISC. from S_2 . The reduction in cyclohexane proceeds exclusively from this quenchable T_2 -state while in 2-propanol 60% reaction from S_2 vs. 40% T_2 -reaction is observed (Fig. 2).

The possible mechanistic paths for the conversion of **1** to **2** are given in the *Scheme*. In the electrochemical reduction of **1** wherein the anion radical **3** is the first intermediate formed, **2** was also the only product [3] [4]. Intermediate **3** is expected to eliminate Br^- rapidly to give the vinyl radical **4**, a species also obtained by homolysis of the C, Br-bond in $[1]^*$. In the electrochemical experiment **4** is converted to **2** by an electron-transfer/protonation sequence. In the photochemical reaction **4** will afford **2** by H-atom abstraction from the solvent. The allylic radical **5** formed either by protonation of **3** or by H-atom abstraction from $[1]^*$ can give **2** by loss of bromine.

The difference in the values of the quantum yields for the $(\pi-\pi^*)$ -induced reaction of **1** in the two solvents (0.19 in cyclohexane vs. 0.07 in 2-propanol) is certainly



meaningful. In the latter solvent 60% of the reaction product stems from S_2 directly and 40% from T_2 , while in cyclohexane only T_2 is reactive (*Fig. 2*). The lower quantum yield in 2-propanol could easily be made plausible by proposing a high rate for internal conversion from S_2 to S_1 or the ground state in this solvent, as compared to cyclohexane. On the other hand rate constants for radiationless transitions from upper excited states should not be very sensitive to the solvent and therefore the reaction in 2-propanol should be as efficient or more so than in cyclohexane (two reactive states *vs.* one). An additional reaction path from S_2 in 2-propanol leading to product *and* allowing for energy dissipation would represent an alternative explanation for the dissimilarities observed. Assuming that besides homolysis occurring in both solvents ($1^* \rightarrow 4$) the key step for the photoreduction in 2-propanol would be electron transfer from the solvent ($1^* \rightarrow 3$) as opposed to H-atom in cyclohexane ($[1]^* \rightarrow 5$), it would be tempting to propose as such step the formation of an exciplex between S_2 and 2-propanol prior to electron transfer.

Financial support by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* is gratefully acknowledged

Experimental Part

Materials. Bromoenone **1** was synthesized according to [8] and purified by chromatography (SiO_2 , CH_2Cl_2). – UV. (C_6H_{12}): λ_{max} 335 nm ($\log \epsilon$ 1.60) and 250 nm ($\log \epsilon$ 3.95).

Gas chromatography was performed at 100° on 5% SE 30 or 25% Carbox 20M on chromosorb W-AW.

Photolyses. Irradiations were performed in a merry-go-round apparatus using either a 16-W low-pressure ($\lambda = 254$ nm) or a 450-W high-pressure Hg-lamp in combination with a K_2CrO_4 filter solution [9] ($\lambda = 313$ nm). Ar-degassed solutions of 10^{-4} mol **1** in 10 ml solvent (pure solvent for direct irradiations and a 1:2-mixture of the solvent and either acetone or benzene in the sensitized runs) containing 100 mg NaHCO_3 and 25 mg tetradecane as internal standard were irradiated for periods from 2–8 h.

Actinometry. Quantum yields were determined in the setting described above using a 0.1M solution of valerophenone in benzene for $\lambda = 313$ nm [10] and a 0.5M aqueous solution of chloroacetic acid for $\lambda = 254$ nm [11].

Quenching experiments were performed as above adding variable amounts of 2,5-dimethyl-2,4-hexadiene or with 10^{-1} M solutions of **1** adding a tenfold excess of 1,3-cyclohexadiene. The rate of cyclohexadiene dimerization [12] by **1** as compared to acetophenone was determined by GC.

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