

Decarbonylation of Adamantan-2-one by Two-photon Excitation with XeCl Laser

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Adamantan-2-one **1** in cyclohexane undergoes decarbonylation to give noradamantane **2** via two-photon absorption of XeCl laser light (308 nm).

Excimer lasers have been used widely in photochemistry.¹ Multi-photon excitation processes are typical features of primary processes upon irradiation of organic compounds with intense laser light. Higher excited singlet and triplet states as well as the lowest excited singlet and triplet states (S_1 and T_1 states) may be produced within the pulse (10–30 ns) of excimer lasers. Generally, these species are believed to decay rapidly to the S_1 and T_1 states within a few picoseconds. We now report the chemical behaviour of a higher excited singlet state of adamantan-2-one. This compound is exceptionally stable towards photoexcitation, though it is categorized with aliphatic ketones which readily undergo various photoreactions. This property will facilitate the elucidation of its reactivity in higher excited states.

A solution of adamantan-2-one **1** shows a typical UV spectrum for an aliphatic ketone [λ_{max} 288 nm (ϵ 19 dm³ mol⁻¹ cm⁻¹) in cyclohexane, corresponding to an n, π^* transition. A cyclohexane solution of **1** (4 cm³; 4×10^{-2} mol dm⁻³) containing adamantane (2×10^{-2} mol dm⁻³) as an internal standard was irradiated for 24 h at 254 nm [60 W low-pressure mercury lamp, UV-D33S (Toshiba) glass filter]. The solution was analysed by GC to indicate complete recovery of **1**. This was in accord with the results of Sasaki *et al.* obtained for **1** in ethanol.² On the other hand, 64% of **1** was consumed to give two products, noradamantane **2** (tricyclo[3,3,1,0^{3,7}]nonane) (isolated yield 42%) and a small amount (yield < 5%) of

2-adamantanol **3**, by irradiation at 308 nm with a XeCl excimer laser for 5 h.[†] Apparently, compound **2** was formed by the loss of the CO group.⁴

To clarify the formation of **2** via a laser-induced photoreaction, the intensity dependence of the reaction was examined for the range 40–160 mJ cm⁻² per pulse. As shown in Fig. 1, initial consumption of **1** and formation of **2** per 1000 pulses (conversion < 25%) were proportional to the square of the laser intensity. This strongly suggests that the present reaction proceeds via two-photon excitation. The formation of **2** was not affected by the presence of 7.6×10^{-2} mol dm⁻³ of biphenyl, a triplet quencher for aliphatic ketones, whose triplet energy E_T is 65 kcal mol⁻¹ ($E_T = 79$ kcal mol⁻¹ for aliphatic ketones; 1 cal = 4.184 J).[‡] This rules out incorporation of a higher triplet state formed by further excitation of the T_1 state of **1** within the pulse width. A triplet state of **1** would be quenched by biphenyl in a diffusion-controlled rate (5×10^9 dm³ mol⁻¹ s⁻¹ for cyclohexane) if it were formed.⁵ The lifetime of the S_1 state of **1** was *ca.* 9 ns,⁶ and therefore the rate for intersystem crossing will be less than 10^8 s⁻¹. The value is comparable with the quenching rate for the presence of 7.6×10^{-2} mol dm⁻³ of biphenyl and must be enough to reduce the formation of **2** via excitation of the T_1 state. Saturation of the solution with oxygen (1.2×10^{-2} mol dm⁻³) suppressed the initial formation of **2** to 70% of that under nitrogen, suggesting a stepwise two-photon excitation mechanism.[§]

Irradiation of a cyclohexane solution of **1** (4 cm³; 2×10^{-2} mol dm⁻³) at 185 nm for 15 h (30 W super low-pressure mercury lamp) gave **2** (16%) together with **3** (50%). This supports the incorporation of a higher excited singlet state of **1** as a key intermediate for the laser-induced decarbonylation of **1**. The yield of **3** was larger than that for the XeCl laser irradiation, probably owing to photochemical decomposition of the solvent. Excitation with the XeCl laser, on the other hand, avoids solvent decomposition. The low yield of **2** in both cases is in accordance with fast internal conversion to the S_1 state, which competes with the decarbonylation process.

Received, 31st May 1994; Com. 4/03215B

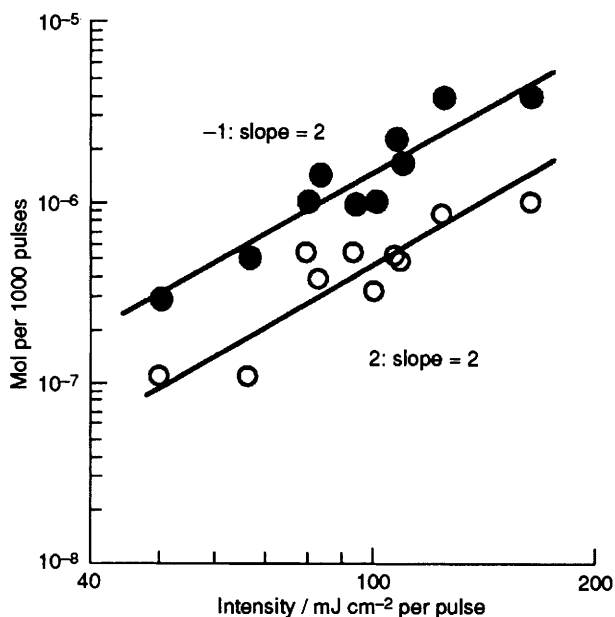
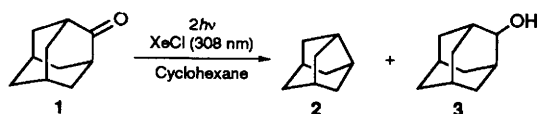


Fig. 1 Laser intensity dependence of the consumption of **1** (closed circle) and formation of **2** (open circle) at 308 nm: [**1**] = 4×10^{-2} mol dm⁻³ in nitrogen-saturated cyclohexane (4 cm³)



Scheme 1

Footnotes

[†] A 30 cm³ portion of the nitrogen-saturated cyclohexane solution containing 218 mg (1.45 mmol) of **1** was irradiated with a XeCl laser (Lumonics Hyper EX-460) with an intensity of 110 mJ cm⁻² per pulse, and a repetition rate of 10 Hz. The mixture was analysed by GC, GCMS and ¹H NMR.³ Colourless crystals (75 mg) of **2** were isolated by column chromatography on silica gel with hexane.

[‡] Singlet energy E_s of biphenyl is 100 kcal mol⁻¹,⁵ which is higher than that of **1** ($E_s = 89$ kcal mol⁻¹, estimated from the onset of its fluorescence). Fluorescence of **1** was not quenched by biphenyl.

[§] At this concentration of oxygen, the intensity of fluorescence of **1** was quenched to 60–70% of that under nitrogen. This is qualitatively in accordance with the results of the reaction, because the lifetime of the S_1 state (9 ns) is shorter than the pulse width (FWHM, 12 ns).

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