Photoreaction of Enolic 1,3-Diketones. Photoketonization and Subsequent Type II-Reaction

Michikazu Yoshioka,*[a] Hideaki Arai,[a] Keiji Ichikawa,[a] and Tadashi Hasegawa[b]

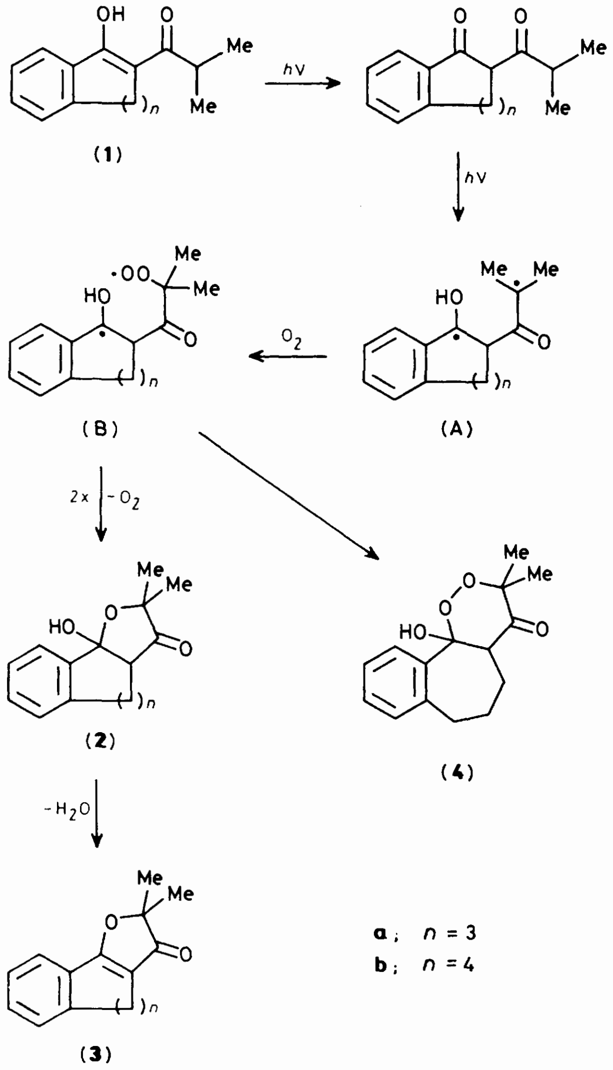
[a] *Department of Chemistry, Saitama University, Shimookubo, Urawa, Saitama 338, Japan*
[b] *Department of Chemistry, Tokyo Gakugei University, Nukuikitamachi, Koganei, Tokyo 184, Japan*

Photolysis of isobutyrylbenzocycloalkenones (**1**) under oxygen gave products arising from the reaction of the type II biradicals with oxygen.

The photochemical enol–keto interconversion of β-diketones and β-keto esters has been studied extensively.[1] U.v. irradiation of some β-dicarbonyl compounds in solution resulted in a shift of their enol–keto equilibrium to the keto form, but on cessation of the irradiation enol form was gradually restored, leading to the thermodynamic enol–keto equilibrium. We now report that the isobutyrylbenzocycloalkenones (**1a,b**), which exist completely in the enol form in solution, undergo photoketonization and that the resulting keto form undergoes a secondary photoreaction, the type II reaction, to produce biradicals which are trapped by oxygen to give oxolanones (**2a,b**), furanones (**3a,b**), and the peroxide (**4**).

Compounds (**1a,b**) were readily available *via* condensation of the corresponding benzocycloalkenones with 2-methylpropanal using methylanilinomagnesium bromide as the condensing agent, followed by oxidation of the ketols with Jones reagent. The u.v. spectra of (**1a,b**) [(**1a**): $\lambda_{max.}$ (hexane) 312 nm (log ε 4.10); (**1b**): $\lambda_{max.}$ (hexane) 305 nm (log ε 4.11)] indicated that they existed in the enol form, and their ^{13}C n.m.r. spectra showed only one carbonyl peak [(**1a**): δ 197.57; (**1b**): δ 203.42], indicating that only the enol form was present in solution.

Irradiation of (**1a,b**) in hexane under nitrogen gave an intractable mixture, but when (**1a**) was irradiated in hexane under oxygen, the oxolanone (**2a**) (m.p. 107—108 °C, 23%),



the furanone (**3a**) (m.p. 99 °C, 14%), and the peroxide (**4**) (m.p. 77—79 °C, 14%) were obtained. Irradiation of (**1b**) in hexane under oxygen gave the oxolanone (**2b**) (m.p. 159—160 °C, 8%) and the furanone (**3b**) (m.p. 98—99 °C, 12%). The structures of the photoproducts were assigned on the basis of their analytical and spectral data and chemical evidence. Deoxygenation of (**4**) using triphenylphosphine gave (**2a**) in 63% yield. Pyrolysis of (**2a, b**) at 160 °C gave (**3a,b**) quantitatively.

The formation of (**2**), (**3**), and (**4**) can be rationalised in terms of initial photoketonization and subsequent 1,5-hydrogen shift from the isobutyryl group to the C-1-carbonyl oxygen in the resulting keto isomer to give the biradical (A). The biradical (A) may interact with molecular oxygen to give the peroxyl radical (B) which may be transformed into (**2**) with generation of oxygen or may ring close to form (**4**). We have previously reported that the type II biradical from 2,4-dimethyl-1-phenylpentane-1,3-dione reacts with oxygen to give the peroxyl radical which is transformed into 2,2,4-trimethyl-5-phenylfuran-3(2*H*)-one with loss of oxygen and water.[2] The furanone (**3**) is easily formed by dehydration of (**2**).

Although it has been shown by spectroscopic analysis that β-diketones are affected by light, resulting in a shift of their enol–keto equilibrium to the keto form,[1] no example of the type II photoreaction of the resulting keto form has been reported. Since all spectral data of (**1a,b**) reveal that they completely exist in the enol form, the present observations provide chemical evidence for the photoketonization and the subsequent type II reaction of the enolic 1,3-diketones.

Received, 18th February 1988; Com. 8/00624E

References

1 P. Markov, *Chem. Soc. Rev.*, 1984, **13**, 69, and references cited therein.

2 M. Yoshioka, M. Oka, Y. Ishikawa, H. Tomita, and T. Hasegawa, *J. Chem. Soc., Chem. Commun.*, 1986, 639.