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Rapid Communication

Photochemical studies on β-ionyl hydrazone

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Direct irradiation of degassed (N_2) *n*-heptane solution of (*E*,*E*)-β-ionone hydrazone results in slow geometric isomerisation of its imine linkage whereas under non-degassed condition it is readily oxidised at both the ring double bond and the imine linkage yielding (*E*)-5,6-epoxy-β-ionone.

Keywords: β-Ionone, β-ionyl hydrazone, photoisomerisation, imine, photooxygenation

(*E*)-β-Ionone (**1**, R=H, **Figure 1**) has been the subject of numerous photochemical studies ever since the first report of its photoreaction appeared five decades ago[1]. On direct photolysis, it affords isomerisation products due to cyclisation and 1,5-hydrogen migration[2-4]. The latter product further undergoes secondary internal photocycloaddition to give a tricyclic oxetan product[3,5]. Irradiation of **1** entrapped in aqueous cyclodextrin cavities, however, has been shown to afford exclusively the product resulting from 1,5-hydrogen migration[6]. Like **1**, 4-hydroxy-β-ionone (**1a**, R=OH) also undergoes photocyclisation and 1,5-sigmatropic hydrogen shift to afford, respectively, the corresponding pyran and retro-γ-ionone[7].

Similarly, irradiation of (*E,E*)-β-ionone oxime ethyl ether **3** has been reported to afford primary photoproducts resulting from geometric isomerisation about the C=N double bond and 1,5-hydrogen shift, both reactions occurring from the excited singlet state of the oxime ether[8]. Analogous photostudy of (*E,E*)-β-ionone hydrazone **2**, however, is not recorded in the literature yet. Herein is reported the preliminary results of the photochemical investigation of **2** carried out under air and nitrogen atmosphere. A solution of **2** not purged with nitrogen undergoes a facile photooxidation at both its imine linkage and ring double bond to furnish epoxyketone **4** while the corresponding reaction under a nitrogen atmosphere apparently leads to isomerisation about its carbon-to-nitrogen double bond (**Scheme I**).

Results and Discussion

Photolysis of solution of 2 not flushed with nitrogen

Examination of the ^{1}H NMR spectra of photomixtures obtained after photolysis of solutions of hydrazone **2** in *n*-heptane, not purged with nitrogen, with 350 nm light (Rayonet lamp) for varying periods of time (0.5-6 hr) invariably showed a pair of doublets located at δ 7.03 and 6.30 whose coupling constants (*J*=15.6 Hz) rule out presence of geometric isomers about the C(7)-C(8) double bond of the substrate. Furthermore, none of the spectra contained features to suggest photoproducts due to either cyclisation or

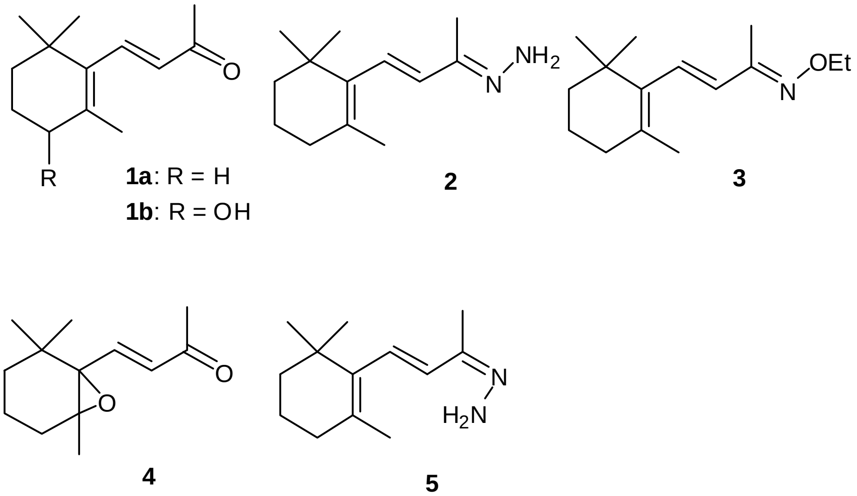
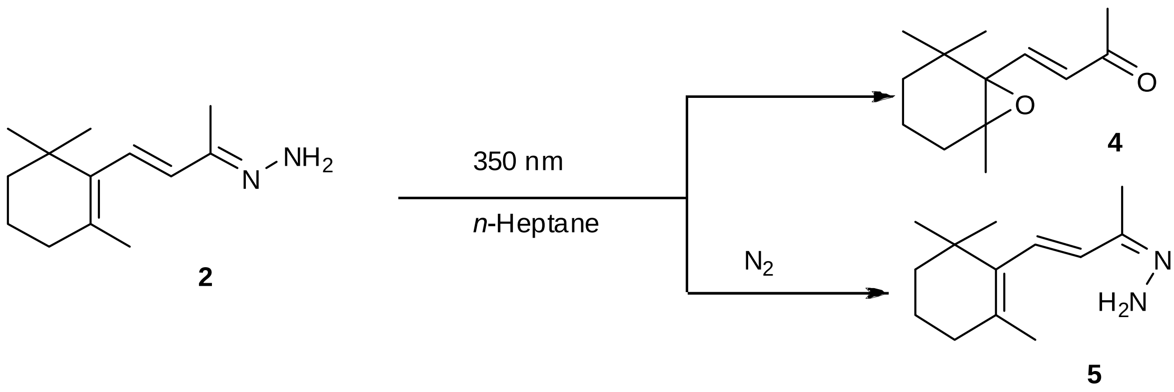


Figure 1



Scheme I

1,5-hydrogen shift, both of which are photoprocesses conventionally observed with **1**. The latter observations also hold for spectra of photomixtures obtained after photolysis of degassed solutions of the hydrazone. The ^{1}H NMR spectrum of the purified photoproduct contained, *inter alia*, a signal centered at δ 1.15(s) suggesting an upfield shift of the C-13 hydrogens relative to those in the starting material. Its ^{13}C NMR spectrum likewise featured, amongst others, pairs of absorption lines located at δ 142.87, 132.60 and 70.79, 66.06, indicative of a pair of olefinic and oxygenated carbon atoms, respectively. The electronic absorption spectrum of the compound showed λ_{max}(methanol) at 294 nm, blue shifted by 18 nm and suggesting a break in extent of conjugation of the double bonds relative to the starting material. The foregoing spectral data are consistent with identification of the photoproduct as 5,6-epoxy-β-ionone **4**, a material that was also isolated in trace amount from a condensation reaction of (*E*)-β-ionone with hydrazine hydrate. The observation that the ^{1}H NMR spectrum of a solution of the hydrazone in *n*-heptane kept in the dark for 5 hr showed no sign of the above mentioned doublets verified that the epoxidation reaction is indeed light-promoted. The involvement of the hydrazono group in promoting the photoepoxidation is inferred from the observation that the ^{1}H NMR spectrum of the photomixture obtained after irradiation under similar conditions of a solution of (*E*)-β-ionone **1** with light of λ 253.7 nm (Rayonet Hg lamp) for 1 hr showed only traces of the signals due to the doublets mentioned earlier. Furthermore, the foregoing photoreaction performed in an oxygen atmosphere in the presence of Rose Bengal in methanol as solvent did not produce **4** thus ruling out the involvement of singlet oxygen in the reaction.

Photooxidation of hydrazones into the corresponding carbonyl compounds has been known for a long time[9,10]. Bartlett and co-workers[11] have also reported on sensitized photooxidation of variously substituted aliphatic and aromatic olefins. Das and his group[12] suggested that singlet oxygen may undergo an "ene" type reaction with **1** to give a hydroperoxide or form the 5,8-peroxy derivative while 5,8-epoxy-β-ionone is reported to be a major degradation product of the reaction of **1** with molecular oxygen[13]. El-Tinay and Chichester[14] demonstrated that the thermal reaction between molecular oxygen and β-carotene resulted in selective epoxidation of the ring double bonds of the pigment, the selectivity being attributed to the higher electron density at the terminal double bond of a conjugated system. While work on the mechanistic aspects of the present photooxidation is underway, it is noteworthy that the present photochemical route offers an additional method for the preparation of **4** (refs. 15-18), which is a useful synthetic intermediate and an effective inhibitor of the tumor promoting agent phorbol diacetate[19].

Photolysis of solution of 2 under nitrogen

Thin layer chromatography (TLC) examination of a photomixture obtained after irradiation of a degassed solution of **2** for 8 hr showed a photoproduct having a lower R_f value (R_f 0.45, 5% ethyl acetate/petroleum ether) than the starting material (R_f 0.63) in the same solvent. Judging by its ^{1}H NMR spectrum, this mixture also contained no products due to photocyclisation or 1,5-sigmatropic hydrogen shift. The purified product contained a pair of doublets located at δ 6.62 and 6.27 with *J*=16.8 Hz thus showing that the *trans* stereochemistry about the C(7)-C(8) double bond of the starting material must have remained intact during the irradiation.

Overlapping with the upper field doublet is a singlet centered at δ 6.30. A prominent new resonance line appearing at δ 125.11 in the ^{13}C NMR spectrum of this photoproduct suggests that the NH_2 unit and C-8 are in a *syn* disposition about the imine linkage[20]. A pair of absorption lines at δ 159.04 and 156.07 is reflective of two imine carbon atoms of the two stereoisomers, **2** and **5**. These observations, together with its blue-shifted λ_{max}(methanol) value of 300 nm relative to that of the starting material [λ_{max} (methanol) 312 nm] favor identification of the photoproduct as (*E*,*Z*)-β-ionone hydrazone, **5**. This photoproduct proved to be quite unstable, decomposing shortly after purification. That the addition of hydrazine to β-ionone[21] did not produce compound **5** may indeed be linked to its instability.

Experimental Section

All the chemicals used in this work were procured from suppliers in Mumbai, India. ^{1}H and ^{13}C NMR spectra were recorded with a Varian VXR 400 MHz FTNMR instrument using TMS as internal standard. Mass spectra were recorded on a Micromass Q-TOF micro instrument. FTIR spectra were recorded with Nicolet Impact-400 series spectrophotometer. UV-Vis absorption spectra were recorded on a Shimadzu UV-160A or JASCO V-570 UV-Vis/NIR spectrophotometer. Reaction products were purified by silica gel column chromatography or by preparative thin layer chromatography.

(*E*,*E*)-β-Ionone hydrazone **2**, prepared following the reported procedure[21] showed the following physicochemical properties: m.p. 96-97°C, lit.[21] m.p. 98°C, UV-Vis (MeOH) λ_{max}/nm (ε, M^{-1} cm^{-1}) 312 (21760); IR (KBr): 3431, 3232, 2957, 2926, 2863, 2824, 2725, 1590, 1400, 1356, 1296, 1026, 971, 770, 598 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.68 (d, *J*=16.8 Hz, H-7), 6.33 (d, *J*=16.4 Hz, H-8), 2.07 (s, H-10), 2.04 (t, *J*=6.0, 6.4 Hz, H-4), 1.76 (s, H-13), 1.64, 1.48 (m, m, H-2 and H-3), 1.06 (s, H-11 and H-12); ^{13}C NMR ($CDCl_3$): δ 160.21, 137.04, 134.17, 134.08, 131.64, 39.79, 34.33, 33.33, 29.09, 21.91, 19.30, 12.94; MS: *m*/*z* (%) 207 (M^+ + H, 9), 190 (14), 176 (100)]. However, along with **2**, 5,6-epoxy-*trans*-β-ionone **4** was also isolated from the reaction mixture as a minor product.

Photolysis

Compound **2** (30 mg, 0.15 mmole) in *n*-heptane (15 mL) was irradiated at 350 nm using Rayonet Hg lamp for 0.5 hr. Purification of the photomixture over silica gel column chromatography using 5% ethyl acetate/petroleum ether afforded **4** (10 mg, 30% yield) as a brown oil.

IR ($CHCl_3$): 2960, 2934, 2868, 1697, 1677, 1626, 1460, 1362, 1254, 984 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 7.03 (d, *J*=15.6 Hz, H-7), 6.30 (d, *J*=15.6 Hz, H-8), 2.28 (s, H-10), 2.07 (t, *J*=6.0 Hz, H-4), 1.92, 1.45 (m, m, H-2 and H-3), 1.15 (s, H-13), 1.07, 0.94 (s, s, H-11 and H-12); ^{13}C NMR ($CDCl_3$): δ 197.80, 142.87, 132.60, 70.79, 66.06, 35.62, 33.70, 29.90, 29.86, 26.06, 25.99, 20.99, 17.03.

A solution of compound **2** prepared as above was flushed with nitrogen for 10 min and irradiated analogously for 8 hr. Purification with preparative TLC (silica gel GF 254, 5% ethyl acetate/petroleum ether) afforded **5** in 14% yield. The product so isolated, however, decomposed shortly afterwards.

^{1}H NMR ($CDCl_3$): δ 6.62 (d, *J*=16.8 Hz), 6.30 (s), 6.27 (d, *J*=16.8 Hz), 2.22 (s), 2.02, 1.74 (s), 1.70 (s), 1.64 (m), 1.47 (m), 1.05 (s), 1.04 (s); ^{13}C NMR ($CDCl_3$): δ 159.04, 156.07, 143.42, 137.25, 137.08, 135.88, 134.17, 133.60, 125.11.

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