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Article

Photochemistry of 1-Hydroxy-2-Indanones: an Alternative Route to Photoenols

***J.C. Netto-Ferreira*[a], *V. Wintgens*[b], *and J.C. Scaiano*[c]**

[a]Departamento de Química, Universidade Federal Rural do Rio de Janeiro,

23851-970 Rio de Janeiro - RJ, Brazil

[b]Laboratoire des Matériaux Moléculaires, C.N.R.S., Thiais, 94320, France

[c]Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

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A irradiação de 1-hidroxi-1,3-difenil-2-indanona leva à formação de dois intermediários atribuídos aos enóis (E,E e Z,E). O enol Z,E tem vida curta e seu possível modo de decaimento resulta na formação de produtos, dentre os quais a orto-benzilbenzofenona é o principal. O enol E,E tem maior estabilidade e apresenta um tempo de vida > 100μs em metanol. Seu decaimento resulta na formação de uma mistura complexa de produtos, onde 10-fenillantrona e 10-hidroxi-10-fenilantrona são os principais. A fotólise por pulso de laser da 1-hidroxi-1,3,3-trifenil-2-indanona mostra a formação de dois possíveis fotoenóis Z ($\tau = 180$ ns) e E ($\tau = 30$ μs). O modo de decaimento destes enóis é a formação de produtos, resultando numa mistura complexa.

Irradiation of 1-hydroxy-1,3-diphenyl-2-indanone (**1**) leads to the formation of two intermediates assigned to the enols (E,E and Z,E). The Z,E-enol is short lived, and its possible decay mode involves product formation from which ortho-benzylbenzophenone is the main product. The longer lived E,E-enol shows a lifetime of > 100 μs in methanol, and its decay results in the formation of a complex mixture of products, with 10-phenylanthrone and 10-hydroxy-10-phenylanthrone being the main ones. Laser flash photolysis of 1-hydroxy-1,3,3-triphenyl-2-indanone (**2**) shows the formation of the two possible photoenols Z ($\tau = 180$ ns) and E ($\tau = 30$ μs). The decay mode for these enols is product formation, resulting in a complex mixture of products.

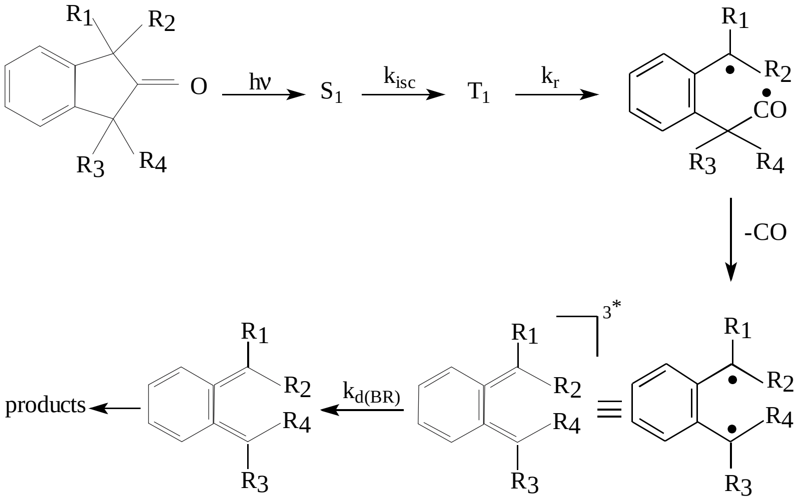
Keywords: photoenols, 1-hydroxy-2-indanones, laser flash photolysis

Introduction

The photochemical decomposition of 2-indanones has been used extensively as a source of *ortho*-xylylenes. This reaction involves the indanone triplet excited state and proceeds through a biradical formed by α-cleavage from this ketone. After loss of carbon monoxide, a second biradical is formed, which is in fact the xylylene triplet excited state. Decay of this biradical results in *ortho*-xylylene formation, which ultimately gives products through either an intra- or an intermolecular pathway (see Scheme 1)[1].

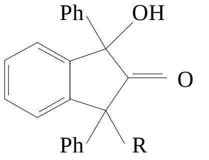
Photoenols can be regarded as hydroxy substituted *ortho*-xylylenes. They are usually formed upon photolysis of aromatic ketones containing *ortho*-alkyl groups. Thus, ketone excitation leads to a mixture of triplet excited states (due to the existence of different ground state conformers for the ketone) which then decay to a rotationally equilibrated 1,4-biradical. This biradical leads to the formation of a mixture of enols. Each component of this “enol mixture” shows very similar spectroscopic characteristics, but quite different kinetic behavior[2-4]. Alternatively, photoenols can also be formed via the thermal opening of substituted benzocyclobutenols[5].

In this paper, we show that the photolysis of hydroxy substituted 2-indanones is a very convenient route to the generation of enols. To show this we have undertaken a de-



Scheme 1.

tailed study of the dynamics of enol formation from 2-indanones having a different substitution pattern, namely 1-hydroxy-1,3-diphenyl-2-indanone (**1**) and 1-hydroxy-1,3,3-triphenyl-2-indanone (**2**).



1 - R = H
2 - R = Ph

Experimental

Materials

The solvents employed were Spectrograde or Gold Label, and were used as received. 1,3-Cyclohexadiene (Aldrich) was bulb-to-bulb distilled just before use. Sodium azide (Aldrich) was used as received.

1-Hydroxy-1,3-diphenyl-2-indanone (**1**) was synthesized in a four-step reaction. The first step involved the formation of 3-phenyl-1-indanone through a Friedel-Crafts reaction between cinnamic acid and benzene[6]. Treatment of this indanone with butylnitrite in acidic ethanol led to 2-isonitroso-3-phenyl-1-indanone[7], which was then hydrolyzed to 1,2-diketo-3-phenylindane by pyruvic acid in an acetic acid/water mixture containing hydrochloric acid. This diketone was then treated with phenylmagnesium bromide, giving **1**. Recrystallization from ethanol yielded colorless needles showing m p = 194-198 @176C (m.p.[7] = 195-200 °C). Spectral data agree well with the proposed structure for **1**.

^{1}H-NMR (200 MHz, CDCl3): δ (ppm) 7.00-7.76 (aromatic protons, 4H, m); 4.93 (CH, 1H, s); 3.08 (OH, 1H, s).

^{13}C-NMR (50.3 MHz, CDCl3): δ (ppm) 216.816 (C=O).

1-Hydroxy-1,3,3-triphenyl-2-indanone (**2**) was also synthesized in a four-step reaction[8]. A Friedel-Crafts reaction between 2,3-diphenyl-1-indanone and benzene gave 2,3,3-triphenyl-1-indanone, which in turn reacted with benzoyl chloride in chloroform/acetic acid, forming 1,1,2-triphenylbenzoyloxyindene. This benzoate was oxidized to 1,1,2-triphenyl-3-benzoyloxy-2,3-epoxy-indane by chromic anhydride in pyridine. Hydrolysis of the epoxy derivative by sodium methoxide in methanol resulted in the formation of **2**. Recrystallization from benzene-hexane yielded colorless needles showing m.p. = 158-159 °C (m.p.[8] = 157-159 °C). Spectral data agree with the proposed structure for **2**.

^{1}H-NMR (200 MHz, CDCl3): δ (ppm) 6.85-7.70 (aromatic protons, 4H, m); 3.40 (OH, 1H, s).

^{13}C-NMR (50.3 MHz, CDCl3): δ (ppm) 214.921 (C=O).

General Techniques

UV-visible spectra were recorded with a Hewlett-Packard 8451A diode array spectrometer.

GC-analyses were carried out on a Perkin-Elmer model 8320 capillary gas chromatograph employing a 12m J&W bonded phase vitreous silica BP1 silicone column. GC-MS analyses were performed on a Hewlett-Packard model 5995 system.

^{1}H- and ^{13}C-NMR spectra were recorded in a Bruker AC 200 spectrometer.

Melting points were determined in a Mel-Temp apparatus and were not corrected.

Product Studies

Typical samples were 1 mL containing 0.03 M of **1** in benzene or trifluoroethanol. The samples were contained in Pyrex tubes and deaerated by bubbling oxygen-free nitrogen. The irradiations were done in a "merry-go-round" apparatus with 9 RPR-3000 lamps. The products were analyzed by GC and GC-MS. The products were not isolated, their identification being based on their mass spectra. An authentic sample of the main product, **3**, was available for comparison.

Laser flash photolysis

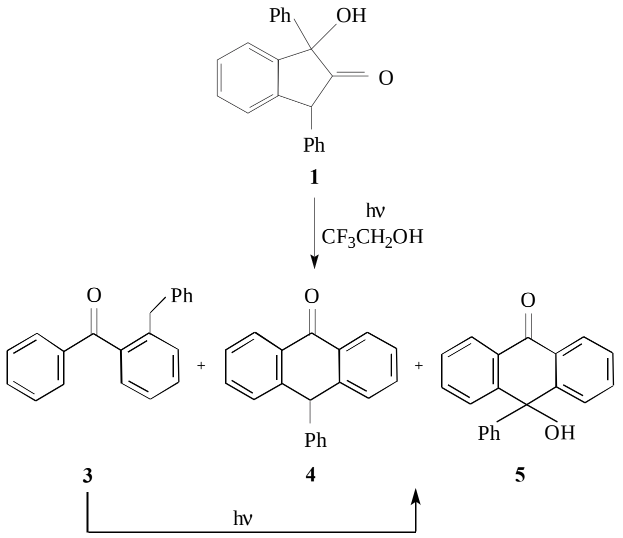
Samples (≈1 mM) were contained in a 7 x 7 mm^2 cell made of Suprasil quartz tubing, and were deaerated by bubbling oxygen-free nitrogen. The samples were irradiated with pulses (308 nm, ≈5 ns, < 20 mJ/pulse) from a Lumonics TE860-2 excimer laser. Our detection system incorporated a monochromator-photomultiplier, and the signals from the RCA-4840 photomultiplier were captured by a Tektronix 2440 transient digitizer and transferred to a Macintosh IIci computer which controlled the system and provided suitable storage and processing facilities through the use of a home-developed program using the LabVIEW-2.2 software. The system was otherwise similar to that reported elsewhere[9,10].

Results

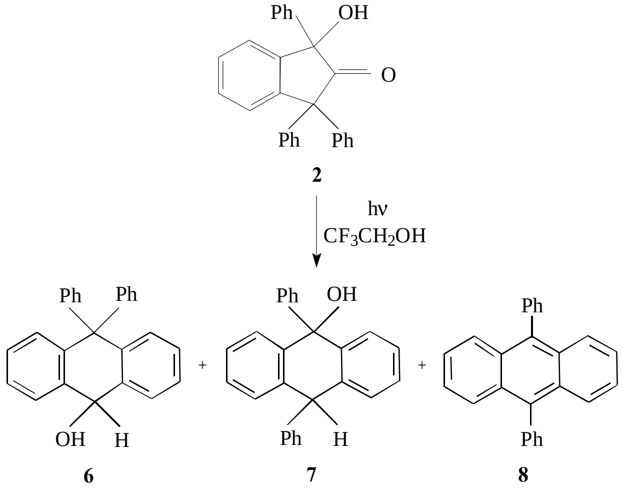
Product studies

Ketone **1** is quite stable upon irradiation in benzene. However, long term irradiation (40 h) of **1** in trifluoroethanol results in the formation of *ortho*-benzylbenzophenone (**3**) as the main product. In addition, a complex mixture of other products is formed, from which 10-phenyl-anthrone (**4**) and 10-hydroxy-10-phenylanthrone (**5**) could be identified. Product **5** is probably formed through oxygen insertion in **4**. It is important to note that the relative yield of **3** compared to **4** and **5** is dependent on irradiation time. This seems to indicate that these products are formed from further irradiation of **3** (Scheme 2). Independent studies of the photochemistry of *ortho*-benzylbenzophenone (**3**) show that **4** and **5** are the main products[11].

The hydroxyindanone **2** shows similar photochemical behavior, being almost unreactive in benzene but forming several products when the reaction is conducted in trifluoroethanol. The main product was identified as 9,9-diphenyl-10-hydroxy-9,10-dihydroanthracene (**6**) and accounts for close to 50% of the total product formation. Two minor products were identified as 9,10-diphenyl-9-hydroxy-9,10-dihydroanthracene (**7**) and 9,10-diphenylanthracene (**8**) (Scheme 3). Surprisingly, we did not obtain any evidence for the formation of *ortho*-diphenylmethylbenzophenone.



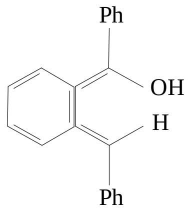
Scheme 2.



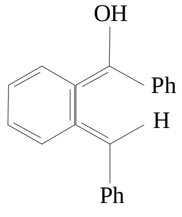
Scheme 3.

Laser flash photolysis

Laser flash photolysis of **1** in methanol led to a readily detectable transient showing maximum absorption at 330 and 435 nm (Fig. 1). The decay monitored at 435 nm showed two components; a short-lived component with a lifetime of $\tau = 2$ μs, and a long-lived species with $\tau = 100$ μs, both insensitive to oxygen. Similar results were obtained in trifluoroethanol, *i.e.*, there was a short and a long-lived component. This spectral and kinetic behavior is in agreement with the data reported for other photoenols[12,13] and we therefore assigned structures **9** and **10** to these species, corresponding to two of the possible photoenols derived from **1**, the Z,E-enol (**9**) and the E,E-enol (**10**), respectively. The same photoenols have been observed in the photochemistry of *ortho*-benzylbenzophenone (**3**)[11].



9 (*Z, E*)



10 (*E, E*)

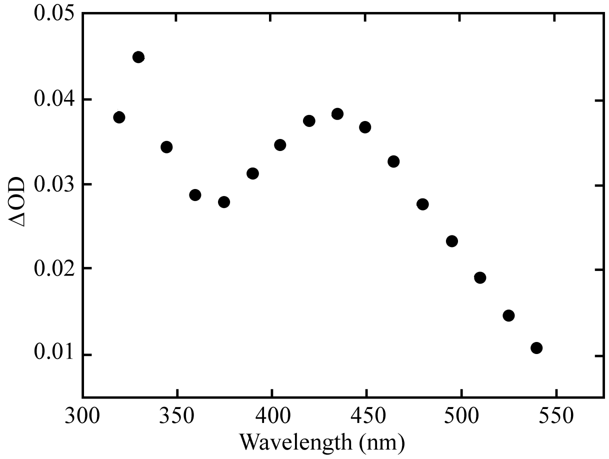
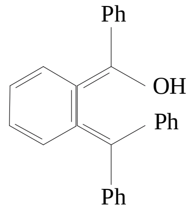


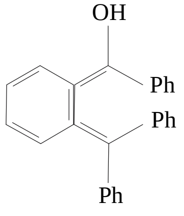
Figure 1. Transient absorption spectrum (recorded 1 μs after the laser pulse) obtained on 308 excitation of 1-hydroxy-1,3-diphenyl-2-indanone (1) in methanol (≈1 mM).

At 330 nm, in trifluoroethanol, we could observe a signal growing-in with the same kinetics as the decay for the *Z,E*-enol. This growth was attributed to product formation, *i.e. ortho*-benzylbenzophenone (**3**), which shows a significant ground state absorption in this region.

1-Hydroxy-1,3,3-triphenyl-2-indanone (**2**) showed almost identical behavior to that of **1**. Laser flash photolysis of **2** in either methanol or trifluoroethanol gave a transient with maximum absorption at 440 nm (Fig. 2) and an end absorption with λ_{max} at 320 nm. In trifluoroethanol, the decay associated with the maximum at 440 nm showed two components with lifetimes of 180 ns (300 ns in methanol) and 30 μs (50 μs in methanol), respectively, both insensitive to oxygen. These two transients were assigned to both enols derived from **2**, the *Z*-enol (**11**) and the *E*-enol (**12**).



11 (*Z*)



12 (*E*)

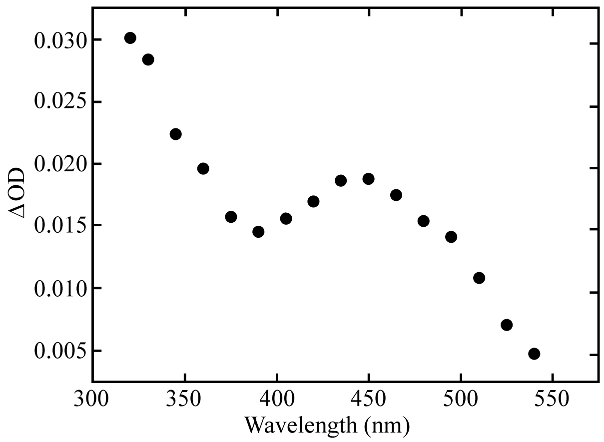
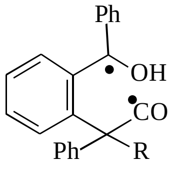


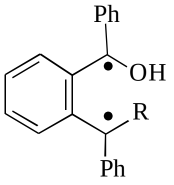
Figure 2. Transient absorption spectrum (recorded 1 μs after the laser pulse) obtained on 308 excitation of 1-hydroxy-1,3,3-triphenyl-2-indanone (2) in methanol (≈1 mM).

Laser flash photolysis experiments in benzene with both **1** and **2** did not lead to any transients that could be assigned to the corresponding enols.

Attempts to detect the biradical precursors to the enols were inconclusive. In the case of **1**, we detected a weak transient (λ_{maxx} = 330 nm) with a lifetime of ≈100 ns in trifluoroethanol. This species was quenched by oxygen. Similarly, in the case of **2**, a transient with λ_{max} at 320 nm and a lifetime of ≈40 ns was detected in methanol. Presumably these intermediates are the biradicals leading to enol formation, although it is not clear if these would be the intermediates before (**13-14**) or after (**15-16**) decarbonylation.



13 - R = H
14 - R = Ph



15 - R = H
16 - R = Ph

In order to further confirm our assignment for the enols derived from **1** and **2**, we performed some quenching experiments using bases to scavenge the long-lived photoenols[14] **10** and **12**. Using sodium azide as a quencher in trifluoroethanol, we measured the quenching rate constants of 3 x 10^7 M^{-1} s^{-1} and 8 x 10^6 M^{-1} s^{-1} for **10** and **12**, respectively.

Discussion

1-Hydroxy-2-indanones provide a method for the preparation of the same photoenols that are normally produced in the photochemistry of *ortho*-substituted benzophenones. In the case of **1**, where four different enols are possible, only two are observed (**9** and **10**). The other two (*E,Z* and *Z,Z*) are presumably too sterically hindered to be formed. The *Z,E-enol* **9** is shorter lived than **10**, due to a symmetry allowed 1,5-hydrogen shift leading to the formation of **3** as the main product. These enols are the same as those produced in the photochemistry of *ortho*-benzylbenzophenone (**3**)[11], and their involvement in the photochemistry of **3** was unequivocally demonstrated by trapping experiments with a series of dienophiles[15]. Further irradiation of **3** can give the cyclization products **4** and **5**, probably through a concerted intramolecular cycloaddition, with **5** being formed *via* an oxygen insertion into the C(10)-H bond. These same products can also be formed directly from the photoenol **10**.

Interestingly, the photolysis of **3** in benzene leads to enol detection, much as it does in polar solvents. In this case, the *E,E* -enol has a lifetime of 470 μs[11]. Therefore, if this enol was formed from **1**, it would be expected that it would be readily detectable. The fact that no enols are detected in the laser photolysis of **1** in benzene and that this molecule is relatively photostable suggest that only "reversible" photochemistry takes place. This reversibility can only occur if the dominant pathway for biradical **13** is the regeneration of **1**, rather than the decarbonylation, ultimately leading to benzophenones via the intermediacy of photoenols.

In the case of **2**, the two possible photoenols, *Z*, **11** and *E*, **12**, can be observed in laser flash experiments. Even though a fast 1,5-hydrogen shift process can again be postulated to explain why the *Z* enol **11** is shorter lived than the corresponding diphenylsubstituted one, *i.e.* **9** we were not able to observe the formation of *ortho*-diphenylmethylbenzophenone. This can be explained by assuming that this ketone is an excellent chromophore at the irradiation wavelength used and is extremely photolabile, leading to its consumption during irradiation. On the other hand, *E*-enol **12** leads to product formation, *i.e.* **6-8**, probably by an intramolecular cycloaddition reaction occurring in a concerted mode.

In conclusion, we were able to show that 1-hydroxy-2-indanones are quite efficient in forming stable photoenols, being an useful alternative method to the formation of this class of intermediates.

Acknowledgments

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