Monatshefte für Chemie 121, 85–87 (1990)

Monatshefte für Chemie
Chemical Monthly

Short Communication

Photochemical Dehydrogenation of 3-Acetyl-3,4-dihydrocoumarin

Ivan Petkov, Anka Bojilova, and **Peter Markov***

Department of Organic Chemistry, University of Sofia, Sofia 1126, Bulgaria

Summary. The ultraviolet irradiation of air-saturated alcoholic solutions of 3-acetyl-3,4-dihydrocoumarin (**1**) leads to the formation of 3-acetylcoumarin (**2**) and 3,3′-diacetyl-3,3′,4,4′-tetrahydro-4,4′-biscoumarin (**3**). The presence of molecular oxygen is an indispensable condition for the occurrence of a photodehydrogenation process, which is quantitatively when effected on silica gel.

Keywords. 3-Acetyl-3,4-dihydrocoumarin; Photochemical dehydrogenation; Coumarin derivatives; photochemical properties.

Photochemische Dehydrierung von 3-Acetyl-3,4-dihydrocumarin (Kurze Mitt.)

Zusammenfassung. Bei UV-Bestrahlung von alkoholischen Lösungen von 3-Acetyl-3,4-dihydrocumarin (**1**) unter O_2 werden 3-Acetylcumarin (**2**) und 3,3′-Diacetyl-3,3′,4,4′-biscumarin (**3**) gebildet. Die Anwesenheit von molekularem O_2 ist für die Photodehydrierung erforderlich, wobei die Umsetzung an Silikagel quantitativ verläuft.

Introduction

The photochemical behaviour of 3,4-dihydrocoumarin was studied previously [1], [2]. In primary or secondary alcohols the ultraviolet radiation initiates alcoholysis resulting in the formation of α-(2-hydroxyphenyl)propionate. A similar process occurs in the dark as well. The presence of electron-acceptor substituents at position 6 in the molecule of 3,4-dihydrocoumarin enhances the rate of phototransformation.

In the present communication the effect of the ultraviolet light on 3-acetyl-3,4-dihydrocoumarin (**1**) was studied. Data on the photochemical behaviour of 3-acetylcoumarin [3] suggest that the possibility of photoexcitation of the carbonyl group in the side chain is of primary importance.

Experimental

^1H nuclear magnetic resonance (NMR) spectra were obtained in deuterochloroform on a Bruker-250 spectrometer. Mass spectra were measured on a Jeol instrument (70 eV) and the chemical ionization was carried out with isobutane. IR spectra were recorded using a UR-20 spectrophotometer. Melting points were determined with a Büchi-510 immersion melting point apparatus and are uncorrected. Analytical thinlayer chromatography (TLC) was performed on precoated silica-gel plates (Silicagel 160) containing a fluorescent indicator. Visualization was performed on precoated silica-gel plates. All solvents used were reagent grade.

3-Acetyl-3,4-dihydrocoumarin (**1**) was synthesized by reduction of 3-acetyl coumarin with sodium borohydride according to [4]. White plates, m.p. 75–79°C; Lit. [5] 72–80°C. IR ($CHCl_3$): 1 715 (C=O, ketone), 1 770 (C=O, lactone) cm^{-1}. ^1H NMR: (ppm) = 3.28, 3.48, 2.68, 2.36.

A solution of **1** (1.0 g, 0.0052 mol) in the respective solvent (300 cm^3) was irradiated under air or argon atmosphere using a photochemical reactor equipped with a 400 W medium pressure arc lamp. The reaction was monitored by TLS.

The reaction mixture was concentrated under reduced pressure and chromatographed over silica gel (200 g "Merck") with ethylacetate/hexane with increasing polarity. Compound **2**: M.p. 120–121°C; Lit. [6] 120°C. IR ($CHCl_3$): 1 690 (C=O, ketone); 1 740 (lactone) cm^{-1}. Compound **3**: M.p. 198–199°C; Lit [3] 199°C. IR (KBr): 1 660 (conjugated ester carbonyl in the enol form); 1 690 (conjugated C=C bond in the enol form); 1 585, 1 488 (*Ar*) cm^{-1}. MS (CI): 378 (M^+).

Results and Discussion

UV irradiation (> 220 nm) of alcoholic solutions of **1** in the presence of atmospheric oxygen causes dehydrogenation resulting in the formation of 3-acetyl coumarin (**2**) and 3,3′-diacetyl-3,3′,4,4′-tetrahydro-4,4′-biscoumarin (**3**).

The influence of the type of alcohol used as a solvent as well as of the presence of oxygen in the reaction system on the ratio of the reaction products and on the quantity of unreacted starting material is illustrated by the data presented in Table 1.

Dehydrogenation of **1** does not occur in the dark. Unlike 3,4-dihydrocoumarin, the 3-acetyl derivative does not undergo photoinduced alcoholysis leading to the opening of the α-pyron ring system. The data summarized in Table 1 show that the alcoholic solvent does not influence substantially the ratio of products **2** and **3**. 3-Acetylcoumarin, however, is the sole product formed in an aprotic solvent (benzene). Photoinduced dehydrogenation of **1** does not take place in the absence of oxygen.

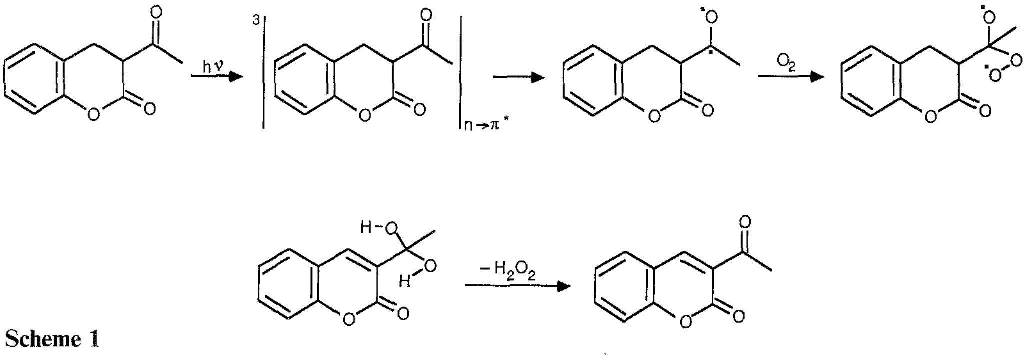
Comparison of our results and the data reported in Ref. [2] suggest that the presence of an acetyl group at position 3 of the α-pyron ring of **1** changes sub-

Table 1. Influence of the solvent on the product composition[a]

Solvent	Products (%)	
	2	**3**
i-Propanol	30	50
i-Propanol[b]	–	–
Ethanol	20	41
t-Butanol	11	44
Benzene	63	–

[a] Concentration: $5.3 \cdot 10^{-3} mol l^{-1}$, duration of UV (> 220 nm) irradiation: 6 hours

[b] In absence of oxygen



Scheme 1

stantially the photochemical behaviour of 3,4-dihydrocoumarin. Taking into account the polar mechanism assumed in Ref. [2] which is in agreement with the conclusions of other investigators (e.g. [7, 8]) it can be concluded that the electron density at carbon atom 4 is substantially reduced and an electrophilic attack leading to the intermediate formation of the respective spiroketone is unprobable.

The established possibility of photochemical dehydrogenation of 3-acetyl-3,4-dihydrocoumarin is probably due to the n → π* excited state arising from the carbonyl group in the side chain (Scheme 1).

The interaction of photoexited aliphatic ketones with molecular oxygen was proved by isotope exchange [9]. The proposed mechanism comprises the intermediate formation of a biradical **4** [10], the conformational peculiarities of which favour the formation of the unstable glycol **5**. The final product is formed as a result of elimination of hydrogen peroxide.

3,3′-Diacetyl-3,3′,4,4′-tetrahydro-4,4′-biscoumarin (**3**) arises as a result of a secondary photoreaction of 3-acetylcoumarin already formed, in accordance with the mechanism proposed in Ref. [3]. Only **3** is obtained by irradiation of an alcoholic solution of **1**, thereby proving assumption.

It is interesting to note that the photoinduced dehydrogenation of **1** if performed on silica gel is quantitative. It is known that the energy ratio of the n → π* and π → π* excited states of some ketones is changed upon excitation occurring on a silica gel surface [11, 12].

References

[1] Anderson J. C., Reese C. R. (1963) J. Chem. Soc.: 1781
[2] Gutsche C. D., Oude-Alink B. A. M. (1968) J. Amer. Chem. Soc. **90**: 5855
[3] Pfoertner K. H. (1976) Helv. Chem. Acta **59**: 834
[4] Wamnoff H., Schornand G., Korte F. (1967) Chem. Ber. **100**: 1296
[5] Dean F. M., Robertson A., Whalley W. B. (1950) J. Chem. Soc.: 895
[6] Knoevenagel E. (1898) Ber. **31**: 732
[7] Coppinger G. M., Bell E. R. (1966) J. Phys. Chem. **70**: 3479
[8] Sandner M. R., Treckler D. J. (1967) J. Amer. Chem. Soc. **89**: 5725
[9] Barltrop J. A., Coyle J. D. (1978) Excited States in Organic Chemistry (russ. ed.). Wiley, New York, p. 266
[10] Srinivasan, R. (1963) Adv. Photochemistry **1**: 89
[11] Griffiths J., Hart H. (1968) J. Amer. Chem. Soc. **90**: 3297
[12] Griffiths J., Hart H. (1968) J. Amer. Chem. Soc. **90**: 5296

Received August 14, 1989. Accepted September 29, 1989