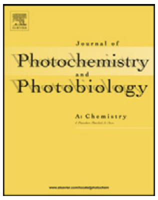
Journal of Photochemistry and Photobiology A: Chemistry 223 (2011) 189–193

Contents lists available at SciVerse ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Photooxidation of camphorquinone in polystyrene matrix

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ARTICLE INFO

Article history:
Received 18 May 2011
Received in revised form 17 August 2011
Accepted 20 August 2011
Available online 3 September 2011

Keywords:
Camphorquinone
1,2-Diketone
Polystyrene
Photooxidation

ABSTRACT

The photoreactivity of low molecular camphorquinone (**CQ**) doped in aerated polystyrene matrix was studied. Irradiation at $\lambda > 380$ nm led mainly to the insertion of one oxygen atom between the carbonyl groups of camphorquinone (**CQ**) and to the formation of camphoric anhydride (**6**). Minor products were cyclopentenecarboxylic acids (**10a**–**c**). Participation of the matrix on **CQ** photooxidation was negligible. The mechanism of photoconversion of CQ has been suggested.

1. Introduction

Camphorquinone (**CQ**) in the presence of H-atom donors is known to be an effective photoinitiator for curing acrylate- and methacrylate-based dental restorative resins [1–3]. **CQ** photochemistry has been studied extensively [4–14]. The structure of its photoproducts depends on the nature of solvent and atmosphere (Schemes 1 and 2). In oxygen-free solutions of **CQ** in benzene and carbon tetrachloride no detectable transformations occurred [4]. The photoreduction of **CQ** in isopropanol and methanol solution was studied by Monroe et al. [5,6]. The products are *endo*-3-hydroxycamphor (**1a**) and *endo*-2-hydroxyepicamphor (**1b**), plus, in methanol, adducts **2a** and **2b**. In toluene or *p*-xylene, 1:1 adducts with solvent molecules (**3a**, **3b**) are the major photoproducts; minor products are hydroxycamphors (**1a**, **1b**) and ring opening products **4a**–**d** [7–10]. In the absence of oxygen the formation of the most products can be explained by a hydrogen abstraction by excited $n \rightarrow \pi^*$ triplet state of carbonyl group of **CQ** producing two primary radicals and subsequent reactions of formed radicals.

Photoreduction (abstraction of hydrogen by excited $n \rightarrow \pi^*$ triplet state of carbonyl group of **CQ**) is the main step in the efficient curing based on the photopolymerization initiated by **CQ** in the presence of alkylamino groups [1,2]. In the presence of oxygen, aftermentioned photooxidation reactions are also important [2].

Photochemical reactions of **CQ** in the presence of molecular oxygen are much more complex and yield products whose structures depend on the specific nature of the solvent and the presence of oxygen (Scheme 2). In benzene, camphonolactone (**5a**) and campholytolactone (**5b**) are obtained in largest yield; other products are hydroxycamphors **1a** and **1b**, camphoric anhydride (**6**), camphoric diacid (**7**), and a mixture of other acids [4]. In other solvents lacking easily abstractable hydrogen atoms, such as carbon tetrachloride and *tert*-butanol, **6** is the main photoproduct [4]. In xylene the only products obtained were **6** and **7** [7]. Similarly, irradiation in cyclohexane yielded **6** and **7** [11]. An early investigation by Brett-Salvelsberg reported formation of **6** in ether solution of **CQ** exposed to sunlight [12,13]. According to Meinwald and Klingele, in methanol, the mixture of hydroxycamphors (**1a**, **1b**) and camphoric diacid monoesters (**8a**, **8b**) was formed [4]. These results markedly differ from those obtained by Gream et al. who isolated **6** and **8b** from a reaction carried out under similar condition [11]. Ji et al. published a method for the synthesis of **6** by irradiation of **CQ** in methanol, ethanol or hexane–H_2O under oxygen atmosphere in 78–85% yields [14]. In anhydrous hexane **6** was not obtained.

Except photoreduction products **1a** and **1b**, the formation of all other products probably has the common intermediate [4,11]. Camphordiacyl peroxide (**9**) (Scheme 2) formed by reaction of $n \rightarrow \pi^*$ triplet state of carbonyl group of **CQ** and molecular oxygen was presumed to be an intermediate for the formation of lactones [4].

CQ irradiated at $\lambda > 400$ nm in aerated polymer matrix does not yield a stable intramolecular diacyl peroxide (**9**) but camphoric anhydride (**6**) was found [15]. However, irradiation of PS film doped with low molecular benzil (**BZ**) at $\lambda > 400$ nm (i.e., the long wavelength edge of the $n \rightarrow \pi^*$ absorption band) led to quantitative formation of benzoyl peroxide [16,17]. Photoperoxidation of polymer bearing covalently bound benzil moieties was used for crosslinking of the polymer and was evaluated as a material for lithographic application [18–23].

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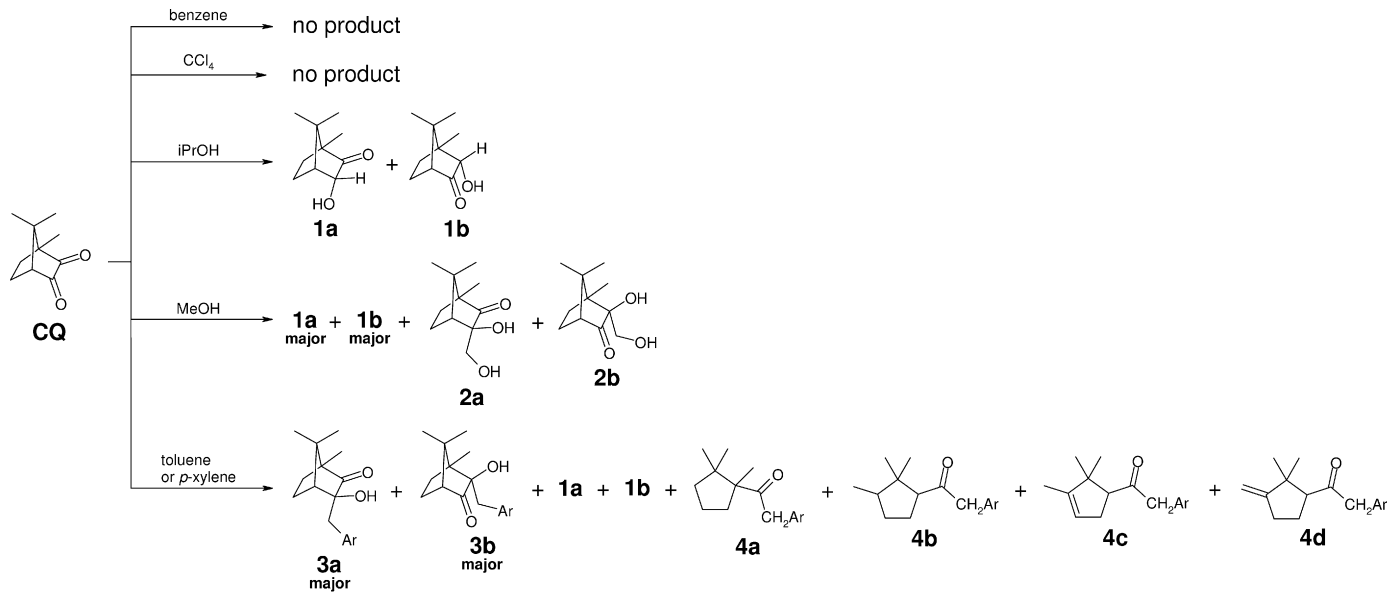
doi:10.1016/j.jphotochem.2011.08.017



Scheme 1. Photochemical reactions of **CQ** in solution under inert atmosphere.

Analogously to **BZ** structures, UV-induced crosslinking may be postulated also with other 1,2-dicarbonyl structures bound to polymer. Therefore, in following paper the polystyrene with pendant **CQ** structures was prepared and its photochemical properties were studied. To understand better the photochemical properties of **CQ** structures bound to polymer chain, prior that, the photochemical study of the low molecular **CQ** in PS was accomplished. The advantage of the low molecular **CQ** model study in comparison with **CQ** bound to polymer is the possibility to separate the products of photooxidation. Therefore, the spectral changes of PS film doped with **CQ** during photooxidation in previous work [15] were extended by the separation and identification of the products by means of NMR and combination of GC and MS in the present work. On the other hand, the elucidation of the nature of photoproducts is also of interest due to the use of **CQ** in dental materials [24].

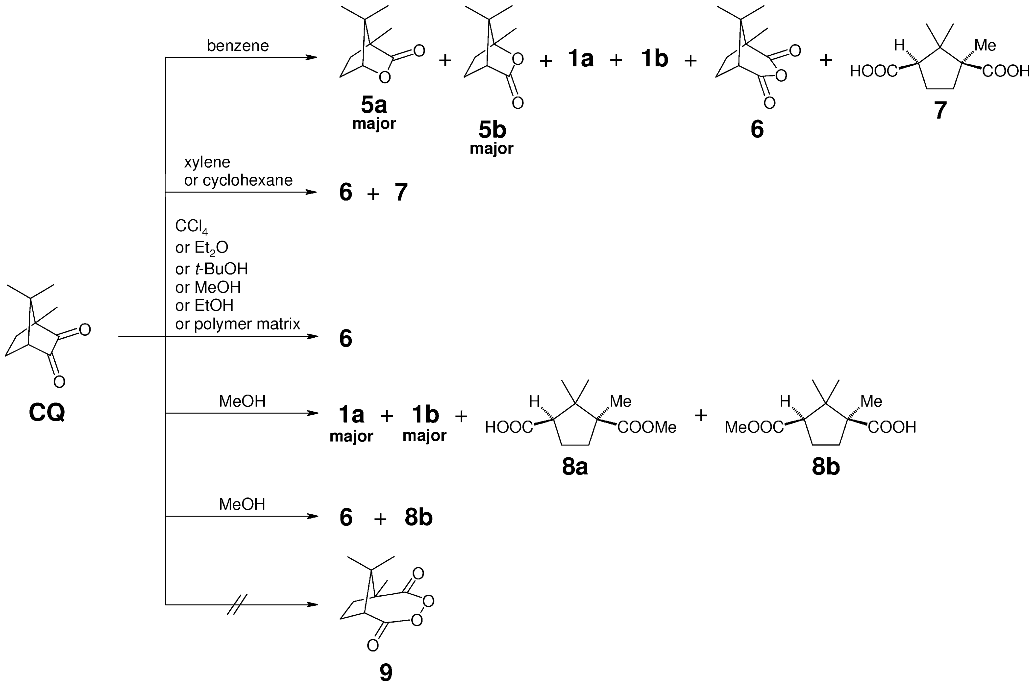
2. Materials and methods

2.1. Materials

(±)-Camphorquinone (Fluka) was used as received. (±)-Camphoric anhydride (**6**) and (±)-camphoric diacid (**7**) were synthesized according to the previously published procedure [15]. All solvents (p.a.) were redistilled before use.

2.2. Characterization

NMR spectra were measured on 600 MHz VNMRS Varian equipped with HCN ^{13}C enhanced salt tolerant cold probe in $CDCl_3$ or DMSO-d_6 at 25 °C using the solvent signal as a reference. Chemical shifts are given in the δ-scale (ppm), with coupling constants



Scheme 2. Photochemical reactions of **CQ** in solution in presence of molecular oxygen.