

## SYNTHESIS OF 6-ETHANIMIDOYL-5H-DIBENZO[a,c][7]ANNULENE-5,7(6H)-DIONE

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### ABSTRACT

A new method for synthesis of 6-ethanimidoyl-5H-dibenzo[a,c][7]annulene-5,7(6H)-dione is presented. The product is obtained from 6-acetyl-5,7-dioxo-6,7-dihydro-5H-dibenzo[a,c]-cyclohepten by applying of the Bucherer-Lieb method for synthesis of hydantoins.

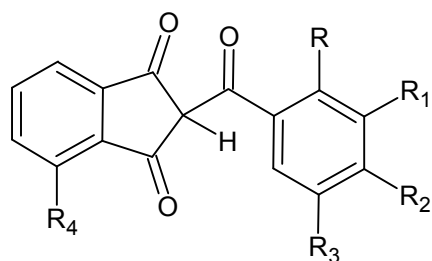
The photochemical characteristics established for the compound make potentially it a source in preparation of photoprotectors.

*Keywords: photoprotectors, 6-ethanimidoyl-5H-dibenzo[a,c][7]annulene-5,7(6H)-dione*

### INTRODUCTION

The method for synthesis of 6-acetyl-5,7-dioxo-6,7-dihydro-5H-dibenzo[a,c]-cycloheptene is developed by us and it is patented [1]. The imine is its first derivative.

There are various organic compounds which are used as UV photoprotectors [2]. p-Aminobenzoates, salicylates, cinnamates, pyrones, benzimidazoles, carbazoles, naphthosulfonates and derivatives of quinones are used for this purpose.



R, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> = H, CH<sub>3</sub>, OCH<sub>3</sub> and NO<sub>2</sub>

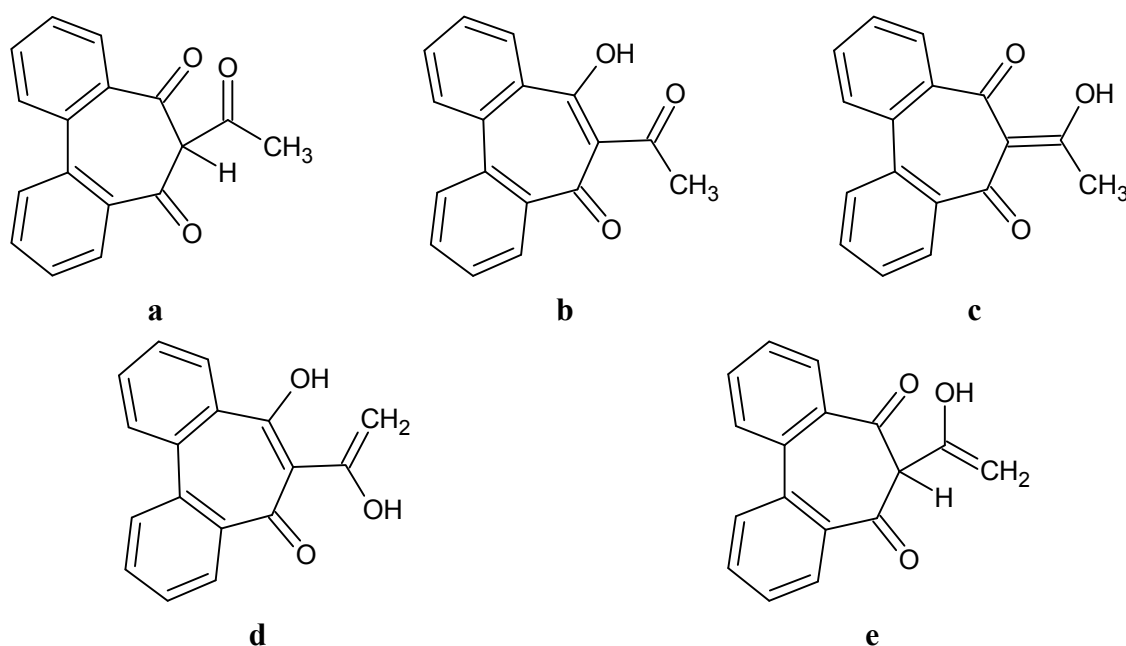
**Figure 1.** Benzoyl-1H-indene-1,3(2H)-diones.

There are 2-substituted benzoyl-1H-indene-1,3(2H)-diones (Fig. 1) which have photoprotection properties [3]. Major shortcomings of these compounds are their relatively low photostability, as well as the difficult synthesis in industrial conditions.

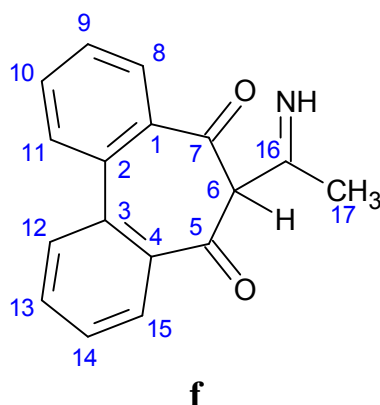
## RESULTS AND DISCUSSION

Recently we showed [4] that irradiation of solutions of 2-acetyl-1,3-indandione, leads to intramolecular proton transfer in the singlet excited state in the molecule. This fact is also observed in 6-acetyl-5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a,c*]-cycloheptene.

The structure of 6-acetyl-5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a,c*]-cycloheptene is confirmed by spectral data (IR, NMR). Quantum-chemical calculations give preference to tautomeric form **c** (Fig. 2).



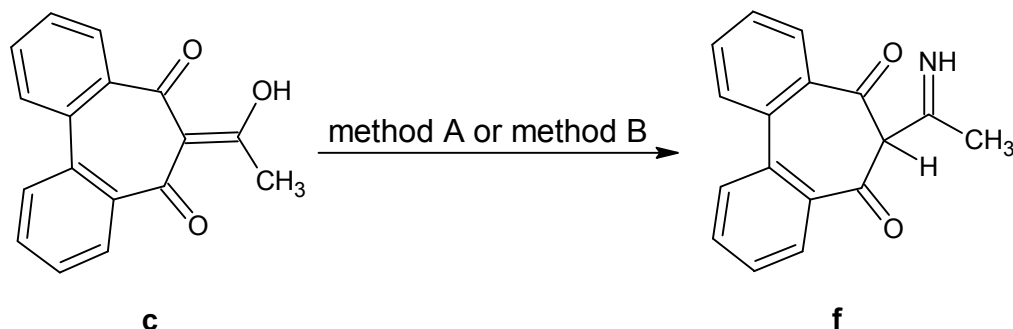
**Figure 2.** Tautomeric forms of 6-acetyl-5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a,c*]-cycloheptene.



**Figure 3.** 6-Ethanimidoyl-5*H*-dibenzo[*a,c*][7]annulene-5,7(6*H*)-dione.

Using the classical Bucherer-Lieb method for obtaining of hydantoin [5] we were able to obtain the relevant imine **f** (Fig. 3). The synthesis of the compound was conducted according to scheme 1.

The product has good photochemical stability, as well as UV absorption in the 290-335 nm range. This fact makes it suitable for preparing of photoprotectors. In this case the protective effect probably refers to photoisomerization processes, which lead to the obtaining of dissociated products with unestablished further effect. The absorption and fluorescent characteristics of the product are better than those published for 2-acetyl-1,3-indandione [6].



**Scheme 1.** Synthesis of 6-ethanimidoyl-5H-dibenzo[a,c][7]annulene-5,7(6H)-dione (**f**).

## EXPERIMENTAL

### I. Instrumentation and methods

All chemicals used are purchased from Merck and Fluka.

The melting points are determined with a Koffler apparatus.

The elemental analysis data are obtained with an automatic analyzer Carlo Erba 1106.

The purity of the compounds is checked by thin layer chromatography on Kieselgel 60 F<sub>254</sub>, 0.2 mm Merck plates.

IR spectra are taken on a 1600 FTIR Perkin-Elmer spectrometer in KBr discs.

NMR spectra are taken on a Bruker DRX-250 spectrometer.

The initial 6-acetyl-5,7-dioxo-6,7-dihydro-5H-dibenzo[a,c]-cycloheptene (**c**) is synthesized on the basis of reference [1].

### II. Synthesis of 6-ethanimidoyl-5H-dibenzo[a,c][7]annulene-5,7(6H)-dione

#### II.1. Method A

0.1 mole of 6-acetyl-5,7-dioxo-6,7-dihydro-5H-dibenzo[a,c]-cycloheptene (**c**), 0.1 mole of NaCN and 0.3 mole of (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> are dissolved in 52 ml of 96% C<sub>2</sub>H<sub>5</sub>OH and 50 ml of water. The reaction mixture is heated while stirring at 45-50 °C for an hour and then refluxed for 3 hours. The solution is concentrated to about two thirds of its volume and, after cooling, is acidified with concentrated HCl to pH 5-6. The mixture is left overnight in a refrigerator for crystallization.

The resulting 6-ethanimidoyl-5H-dibenzo[a,c][7]annulene-5,7(6H)-dione (**f**) is recrystallised from ethanol/water.

Yield: 68 %.

M.p.: 145-146 °C.

Rf (ethyl acetate : petroleum ether = 1 : 2) = 0.78.

Rf (chloroform : methanol = 10 : 1) = 0.43.

Elemental analysis data, anal. calcd. (found) / %: C – 77.55 (77.41); H – 4.98 (4.93); N – 5.32 (5.27).

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu_{\text{NH}}$  = 3314, 3187;  $\nu_{\text{C=O}}$  = 1687;  $\nu_{\text{C=N}}$  = 1634;  $\nu_{\text{arom.}}$  = 3065, 1523;  $\nu_{\text{CH}_3}$  = 2936;  $\nu_{\text{o-disub. core}}$  = 733.

$^1\text{H-NMR}$  (DMSO- $\text{d}_6$ , ppm):  $\delta_{\text{CH}_3}$  – 2.53;  $\delta_{\text{arom.}}$  – 7.42-7.69;  $\delta_{\text{CH}}$  – 8.9;  $\delta_{\text{NH}}$  – 9.86.

## II.2. Method B

0.1 mole of 6-acetyl-5,7-dioxo-6,7-dihydro-5*H*-dibenzo[*a,c*]-cycloheptene (**c**), 0.22 mole of NaCN, 0.15 mole  $(\text{NH}_4)_2\text{CO}_3$ , 200 ml of  $\text{C}_2\text{H}_5\text{OH}$  and 200 ml of aqueous ammonia are heated in an autoclave at 120 °C for 2 hours. The resulting product (**f**) is filtered, washed with water and diethyl ether and recrystallised from ethanol/water.

Yield: 56 %.

The physicochemical parameters and spectral data of thus obtained compound are identical with those of the product synthesized by method A.

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