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Photocyclization of 1,4-Naphthaquinone with β-Alanine

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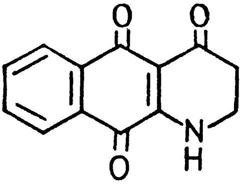
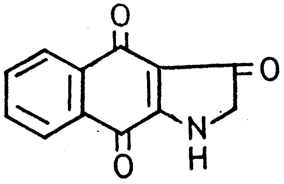
1,2,3,4-Tetrahydro benz[g] quinoline-4,5,10-trione was isolated in quantitative yield via photocycloaddition of β-alanine to 1,4-naphthaquinone in ethanol using high pressure mercury lamp as well as sunlight irradiation.

INTRODUCTION

The thermal reaction of 1,4-napthaquinone (NQ) and amino acids is well known[1,2]. Loven[1] has shown that reaction of two moles of NQ and one mole of β-alanine in refluxing ethanol for 8–10 hrs afforded 1,2,3,4-tetrahydro benz[g] quinoline, 4,5,10-trione (1). The benzindol trione (2) has been obtained later through an analogous reaction[2] of glycine with NQ. It has been observed that the photocycloaddition of amino acids to aromatic or aliphatic quinones have not received the much attention as far as the other different types of reagents[3–6]. Here we report the photochemical behaviour of 1,4-naphthaquinone when irradiated in presence of β-alanine using high presure mercury lamp and sunlight photolysis in ethanol solution.



(1)



(2)

Pyrex-filter sunlight irradiation of the pale greenish yellow alcoholic solution of 1,4-naphthaquinone (2 mol) and β-alanine (1 mol) produced a deep brown solution after four days affording 50% yield of the cyclized compound (1). Photolysis of the same molar ratios of the reactants using 150 W high pressure mercury lamp in ethanol gave the deep brown solution after 5 hrs. resulting in the formation of the cyclized compound (1) in 79% yield. The photolysis time was controlled via TLC comparing to the authentic sample[1]. The first detection of the compound (1) observed after $1\frac{1}{2}$ hrs., just above the start line as brownish

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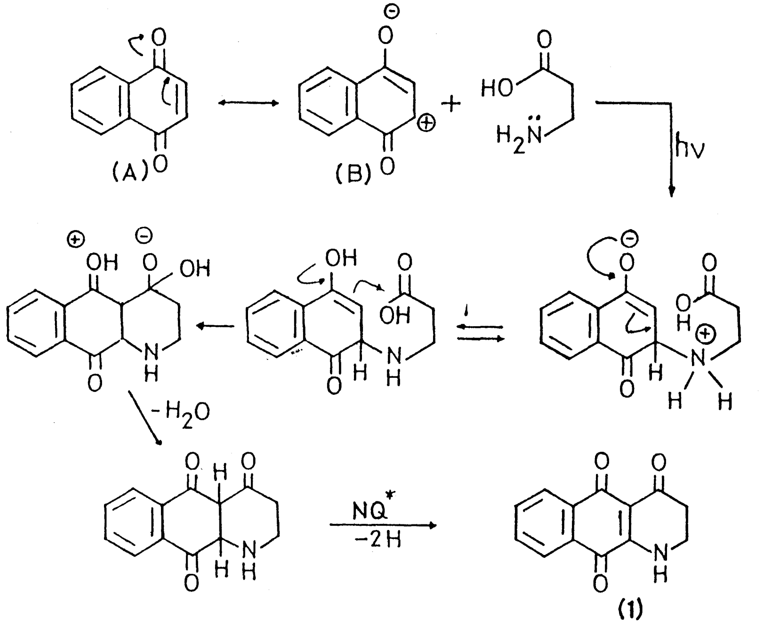
orange spot in toluene/ethylacetate (4 : 1) with a very few negligible spots comparing with the thermal reaction behaviour. Photolysis of equimolar amounts of the reactants under the same conditions afforded the cyclized compound (1) in a chemical yield much smaller than when a (2 : 1) ratio was applied. The cyclobutane dimers have not been found among the photoproducts[7] in each of the above trials. The control experiment was carried out for two weeks in dark at room temperature without any additional spots.

The following assumption may be presented to the enchacement of efficiency of the known thermal reaction[1] by light which may act in two ways:

(i) It postulates an excited state in which the contribution of (B) is larger than in the ground state and thus the addition of β-alanine is eased.

(ii) It acts as a better oxidant (in the excited state NQ*) than in the ground state and two hydrogen atoms have to be removed in the overall process as shown in the following:



(1)

EXPERIMENTAL

High pressure 150 W mercury lamp at room temperature was used; 1,4-napthaquinone was recrystallized from benzene, then sublimed under reduced pressure; β-alanine (Merck) used as received, spectral grade ethanol was used. The photolysis time was allowed and the reaction products were controlled by means of TLC. The analytical and spectroscopic data of the product were carried out in the microanalytical center at Cairo University and show identical analysis as the authentic sample.

General Procedure of Photolysis

(a) Via 150 W high pressure mercury lamp at room temperature: A solution of 1,4-naphthaquinone (1 g, 2 mol) in 40 ml ethanol was added to 30 ml ethanolic solution of β-alanine (0.3 g, 1 mol) and the mixture filled up to a total volume of 250 ml. The yellowish green mixture was photolyzed for 6 hrs, the deep brown solution was filtered concentrated to about 125 ml. The precipitate formed by addition of cold water was washed several times with cold water and crystallized from ethanol. The solid brown product was sublimed to recover unreacted 1,4-naphthaquinone. Recrystallization afforded deep brown needles identical to the authentic sample, m.pt. 184°C; Lit[1], 186°C; yield 79%.

(b) Sunlight Irradiation: The same molar amounts were exposed to sunlight in a sealed pyrex flask for four days with stirring, filtered, evaporated till dryness, washed with water, dried, then sublimed to recover unreacted 1,4-naphthaquinone, dissolved in ethanol, reprecipitated with cold water, filtered and recrystallized from ethanol affording deep crystalline needles in 50% yield, identical with the authenhtic sample.

(c) Preparation of compound (1) according to Ref 1: A mixture of 1,4-naphthaquinone (3 g, 2 mol) and β-alanine (1.3 g, 1 mol) was refluxed in 100 ml ethanol for 8 hrs on a water bath and the yellow-green solution was turned to deep brown. The reaction mixture was poured into ice/water mixture (200 ml) and left aside for overnight at room temperature, the deep precipitate was filtered, washed with cold water, crystallized from ethanol into crystalline brown needles; 60% yield; m.pt. 184°C.

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