

A Facile Preparation of Red Aminoquinones by Direct Irradiation of 1,4-Benzoquinone and Naphthoquinones in Diethylamine

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Some quinones such as 1,4-benzoquinone **2**, 1,4-naphthoquinone **3** and 1,2-naphthoquinone **4** dissolved in diethylamine were irradiated with 300 nm UV light to afford red aminoquinones **6**, **7**, and **9** as the major products. Irradiation of a solution of a primary product, *i.e.*, 2,5-bis(diethylamino)-1,4-benzoquinone **6** in benzene gave 2,5-bis(ethylamino)-1,4-benzoquinone **10** in 80% yield, along with an oxazoline **11** in 19% yield via photochemical deethylation. A solution of 2-diethylamino-1,4-naphthoquinone **7** in benzene was also irradiated under the same condition, in which 2-ethylamino-1,4-naphthoquinone **12** was obtained in ca. 100% yield.

key words: 1,4-benzoquinone, 1,4-naphthoquinone, 1,2-naphthoquinone, diethylamine, photoreaction

INTRODUCTION

The photochemistry of quinones has been a subject of extensive investigations. Various compounds were found to be produced *via* the primary process in numerous photoreactions such as reduction, cycloaddition, substitution and decomposition[1]. Particularly, photoinduced electron transfer between quinones and amines has been of great interest, because some quinones play a major role in the redox electron-transfer chains of living systems [1-4]. Amines have been used to get a variety of compounds derived from quinones under the various conditions [5-8]. The photochemistry of carbonyl compounds, including quinones, with amines is also of particular interest since it is an efficient process for the synthesis of diols or other types of reductive photoproducts [9-11]. We have reported reductive photoadditions of carbonyl compounds to *N,N*-dimethylaniline, in which ethanolamines are produced as the major products [12]. Irradiation of anthraquinone under the similar condition also gave the same type of photoadduct. In connection with the photoreactions of quinones with amines, we selected some liquid amines, such as diethylamine, triethylamine and *n*-propylamine, to compare the photoproducts. Here we observed the formation of diethylamino- and ethylaminoquinones, when irradiated quinones such as 1,4-benzoquinone, 1,4-naphthoquinone and 1,2-naphthoquinone in diethylamine with 300 nm UV light.

MATERIALS AND METHODS

Materials

Some quinones and amines such as 1,4-benzoquinone, 1,4-

naphthoquinone, 1,2-naphthoquinone, diethylamine, triethylamine and *n*-propylamine were purchased from Aldrich Chemical Co. and used without further purification. Silica gel (Kieselgel 60 F254, Merck Co.) was used for thin layer chromatography. Silica gel (Kieselgel G, 230-400 mesh) was purchased from Merck Co. for liquid column chromatography. Hexane, ethyl acetate and benzene were obtained from Ducksan Chemical Co.

Methods

¹H and ¹³C NMR spectra were recorded on a Jeol JMN EX-400 spectrometer. Proton chemical shift are reported in ppm downfield from tetramethylsilane (TMS), and ¹³C resonances were recorded using the CDCl₃ resonance (77.0 ppm) of the solvent as an internal standard and reported in ppm downfield from TMS. Infrared (IR) spectra were recorded on a Nicolet 5-DXB Fourier transform spectrophotometer in KBr pellets or NaCl cell, in which peaks are reported in reciprocal centimeters (cm⁻¹). Ultraviolet (UV) spectra were recorded on a Beckman DU 7500 spectrophotometer. Mass spectra were determined at 40-70 eV with a Hewlett-Packard 5985 GC/MS spectrometer by electron impact (EI) method. All photoreactions were carried out under dry nitrogen atmosphere in oven-dried glassware. Evaporation of solvents was carried out with a rotary evaporator using vacuum pump.

Photoreactor

Irradiation was carried out with a Rayonet photochemical reactor (Model RPR-208, Southern New England Ultraviolet Co.) equipped with 300 nm UV lamps, water-cooled reaction vessel and a cooling fan.

Irradiation and Characterization

Quinones (2 mmol) were dissolved in 10 mL of amines. The reaction mixtures were purged with dry nitrogen gas to remove molecular oxygen gas for 30 min before irradiation with 300 nm

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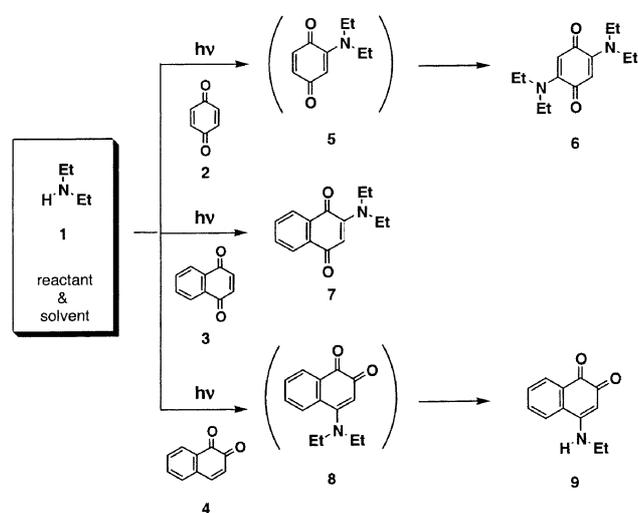
UV lamps for 24 h. Progress of the photoreactions was analyzed by TLC and NMR spectra. A rotary evaporator was used to remove the solvents, and the products **6**, **7**, and **9** were isolated by liquid column chromatography using hexane and ethyl acetate as the eluents. Solutions of 0.5 mmol of diethylaminoquinones **6** and **7** in 30 mL of benzene were irradiated with 300 nm UV light for 24 h to give mono-ethyl derivatives, **10** and **11** and **12**. The photoproducts were characterized by representative spectral data such as UV, IR, NMR and mass spectra.

Spectral Data

6: UV(MeOH) λ_{\max} 525, 375 nm; IR(KBr) 3073, 2722, 2865, 1622, 1542, 1454, 1320, 1246, 1152, 1078, 863, 796, 682 cm^{-1} ; $^1\text{H-NMR}(\text{CDCl}_3)$ δ 5.4(2H, s), 3.5(8H, q), 1.2(12H, t); $^{13}\text{C-NMR}(\text{CDCl}_3)$ δ 182, 150, 100, 47; Mass(EI) m/e 250. **7**: $^1\text{H-NMR}(\text{CDCl}_3)$ δ 8.0-7.6(4H), 6.8(1H, s), 3.5(4H, q), 1.3(12H, t), Mass (EI) m/e 229. **9**: $^1\text{H-NMR}(\text{CDCl}_3)$ δ 8.0-7.5(4H), 5.8(NH, s), 5.6(1H, s), 3.2(2H, q), 1.2(3H, t); Mass (EI) m/e 201. **10**: $^1\text{H-NMR}(\text{CDCl}_3)$ δ 6.4(2NH, s), 5.2(2H, s), 3.1(4H, q), 1.2(6H, t); Mass(EI) m/e 194. **11**: $^1\text{H-NMR}(\text{CDCl}_3)$ δ 6.4(1H, s), 5.4(1H, s), 3.6(1H, q), 3.1(1H, q), 1.2(3H, t), 0.9(3H, d); Mass(EI) m/e 193. **12**: $^1\text{H-NMR}(\text{CDCl}_3)$ δ 8.03(1H, d), 7.98(1H, d), 7.66(1H, t), 7.55(1H, t), 5.8(2NH, s), 5.7(1H, s), 3.2(2H, q), 1.3(3H, t); Mass (EI) m/e 201.

RESULTS AND DISCUSSION

In our previous work, it was found that ethanolamines are produced from the photoreactions of some carbonyl compounds including anthraquinone in an aromatic tertiary amine, *i.e.*, *N,N*-dimethylaniline. However, in the case of diethylamine **1**, different types of products were observed. Direct irradiation of some quinones **2**, **3** and **4** in diethylamine afforded red aminoquinones *via* photosubstitution reactions. Irradiation of 1,4-benzoquinone **2** in diethylamine **1** for 24 h afforded red 2,5-bis(diethylamino)-1,4-benzoquinone **6** in

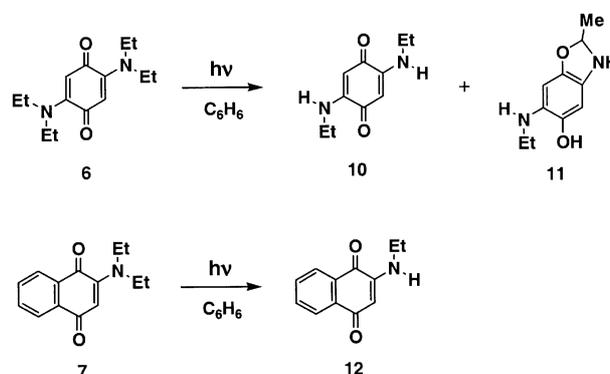


Scheme 1.

75% yield, in which the primary product **5** was not observed as shown in Scheme 1. Irradiation of 1,4-naphthoquinone **3** in diethylamine for 24 h gave 2-diethylamino-1,4-naphthoquinone **7** in 60% yield. Interestingly, irradiation of 1,2-naphthoquinone **4** in diethylamine for 24 h yielded 4-ethylamino-1,2-naphthoquinone **9** *via* photo-deethylation of the primary product **8**.

The photo-deethylation product, like **9**, was also found to be produced when a solution of 2,5-bis(diethylamino)-1,4-benzoquinone **6** (125 mg, 0.5 mmol) in 30 mL of benzene was further irradiated with 300 nm UV light for 24 h, in which 2,5-bis(ethylamino)-1,4-benzoquinone **10** was isolated in 80% yield, along with an oxazoline **11** in 19% yield, as shown in Scheme 2. The formation of **11** could be rationalized by the initial H-abstraction of the excited carbonyl group, followed by cyclization to give a 5-membered ring. A solution of 2-diethylamino-1,4-naphthoquinone **7** in benzene was also further irradiated under the same condition to give 2-ethylamino-1,4-naphthoquinone **12** in *ca.* 100% yield.

On the other hand, irradiation of some quinones in triethylamine gave rise to many kinds of products, and it was found to be difficult to separate adduct from the complex mixtures. In the case of *n*-propylamine, the same type of products such as 2,5-bis(*n*-propylamino)-1,4-benzoquinone, 2-(*n*-propylamino)-1,4-naphthoquinone, and 4-(*n*-propylamino)-1,2-naphthoquinone were produced, when irradiated **2**, **3**, and **4** in liquid *n*-propylamine under the similar condition. All these photoproducts obtained from quinones and amines are red-colored applicable



Scheme 2.

Table 1. The longest absorption band (λ_{\max}) of 1,4-benzoquinone, naphthoquinones and aminoquinones observed in methanol at room temperature.

1,4-Benzoquinone and photoproducts (λ_{\max})	1,4-Naphthoquinone and photoproducts (λ_{\max})	1,2-Naphthoquinone and photoproduct (λ_{\max})
2 (333 nm)	3 (332nm)	4 (397 nm)
6 (465 nm)	7 (438 nm)	8 (-)
10 (450 nm)	12 (430 nm)	9 (430 nm)

-: not isolated.

for the development of dyes. The longest absorption bands of these red aminoquinones were determined in methanol at room temperature and summarized in Table 1.

In conclusion, we found that various red aminoquinones are produced from direct irradiation of quinones in liquid amines in good yields. Diethylaminoquinones are converted to the corresponding mono-ethyl derivatives, when irradiated them in benzene. Irradiation of quinones in aliphatic tertiary amine such as triethylamine did not give any adducts. The photochemistry of benzoquinones and naphthoquinones in aromatic tertiary amines, *i.e.*, aniline derivatives is under investigation.

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