Monatshefte für Chemie 113, 1059—1061 (1982)

Monatshefte für Chemie
Chemical Monthly

The Dealkylation of 2-Diethylamino-3*H*-phenothiazin-3-one

Short Communication

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(Received 10 May 1982. Accepted 24 May 1982)

2-Diethylamino-3*H*-phenothiazin-3-one was dealkylated to 2-ethylamino-3*H*-phenothiazin-3-one either by photolysis or pyrolysis.

(Keywords: 2-Ethylamino-3H-phenothiazin-3-one; 3H-Phenothiazin-3-one)

Entalkylierung von 2-Diethylamino-3H-phenothiazin-3-on (Kurze Mitteilung)

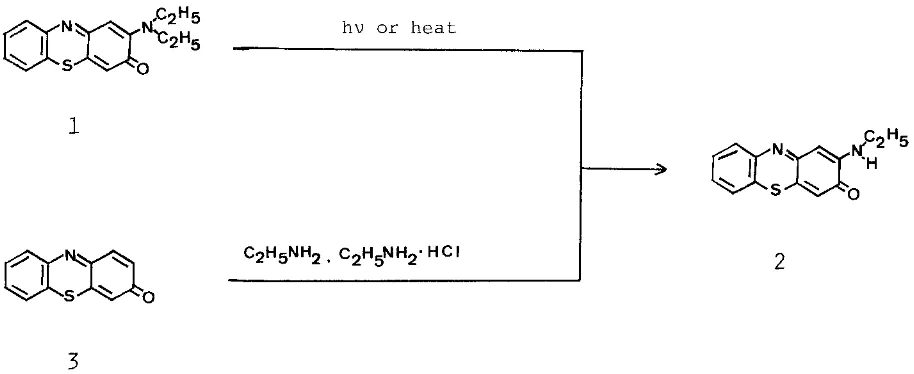
Die Titelverbindung wurde durch Photolyse oder Pyrolyse zu 2-Ethylamino-3*H*-phenothiazin-3-on entalkyliert.

In the previous communication, the reaction of 5*H*-benzo[a]-phenothiazin-5-one with aldehydes was investigated and structures were assigned to the reaction products[1]. As a part of the general problem of the study of the photochemical reactivity of quinone imines, we now report the dealkylation of 2-diethylamino-3*H*-phenothiazin-3-one.

When a benzene solution of 2-diethylamino-3*H*-phenothiazin-3-one (**1**) was irradiated in a Pyrex vessel for 7.5 h with a high-pressure mercury lamp, the corresponding monoethyl compound **2** was obtained in 92% yield.

The IR spectrum of compound **1** did not show an absorption in the region 3 500-3 300 cm^{-1}, but that of photoproduct of **1** exhibited an absorption at 3 320 cm^{-1} due to the amino group. The NMR spectrum of **1** exhibited two close triplets in the region 1.59-0.69 ppm and two close quartets in the region 3.83-3.15 ppm, respectively, due to the methyl and methylene protons. However, the NMR spectrum of the photoproduct showed a triplet at 1.21 ppm, a quartet at 3.31 ppm, and a singlet in the region 6.01-5.41 ppm, respectively, due

0026-9247/82/0113/1059/$ 01.00



to the methyl, methylene, and amine protons. Furthermore, the photoproduct was identified as **2** by the direct comparison with a sample prepared by an alternate route.

The same compound **2** could also be obtained (72% yield) by the pyrolysis of **1** in *N*,*N*-dimethylformamide. On the other hand, compound **2** was dealkylated to 2-amino-3*H*-phenothiazin-3-one neither by photolysis nor pyrolysis under the same condition.

Experimental

Melting points were determined on a Yanagimoto micromelting apparatus and are uncorrected. The infrared spectra were recorded on a Jasco DS 701 G spectrometer. Nuclear magnetic resonance spectra were determined on a Hitachi R-20 B spectrometer using tetramethylsilane as an internal reference. Mass spectra were determined on a Hitachi M-52 spectrometer.

2-Diethylamino-3*H*-phenothiazin-3-one was obtained according to the reported method[2].

Dealkylation of 2-diethylamino-3H-phenothiazin-3-one (**1**)

Method A (*Photolysis*)

A solution of **1** (25 mg) in benzene (40 ml) was irradiated for 7.5 h in a Pyrex glass from outside by means of 100 Watt high-pressure mercury arc lamp in a nitrogen atmosphere through a 7 cm-thick layer of cold water (0-5 °C). After the removal of the solvent under reduced pressure, the residue was chromatographed on an aluminium oxide column using benzene as an eluent. The red-brown solid was obtained in 92% yield.

The structure of the product was then identified by direct comparison of IR, ^{1}H-NMR, and mass spectra with those of authentic materials.

Method B (*Pyrolysis*)

A solution of **1** (30 mg) in *N*,*N*-dimethylformamide (2 ml) was refluxed for 1.5 h, cooled, poured into ice cold water, and filtered. The precipitate was chromatographed on a aluminium oxide column using benzene as an eluent. The red-brown solid was obtained in 72% yield. The product was identified as **2**.

2-Ethylamino-3H-phenothiazin-3-one (**2**)

A solution of 3*H*-phenothiazin-3-one (**3**) (0.44 g, 0.002 mol), ethylamine (3 ml), and ethylamine hydrochloride (1 g, 0.012 mol) in *N*,*N*-dimethylformamide (20 ml) was stirred for 1.5 h at room temperature, after which the reaction mixture was poured into water (200 ml), and the precipitate was collected. The crude product was purified by chromatography on an aluminium oxide column (benzene as eluent).

Compound **2** gave red-brown crystals; M.p. 145°; yield 10%.

IR (KBr): 1627 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): 1.29 (t, 3 H, CH_3 group), 3.31 (q, 2 H, CH_2 group), 5.41-6.01 (s, 1 H, NH group), 6.36 (s, 1 H, arom.), 6.79-7.52 (m, 4 H, arom.), 7.64-7.90 (m, 1 H, arom.).

MS: $m/s = 256$ (M^+).

$C_{14}H_{12}N_2OS$ (256.3). Calcd. C 65.60 H 4.72 N 10.93%.
Found. C 65.78 H 4.78 N 10.67%.

References

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