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The Dehalogenation of the Halo Substituted 5*H*-Benzo[a]phenothiazin-5-ones and 3*H*-Phenothiazin-3-ones

Short Communication

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6-Bromo- and 6-chloro-5*H*-benzo[a]phenothiazin-5-ones were dehalinated to 5*H*-benzo[a]phenothiazin-5-one in the presence of sodium hydrosulfite (disodiumdithionite · 2 H_2O) dissolved in aqueous pyridine under nitrogen atmosphere.

(Keywords: 5H-Benzo[a]phenothiazin-5-one; 6-Bromo-5H-benzo[a]phenothiazin-5-one; 6-Chloro-5H-benzo[a]phenothiazin-5-one; 3H-Phenothiazin-3-one)

Enthalogenierung von halogensubstituierten 5H-Benzo[a]phenothiazin-5-onen und 3H-Phenothiazin-3-onen

6-Brom- und 6-Chlor-5*H*-benzo[a]phenothiazin-5-on lassen sich in wäßrigem Pyridin in Gegenwart von Natriumdithionit unter Stickstoff zu 5*H*-Benzo[a]phenothiazin-3-on enthalogenieren.

In the previous communication, the reaction of 5*H*-benzo[a]phenoxazin-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 reactivity of quinone imines, we now report the dehalogenation of the halo substituted 5*H*-benzo[a]phenothiazin-5-one (**1**) and 3*H*-phenothiazin-3-one (**2**).

In this work, 6-bromo-5*H*-benzo[a]phenothiazin-5-one (**1a**) was prepared by condensation of zinc thiolate of 2-amino-benzenethiol with 2,3-dibromo-1,4-naphthoquinone in refluxing methanol. The dehalogenation of the compound **1** easily proceeded in the aqueous pyridine under nitrogen atmosphere and gave the compound **3** in quantitative

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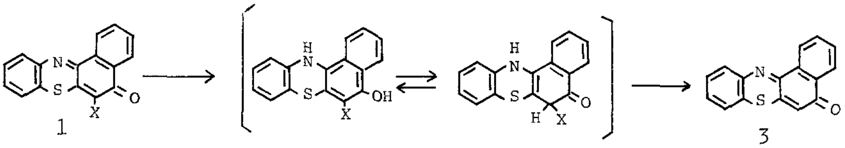
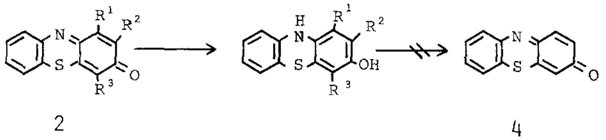
yield. This replacement of the halo group by a hydrogen atom under such mild conditions is intriguing. The structures of products were determined by elemental and from spectroscopic data. In particular,



1a, X = Br
1b, X = Cl



2	R^1	R^2	R^3
a	Cl	H	H
b	H	Cl	H
c	H	H	Cl

the NMR spectrum of products ($CDCl_3$) exhibited a characteristic singlet at 6.70 ppm due to olefinic proton, but those of compound **1** did not show any evidence assigned to this kind of proton. Furthermore, the products were identified by direct comparison with sample prepared by an alternate route[2]. On the other hand, compound **2** did not dehalogenate to 3*H*-phenothiazin-3-one (**4**) under the same condition. The difference in the reactivity of the halo group may be attributed to the annelated benzene ring.

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.

6-Chloro-5*H*-benzo[a]phenothiazin-5-one[2] and halo substituted 3*H*-phenothiazin-3-one[3] were obtained according to the reported methods.

6-Bromo-5H-benzo[a]phenothiazin-5-one (**1a**)

A mixture of the zinc thiolate of 2-aminobenzenethiol (1.57 g, 0.005 mol), and 2,3-dibromo-1,4-naphthoquinone (3.17 g, 0.01 mol) in ethanol (100 ml) was stirred for 1 h at room temperature and then heated under reflux 2 h. The solid which deposited on cooling was filtered off, washed with aqueous 5% hydrochlorid acid, and recrystallized from ethanol.

Compound **1a** gave red crystals; M.p. 190°; yield 85%.

IR (KBr): 1642 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): 7.34–7.97 (m, 6 H, arom.), 8.15–8.35 (m, 1 H, arom.), 8.67–8.95 (m, 1 H, arom.).

MS: *m*/e = 341 (M^+).

$C_{16}H_8BrNOS$ (342.2). Calcd. C 56.16, H 2.36, N 4.09.
Found C 56.36, H 2.36, N 3.96.

5H-benzo[a]phenothiazin-5-one (**3**)

A suspension of the halo substituted 5*H*-benzo[a]phenothiazin-5-one (**1**) (0.01 mol), sodium hydrosulfite (disodiumdithionite, 15.1 g, 0.1 mol), benzene (10 ml), and dioxane (20 ml) in 30 ml of water was bubbled with nitrogen for 20 min. After reduction of the starting materials, the suspension was then heated to reflux. At the beginning of the refluxing 25 ml of pyridine was added to the mixture and the refluxing was continued for 2.5 h under nitrogen atmosphere. After removal of the organic solvents under reduced pressure, the precipitate was collected, washed well with water and 5% aqueous acetic acid and recrystallized from benzene. Compound **3** was obtained from compound **1a** or **1b** in 98 or 97% yield, respectively.

Compound **3** gave red crystals; M.p. 177°.

IR (KBr): 1636 cm^{-1} (C=O).

^{1}H-NMR ($CDCl_3$): 7.14–7.86 (m, 6 H, arom.), 8.04–8.22 (m, 1 H, arom.), 8.54–8.78 (m, 1 H, arom.).

$C_{16}H_9ONS$ (263.3). Calcd. C 72.98, H 3.45, N 5.33.
Found C 72.86, H 3.32, N 5.35.

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