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6-Alkylthio- and 6-phenylthio-5*H*-benzo[*a*]phenothiazin-5-ones were prepared by the photochemical reaction of 5*H*-benzo[*a*]phenothiazin-5-one with alkylthiols and thiophenol. The structures of newly prepared compounds were determined by elemental analysis, spectroscopic methods (ir, nmr and ms) and comparison with a sample prepared by an alternate route.

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Reactions of quinone with alkyl- and arylthiols have been studied by several workers (1-9), but there have been few studies on those of quinone imines (10-13). In a previous paper, the photochemical reaction of 5*H*-benzo[*a*]phenothiazin-5-one (**1**) with aldehydes was investigated and structures were assigned to the reaction products (14).

As part of the general problem of the study of the photochemical reaction of 5*H*-benzo[*a*]phenothiazin-5-one (**1**) with various hydrogen donors, we have extended the investigation to the photochemical reactions of 5*H*-benzo[*a*]phenothiazin-5-one (**1**) with alkylthiols and thiophenol. In this experiment, ultraviolet light from a 100 watt high-pressure mercury lamp was used. A benzene solution of 5*H*-benzo[*a*]phenothiazin-5-one (**1**) and the alkylthiols **2a-e** were irradiated in a nitrogen atmosphere at 5° for 10 hours and then bubbled with air for several minutes. The photoproducts (**3a-e**) obtained were chromatographed on silica gel and recrystallized from ethanol. When thiophenol (**2f**) was used in place of alkylthiols **2a-e**, 6-phenyl-

thio-5*H*-benzo[*a*]phenothiazin-5-one (**3f**) was obtained in fairly good yield.

The structures of the photoproducts **3a-f** were fully supported by microanalytical results and spectral data. In particular, the <sup>1</sup>H-nmr spectrum (deuteriochloroform) of **1** exhibited a characteristic singlet at δ 6.70 (1H) due to the olefinic proton, but those of the photoproducts **3a-f** of **1** with **2a-e** and **2f** did not show a characteristic singlet at δ 6.70 (1H). The photoproducts **3a-f** thus obtained were identical in every respect with a sample prepared by an alternate route. This route involves the condensation of 2-aminothiophenol (**4**) with an appropriate 2-alkylthio-3-chloro-1,4-naphthoquinones **5a-d** or 2-alkylthio- and 2-arylthio-1,4-naphthoquinones **5e,f** to furnish the corresponding 6-substituted-5*H*-benzo[*a*]phenothiazin-5-ones **3a-f**.

The present report offers a facile method for the synthesis of 6-alkylthio- and 6-arylthio-5*H*-benzo[*a*]phenothiazin-5-ones from readily available starting material.

SCHEME I

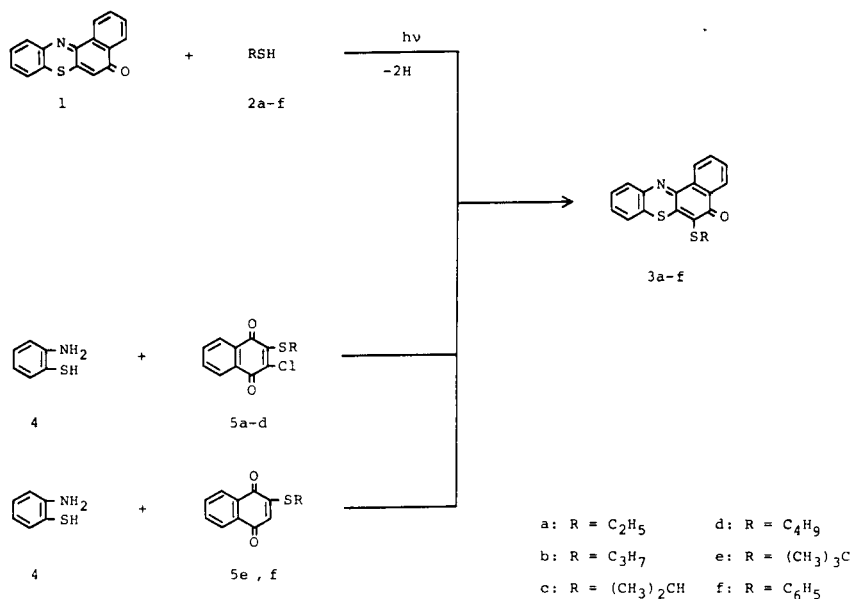
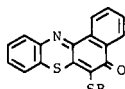


Table 1  
6-Alkylthio- and 6-Phenylthio-5*H*-benzo[*a*]phenothiazin-5-one, **3a-f**



Compound	R	Procedure Yield, %	Mp °C	Molecular Formula	Elemental Analysis		
					Analysis Calcd. (Found)	C	H
<b>3a</b>	C <sub>2</sub> H <sub>5</sub>	A, 49 (a)	175-176	C <sub>18</sub> H <sub>13</sub> NOS <sub>2</sub> (323.4)	66.87 (66.48)	4.02 (3.82)	4.33 (4.05)
		B, 45 (b)					
<b>3b</b>	C <sub>3</sub> H <sub>7</sub>	A, 49 (a)	150-151	C <sub>19</sub> H <sub>15</sub> NOS <sub>2</sub> (337.4)	67.66 (67.40)	4.45 (4.54)	4.15 (3.94)
		B, 40 (b)					
<b>3c</b>	(CH <sub>3</sub> ) <sub>2</sub> CH	A, 52 (a)	178-179	C <sub>19</sub> H <sub>15</sub> NOS <sub>2</sub> (337.4)	67.66 (67.68)	4.45 (4.25)	4.15 (4.04)
		B, 35 (b)					
<b>3d</b>	C <sub>6</sub> H <sub>5</sub>	A, 56 (a)	99-100	C <sub>20</sub> H <sub>17</sub> NOS <sub>2</sub> (351.4)	68.38 (68.66)	4.84 (4.82)	3.99 (4.03)
		B, 38 (b)					
<b>3e</b>	(CH <sub>3</sub> ) <sub>3</sub> C	A, 54 (a)	188-189	C <sub>20</sub> H <sub>17</sub> NOS <sub>2</sub> (351.4)	68.38 (68.58)	4.84 (4.84)	3.99 (3.74)
		C, 10 (b)					
<b>3f</b>	C <sub>6</sub> H <sub>5</sub>	A, 71 (a)	256-257	C <sub>22</sub> H <sub>13</sub> NOS <sub>2</sub> (371.4)	71.16 (70.94)	3.50 (3.36)	3.77 (3.52)
		C, 20 (b)					

(a) Yield of product based on 5*H*-benzo[*a*]phenoxazin-5-one consumed. (b) Yield of isolated product.

Table 2  
Spectroscopic Data of 6-Alkylthio- and 6-Phenylthio-5*H*-benzo[*a*]phenothiazin-5-one, **3a-f**

Compound	Mass	Infrared Spectrum cm <sup>-1</sup>	<sup>1</sup> H NMR Spectrum (Deuteriochloroform)	
			ppm	
<b>3a</b>	323 (M <sup>+</sup> )	2970; 2860; 1627 (C=O); 1598; 1499; 1302; 770	1.10-1.42 (t, 3H), 2.90-3.34 (q, 2H), 7.27-7.94 (m, 6H, arom.), 8.10-8.33 (m, 1H, arom.), 8.62-8.82 (m, 1H, arom.)	
<b>3b</b>	337 (M <sup>+</sup> )	2970; 2870; 1623 (C=O); 1598; 1497; 1301; 769	0.80-1.18 (t, 3H), 1.40-1.78 (m, 2H), 3.06-3.18 (t, 2H), 7.25-7.98 (m, 6H, arom.), 8.18-8.33 (m, 1H, arom.), 8.60-8.86 (m, 1H, arom.)	
<b>3c</b>	337 (M <sup>+</sup> )	2970; 2860; 1618 (C=O); 1590; 1490; 1290; 764	1.26 (s, 3H), 1.36 (s, 3H), 3.60-4.30 (m, 1H), 7.27-7.90 (m, 6H, arom.), 8.12-8.40 (m, 1H, arom.), 8.65-8.90 (m, 1H, arom.)	
<b>3d</b>	351 (M <sup>+</sup> )	2970; 2880; 1632 (C=O); 1600; 1500; 1301; 768	0.70-1.10 (t, 3H), 1.30-1.83 (m, 4H), 2.93-3.26 (t, 2H), 7.30-7.90 (m, 6H, arom.), 8.15-8.37 (m, 1H, arom.), 8.67-8.92 (m, 1H, arom.)	
<b>3e</b>	351 (M <sup>+</sup> )	2980; 2860; 1627 (C=O); 1598; 1496; 1296; 768	1.44 (s, 9H), 7.30-7.92 (m, 6H, arom.), 8.16-8.37 (m, 1H, arom.), 8.65-8.90 (m, 1H, arom.)	
<b>3f</b>	371 (M <sup>+</sup> )	1618 (C=O); 1584; 1484; 1295; 753	6.95-7.90 (m, 11H, arom.), 8.10-8.38 (m, 1H, arom.), 8.61-8.91 (m, 1H, arom.)	

## EXPERIMENTAL

Melting points were determined on a Yanagimoto micromelting apparatus and are uncorrected. The infrared spectra were recorded on a Jasco DS 701G spectrometer. Absorption frequencies are equated in reciprocal centimeters. Nuclear magnetic resonance spectra were determined on a Hitachi R-20B spectrometer using tetramethylsilane as an internal reference. Chemical shifts are quoted in parts per million (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Mass spectra were determined on a Hitachi M-52 spectrometer.

General Procedure A for the Photochemical Synthesis of 6-Alkylthio- and 6-Arylthio-5*H*-benzo[*a*]phenothiazin-5-ones, **3a-f**.

5*H*-Benzo[*a*]phenothiazin-5-one (**1**) (0.16 g, 0.6 mmole) and an alkylthiol (or a thiophenol) (3 mmole) were dissolved in benzene (90 ml). The solution was irradiated in a Pyrex glass tube for 10 hours 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°) and then bubbled with air for several minutes. After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica gel column (benzene as eluent). The photoproducts **3** thus obtained were further purified by recrystallization from ethanol.

General Procedure B for the Preparation of 6-Alkylthio-5*H*-benzo[*a*]phenothiazin-5-ones, **3a-d**.

A suspension of 2-alkylthio-3-chloro-1,4-naphthoquinone (**5a-d**) (10 mmole) and 2-aminothiophenol (**4**) (1.25 g, 10 mmole) in dry pyridine (60 ml) was stirred for 1 hour at room temperature and then heated under reflux for 2.5 hours. After cooling, an equal volume of methanol was added. The precipitate was collected and recrystallized from ethanol.

Procedure C for the Preparation of 6-*t*-Butylthio- and 6-Phenylthio-5*H*-benzo[*a*]phenothiazin-5-ones, **3e,f**.

A solution of 2-aminothiophenol (**4**) (1.25 g, 10 mmole) in 15% aqueous hydrochloric acid (50 ml) was added to a solution of 6-phenylthio-1,4-naphthoquinone (**15**) (**5f**) (2.68 g, 10 mmole) in ethanol (250 ml), and the mixture was stirred at room temperature for 20 hours. Iron(III) chloride hexahydrate (10.8 g, 40 mmole) was then added with stirring and the mixture set aside overnight. The precipitate was collected, washed well with water, and recrystallized from ethanol. *t*-Butylthio-5*H*-benzo[*a*]phenothiazin-5-one was prepared by condensation of **4** with **5e** just as was **3f**.

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