The Photochemical Reaction of 5*H*-Benzo[*a*]phenothiazin-5-ones with Aldehydes

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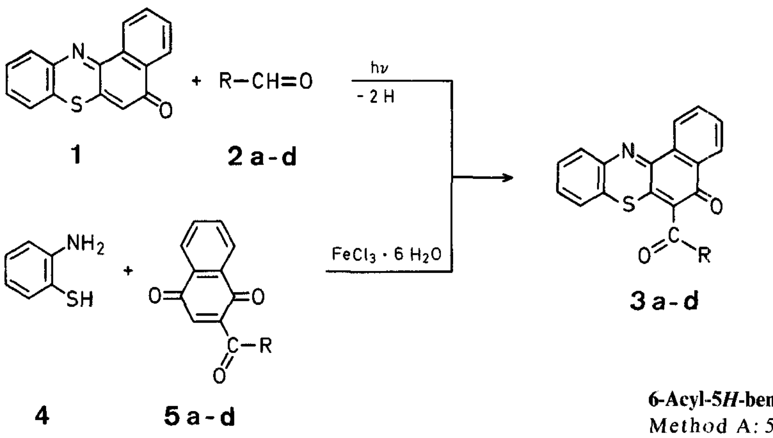
Light-induced reactions between quinones and aldehydes have been extensively studied by several workers[1-7], but there have been few studies on those of quinone imines, probably because of their instability[8-11]. In the present work, 5H-benzo[a]phenothiazin-5-one (**1**) was chosen as the quinone imine. It seemed that it would be interesting to investigate what type of reaction occurs between aldehydes and 5*H*-benzo[*a*]phenothiazin-5-one (**1**) on irradiation.

Although benzophenothiazones are receiving some attention, the recorded synthetic methods are tedious and only a few substituted derivatives have been hitherto reported[12-15]. In view of a potential interest for this class of compounds in pharmacology, we report a novel route for the synthesis of some 5*H*-benzo[*a*]phenothiazin-5-one derivatives **3a-d**. 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 aldehydes **2** was irradiated in a nitrogen atmosphere at 5 °C for 15 h and then bubbled with air for several minutes. The photoproducts **3** obtained were chromatographed on silica gel and recrystallized from benzene/ethanol.

6-Acyl-5*H*-benzo[*a*]phenothiazin-5-ones **3** were synthesized thus in fairly good yields. The presence of small amounts of unidentified products in the reaction mixture was detected by T.L.C. The structures of the photoproducts were fully supported by microanalytical results and spectral data. The photoproducts thus obtained were identical in every respect with a sample prepared by an alternate route (Method B; **4**+**5**→**3**).

The present photochemical reaction might provide a new synthetic route to quinone imine derivatives. The detailed mechanism is not clear at present and further studies are in progress.



	a	b	c	d
R	CH_3	C_2H_5	n-C_4H_9	C_6H_5

6-Acyl-5*H*-benzo[*a*]phenothiazin-5-ones 3; General Procedure:

Method A: 5*H*-Benzo[*a*]phenothiazin-5-one (**1**, 0.13 g, 0.5 mmol) and an aldehyde **2** (10 mmol) are dissolved in benzene (60 ml). The solution is irradiated in a pyrex glass tube for 15 h 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) and

Table. 6-Acyl-5*H*-benzo[*a*]phenothiazin-5-ones **3a-d**

Product	Yield [%] by Method[a] A[b]	B[c]	m.p. [°C][d]	Molecular formula[e]	M.S. *m/e*	I.R. (KBr)[f] ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$)[g] δ [ppm]
3a	90	15	242–243	$C_{18}H_{11}NO_2S$ (305.4)	305 (M^+)	1635, 1400	2.81 (s, 3H); 7.51–7.88 (m, 6H_{arom}); 8.21–8.41 (m, 1H_{arom}); 8.81–9.01 (m, 1H_{arom})
3b	85	12	194–195	$C_{19}H_{13}NO_2S$ (319.4)	319 (M^+)	1635, 1415	1.04–1.40 (t, 3H); 3.05–3.45 (q, 2H); 7.51–7.85 (m, 6H_{arom}); 8.25–8.45 (m, 1H_{arom}); 8.75–9.00 (m, 1H_{arom})
3c	63	11	170–171	$C_{20}H_{15}NO_2S$ (333.4)	333 (M^+)	1635, 1415	0.81–1.31 (t, 2H); 1.54–2.01 (m, 2H); 3.03–3.36 (t, 3H); 7.46–8.03 (m, 6H_{arom}); 8.11–8.41 (m, 1H_{arom}); 8.68–8.96 (m, 1H_{arom})
3d	70	10	266–267	$C_{23}H_{13}NO_2S$ (367.4)	367 (M^+)	1670, 1620	7.18–8.02 (m, 11H_{arom}); 8.11–8.34 (m, 1H_{arom}); 8.14–9.01 (m, 1H_{arom})

[a] Reaction procedure A and B are described at the beginning of experimental section.

[b] Yield of product based on 5*H*-benzo[*a*]phenothiazin-5-one consumed.

[c] Yield of isolated product.

[d] m.p.s were measured on a Yanagimoto micromelting apparatus and are uncorrected.

[e] All products gave satisfactory microanalysis with the following maximum derivations from the calculated values; C, ±0.30; H, ±0.21; N, ±0.25.

[f] I.R. spectra were recorded with a Jasco DS 701 G spectrometer.

[g] ^{1}H-N.M.R. spectra were taken on a Hitachi R-20 B spectrometer using TMS as internal standard.

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then bubbled with air for several minutes. After the removal of the solvent under reduced pressure, the residue is chromatographed on a silica gel column (benzene/chloroform 1:1 as eluent). The photoproducts **3** thus obtained are further purified by recrystallization from benzene/ethanol.

Method B: 6-Acyl-5*H*-benzo[*a*]phenothiazin-5-ones are synthesized using a slight modification of the procedure described by Akatsuka et al.[14]. A solution of 2-aminothiophenol (**4**; 1.25 g, 0.01 mol) in 15% aqueous hydrochloric acid (60 ml) is added to a solution of 6-acyl-1,4-naphthoquinone **5** (0.01 mol) in ethanol (250 ml), and the mixture is stirred at room temperature for 18 h. Iron(III) chloride hexahydrate (10.8 g, 0.04 mol) is then added with stirring and the mixture set aside overnight. The precipitate is collected, washed well with water, and recrystallized from benzene/ethanol.

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