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Simple Synthesis of 6-Alkyl-5*H*-benzo[a]phenoxazin-5-ones

Short Communication

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6-Alkyl-5*H*-benzo[a]phenoxazin-5-ones were prepared by the reaction of 5*H*-benzo[a]phenoxazin-5-one with carboxylic acid in the presence of silver ion and peroxydisulfate.

(Keywords: 5H-Benzo[a]phenoxazin-5-one; 6-Ethyl-5H-benzo[a]phenoxazin-5-one; 6-Methyl-5H-benzo[a]phenoxazin-5-one)

Eine einfache Synthese von 6-Alkyl-5H-benzo[a]phenoxazin-5-onen (Kurze Mitteilung)

6-Alkyl-5*H*-benzo[a]phenoxazin-5-one wurden mittels Reaktion von 5*H*-Benzo[a]phenoxazin-5-onen mit Carbonsäuren in Gegenwart von Silberionen und Peroxydisulfat dargestellt.

In the previous communication, the photochemical reaction of 5*H*-benzo[a]phenoxazin-5-one (**1**) with aldehydes was investigated[1]. There have been few studies on the reactions of quinone imines with alkyl radicals, although those of quinone have extensively been studied by many investigators[2–6]. In view of a potential interest for phenoxazone derivatives in pharmacology, we now reported the reactions of **1** with nucleophilic radicals generated in the silver ion catalysed oxidation of carboxylic acid with peroxydisulphate[7].

6-Alkyl-5*H*-benzo[a]phenoxazin-5-ones (**3a-e**) were prepared by reacting **1** with alkyl radicals in an aqueous acetonitrile at 75–80 °C. The structures of these compounds **3** were fully supported by microanalytical results and spectral data. In particular, the NMR spectrum of **1** ($CDCl_3$) exhibited a characteristic singlet at 6.30 ppm due to the olefinic

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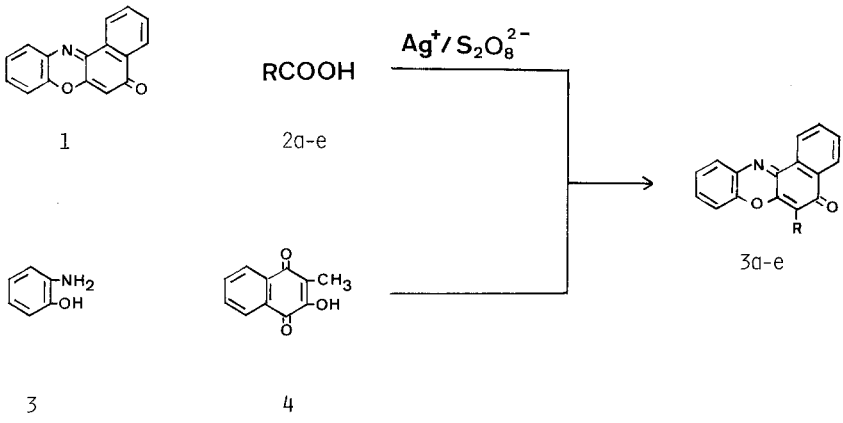
proton, but those of **3** did not any evidence assigned to this kind of proton. Furthermore, the compound **3a** was identified by direct comparison with a sample prepared by an alternate route.



	a	b	c	d	e
R	CH_3	C_2H_5	C_3H_7	$(CH_3)_2CH$	$(CH_3)_3C$

The present report might provide a new synthetic route to quinone imine derivatives. The detailed mechanism is not clear at present and a further study is in progress.

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. The elemental analyses (C, H, N) for **3a-e** were in full agreement with the corresponding calculated values.

6-Methyl-5H-benzo[a]phenoxazin-5-one (**3a**)

Method (A)

To a vigorously stirred suspension of 5*H*-benzo[a]phenoxazin-5-one **1** (0.49 g, 0.002 mol), the carboxylic acid **2** (0.015 mol), and silver nitrate (0.2 g) in acetonitrile (100 ml) and water (40 ml) were added a solution of ammonium peroxydisulfate (2.04 g, 0.009 mol) in water (25 ml) during 40 min at 75–80 °C and the mixture was stirred and heated for a further 30 min. After removal of

the organic solvent under reduced pressure, the precipitate was collected, washed well with water, and chromatographed over a aluminium oxide column eluted with benzene. The solid obtained on concentration of the eluate was recrystallized from benzene. Compound **3a** gave yellow crystals; M. p. 209°; yield 38%.

IR (KBr): 1628 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): 2.11 (s, 3H, CH_3 group), 7.05-7.79 (m, 6H, arom.), 7.99—8.31 (m, 1H, arom.), 8.36-8.64 (m, 1H, arom.). MS: $m/e = 261$ (M^+).

Method (B)

A mixture of 2-aminophenol **4** (0.44 g, 0.004 mol) and 2-hydroxy-3-methyl-1,4-naphthoquinone **5** (1.69 g, 0.009 mol) in 10 ml of 90% aqueous acetic acid was heated at 100 °C for 2.5 h. After the removal of the solvent under reduced pressure, the residue was chromatographed on aluminium oxide column using benzene as an eluent. The crude product was further purified by recrystallization from benzene and identified (M. p., IR, ^{1}H-NMR, and MS) as **3a**. Yield 3%.

6-Alkyl-5H-benzo[a]phenoxazin-5-ones (**3b-e**)

Compounds **3b-e** were prepared by the reaction of **1** with **2b-e**.

Compound **3b** gave yellow crystals; M. p., 165°; yield 27%. IR (KBr): 1632 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): 1.18 (t, 3H, CH_3 group), 2.63 (q, 2H, CH_2 group), 6.86-7.69 (m, 6H, arom.), 7.94-8.15 (m, 1H, arom.), 8.16-8.53 (m, 1H, arom.). MS: $m/e = 275$ (M^+).

Compound **3c** gave yellow crystals; M. p. 138°; yield 24%. IR (KBr): 1634 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): 1.07 (t, 3H, CH_3 group), 1.33-1.89 (m, 2H, CH_2 group), 2.13 (t, 2H, CH_2 group), 6.90-7.77 (m, 6H, arom.), 7.94-8.27 (m, 1H, arom.), 8.32-8.64 (m, 1H, arom.). MS: $m/e = 289$ (M^+).

Compound **3d** gave yellow crystals: M. p. 177°; yield 40%. IR (KBr): 1635 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): 1.35 (d, 6H, CH_3 group), 3.63 (q. 1H, CH group), 6.81-7.68 (m, 6H, arom.), 7.88-8.18 (m, 1H, arom.), 8.27-8.53 (m, 1H, arom.). MS: $m/e = 289$ (M^+).

Compound **3e** gave yellow crystals: M. p. 200°; yield 42%. IR (KBr): 1630 cm^{-1} (C=O). ^{1}H-NMR ($CDCl_3$): 1.53 (s, 9H, CH_3 group), 6.91-7.68 (m, 6H, arom.), 7.93-8.15 (m, 1H, arom.), 8.33-8.55 (m, 1H, arom.). MS: $m/e = 303$ (M^+).

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