The Alkylation of 3H-Phenoxazin-3-one Derivatives

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2-Alkyl-, 4-alkyl-, and 2,4-dialkyl-3H-phenoxazin-3-ones were prepared by reacting 3H-phenoxazin-3-one with alkyl radicals in aqueous acetonitrile at 70-75°. The alkyl radicals were generated from the silver catalysed oxidative decarboxylation of acids with peroxydisulphate.

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The addition of alkyl and aryl radicals to quinone has been extensively studied by several workers (1-5) and the high reactivity of quinones toward free readicals is well known (6-8). There have been few studies on those of imino quinones, probably because of their instability. In previous papers, the photochemical reactions of iminoquinones with aldehydes and alkylthiols were investigated and structures were assigned to the reaction products (9,10). As part of the general problem of the study of the reactivity of imino quinones, we have extended the investigation to the reaction of 3H-phenoxazin-3-one derivatives with alkyl radicals.

The alkyl radicals were generated from the silver catalysed oxidative decarboxylation of acid with peroxydisulfate (11). 2-alkyl-, 4-alkyl-, and 2,4-dialkyl-3H-phenoxazin-3one (3, 4, 5) were prepared by the reaction of 3H-phenoxazin-3-one (1) with alkyl radicals in aqueous acetonitrile at 70-75°. Furthermore, compound 5 was obtained by the reaction of 3a with alkyl radicals under the same condition. The results are summarized in Table 1.

Scheme I

Table 1 Physical Properties of 3H-Phenoxazin-3-one Derivatives

Compound No.	R,	R ₂	Yield, %	Mp, °C	Molecular Formula		emental Analys Calcd. (Found) H	
3a	CH ₃	Н	17	204-206	C ₁₃ H ₉ NO ₂ (211.2)	73.92 (73.85)	4.29 (4.39)	6.63 (6.38)
3 b	C_2H_s	Н	27	170-172	C ₁₄ H ₁₁ NO ₂ (225.2)	74.65 (74.35)	4.92 (4.85)	6.22 (5.89)
4a	Н	CH3	12	168-170	C ₁₃ H ₉ NO ₂ (211.2)	73.93 (73.82)	4.29 (4.26)	6.63 (6.31)
5a	CH3	CH ₃	6 (a) 19 (b)	181-182	C ₁₄ H ₁₁ NO ₂ (225.2)	74.65 (74.61)	4.92 (5.01)	6.22 (6.11)
5Ь	C_2H_5	C_2H_5	9	98-99	C ₁₆ H ₁₅ NO ₂ (253.3)	75.88 (75.67)	5.97 (5.71)	3.53 (5.42)
5c	CH ₃	C_2H_5	23 (b)	140-141	C ₁₅ H ₁₃ NO ₂ (239.3)	75.30 (74.97)	5.48 (5.23)	5.85 (5.64)

⁽a) The compound was obtained by the reaciton of 1 with 2a. (b) The compound was obtained by the reaction of 3a with 2a,b.

Table 2
Spectroscopic Data of 3H-Phenoxazin-3-one Derivatives

Compound No.	Mass	Infrared Spectrum cm ⁻¹	'H NMR Spectrum (deuteriochloroform) ppm
3а	211	1650 (C=O); 1618; 1584; 1518; 1464; 1164; 906; 757	2.13 (s, 3H, CH ₃), 6.23 (m, 1H, aromatic), 7.01-7.46 (m, 4H, aromatic), 7.58-7.83 (m, 1H, aromatic)
3Ь	225	1650 (C=O); 1610; 1582; 1514; 1458; 1160; 878; 745	1.28 (t, 3H, CH ₃), 2.54 (q, 2H, CH ₂), 6.22 (s, 1H, aromatic), 6.90-7.47 (m, 4H, aromatic), 7.53-7.83 (m, 1H, aromatic)
4 a	211	1648 (C=0); 1618; 1577; 1516; 1462; 1176; 837; 752	2.08 (s, 1H, CH ₃), 6.64-7.51 (m, 5H, aromatic), 7.56-7.73 (m, 1H, aromatic),
5a	225	1651 (C=O); 1614; 1586; 1509; 1459; 1187; 874; 748	2.06 (s, 3H, CH ₃), 2.17 (s, 3H, CH ₃), 6.98-7.41 (m, 4H, aromatic), 7.57-7.76 (m, 1H, aromatic)
5b	253	1646 (C=O); 1608; 1584; 1512; 1458; 1178; 878; 754	1.13 (t, 6H, CH ₃), 2.61 (q, 4H, CH ₂), 6.93-7.42 (m, 4H, aromatic), 7.48-7.83 (m, 1H, aromatic)
5 c	239	1649 (C=O); 1618; 1586; 1514; 1457; 1187; 897; 757	1.11 (t, 3H, CH ₃), 2.16 (s, 1H, CH ₃), 2.63 (q, 2H, CH ₂), 7.03-7.43 (m, 4H, aromatic), 7.48-7.84 (m, 1H, aromatic)

The structures of the compounds 3-5 were determined by elemental analysis and from spectroscopic data. In particular, the nmr spectra (deuteriochloroform) of 1 exhibited a characteristic singlet at 6.30 ppm due to the olefinic proton but those of 4 and 5 did not show any evidence that could be assigned to this type of proton. Therefore, the addition of alkyl radicals did occur at the 4-position of 1. On the other hand, the nmr spectrum of 3 exhibited a characteristic singlet at 6.30 ppm and compound 3a thus obtained was identical in every respect with a sample prepared by the previously reported method (12). Consequently, compounds 3 were identified as 2-alkyl-3H-phenoxazin-3-ones. Furthermore, compound 5a obtained by the reaction of 1 with 2a was identical in every respect with a sample prepared by the reaction of 3a with 2a.

The presently available method for the preparation of 2-alkyl- and 2,4-dialkyl-3*H*-phenoxazin-3-ones has the disadvantage of the very poor overall yield of the multi-step procedures (12,13). Therefore, the present note provides a new synthetic route to iminoquinone derivatives.

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 reported in reciprocal centimeters. Nuclear magnetic resonance spectra were determined on a Hitachi R-20B spectrometer using tetramethylsilane as an internal reference. Chemical shifts are reported 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 for the Alkylation of 3H-Phenoxazin-3-one (1) and 2-Methyl-3H-phenoxazin-3-one (3a).

To a vigorously stirred suspension of 3*H*-phenoxazin-3-one (1) (0.2 g, 1 mmole) or 2-methyl-3*H*-phenoxazin-3-one (3a), the carboxylic acid (2) (10 mmoles) and silver nitrate (0.17 g, 1 mmole) in acetonitrile (50 ml) and water (20 ml) was added a solution of ammonium peroxydisulfate (0.45 g, 2 mmoles) in water (25 ml) during a period of 45 minutes at 70-75°. The mixture was stirred and heated for an additional 15 minutes. After removal of the organic solvent under reduced pressure, the precipitate was collected, washed well with water and chromatographed over an aluminium oxide column and eluted with benzene. The solid obtained on concentration of the eluate was recrystallized from benzene.

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