

Photoalkylation of Phenanthro[9,10-*d*]oxazole (I)

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The photochemical reaction of phenanthro[9,10-*d*]oxazole with ethanol, 1-propanol, 2-propanol, or diethyl ether resulted in the substitution of the 1- and/or 2-hydroxyalkyl and/or alkyl groups at the position 2.

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Photoalkylations of nitrogen heteroaromatics have received considerable attention in recent years from the synthetic and mechanistic views of point (2)-(17). In general, these reactions involve the addition of alcohol, ether, or amine to C=N and =N-C=N linkages. However, there have been no reports on the photoalkylation of a system having a -O-C=N linkage. Therefore, it is of interest to investigate whether such a system is photochemically susceptible to the same solvent addition. This report describes results of our studies on the photochemical behavior of phenanthro[9,10-*d*]oxazole (I) in ether or hydroxylic solvents. During the investigation we have found a novel example of C-methylation by ethanol solvent.

Irradiation with ultraviolet light longer than 300 nm under nitrogen of phenanthro[9,10-*d*]oxazole (I) in an alcoholic solvent (ethanol, 1-propanol, or 2-propanol) or in diethyl ether led to the substitution of the appropriate moiety for the hydrogen atom at the position 2. The resulting substituent was dependent on the solvent used and was the corresponding hydroxyalkyl and alkyl groups. The reactions studied are summarized in Table I and can be presented as shown in Scheme 1.

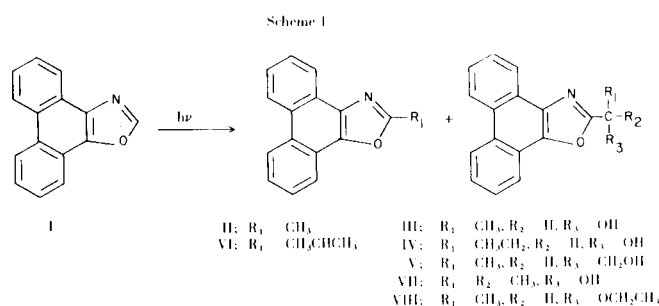
Table I

Photoalkylation of Phenanthro[9,10-*d*]oxazole (I)

Solvent	Time (hour)	Recovered (%)	Products (%) (a)
Ethanol	89	49	II (14.6), III (0.7)
1-Propanol	38	4.7	IV (33.2), V (1.3)
2-Propanol	8	—	VI (3.4), VII (35.9)
Diethyl ether	30	52.1	VIII (7.5), III (4.4)

(a) Yields are based on the total amount of the starting material.

Products were isolated by column chromatography on silica gel after the removal of the solvent under reduced pressure. The progress of the reactions was followed by thin-layer chromatography. The structures of compounds



III-VIII were confirmed by elemental analyses as well as by uv, nmr, and mass spectra. The identification of II was done by comparison with an authentic sample (18) by m.p., ir, and nmr spectral criteria. Spectral data for the products are given in Table 2.

The present result confirms that phenanthro[9,10-*d*]oxazole (I) in alcoholic solvents or diethyl ether undergoes photoalkylation on the carbon of the -O-C=N linkage, as in the case of a system having a C=N linkage previously reported. Thus, most of the photoalkylation described here can be accommodated by analogy with the pathway proposed by Stermitz, *et al.*, (7).

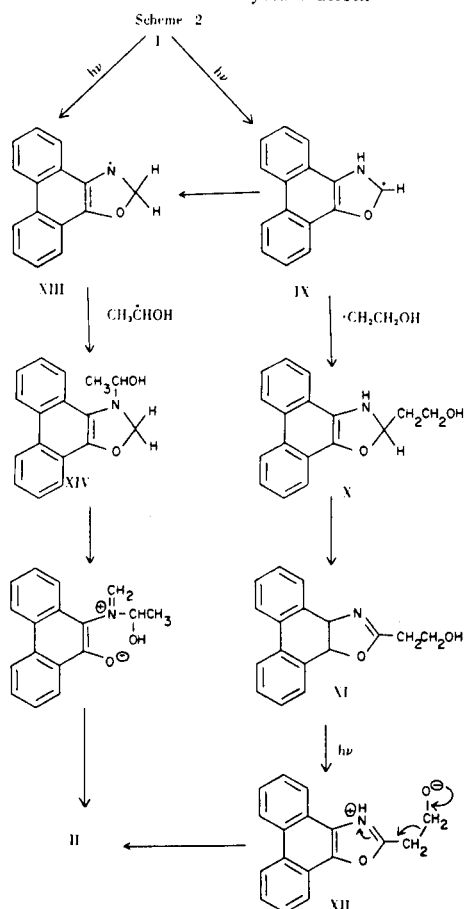
Noteworthy features are that, in 1-propanol, the product V arising from the  $\beta$ -hydrogen abstraction was produced (19), and that the formation of II is a novel example of C-methylation by the solvent ethanol. Formation of the product II is not quite consistent with the literatures on the photoalkylations of nitrogen heteroaromatics by alcohols.

Two structurally distinct mechanistic paths may be considered for the formation of this product II as shown in Scheme 2. One mechanism involves the formation of XI, arising by  $\beta$ -hydrogen abstraction from ethanol solvent, which undergoes further photoelimination to the observed product II *via* an intermediate XII (20). Although we have no sufficient evidence to suppose XI as the precursor of II, a support for such an idea has been found in the photoelimination described by Stermitz, *et al.*, (7), (14),

Table 2

Spectral Data for Photoproducts				
Compounds	M.p. (°C)	Nmr ( $\delta$ ppm) (a)	Ir ( $\text{cm}^{-1}$ ) (b)	Elemental analysis (d)
III	145-147	1.85 (d, 3H, $J = 7$ Hz, $\text{CH}_3\text{CH}-$ ), 3.55 (broad, 1H, OH) (c), 5.31 (q, 1H, $J = 7$ Hz, $-\text{CHCH}_3\text{OH}$ ), 7.5-8.7 (m, 8H, aromatic)	3250	Calcd. for $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$ : C, 77.55; H, 4.98; N, 5.32. Found: C, 77.52; H, 4.93; N, 5.53. Mol. wt. 263
IV	152-152.5	1.10 (t, 3H, $J = 7$ Hz, $\text{CH}_3\text{CH}_2-$ ), 2.16 (quintet, 2H, $J = 7$ Hz, $\text{CH}_3\text{CH}_2-$ ), 3.97 (broad, 1H, OH) (c), 5.08 (t, 1H, $J = 7$ Hz, $-\text{CHOH}$ ), 7.5-8.7 (m, 8H, aromatic)	3260	Calcd. for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ : C, 77.96; H, 5.45; N, 5.05. Found: C, 78.11; H, 5.52; N, 4.88. Mol. wt. 277
V	147-149	1.52 (d, 3H, $J = 7$ Hz, $\text{CH}_3\text{CH}-$ ), 3.05 (broad, 1H, OH) (c), 3.48 (sextet, 1H, $J = 7$ Hz, $\text{CH}_3\text{CH}-$ ), 4.08 (d, 2H, $J = 7$ Hz, $-\text{CH}_2\text{OH}$ ), 7.5-8.7 (m, 8H, aromatic)	3270	Calcd. for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}$ : C, 77.96; H, 5.45; N, 5.05. Found: C, 77.79; H, 5.43; N, 5.03. Mol. wt. 277
VI	80-81	1.55 (d, 6H, $\text{CH}(\text{CH}_3)_2$ ), 3.38 (septuplet, $J = 7$ Hz, CH-), 7.5-8.7 (m, 8H, aromatic)		Calcd. for $\text{C}_{18}\text{H}_{15}\text{ON}$ : C, 82.73; H, 5.79; N, 5.36. Found: C, 82.92; H, 6.19; N, 5.12. Mol. wt. 261
VII (e)	78	1.85 (s, 6H, $\text{C}(\text{CH}_3)_2$ ), 2.81 (broad, 3H, OH, $\text{H}_2\text{O}$ ) (c), 7.5-8.7 (m, 8H, aromatic)	3440	Calcd. for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}\cdot\text{H}_2\text{O}$ : C, 73.20; H, 5.80; N, 4.74. Found: C, 73.25; H, 5.73; N, 4.74. Mol. wt. 277
VIII	oil	1.25 (t, 3H, $J = 7$ Hz, $-\text{CH}_2\text{CH}_3$ ), 1.78 (d, 3H, $J = 7$ Hz, $\text{CH}_3\text{CHO}-$ ), 3.63 (q, 2H, $J = 7$ Hz, $-\text{OCH}_2\text{CH}_3$ ), 4.90 (q, 1H, $J = 7$ Hz, $\text{CH}_3\text{CHO}-$ ), 7.4-8.8 (m, 8H, aromatic)	1110	Calcd. for $\text{C}_{19}\text{H}_{17}\text{O}_2\text{N}$ : C, 78.33; H, 5.88; N, 4.81. Found: C, 78.03; H, 5.78; N, 4.56. Mol. wt. 291

(a) Measured in deuteriochloroform using TMS as an internal standard. (b) Determined with a JASCO DS-701G infrared spectrometer. (c) Deuterium exchangeable. (d) Molecular weights were determined with a JEOL JMS-01SG-2 mass spectrometer. (e) This material has one molecule of water of crystallization.



who have reported that 2-substituted quinoline, isoquinoline, or pyridine having a  $\gamma$ -hydrogen on the side chain undergoes a photoelimination to yield the methyl substituted heterocycle. An alternative and attractive one-step route would involve the unusual dihydro-intermediate XIV which might be formed by direct hydrogen abstraction to the carbon end of the  $-\text{O}-\text{C}=\text{N}$  linkage or by the migration of the hydrogen abstracted from ethanol from nitrogen to carbon prior to the coupling takes place (21). This intermediate XIV would be expected to undergo ring cleavage and ring closure with the concomitant elimination of methanol to the methylated product II. Mechanistic studies to distinguish between these two possibilities are in progress.

#### EXPERIMENTAL

Phenanthro[9,10-*d*]oxazole (I) was prepared according to the literature method (22). Irradiations were conducted in an immersion reactor employing 100 W or 400 W-high pressure mercury lamp through a Pyrex filter. A stream of dry nitrogen was led through the solution prior to irradiation and continued throughout the irradiation. Solvents used for irradiations were reagent grade and redistilled. Column chromatography was carried out on Mallinckrodt silica gel (100 mesh). Thin-layer chromatography was carried out on Wakogel B-O silica gel using iodine vapor for detection.

Photolysis of Phenanthro[9,10-*d*]oxazole (I).

(A) A solution of I (2.625 g.) in refluxing ethanol (600 ml.) was irradiated for 89 hours. After the solvent was removed, the

residue was chromatographed on silica gel eluted with chloroform to be fractionated to three fractions in their order of elution. The first fraction gave the unreacted starting material (1.310 g.). The second fraction, after purification by rechromatography eluted with benzene-petroleum ether (2:1) and recrystallization from ethanol gave II (0.403 g.), m.p. 150-151°, established by comparison of an authentic sample. The last fraction, after rechromatography eluted with chloroform, gave a viscous oil. By addition of cold diethyl ether, crystals of III were precipitated. Further purification by sublimation (120°, 10<sup>-5</sup> mm Hg) gave needles (0.020 g.).

(B) A solution of I (1.929 g.) in 1-propanol (840 ml.) was irradiated at 68° for 38 hours. The usual work-up as above and column chromatography eluted with chloroform led to the starting material (0.091 g.), IV (0.807 g.), and V (0.032 g.). These products were then purified by column chromatography using a mixture of ethyl acetate and benzene (1:5) as the eluent and recrystallization from ethanol.

(C) A solution of I (1.320 g.) in 2-propanol (635 ml.) was irradiated at 76° for 8 hours. The usual work-up as above and chromatography eluted with chloroform led to the products VI (0.053 g.) and VII (0.635 g.). These products were further purified by recrystallization from ethanol, and acetone-water, respectively.

(D) A solution of I (1.971 g.) in diethyl ether (840 ml.) was irradiated at 32° for 30 hours. After the solvent was removed, the residue was chromatographed on silica gel eluted with chloroform to be fractionated to three fractions in order of elution. The first fraction, after purification by subsequent chromatography using a mixture of ethyl acetate and *n*-hexane (1:5) as the eluent, gave VIII (0.119 g.). The second fraction gave the starting material (1.028 g.). The last fraction, after purification by rechromatography using a mixture of ethyl acetate and chloroform (1:5) as the eluent, gave III (0.013 g.).

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