# Photochemical Behavior of Some Substituted Benzophenoxazinones



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Irradiation of some substituted benzophenoxazinones in methanol solution by visible light yields dimerization and substitution products. A possible radical mechanism is proposed and validated by quantum mechanical computations.

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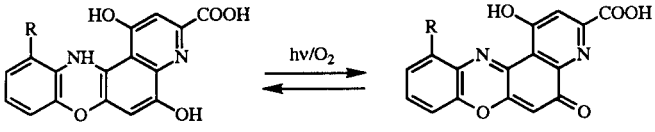
## Introduction.

Skin and eye colors of invertebrates are for the most part due to ommochromes [1], a class of naturally occurring phenoxazinonic pigments. The red dihydroxanthommatin and the yellow xanthommatin (Figure 1) are the most representative ommochromes.

Although these cell pigments are widespread in the invertebrate photoreceptors and show a very interesting redox photochromism, their role and chemistry are still largely unknown.




Dihydroxanthommatin
R = $COCH_2CH(NH_2)COOH$

Xanthommatin

Figure 1

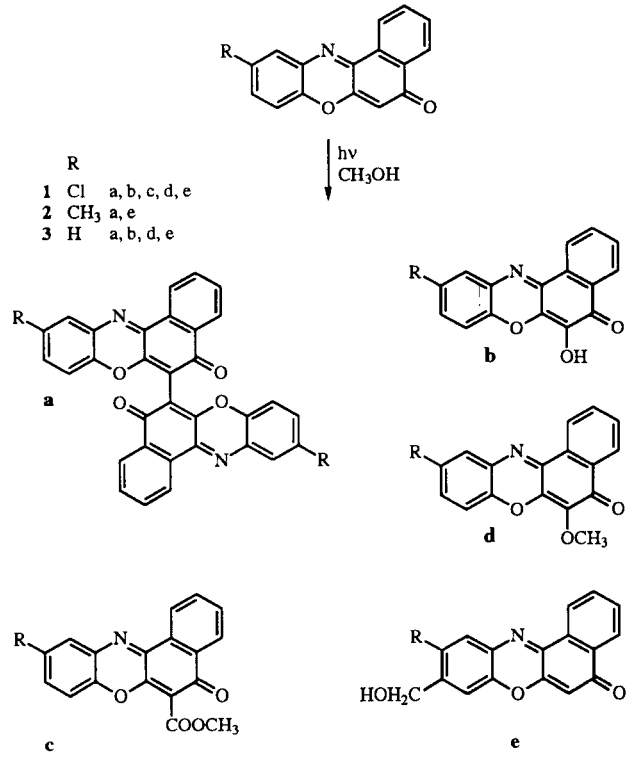
Our interest in the photoreactivity of ommochromes by visible light [2,3], as well as in the radical oxidation of phenols and aromatic amines [4,5], led us to explore the behavior of some substituted benzophenoxazinones as models of the light-sensitive ommochromes.

In the present paper we attempt to interpret the reactivity of some iminoquinones irradiated in methanol by visible light on the basis of knowledge of the quinone chemistry. The Scheme 1 shows the products recovered from the irradiated solutions of 10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1**) [6], 10-methyl-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**2**) [6] and 5*H*-benzo[3,2-*a*]phenoxazin-5-one (**3**) [6].

## Results and Discussion.

A $10^{-2}$ *M* solution of **1** in methanol was irradiated by a solar lamp (Osram 600 W) in a quartz flask at 25° as long as the starting material disappeared. The mixture, dried *in vacuo*, and analyzed by tlc afforded five colored products: 6-6'-di-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1a**), 6-hydroxy-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1b**), 6-carbomethoxy-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1c**), 6-methoxy-10-chloro-5*H*-benzo[3,2-*a*]-phenoxazin-5-one (**1d**), and 9-hydroxymethyl-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1e**) (Scheme 1). The structures were established by spectral (uv, ir, nmr, ms) and elemental analyses

Scheme 1




Compound **1b** was also converted into its methyl derivative, by treating with diazomethane in methanol.

Comparison of chromatographic and spectroscopic properties showed that the orange **1d** product, present in the irradiated solution of **1**, is identical to the methyl derivative of **1b**.

Methanol solutions of **2** and **3** (Scheme 1), irradiated under the same conditions and analyzed chromatographically, afforded the colored compounds **2a**, **2e** and **3a**, **3b**,

**3d** and **3e**, respectively. Spectral data and elemental analyses are summarized in the experimental.

The Table 1 reports the yields of the photochemical irradiation of the phenoxazinones **1**, **2**, and **3** in methanol and the product distribution after four hours of reaction.

Table 1

Reaction Yields (% in moles) and Product Distribution after Four Hours of Uninterrupted Irradiation of Phenoxazinones **1**, **2**, **3** in methanol ($10^{-2}$ *M*). Irradiation Reaction was Performed by a Solar Lamp, Osram 650 W, at 25°. **a**, **b**, **c**, **d**, **e** = mole 10 $M^{-3}$

| $10^{-2}M$ R | | yield % in moles | **a** | **b** | **c** | **d** | **e** |
|---|---|---|---|---|---|---|---|
| **1** | Cl | 54.5 | 1.30 | 0.50 | 0.34 | 0.78 | 1.23 |
| **2** | $CH_3$ | 70.2 | 3.02 | | | 0.98 | |
| **3** | H | 56.3 | 1.66 | 0.79 | | 0.51 | 1.01 |

Whereas the methanol solutions of the 5*H*-benzo[3,2-*a*]-phenoxazin-5-ones, **1**, **2** and **3** are stable in the dark, they react under visible light irradiation, suggesting that excited forms of the iminoquinone system could play a role in the reaction.

Although the quinone photochemistry has been studied extensively, the behavior of iminoquinones is still not completely understood. In the light-induced intermolecular reactions of quinones in alcohol, there is still controversy about whether the primary reaction of the excited quinone is an electron transfer followed by proton transfer or a direct hydrogen atom transfer from the α-position of the alcohol to the excited quinone. Nevertheless, both reaction mechanisms give a semiquinone radical intermediate [7].

product formation: oxygen and nitrogen, present in the quinoniminic system, could compete each other, affording the intermediates **A** and **B** (Scheme 2), which direct the subsequent reactivity towards 6 and 9 positions, respectively.

The presence on the 10 position of the benzophenoxazinone system of the electron-withdrawing chlorine seems to decrease whereas the electron-donating methyl group seems to increase the reaction yield; the less the system is reactive, the more numerous the products are.

Moreover, the product distribution suggests the hypothesis that the relative stability of the two intermediate radicals **A** and **B** could affect the reaction yields.

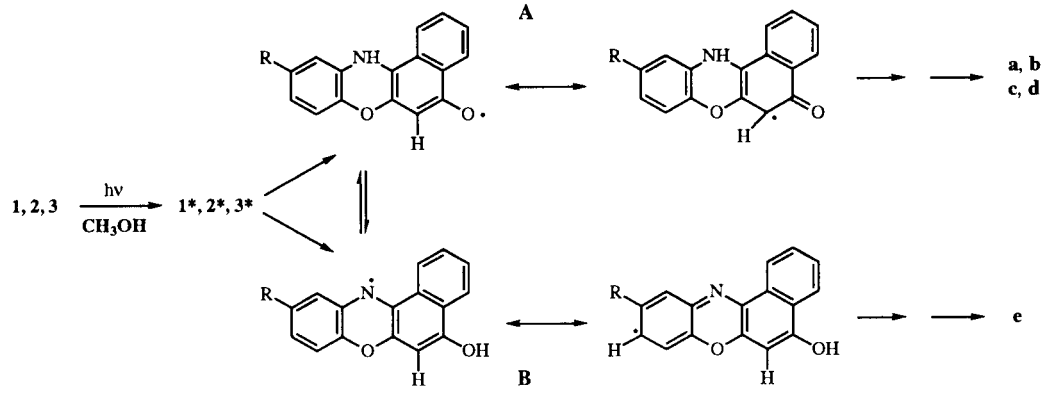
Therefore, the species **A** and **B** have been characterized by semiempirical AM1 computations [8], using the MOPAC/6 program [9] and the half-electron approximation [10] for open-shell systems. The geometry of the **A** and **B** radicals, resulting from **1**, **2**, and **3**, has been fully optimized with the only constraint of $C_S$ symmetry. The results, collected in Table 2, show that the **A** radical always remains more stable, irrespective of substitution at C10.

Table 2

Relative Stability of **A** and **B**-Intermediates in Kcal/mol, at 298K, Computed using the MOPAC/6 Program

| | **A** | | | **B** | | |
|---|---|---|---|---|---|---|
| | ΔH° | % Calcd. | Found | ΔH° | % Calcd. | Found |
| **1** | 29.42 | 77.4 | 77 | 30.17 | 22.6 | 23 |
| **2** | 28.10 | 84.6 | 86 | 29.12 | 15.4 | 14 |
| **3** | 35.65 | 82.2 | 82 | 36.56 | 17.8 | 18 |

Scheme 2




Analogously with the quinone photochemistry, the phenoxazinones **1-3**, irradiated by visible light in methanol, could give rise to excited forms **1***, **2***, **3***, which, decaying by a hydrogen abstraction or by electron transfer, could yield a semiquinonimine radical involved in the

According to the quinone chemistry, the products **a**, **b**, **c**, and **d** seem to arise from the intermediate **A** while **e** seems to arise from intermediate **B**. The products **1-3a** could be formed by an oxidative coupling of **A**, after tautomerization followed by oxidation. The oxidant agent in

solution could be either the starting phenoxazinones or air. Since hydroxyphenoxazines are very unstable compounds and easily yield phenoxazinones, no disproportionation reaction could be observed.

On the other hand, photooxidative couplings of quinones have been reported in the irradiation of 5-bromouracil [11] and in the irradiation of 2-methyl and of 2-hydroxy-1,4-naphthoquinone, model compounds of naturally occurring vitamins and [12]. The photochemical oxidative dimerization was also hypothesized in the formation of actinorhodin, a naturally occurring antibiotic [11].

The hydroxylation reaction yielding **1b** and **3b** is widely reported in the quinone chemistry [7,13]. It has been suggested that hydroxy radicals are formed in the irradiated solutions of quinones containing either water or oxygen. The hydroxy radical could couple with the stable **A** semiquinone radical and, after tautomerization and oxidation, affords **1b** and **3b**. Also the 6-carbomethoxy derivative, recovered from the irradiated mixture of **1**, probably arises from a coupling between **A** and radical by-products of the methanol oxidation, HCOH and HCOOH. Oxidation and esterification reaction could take place in another step. The occurrence of methoxy derivatives **1d** and **3d** could be due either to a coupling between **A** and the methoxy radical or to a substitution reaction on **1b** and **3b**, respectively. On this topic, we reported the isolation of 1,6-dimethoxy-11-(β-aspartoyl-*N*-acetylmethyl ester)-5*H*-pyrido[3,2-*a*]phenoxazin-5-one arising from the irradiated solution of 1-methoxy-11-(β-aspartoyl-*N*-acetylmethyl ester)-5*H*-pyrido[3,2-*a*]phenoxazin-5-one in acidic methanol [2]. Solvent addition products, **1e** and **3e,** probably arise from a coupling between **B** and the alcohol carbon-radical. On the last reaction the addition of methanol and ethanol to 1,4-diaminoanthraquinone was reported [14].

In conclusion, many evidences indicate that, in methanol solution and under visible light irradiation, the iminoquiquinone system present in the phenoxazinones gives rise to an excited state which seems to decay yielding an equilibrium mixture of two sequinonimine radicals **A** and **B**. Independently from the way in which these radicals are produced, the substituent effect, modifying the ratio between the two possible intermediates, correctly reproduces the product distribution and supports the proposed hypothesis of the products formation.

## EXPERIMENTAL

Melting points were determined with a Kofler apparatus and are uncorrected. Electron impact (ei) mass spectra were obtained at 70 ev on a VG ZAB 2F spectrometer. The purity of the compounds was checked by ascending tlc on F254 Merck's precoated silica-gel plates (0.25 mm) with fluorescent baking.

The ir spectra were taken on a Perkin-Elmer 399 spectrophotometer in potassium bromide. The $^1$H nmr spectra, recorded in deuteriochloroform and reported in δ, were recorded on a Bruker 270 MHz spectrometer with TMS as internal reference.

General Procedure for the Irradiation of Benzophenoxazinones **1**, **2**, and **3**.

A solution $10^{-3}$ *M* of phenoxazinone in methanol was irradiated, 24 hours, in a quartz flask at 25°, by sunlight lamp 650 W OSRAM at 10 cm of distance. When the starting material disappeared, the reaction mixture was concentraded *in vacuo* and analyzed by tlc (silica gel 1 mm) using chloroform as eluent.

The chromatograms afforded the products **1a,b,c,d,e**, **2a,e**, **3a,b,d,e**, respectively from **1**, **2**, and **3**.

6-6'-Di-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1a**).

The product was collected as a yellow powder, mp 221-222°; ir: 1665, 1625 cm$^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 446 nm (3.22), 354 (3.34); $^1$H nmr (deuteriochloroform): δ 8.80 (2H, dd, J = 7.2, $J_m$ = 2.0 Hz), 8.30 (2H, dd, J = 7.2, $J_m$ = 2.2 Hz), 7.86 (2H, d, $J_m$ = 2.4 Hz), 7.82 (2H, dt, J = 7.2, $J_m$ = 2.2 Hz), 7.80 (2H, dt, J = 7.2, $J_m$ = 2.0 Hz), 7.33 (2H, dd, J = 8.8, $J_m$ = 2.4 Hz), 7.03 (2H, d, J = 8.8 Hz); ms: 560 (93%, M+).

*Anal.* Calcd. for $C_{32}H_{14}Cl_2N_2O_4$: C, 68.47; H, 2.51; N, 4.99. Found: C, 68.54; H, 2.52; N, 5.00.

6-Hydroxy-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1b**).

The product was collected as a red powder, mp 250-251°; ir: 3078, 1660, 1625 cm$^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 485 nm (3.49), 360 (3.61); $^1$H nmr: δ 8.74 (1H, dd, J = 8.7, $J_m$ = 2.2 Hz), 8.31 (1H, dd, J = 8.7, $J_m$ = 2.2 Hz), 7.79 (1H, dt, J = 8.7, $J_m$ = 2.2 Hz), 7.77 (1H, dt, J = 8.7, $J_m$ = 2.2 Hz), 7.54 (1H, d, $J_m$ = 2.4 Hz ), 7.39 (1H, dd, J = 9.1, $J_m$ = 2.4 Hz), 7.32 (1H, d, J = 9.1 Hz), 9.30 (1H, bs, DCl exchangeable); ms: 297 (71%, M+), 287 (100, M$^-$OH).

*Anal.* Calcd. for $C_{16}H_8ClNO_3$: C, 64.55; H, 2.71; N, 4.71. Found: C, 64.41; H, 2.72; N, 4.73.

A solution of **1b** (30 mg) in methanol was treated with diazomethane in diethyl ether and converted to the methyl derivative. Spectral and elemental analyses showed that this compound is equal to **1d**.

6-Carbomethoxy-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1c**).

This red-orange crystalline compound had mp 244-245°; ir: 1733 cm$^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 441 (2.82), 356 (2.80) nm; $^1$H nmr: δ 8.72 (1H, dd, J = 6.8, $J_m$ = 2.3 Hz), 8.33 (1H, dd, J = 6.7, $J_m$ = 2.4 Hz), 7.89 (1H, d, $J_m$ = 2.3 Hz), 7.85 (1H, dt, J = 6.8, $J_m$ = 2.4 Hz), 7.82 (1H, dt, J = 6.7, $J_m$ = 2.3 Hz), 7.50 (1H, dd, J = 8.8, $J_m$ = 2.3 Hz), 7.35 (1H, d, J = 8.8 Hz), 4.04 (3H, s); ms: 339 (100%, M+), 308 (60, M$^-$OMe).

*Anal.* Calcd. for $C_{18}H_{10}ClNO_4$: C, 63.64; H, 2.97; N, 4.12. Found: C, 63.59; H, 2.96; N, 4.10.

6-Methoxy-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1d**).

The product was collected as a yellow powder, mp 164-165°; ir: 1670, 1620 cm$^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 456 nm (2.94), 355 (3.05); $^1$H nmr: δ 8.69 (1H, dd, J = 6.5, $J_m$ = 2.7 Hz), 8.32 (1H, dd, J = 5.7, $J_m$ = 3.5 Hz), 7.81 (1H, d, $J_m$ = 2.4 Hz), 7.79 (1H, dt, J = 6.5, $J_m$ = 2.7 Hz), 7.79 (1H, dt, J = 5.7, $J_m$ = 3.5 Hz), 7.42 (1H, dd, J = 8.8, $J_m$ = 2.4 Hz ), 7.33 (1H, d, J = 8.8 Hz), 4.13 (3H, s); ms: 311 (100%, M+), 280 (71, M$^-$OMe).

*Anal.* Calcd. for $C_{17}H_{10}ClNO_3$: C, 65.50; H, 3.23; N, 4.49. Found: C, 65.66; H, 3.24; N, 4.50.

9-Hydroxymethyl-10-chloro-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**1e**).

The product was collected as yellow powder of mp 242-243°; ir: 3540, 1667, 1610 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 443 (3.85) 356 (3.61) nm; $^1H$ nmr: δ 8.71 (1H, dd, J = 7.1, $J_m$ = 2.2 Hz), 8.24 (1H, dd, J = 6.8, $J_m$ = 2.4 Hz), 7.83 (1H, s), 7.80 (1H, dt, J = 7.1, $J_m$ = 2.4 Hz), 7.78 (1H, dt, J = 6.8, $J_m$ = 2.2 Hz), 7.56 (1H, s) 6.46 (1H, s), 4.85 (2H, bs), 3.20 (1H, bs, deuteriumoxide exchangeable); ms: 311 (70%, M+), 310 (100%, M-H).

*Anal.* Calcd. for $C_{17}H_{10}ClNO_3$: C, 65.50; H, 3.23; N, 4.49. Found: C, 65.75; H, 3.21; N, 4.51.

6-6'-Di-10-methyl-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**2a**).

The product was collected as orange crystals, mp 173-174°; ir: 1668, 1620 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 454 nm (4.10), 359 (4.19); $^1H$ nmr: δ 8.82 (2H, dd, J = 5.2, $J_m$ = 0.8 Hz), 8.38 (2H, dd, J = 4.1, $J_m$ = 0.9 Hz), 7.82 (2H, dt, J = 5.2, $J_m$ = 0.9 Hz), 7.77 (2H, dt, J = 4.1, $J_m$ = 0.8 Hz), 7.67 (2H, d, $J_m$ = 1.1 Hz), 7.17 (2H, dd, J = 5.6, $J_m$ = 1.1 Hz), 6.97 (2H, d, J = 5.6 Hz), 2.43 (6H, s); ms: 520 (100%, M+).

*Anal.* Calcd. for $C_{34}H_{20}N_2O_4$: C, 78.45; H, 3.87; N, 5.38. Found: C, 78.56; H, 3.86; N, 5.40.

9-Hydroxymethyl-10-methyl-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**2e**).

The product was collected as a yellow powder, mp 237-238°; ir: 3538, 1665, 1612 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 449 (3.82) 3.63 (4.30) nm; $^1H$ nmr: δ 8.71 (1H, dd, J = 6.9, $J_m$ = 2.4 Hz), 8.30 (1H, dd, J = 6.7, $J_m$ = 2.3 Hz), 7.78 (1H, dt, J = 6.9, $J_m$ = 2.3 Hz), 7.75 (1H, dt, J = 6.7, $J_m$ = 2.4 Hz), 7.60 (1H, s), 7.44 (1H, s), 7.36 (1H, s), 6.43 (2H, s), 2.36 (3H, s), 3.32 (1H, bs, deuteriumoxide exchangeable); ms: 291 (70%, M+), 290 (100, M-H).

*Anal.* Calcd. for $C_{18}H_{13}NO_3$: C, 74.22; H, 4.50; N, 4.81. Found: C, 74.19; H, 4.48; N, 4.79.

6-6'-Di-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**3a**).

The product was collected as an orange powder, mp 249-250°; ir: 1665 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 439 nm (4.62), 356 (4.72); $^1H$ nmr: δ 8.84 (2H, dd, J = 6.0, $J_m$ = 1.7 Hz), 8.39 (2H, dd, J = 7.2, $J_m$ = 1.5 Hz), 7.87 (2H, dd, J = 7.7, $J_m$ = 1.1 Hz), 7.81 (2H, dt, J = 7.2, $J_m$ = 1.7 Hz), 7.79 (2H, dt, J = 6.0, $J_m$ = 1.5 Hz), 7.78 (2H, dt, J = 7.7, $J_m$ = 2.2 Hz), 7.31 (2H, dt, J = 7.7, $J_m$ = 1.1 Hz), 7.09 (2H, dd, J = 7.7, $J_m$ = 2.2 Hz); ms: 492.

*Anal.* Calcd. for $C_{32}H_{16}N_2O_4$: C, 78.04; H, 3.27; N, 5.69. Found: C, 78.15; H, 3.28; N, 5.70.

6-Hydroxy-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**3b**).

The product was collected as a red powder, mp 250-251°; ir: 3075, 1662, 1620 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 440 nm (3.49), 360 (3.61); $^1H$ nmr: δ 8.55 (1H, dd, J = 7.8, $J_m$ = 1.9 Hz), 8.15 (1H, dd, J = 7.0, $J_m$ = 1.5 Hz), 7.68 (1H, dt, J = 7.8, $J_m$ = 1.5 Hz), 7.65 (1H, dt, J = 7.0, $J_m$ = 1.9 Hz), 7.52 (1H, dd, J = 7.8, $J_m$ = 1.5 Hz), 7.24 (1H, dt, J = 7.8, $J_m$ = 1.5 Hz), 7.16 (1H, dd, J = 7.8, $J_m$ = 1.5 Hz), 7.11 (1H, dt, J = 7.8, $J_m$ = 1.5 Hz), 9.27 (1H, s, DCl exchangeable); δ ms: 263 (82%, M+) 262 (100, M-H).

*Anal.* Calcd. for $C_{16}H_9NO_3$: C, 73.00; H, 3.45; N, 5.32. Found: C, 73.06; H, 3.46; N, 5.34.

6-Methoxy-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**3d**).

The product was collected as a yellow powder, mp 165-166°; ir: 1670, 1620 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 446 (3.51), 359 (3.50) nm; $^1H$ nmr: δ 8.77 (1H, dd, J = 8.4, $J_m$ = 1.6 Hz), 8.39 (1H, dd, J = 7.8, $J_m$ = 2.0 Hz), 7.89 (1H, dt, J = 7.1, $J_m$ = 2.1 Hz), 7.81 (1H, dt, J = 7.8, $J_m$ = 1.6 Hz), 7.78 (1H, dd, J = 8.4, $J_m$ = 2.0 Hz), 7.55 (1H, dd, J = 7.8, $J_m$ = 2.1 Hz), 7.51 (1H, dt, J = 7.8, $J_m$ = 2.0 Hz), 7.41 (1H, dt, J = 7.8, $J_m$ = 2.0 Hz), 4.15 (3H, s); ms: 277 (100%, M+).

*Anal.* Calcd. for $C_{17}H_{11}NO_3$: C, 73.64; H, 4.00; N, 5.05. Found: C, 73.69; H, 4.02; N, 5.07.

9-Hydroxymethyl-5*H*-benzo[3,2-*a*]phenoxazin-5-one (**3e**).

The product was collected as a yellow powder, mp 252-253°; ir: 3540, 1665, 1613 $cm^{-1}$; uv (chloroform): $\lambda_{max}$ log (ε) 424 (3.40) 370 (3.38) nm; $^1H$ nmr: δ 8.70 (1H, dd, J = 8.1, $J_m$ = 2.4 Hz), 8.27 (1H, dd, J = 8.1, $J_m$ = 2.2 Hz), 7.85 (1H, d, J = 8.1 Hz), 7.78 (1H, dt, J = 8.1, $J_m$ = 2.2), 7.76 (1H, dt, J = 8.1, $J_m$ = 2.2 Hz), 7.53 (1H, dd, J = 8.1, $J_m$ = 2.2 Hz), 7.35 (1H, d, $J_m$ = 2.2), 7.30 (1H, s, deuteriumoxide exchangeable), 6.42 (1H, s), 4.80 (2H, s); ms: 277 (75%, M+), 276 (100, M-H).

*Anal.* Calcd. for $C_{17}H_{11}NO_3$: C, 73.64; H, 4.00; N, 5.05. Found: C, 73.53; H, 4.03; N, 5.03.

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