The acidic, methyl isobutyl ketone extracted aqueous filtrate was treated as in the preceding procedure to obtain potassium phenethicillin in 12.7% yield.

After the 6-APA was removed, the methyl isobutyl ketone filtrate was concentrated *in vacuo* to a brown solid: weight, 1.05 g; mp 164.3–166.5°. This was recrystallized twice from a boiling mixture of 2-propanol and water (3:1). Darco KB was used in the first recrystallization. A white, crystalline sample of 3,4-dihydro-2,2-dimethyl-2H-1,4-benzoxazin-3-one (**6b**) was obtained: weight, 0.45 g (36.8%); mp 165.6–166.1° (lit.[23] mp 161.5°); $\nu_{max}^{KBr}$ 2900–3200 (NH, CH), 1690 (C=O), 1251 (Ph-O-C), and 760 $cm^{-1}$ (aromatic hydrogens). An aqueous solution of this compound gave no color change when treated with 5% aqueous ferric chloride solution.

*Anal.* Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 68.00; H, 6.41; N, 8.21.

In a similar manner, 3,4-dihydro-2H-1,4-benzoxazin-3-one (**6a**) was obtained after the catalytic reduction of potassium 6-(*o*-nitrophenoxyacetamido)penicillanate under hydrogen pressure: mp 171.0–174.8° (lit.[24] mp 173.5°); $\nu_{max}^{KBr}$ 2900–3200 (NH, CH), 1700 (C=O), 1220 (Ph-O-C), and 748 $cm^{-1}$ (aromatic hydrogens). An aqueous solution of this compound did not change color when treated with 5% aqueous ferric chloride solution.

(23) C. A. Bischoff, *Chem. Ber.*, **33**, 931 (1900).

(24) W. A. Jacobs and M. Heidelberger, *J. Am. Chem. Soc.*, **39**, 2188 (1917).

# Photochemistry of 2-Alkylaminophenoxaz-3-ones.[1a] II

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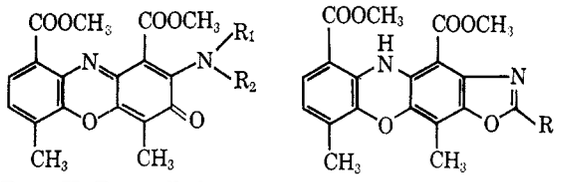
As a continuation of our previous study[2] the photochemistry of 2-dialkylaminophenoxaz-3-ones has been investigated. In general these compounds have been found to be more photoreactive than the corresponding monoalkylaminophenoxaz-3-ones. The 2-dimethylaminophenoxaz-3-one **4** underwent photochemical demethylation. Irradiation of the 2-polymethyleniminophenoxaz-3-ones gave various products depending upon the size of the polymethylenimine ring. The phenoxazones **9**, **11**, and **12** gave novel pentacyclic compounds **23**, **25**, and **26**, respectively. Stable dihydrophenoxaz-3-ones have been obtained by the reduction of compounds **10**, **11**, and **12**.

In an earlier paper,[2] we described the preparation and photochemistry of 2-monoalkylaminophenoxaz-3-ones **1**. Depending upon the nature of the 2-alkylamino substituent, an oxazolophenoxazine **2** or an oxazolinophenoxazine **3** was observed to be the photoproduct (Scheme I). We have now extended our studies to the photochemistry of 2-dialkylamino- and 2-polymethyleniminophnoxaz-3-ones.

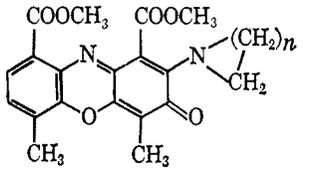
SCHEME I

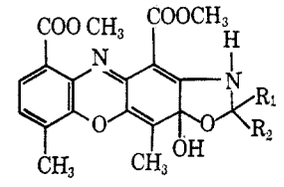


**1**, $R_1$ = H, $R_2$ = alkyl
**4**, $R_1$ = $R_2$ = $CH_3$
**6**, $R_1$ = H, $R_2$ = $CH_2CH(OCH_3)_2$
**7**, $R_1$ = H, $R_2$ = $CH_2CH_2OCH_3$
**13**, $R_1$ = H, $R_2$ = $CH_3$



**2**, R = H
**16**, R = $CH(OCH_3)_2$
**17**, R = $CH_2OCH_3$





**3**, $R_1$ = $R_2$ = alkyl
**5**, $n$ = 1
**8**, $n$ = 2
**9**, $n$ = 3
**10**, $n$ = 4
**11**, $n$ = 5
**12**, $n$ = 6

The phenoxaz-3-ones[3] **4** to **12** were prepared from the corresponding 2-chlorophenoxaz-3-one by treatment with an appropriate amine as described in the preceding paper.[3] With the exception of the ethyleniminophenoxaz-3-one **5**, all of these products were found to be much more light sensitive than the corresponding monosubstituted compounds. Purification of these compounds had to be carried out by crystallization in the absence of light and all except **5** and **8** decomposed during thin layer chromatography (tlc). The nmr spectra of all the phenoxaz-3-ones were consistent with assigned structures (*cf.* Experimental Section).

**Photolysis of 2-Dialkylaminophenoxaz-3-ones.**—Irradiation of 2-dimethylaminophenoxaz-3-one **4** gave an unstable intermediate (Experimental Section) which on work-up formed 2-methylaminophenoxaz-3-one[3] **13**. The first step in this demethylation process appears to be the formation of a zwitterionic compound **14** and the latter then gives **13** by hydrolysis and oxidation. An alternative cyclization of **14** to the oxazoline **15** did not take place probably because of the ease of hydrolysis of the former (Scheme II). The intermediates derived from the irradiation of 2-polymethyleniminophenoxaz-3-ones may be less susceptible to hydrolysis than **14**, thus providing an opportunity for cyclization. It was, therefore, decided to study the photochemistry of a series of 2-polymethyleniminophenoxaz-3-ones.

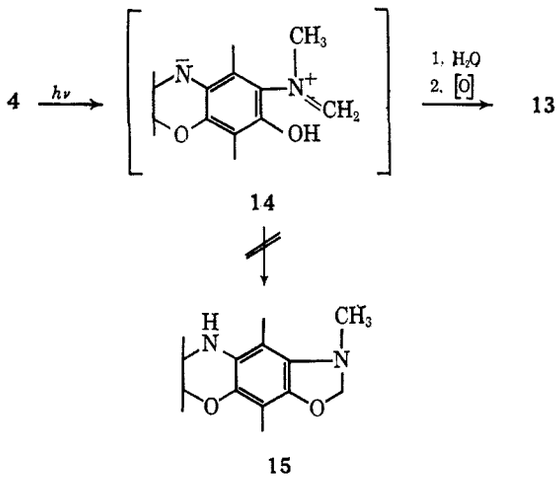
The ethyleniminophenoxaz-3-one **5**, the first member of this series, did not give any identifiable product upon photolysis in benzene; most of the starting

(1) (a) This work was supported by Grant No. DA-ARO(D)-31-124-G250 and Contract No. DA-31-124-ARO(D)-169 with the U. S. Army Research Office; (b) Department of Chemistry, North Carolina State University, Raleigh, N. C.

(2) S. G. Levine and M. C. Wani, *J. Org. Chem.*, **30**, 3185 (1965).

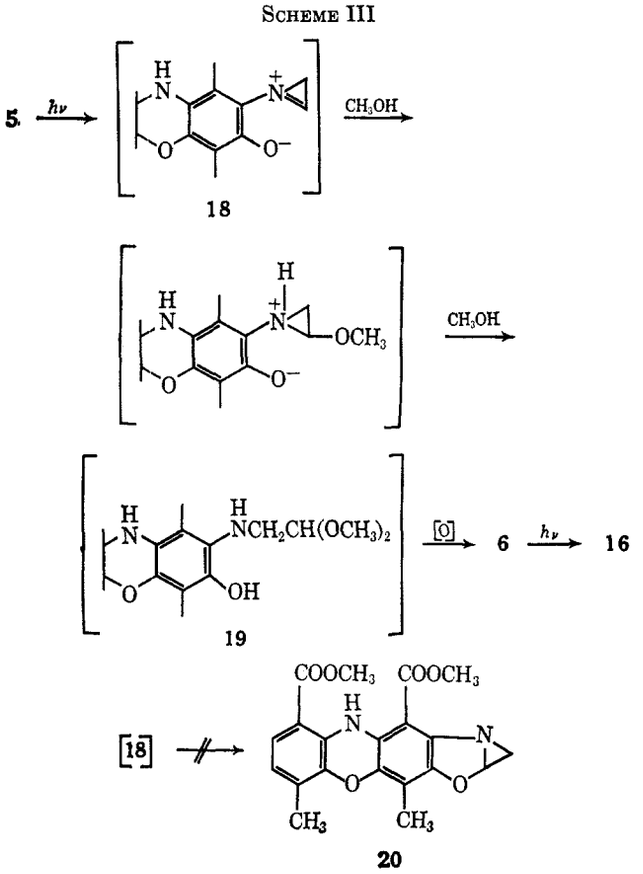
(3) In connection with the preparation of 2-azetidinophenoxaz-3-one **8**, it is interesting to note that, although the nmr spectrum of the sample of azetidine prepared according to the method of I. M. Roberts and D. Horvitz [*Chem. Abstr.*, **58**, 10172 (1963)] indicated the presence of allylamine, the product was pure **8** as shown by its tlc and nmr spectrum. Since a large excess of the amine was used, a possible explanation of this observation may lie in the greater nucleophilicity of azetidine over allylamine.

SCHEME II

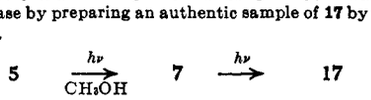


material was recovered unchanged. However, small amounts of a fluorescent product could be isolated as the only stable product from the photolysis mixture when 25% methanol in benzene was used as a solvent. This fluorescent product was found to be identical with the oxazole **16** obtained by the photolysis or pyrolysis[3] of 2-$\beta$,$\beta$-dimethoxyethylaminophenoxaz-3-one **6**.[4] The oxazole **16** may arise through the sequence of steps in Scheme III. Since the reaction was carried out in an

SCHEME III



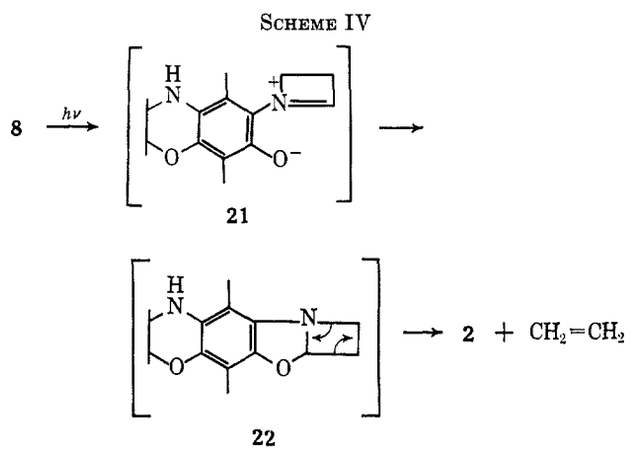
(4) It was first thought that the fluorescent product might be the oxazole **17** resulting from the photolysis of 2-$\beta$-methoxyethylaminophenoxaz-3-one **7**. The latter could have originated from the light-catalyzed addition of methanol to the ethylenimine ring of **5**. Subsequently, it was proved that this was not the case by preparing an authentic sample of **17** by the photolysis or pyrolysis[3] of **7**.



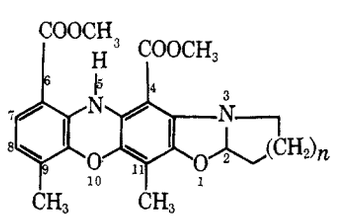
atmosphere of nitrogen, the oxidation of **19** to **6** probably took place with the unreacted **5**. Cyclization of the zwitterionic intermediate **18** to the pentacyclic compound **20** did not occur presumably because of the strain involved in the latter structure (Scheme III).

Photolysis of 2-azetidinophenoxaz-3-one **8** likewise failed to yield a pentacyclic product. The fluorescent substance actually obtained was identified as the unexpected oxazole **2** previously prepared by the photolysis or pyrolysis[3] of **13**. This photochemical degradation could have taken place *via* ring closure of the intermediate zwitterion **21** to the pentacyclic compound **22** followed by fragmentation of the latter (Scheme IV).

SCHEME IV



A stable pentacyclic product was, however, obtained by photolysis of the pyrrolidinophenoxaz-3-one **9**. In agreement with structure **23**, the nmr spectrum of

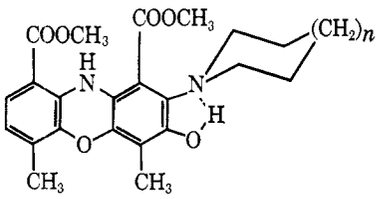


**23**, $n=0$
**24**, $n=1$
**25**, $n=2$
**26**, $n=3$

this substance showed a peak at $\tau$ 4.14 (triplet) attributable to the proton on C-2 of the oxazoline ring. Examination of a molecular model of **23** reveals that the conformer with a *trans*- 2,3 ring juncture is very highly strained and the compound probably exists predominantly in the *cis* form. Compound **23** could be converted back to **9** by catalytic hydrogenation followed by oxidation.

Photolysis of the higher homologs **10**, **11**, and **12** led to analogous pentacyclic products **24**,[5] **25**, and **26**, each of which exhibited an nmr signal near $\tau$ 4.1. These three substances were further characterized by hydrogenation to crystalline dihydro compounds **27**, **28**, and **29**. The product, in each case, was stable to air oxidation in solution as well as in the crystalline state. This behavior is in contrast to the generally observed tendency of dihydrophenoxazones to revert

(5) Compound **24** was obtained as an oil only, even after preparative tlc. The spectral properties of this oil were similar to those of **23**.



**27**, $n=1$
**28**, $n=2$
**29**, $n=3$

to the parent substances on exposure to air. The dihydrophenoxazones from **4**, **5**, **8**, and **9** behaved typically and could not be isolated.

We may conclude that in this series of reactions as in those previously described,[2] the initial step of the photochemical process appears to be that of hydrogen abstraction from the dialkylamino group by the excited quinone carbonyl. The subsequent course of the reaction depends, in each case, upon the nature of the dialkylamino group.

## Experimental Section[6]

**General Procedure for the Preparation of 4,6-Dimethyl-1,9-dicarbomethoxy-2-alkylaminophenoxaz-3-ones.**—A solution (1.0 ml/mg) of 2-chlorophenoxaz-3-one[2] in dry tetrahydrofuran was treated with a large excess (10–15-fold) of the appropriate alkylamine and allowed to stand in the dark for 18–20 hr at room temperature. The excess amine and the solvent were removed under reduced pressure. The chloroform solution of the residue was shaken several times with water, dried, and evaporated. The product was crystallized from ethyl acetate.

The following mono- and dialkylaminophenoxaz-3-ones were prepared by the above procedure.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-dimethylaminophenoxaz-3-one** (**4**) was obtained in 90% yield: mp 171–172°; $\lambda_{max}^{MeOH}$ 228, 254, 438, and 458 mμ;[7] $\nu_{max}^{KBr}$ 2950, 1720, 1630, 1597, 1565 cm$^{-1}$; nmr τ 2.42, 2.75 (aromatic protons), 6.04, 6.08 (O-methyl), 6.89 (N-methyl), 7.57, 7.87 (ring methyl).

*Anal.* Calcd for $C_{20}H_{20}N_2O_6$: C, 62.49; H, 5.24; N, 7.29. Found: C, 62.78; H, 5.42; N, 7.56.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-(1′-ethylenimino)phenoxaz-3-one** (**5**) was obtained in 90% yield: mp 213–215°; $\lambda_{max}^{MeOH}$ 242 mμ (ε 35,941), 418 mμ (ε 29,814); $\nu_{max}^{Nujol}$ 1720, 1695, 1610, 1565 cm$^{-1}$; nmr τ 2.41, 2.53 (aromatic protons), 6.05, 6.07 (O-methyl), 7.53, 7.82 (ring methyl), 8.63 (methylene).

*Anal.* Calcd for $C_{20}H_{18}N_2O_6$: C, 62.82; H, 4.75; N, 7.33. Found: C, 62.62; H, 4.74; N, 7.54.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-β,β-dimethoxyethylaminophenoxaz-3-one** (**6**) was obtained in 90% yield: mp 120–122°; $\lambda_{max}^{MeOH}$ 224 mμ (ε 19,510), 250 (24,830), 422 (23,943), 444 (27,490); $\nu_{max}^{KBr}$ 3430, 3310 2955, 2835, 1725, 1705, 1600, 1515 cm$^{-1}$; nmr τ 2.32, 2.47 (ring protons), 3.34 (NH), 5.38 (methine), 6.47 (methylene), 6.00, 6.03, 6.58 (O-methyl), 7.49, 7.80 (ring methyl).

*Anal.* Calcd for $C_{22}H_{24}N_2O_8$: C, 59.45; H, 5.44; N, 6.30. Found: C, 59.82; H, 5.68; N, 6.63.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-β-methoxyethylaminophenoxaz-3-one** (**7**) was obtained in 91% yield: mp 125–127°; $\lambda_{max}^{MeOH}$ 226 mμ (ε 19,881), 250 (28,179), 436 (25,692), 442 (29,008); $\nu_{max}^{KBr}$ 3430, 3295, 2950, 1715, 1622, 1585, 1515 cm$^{-1}$; nmr τ 2.35, 2.50 (ring protons), 3.25 (NH), 6.43 (methylene), 6.05, 6.08, 6.60 (O-methyl), 7.50 7.83 (ring methyl).

*Anal.* Calcd for $C_{21}H_{22}N_2O_7$: C, 60.86; H, 5.35; N, 6.76. Found: C, 61.05; H, 5.29; N, 6.58.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-(1′-azetidino)phenoxaz-3-one** (**8**) was obtained in 75% yield: mp 182–184°; $\lambda_{max}^{MeOH}$ 230 mμ (ε 24,576), 252 (31,711), 434 (25,368), 454 (28,540); $\nu_{max}^{Nujol}$ 1710, 1627, 1600, 1560 cm$^{-1}$; nmr τ 2.45, 2.70 (ring protons), 5.4 (N-methylene), 6.05 (O-methyl)), 7.52, 7.90 (ring methyl), 8.55 (methylene).

*Anal.* Calcd for $C_{21}H_{20}N_2O_6$: C, 63.63; H, 5.09; N, 7.07. Found: C, 63.81; H, 5.33; N, 6.78.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-(1′-pyrrolidino)phenoxaz-3-one** (**9**) was obtained in 93% yield: mp 164–165°; $\lambda_{max}^{MeOH}$ 228, 254, 438, 456[7] mμ; $\nu_{max}^{KBr}$ 2950, 1710, 1620, 1597, 1530 cm$^{-1}$; nmr τ 2.50, 2.79 (aromatic protons), 6.08 6.10 (O-methyl), 6.15 (N-methylene), 7.55, 7.85 (C-methyl), 8.10 (methylene).

*Anal.* Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.06; H, 5.44; N, 6.99.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-(1′-piperidino)phenoxaz-3-one** (**10**) was obtained in 90% yield: mp 155–157°; $\lambda_{max}^{MeOH}$ 230, 252, 438, 460[7] mμ; $\nu_{max}^{KBr}$ 2935, 2850, 1725, 1615, 1590, 1550 cm$^{-1}$; nmr τ 2.47, 2.70 (aromatic protons); 5.99, 6.03 (O-methyl), 6.58 (N-methylene), 7.54, 7.85 (ring methyl), 8.27 (methylene).

*Anal.* Calcd for $C_{23}H_{24}N_2O_6$: C, 65.08; H, 5.70; N, 6.60. Found C, 64.89; H, 5.96; N, 6.75.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-(1′-hexamethylenimino)-phenoxaz-3-one** (**11**) was obtained in 64% yield: mp 145–147°; $\lambda_{max}^{MeOH}$ 230, 254, 436, 460[7] mμ; $\nu_{max}^{KBr}$ 2935, 2686, 1725, 1625, 1600, 1552 cm$^{-1}$; nmr τ 2.47, 2.67 (aromatic protons), 6.02, 6.04 (O-methyl), 6.37 (N-methylene), 7.54, 7.85 (C-methyl), 8.27 (methylene).

*Anal.* Calcd for $C_{24}H_{26}N_2O_6$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.30; H, 5.91; N, 6.91.

**4,6-Dimethyl-1,9-dicarbomethoxy-2-(1′-heptamethylenimino)-phenoxaz-3-one** (**12**) was obtained in 60% yield: mp 166–168°; $\lambda_{max}^{MeOH}$ 236, 256, 440, 460[7] mμ; $\nu_{max}^{KBr}$ 2925, 2860, 1720, 1620, 1545 cm$^{-1}$; nmr τ 2.47, 2.79 (aromatic protons), 6.04 (O-methyl), 6.39 (N-methylene), 7.52, 7.85 (C-methyl), 8.27 (methylene).

*Anal.* Calcd for $C_{25}H_{28}N_2O_6$: C, 66.36; H, 6.24; N, 6.19. Found: C, 66.67; H, 6.20; N, 6.54.

**Photolysis. General Method.**—Irradiations were conducted using 40 mg of phenoxazone in 300 ml of benzene (solvent A) or 25% methanol in benzene (solvent B) under a nitrogen atmosphere using a 200-w source in a Hanovia water-cooled immersion unit with a pyrex filter. The irradiation time was 2 hr for the phenoxaz-3-ones **5** and **7** and 6 hr for **6**. In all other cases the irradiation time was 15 min. Solvent was removed under reduced pressure and the residue was subjected to an appropriate work-up procedure.

**Photolysis of 4 in Solvent B. 4,6-Dimethyl-1,9-dicarbomethoxy-2-methylaminophenoxaz-3-one** (**13**).[2]—A tlc[6] of the total photolysis mixture indicated the presence of an unstable material which formed two spots with the progress of chromatography. An attempt to purify the product by crystallization was unsuccessful. Therefore, an ethyl acetate solution of the product mixture was exposed to air for 5 hr and then concentrated to yield 29 mg of **13** identified by comparison with an authentic sample of the same.

**2-Dimethoxymethyl-4,6-dicarbomethoxy-9,11-dimethyl-5H-oxazolo[4,5-*b*]phenoxazine** (**16**). **A1. By Photolysis of 6 in Solvent A.**—The chloroform solution of the gummy residue was passed through a short column of alumina (activity IV). The product (25%) was crystallized from ethyl acetate.

**A2. By Photolysis of 5 in Solvent B.**—Attempted photolysis in solvent A led largely to recovered starting material. Photolysis was then performed in solvent B. The photolysis mixture was subjected to liquid–liquid partition chromatography (llpc) on a Celite column (45 × 1.5 cm) using cyclohexane–dimethylformamide as a two-phase solvent system.[2] The faster moving nonfluorescent compound (10 mg) was unstable and, therefore, no further work was possible. A work-up of the fluorescent fractions gave 3 mg of **16** identified by comparison with an authentic sample of the same. A considerable amount of the polar material stayed at the origin of the column.

**B. By Pyrolysis of 6.**—A solution of 34 mg of **6** in 5 ml of xylene was refluxed for 12 hr. Excess solvent was removed under reduced pressure on a steam bath. A chloroform solution of the residue was passed through a short column of alumina (activity

(6) The melting points were determined on a Kofler microscope hot stage and are uncorrected. The analyses were carried out by Micro-Tech Laboratories, Skokie, Ill. The infrared spectra were determined on a Perkin-Elmer 221 spectrophotometer. The ultraviolet absorption spectra were measured by means of a Bausch and Lomb recording spectrophotometer, Model 505. Nuclear magnetic resonance spectra were recorded on Varian HR-60 and A-60 instruments using deuteriochloroform as solvent andte tra methylsilane (0 cps) as an internal standard. Chemical shifts are reported in τ units. Thin layer chromatography was performed in all cases on silica gel G using 5% acetone in chloroform as the eluting solvent.

(7) Since the compounds **4**, **9**, **10**, **11**, and **12** (*vide infra*) underwent a rapid photochemical change, a correct estimate of the ε values could not be obtained.

IV) and the product (81%) was crystallized from ethyl acetate: mp 173–175°; $\lambda_{max}^{MeOH}$ 226 mμ (ε 39,816), 251 (36,276), 418 (17,696); $\nu_{max}^{KBr}$ 3430, 3270, 2950, 2830, 1700, 1635, 1560, 1505 cm$^{-1}$; nmr τ 2.67, 3.60 (aromatic protons), 4.4 (methine), 5.95, 6.08 (carbomethoxy methyl), 6.48 (ether methyl), 7.70, 7.89 (ring methyl).

*Anal.* Calcd for $C_{22}H_{22}N_2O_8$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.66; H, 5.03; N, 6.75, 6.84.

**2-Methoxymethyl-4,6-dicarbomethoxy-9,11-dimethyl-5H-oxazolo[4,5-*b*]phenoxazine (17). A. By Photolysis of 7 in Solvent A.**—Approximately one-half of the residue was subjected to a preparative tlc on a silica gel G plate (20 × 20 × 0.1 cm) using 10% acetone in chloroform. The desired fluorescent band was eluted with ethyl acetate–chloroform. The total yield of **17** was 20%.

**B. By Pyrolysis.**—A solution of 50 mg of **7** in 5 ml of xylene was refluxed for 50 hr. The reaction mixture was processed in the same manner as that employed for the pyrolytic preparation of **16**. The product (41%) crystallized as plates from methanol: mp 180–182°; $\lambda_{max}^{MeOH}$ 226 mμ (ε 38,765), 250 (34,641), (17,320); $\nu_{max}^{KBr}$ 3440, 3275, 2955, 2850, 1705, 1645, 1560, 1510 cm$^{-1}$; nmr τ 2.67, 3.60 (aromatic protons), 5.32 (O-methylene), 5.93, 6.08 (carbomethoxy methyl), 6.48 (ether methyl), 7.70, 7.87 (ring methyl).

*Anal.* Calcd for $C_{21}H_{20}N_2O_7$: C, 61.16; H, 4.89; N, 6.79. Found: C, 61.42; H, 5.01; N, 6.48.

**Photolysis of 8 in Solvent A. 4,6-Dicarbomethoxy-9,11-dimethyl-5H-oxazolo[4,5-*b*]phenoxazine (2).**[2]—The crude product was dissolved in chloroform and passed through a short column of alumina (activity IV). Crystallization from ethyl acetate gave 26 mg of **2** identified by comparison with an authentic sample.

**Photolysis of 9 in Solvent A. 4,6-Dicarbomethoxy-9,11-dimethyl-2,3-trimethyleneoxazolino[4,5-*b*]phenoxazine (23).**—An ether solution of the residue was passed through a short column of silica gel G. The product (30 mg) crystallized from the eluate: mp 175–176.5°; $\lambda_{max}^{MeOH}$ 230 mμ (ε 46,612), 440 mμ (ε 17,237); $\nu_{max}^{CS_2}$ 3425, 3315, 2955, 2943, 1700, 1645, 1560, 1500 cm$^{-1}$; nmr τ −0.86 (NH), 2.69, 3.59 (aromatic protons), 4.14 (oxazoline proton), 6.00 6.09 (O-methyl), 7.00 (broad, N methylene), 7.87, 7.94 (aromatic methyl), 8.15 (broad, methylene).

Catalytic hydrogenation (*vide infra*) of **23** followed by oxidation gave **9**.

*Anal.* Calcd for $C_{22}H_{22}N_2O_6$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.48, 64.63; H, 5.31, 5.38; N, 6.67.

**Photolysis of 10 in Solvent B.**—Removal of solvent gave a yellow oil which appeared to be homogeneous by tlc.[6] This substance could not be crystallized even after attempted purification by preparative tlc.[6] The ultraviolet, infrared, and nmr spectra of this oil were very similar to those of **23**: $\lambda_{max}^{MeOH}$ 228, 434 mμ; $\nu_{max}^{KBr}$ 3450, 3315, 2940, 2845, 1695, 1635, 1560, 1500 cm$^{-1}$; nmr τ −0.76 (NH), 2.67, 3.60 (aromatic protons), 4.90 (oxazoline proton), 6.00, 6.06 (O-methyl), 7.04 (broad, N-methylene), 7.86 (aromatic methyl), 8.38 (broad, methylene).

Catalytic hydrogenation (*vide infra*) converted the yellow oil to the dihydrophenoxaz-3-one **27** also obtainable by the reduction of **10**.

**Photolysis of 11 in Solvent A. 4,6-Dicarbomethoxy-9,11-dimethyl-2,3-pentamethyleneoxazolino[4,5-*b*]phenoxazine (25).**—The work-up procedure was the same as for the preparation of **23**. The yield was 50%: mp 127–128°; $\lambda_{max}^{MeOH}$ 234 mμ (ε 36,892 440 mμ (ε 11,399); $\nu_{max}^{CS_2}$ 3320, 3265, 2935, 2850, 1715, 1690 cm$^{-1}$; nmr τ −0.70 (NH), 2.74, 3.60 (aromatic protons), 4.47 (oxazoline proton), 6.02, 6.10 (O-methyl), 6.90 (broad, N-methylene), 7.87, 7.94 (aromatic methyl), 8.27 (methylene).

*Anal.* Calcd for $C_{24}H_{26}N_2O_6$: C, 65.74; H, 5.98. Found: C, 65.54; H, 5.97.

**Photolysis of 12 in Solvent A. 4,6-Dicarbomethoxy-9,11-dimethyl-2,3-hexamethyleneoxazolino[4,5-*b*]phenoxazine (26).**—The work-up procedure was the same as for the preparation of **23**. The yield was 75%: mp 154–156°; $\lambda_{max}^{MeOH}$ 234 mμ (ε 32,580), 440 mμ (ε 9050); $\nu_{max}^{CS_2}$ 3320, 3265, 2935, 2850, 1710, 1690 cm$^{-1}$; nmr τ −0.60 (NH), 2.74, 3.60 (aromatic protons), 4.47 (oxazoline proton), 6.04, 6.10 (O-methyl), 6.90 (broad, N-methylene), 7.89, 7.97 (aromatic methyl), 8.27 (methylene).

*Anal.* Calcd for $C_{25}H_{28}N_2O_6$: C, 66.36; H, 6.24; N, 6.19. Found: C, 65.99; H, 6.30; N, 6.32.

**Catalytic Hydrogenation.**—The reductions were carried out in benzene or methanol in the presence of platinum oxide at room temperature and pressure. The following dihydrophenoxaz-3-ones, **27**, **28**, and **29**, were obtained by this procedure. Compound **27** could also be obtained by the hydrogenation of the yellow oil resulting from the photolysis of **10**.

**4,6-Dimethyl-1,9-dicarbomethoxy-3-hydroxy-2-(1′-piperidino)-phenoxazine (27)** melted at 182–184°: $\lambda_{max}^{MeOH}$ 226 mμ (ε 46,909), 408 mμ (ε 14,499); $\nu_{max}^{KBr}$ 3430, 3310, 2930, 2850, 1720, 1690, 1630, 1560, 1500 cm$^{-1}$; nmr τ 0.14 (NH), 2.42 (OH), 2.72, 3.59 (aromatic protons), 5.95, 6.12 (O-methyl), 6.95 (broad, N-methylene), 7.87 (aromatic methyl), 8.32 (methylene).

*Anal.* Calcd for $C_{23}H_{26}N_2O_6$: C, 64.77; H, 6.15; N, 6.57. Found: C, 65.00; H, 6.29; N, 6.65.

**4,6-Dimethyl-1,9-dicarbomethoxy-3-hydroxy-2-(1′-hexamethylenimino)phenoxazine (28)** melted at 178–180°: $\lambda_{max}^{MeOH}$ 226 mμ (ε 35,236), 410 mμ (ε 11,451); $\nu_{max}^{KBr}$ 3450, 3335, 2935, 2855, 1720, 1690, 1565, 1505 cm$^{-1}$; nmr τ −0.20 (NH), 2.24 (OH), 2.72, 3.59 (aromatic protons), 6.00, 6.12 (O-methyl), 7.40 (broad, N-methylene), 7.87 (aromatic methyl), 8.29 (methylene).

*Anal.* Calcd for $C_{24}H_{28}N_2O_6$: C, 65.44; H, 6.41; N, 6.36. Found: C, 65.55; H, 6.48; N, 6.44.

**4,6-Dimethyl-1,9-dicarbomethoxy-3-hydroxy-2-(1′-heptamethylenimino)phenoxazine (29)** melted at 203–205°: $\lambda_{max}^{MeOH}$ 226 mμ (ε 29,997), 410 mμ (ε 8635); $\nu_{max}^{KBr}$ 3430, 3335, 3000, 2925, 2855, 1715, 1685, 1560, 1500 cm$^{-1}$; nmr τ −0.23 (NH), 2.10 (OH), 2.70, 3.57 (aromatic protons), 6.00, 6.10 (O-methyl), 6.90 (broad, N-methylene), 7.85 (aromatic methyl), 8.27 (methylene).

*Anal.* Calcd for $C_{25}H_{30}N_2O_6$: C, 66.06; H, 6.65; N, 6.16. Found: C, 66.10; H, 6.61; N, 6.36.

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