Formation of Dihydrotriphenodioxazines and Dihydroisotriphenodioxazines by Acidic Treatment of Some Substituted 3*H*-Phenoxazin-3-ones: Isolation and Characterization. A New Perspective in the Chemistry of Ommochromes[1]

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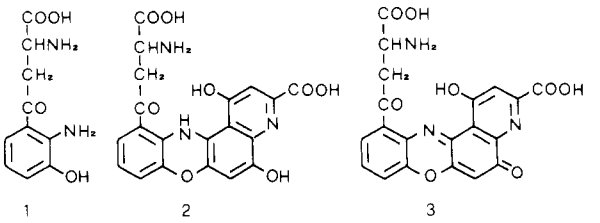
Cleavage of the substituted 3*H*-phenoxazin-3-one system is observed in acidic medium. Isolation and characterization of 1,9-dicarbomethoxy-2-hydroxy-3*H*-phenoxazin-3-one (**5a**) and 1,8,13-tricarbomethoxy-7,14-dihydrotriphenodioxazine (**6a**), of 1,9-diacetyl-2-hydroxy-3*H*-phenoxazin-3-one (**5b**) and 1,8,13-triacetyl-7,14-dihydrotriphenodioxazine (**6b**), of 2,7-dicarbomethoxy-4-hydroxy-3*H*-phenoxazin-3-one (**5c**) and 3,8,13-tricarbomethoxy-7,14-dihydroisotriphenodioxazine (**6c**), and of 2,7-diacetyl-4-hydroxy-3*H*-phenoxazin-3-one (**5d**) and 3,8,13-triacetyl-7,14-dihydroisotriphenodioxazine (**6d**) from the treatment in methanol–0.2 N H_2SO_4 of 1,9-dicarbomethoxy-2-amino-3*H*-phenoxazin-3-one (**4a**), 1,9-diacetyl-2-amino-3*H*-phenoxazin-3-one (**4b**), 2,7-dicarbomethoxy-4-amino-3*H*-phenoxazin-3-one (**4c**), and 2,7-diacetyl-4-amino-3*H*-phenoxazin-3-one (**4d**), respectively, are reported. A probable mechanism for the formation of the reaction products is presented.

The phenoxazinonic system,[2] present in the ommochrome pigments, is formed by oxidation reaction of an aminoacid, the 3-hydroxykynurenine (**1**).[3] These pigments, as dihydroxanthommatin (**2**) and xanthommatin (**3**), have been found labile in both acidic[4] and alkaline solution (Chart I). To explore the reason for this behavior, we studied the reactions of several model phenoxazinones in acidic conditions. We examined some substituted 3*H*-phenoxazin-3-ones in acidic medium similar to the extraction mixture of naturally occurring ommochromes and found them to be unstable: in fact, several reactions took place on the phenoxazinonic ring and some products with interesting redox properties were formed.

Chart I



Results

When a solution of 1,9-dicarbomethoxy-2-amino-3*H*-phenoxazin-3-one (**4a**) in methanol–H_2SO_4 was refluxed for 1 h, two products were isolated as well as 15% unreacted **4a**. The major compound (40%) was the hydroxyphenoxazinone **5a**. A very minor, yellow product was shown to be **6a**. These substances, **5a** and **6a**, were separated and purified by chromatography and the structures established by elemental analyses and spectral data (IR, ^1H NMR, UV, MS).

The product **5a** was identified as 1,9-dicarbomethoxy-2-hydroxy-3*H*-phenoxazin-3-one. Its ^1H NMR ($CDCl_3$) spectrum showed an AMX aromatic pattern: the C-7 proton appeared as a triplet (δ 7.35) and the C-6 proton (δ 7.53) was a doublet, as was the C-8 proton (δ 8.07), this last one at lower field due to the near presence of the carbomethoxy group. The C-4 proton (δ 6.52) appeared as a clearly distinguishable singlet, and the carbomethoxy groups were separated singlets (δ 3.90, 3.80). The mass spectrum ($M^{+\cdot}$ 329) showed an intensive peak, characteristic of the quinone structure,[5] and the IR spectrum was in clear agreement with that of the reported phenoxazinones.[6] Whereas the UV spectrum of **5a** in chloroform showed stable maxima at 446–24 nm, the methanol–H_2SO_4 solution showed maxima at 412–33 nm that disappeared in time. A new maximum at 334 nm (two shoulders at 412–33 nm) appeared, although thin-layer chromatography indicated the presence of **5a** only. This result indicated that the hemiketal **5'a** is formed from the 2-hydroxyphenoxazin-3-one-substituted system. This typical hemiketal formation is an equilibrium reaction and has been widely described.[7]

The product **6a** was identified as 1,8,13-tricarbomethoxy-7,14-dihydrotriphenodioxazine by elemental analysis, spectral data, and oxidation reaction. Its ^1H NMR spectrum ($CDCl_3$), typical of a phenoxazinic compound, showed seven aromatic protons, two N protons, and three carbomethoxy proton signals. The hydrogen atoms at C-2 and C-9 appeared as two almost overlapping doublets (δ 7.35) at the lowest field, because of the electron-withdrawing character of the nearby carbomethoxy groups. The C-3 and C-10 protons appeared (δ 6.55) as undistinguishable triplets; the C-4 and C-11 protons (δ 6.65, 6.75) appeared as distinguishable doublets; the C-6 proton (δ 6.03) was a singlet. The N-14 (δ 10.25) proton appeared at a lower field than the N-7 proton (δ 8.47) signal, because of the marked electron-withdrawing effect of the two carbomethoxy groups. The IR spectrum showed the characteristic stretching of an α,β-unsaturated associated and unassociated carbomethoxy group (1680, 1725 cm^{-1}) and of NH stretching (3340 cm^{-1}) and supported the proton assignment. When a chloroform solution of **6a** was irradiated with a halogen superphotolamp (Osram 650 W), the red-fluorescent (λ_{max} 482, 517 nm) triphenodioxazine **7a** was formed, and the photoxidation reaction was almost complete in 30 min at 18 °C. The compound **7a**, the 1,8,13-tricarbomethoxytriphenodioxazine, was purified by chro-

(1) This work was supported by a grant from the Consiglio Nazionale delle Riverche.

(2) M. Ionescu and H. Mantsch, *Adv. Heterocycl. Chem.*, 8, 83 (1967).

(3) A. Butenandt and W. Schäfer in "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters and Related Fields", Academic Press, New York, 1962, pp 13–33.

(4) A. Bolognese and G. Scherillo, *Experientia*, **30**, 225 (1974).

(5) N. L. Zeller in "The Chemistry of the Quinonoid Compounds", S. Patai, Ed., Wiley, New York, 1974, Part I, p 231.

(6) N. L. Agarwal and W. Schäfer, *J. Org. Chem.*, **45**, 2155 (1980).

(7) W. Schäfer and H. Schlude, *Tetrahedron Lett.*, 2161 (1968).

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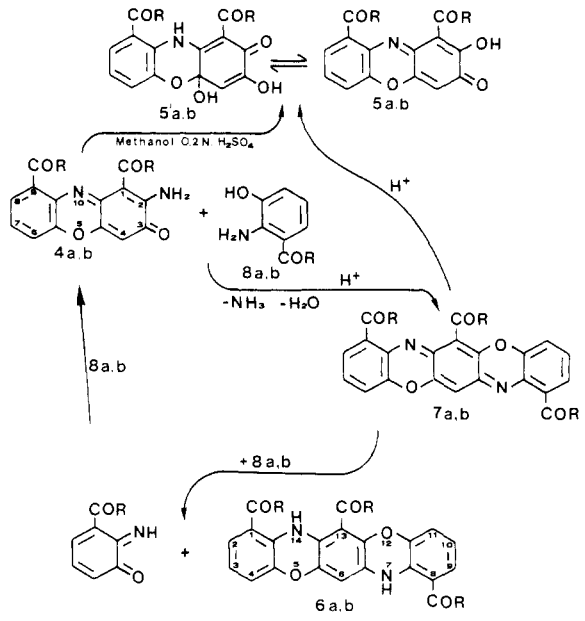


a:R=OCH_3 b:R=CH_3

matography and identified. The mass spectrum showed a molecular peak at M^+ 460; the ^1H NMR ($CDCl_3$) showed the C-6 proton as a sharp singlet at δ 6.62 and the aromatic protons between 7.44 and 7.19; the IR spectrum showed strong absorptions at 1720 and 1690 cm^{-1}, due to unassociated carbomethoxy and quinonediimine groups, but was devoid in the OH or NH region. Whereas the dihydrotriphenodioxazine **6a** is stable in acidic alcoholic medium, the corresponding **7a** decomposed. Chromatographic analysis of the mixture of **7a** in methanol–H_2SO_4 (0.2 N, 9:1, v/v) showed, after 30 min, the presence of **5a** and **8a** only.

The structure of **6a**, in good agreement with the reported spectral data, is also supported by the formation of the oxidized product **7a**, where the *p*-quinonediimine group is present. Such a structure confirmed the N-7 and N-8 positions in **6a**. The carbomethoxy group is, without doubt, on C-8 because the acidic degradation of **7a** yielded **5a** and **8a**. The 2-hydroxy-3-aminobenzoic acid methyl ester was never recovered.

These unusual results on the unstability of the phenoxazinonic system in acidic medium seemed to us to be worthy of further investigations, and other substituted 3*H*-phenoxazin-3-ones were examined.

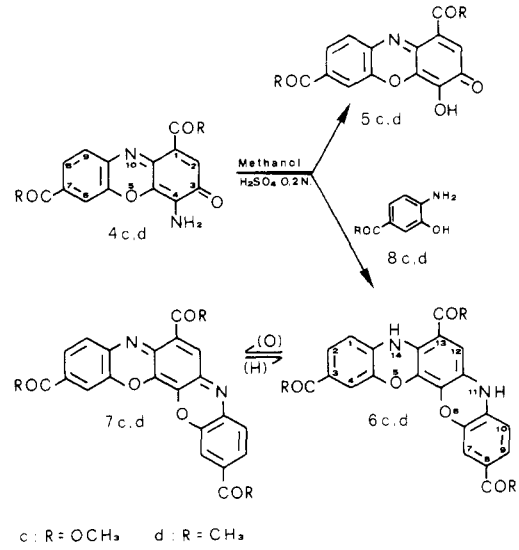
The acidic solution of the 1,9-diacetyl-2-amino-3*H*-phenoxazin-3-one (**4b**), like that of the described **4a**, yielded the corresponding **5b**[8] and **6b** (Scheme I).

Likewise, the 2,7-dicarbomethoxy-4-amino-3*H*-phenoxazin-3-one (**4c**) and the 2,7-diacetyl-4-amino-3*H*-phenoxazin-3-one (**4d**) in methanol–H_2SO_4 were unstable and decomposed to yield the corresponding 4-hydroxyphenoxazinones **5c** and **5d** and the dihydroisotriphenodioxazines **6c** and **6d** (Scheme II).

Both the triphenodioxazines **7a,b** and the isotriphenodioxazines **7c,d** are formed either by photooxidation or by "shaking" their chloroformic solutions and aqueous ferricyanide.

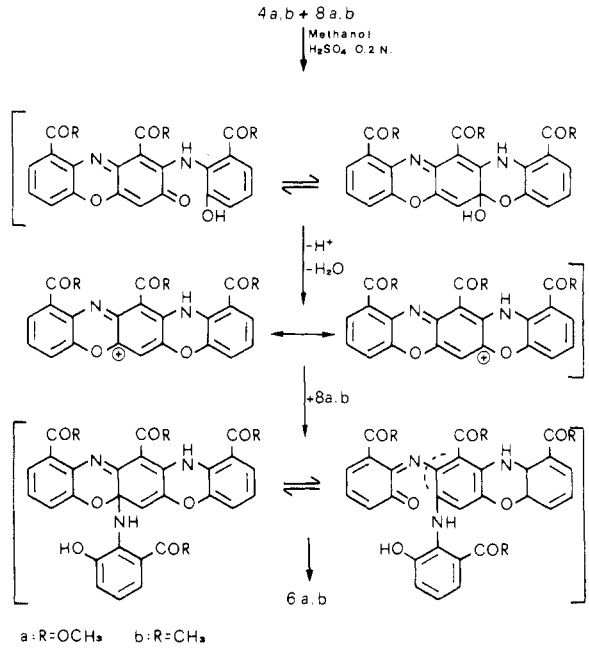
For some indication to the mechanism of this reaction, **4a** was refluxed, for 1 h, in methanol–H_2SO_4 (0.2 N, 9:1, v/v) with the *o*-aminophenol **8a** (in excess). **5a** and **6a**

Scheme II



c: R=OCH_3 d: R=CH_3

Scheme III



a:R=OCH_3 b:R=CH_3

were recovered from the reaction mixture, but the yield of **6a** increased to almost 40%. Therefore, **4a** was also refluxed, under the above reported conditions, with another *o*-aminophenol, **8b**. In addition to the expected 1,13-dicarbomethoxy-8-acetyl-7,14-dihydrotriphenodioxazine (**6e**), 1,8,13-triacetyl-7,14-dihydrotriphenodioxazine (**6b**) was recovered (Scheme III). When **4b** was refluxed with **8a**, the 1,13-diacetyl-8-carbomethoxy-7,14-dihydrotriphenodioxazine (**6f**) and the 1,8,13-tricarbomethoxy-7,14-dihydrotriphenodioxazine (**6a**) were recovered. Elemental analyses and spectral data are reported in the Experimental Section.

It is noteworthy that neither **6a** nor **7a** was recovered when **8a** was added to **5a** in acidic methanol.

Discussion

Butenandt and his co-workers have reported[8] that 9-acetyl-2-hydroxy-3*H*-phenoxazin-3-one and 1,8-diacetyltriphenodioxazine are formed by heating 2-amino-3-hydroxyacetophenone hydrochloride with dihydroxybenzoquinone in butanol. Similar products were obtained

(8) A. Butenandt, E. Biekert, and G. Neubert, *Justus Liebigs Ann. Chem.*, **602**, 72 (1960).

by acidic treatment of **4** in methanol.

The main products **5** are formed when H_2O, present in the reaction mixture, attacks the NH_2 group with elimination of NH_4^+. In acidic medium, **5** subsequently reacts with H_2O to yield the hemiketals **5'**. According to Schäfer, this is a reversible reaction.[7]

The products **6** are formed by reaction of **4** with **8**; the latter[8] are present in the reaction mixture either because they are added or because they develop from the cleaving of the oxygen and nitrogen bridges of the phenoxazinones **4**.

Most of the reported reactions between substituted quinones and *o*-aminophenols involve either the condensation reaction[9] or the attack of the *o*-aminophenol amino group on the quinone substituent and subsequent ring closure.[5,10]

Schemes I and III show two possible mechanisms for the reaction examined above. In Scheme III, the NH_2 group of **8a** substitutes the amino group of **4a**. Subsequently, the addition of the OH group of **8a** to the quinone carbonyl group forms the hemiketal. The intermediate carbonium ion, formed in acidic medium, is resonance stabilized. It could react with a second molecule of aminophenol, in either position, giving the products.

In practice, what happens is that the 1,13-dicarbomethoxy-8-acetyl-7,14-dihydrotriphenodioxazine (**6e**) and 1,8,13-triacetyl-7,14-dihydrotriphenodioxazine (**6b**) were only recovered from the reaction mixture of **4a** and **8b** in acidic methanol. Despite numerous attempts, we have not been able to find any evidence for the presence of 1,8-diacetyl-13-carbomethoxy-7,14-dihydrotriphenodioxazine or of other intermediate products, under the cited conditions.

The same results were obtained from the reaction of **4b** and **8a** in acidic methanol: only the 1,13-diacetyl-8-carbomethoxy-7,14-dihydrotriphenodioxazine (**6f**) and the 1,8,13-tricarbomethoxy-7,14-dihydrotriphenodioxazine (**6a**) were recovered.

Isolation of **6e** and **6b** and of **6f** and **6a** from the reaction mixtures of **4a** and **8b** and of **4b** and **8a**, respectively, and the absence of more significance here, of the 1,8-diacetyl-8-carbomethoxy-7,14-dihydrotriphenodioxazine and of the 1,8-dicarbomethoxy-13-acetyl-7,14-dihydrotriphenodioxazine seem to exclude the formation of an intermediate carbonium ion (Scheme III).

In Scheme I the products **4** condense with the *o*-aminophenols to yield the triphenodioxazines **7**. Isolation of **6a** instead of the acid labile **7a** may be dependent on the free *o*-aminophenol **8a** present in the reaction mixture.

In fact we noted that free **8a** is able to reduce **7a** both in neutral chloroformic solution and in the acidic reaction mixture. The reduction of **7a**, under the reaction conditions, is noted to be faster than the reported decomposition. The formed *o*-iminoquinone probably reacts with **8a**, present in excess, to yield the phenoxazinone **4a**. In this way, **6b** and **6a** may be formed in the reaction mixture of **4a** and **8b** and of **4b** and **8a**, respectively, from the in situ synthesized phenoxazinones **4b** and **4a**.

The substances **4** have been studied as chemical models of some animal pigments. The reported results demonstrate that the examined phenoxazinones **4** are H^+-labile systems and that the corresponding dihydro- and dihydroisotriphenodioxazines undergo photochemical reactions by visible light.

The phenoxazinonic ring is the only product of the oxidation reaction of *o*-aminophenol, but, in the absence of oxidizing agents, it undergoes several transformations, the precise transformations depending on the medium, and yields more complicated structures. The possibility that similar reactions take place under biological conditions could explain the great number of naturally occurring ommochromes.[11,12] These pigments, present in the photoreceptors of invertebrates, are largely unknown both as to structure and biological role. One the other hand, the reported photooxidation of the **6** models examined above and the reduction of **7** by the corresponding *o*-aminophenol **8** could form an oxidation–reduction cyclic system, associated with visual pigments, whose sensitivity to light spans the visible spectrum (ca. 440–660 nm):

$$6 \underset{8}{\overset{h\nu/O_2}{\rightleftharpoons}} 7$$

Experimental Section

The UV spectra were recorded with a Perkin-Elmer 550 S spectrophotometer. The fluorescence spectra were recorded with a Spex fluorimeter. The IR spectra were taken on Perkin-Elmer 399 spectrophotometer in chloroform. ^1H NMR spectra (reported in δ) were recorded on a Bruker 270-MHz spectrometer with Me_4Si as internal reference. Mass spectra were obtained with a VG ZAB 2F mass spectrometer (electron energy 70 eV, ion source temperature 250 °C). Melting points were determined with a Kofler apparatus and are uncorrected. The purity of the compounds was checked by ascending TLC on Merck's precoated silica gel F-254 plates (0.25 mm) with fluorescent backing, using the following mixture I: benzene–chloroform–methanol (45:45:10).

Disubstituted-amino-3*H*-phenoxazin-3-one (4a,[13] 4b,[8] 4c, and 4d). General Procedure. All these **4** were synthesized according to the published methods by oxidation of **8**. All the products were purified by column chromatography (silica gel, 10% deactivated, benzene as eluent) and repurified by TLC (silica gel, 0.5 mm, mixture I as eluent).

2,7-Dicarbomethoxy-4-amino-3*H*-phenoxazin-3-one (4c). Anal. Calcd for $C_{16}H_{12}O_6N_2$: C, 58.54; H, 3.68; N, 8.53. Found: C, 58.39; H, 3.57; N, 8.40. ^1H NMR ($CDCl_3$) δ 8.03 (2 H, m), 7.85 (1 H, d), 6.49 (1 H, s), 3.96 (3 H, s), 3.99 (3 H, s); IR ($CHCl_3$) 3470–3320 (NH_2), 1725 ($COOCH_3$), 1670 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 444 (4.21), 416 (4.21); mass spectrum, *m/e* 328 (M^+), 297, 269, 238, 210; mp 228–30 °C.

2,7-Diacetyl-4-amino-3*H*-phenoxazin-3-one (4d). Anal. Calcd for $C_{16}H_{12}O_4N_2$: C, 64.86; H, 4.08; N, 9.46. Found: C, 64.79, H, 4.02; N, 9.13. ^1H NMR ($CDCl_3$) δ 7.91 (2 H, m), 7.80 (1 H, d), 6.54 (1 H, s), 3.10 (3 H, s), 2.84 (3 H, s); IR ($CHCl_3$) 3420–3300 (NH_2), 1690 ($COCH_3$), 1650 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 448 (4.18), 428 (4.18); mass spectrum, *m/e* 296 (M^+); mp 202–3 °C.

Reaction of 4 in Methanol–0.2 N H_2SO_4 (9:1, v/v). General Procedure. A 100-mg sample of **4** was added to 20 mL of methanol–0.2 N H_2SO_4 and heated to reflux for 1 h. The mixture, cooled to room temperature and neutralized, was extracted with chloroform. The chloroformic solutions were dried, concentrated in vacuo, placed on TLC plates (F-254 Merk, silica gel), and developed with the mixture I. The chromatograms showed three products: **4**, **5**, and **6**. Three colored bands afforded **4a** (15 mg), **5a** (40 mg) and **6a** (4 mg), **4b** (11 mg), **5b** (32 mg) and **6b** (5 mg), **4c** (9 mg), **5c** (27 mg) and **6c** (8 mg), and **4d** (12 mg), **5d** (30 mg) and **6d** (9 mg), respectively.

1,9-Dicarbomethoxy-2-hydroxy-3*H*-phenoxazin-3-one (5a). Anal. Calcd for $C_{16}H_{11}O_7N$: C, 58.36; H, 3.37; N, 4.25. Found: C, 57.93; H, 2.72; N, 4.01. ^1H NMR ($CDCl_3$) δ 8.07 (1 H, d), 7.53 (1 H, d), 7.35 (1 H, t), 6.52 (1 H, s), 3.90 (3 H, s), 3.80 (3 H, s); IR ($CHCl_3$) 1700 ($COOCH_3$), 1655 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max}

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(10) W. Schäfer, T. Geyer, and H. Schlude, *Tetrahedron*, **28**, 3811 (1972).
(11) B. Linzen, *Adv. Insect Physiol. Chem.*, **10**, 117 (1974).
(12) G. Prota in "Marine Natural Products", P. J. Scheuer, Ed., Academic Press, New York, 1980, Vol. III.
(13) J. Angyal, E. Bullock, W. G. Hanger, W. C. Howell, and A. W. Johnson, *J. Chem. Soc.*, 1592 (1957).

nm (log ϵ) 477_s, 446 (4.10), 424 (4.10), 398_s; mass spectrum, m/e 331 (M + 2), 329 (M^+), 299, 267, 239, 211; mp 231–2 °C after recrystallization in benzene.

2,7-Dicarbomethoxy-4-hydroxy-3*H*-phenoxazin-3-one (5c). Anal. Calcd for $C_{16}H_{11}O_7N$: C, 58.36; H, 3.37; N, 4.25. Found: C, 57.98; H, 3.32; N, 4.19. ^1H NMR ($CDCl_3$) δ 8.06 (1 H, d, J = 9; meta coupled J = 1 Hz), 8.07 (1 H, s, meta coupled J = 1 Hz), 7.77 (1 H, d, J = 9 Hz), 6.57 (1 H, s), 3.97 (6 H, s); IR ($CHCl_3$) 1690 ($COOCH_3$), 1650 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 470_s, 445 (3.9), 426 (3.9), 390_s; mass spectrum, m/e 331 (M + 2), 329 (M^+); mp 241–2 °C after recrystallization in benzene.

2,7-Diacetyl-4-hydroxy-3*H*-phenoxazin-3-one (5d). Anal. Calcd for $C_{16}H_{11}O_5N$: C, 64.64; H, 3.73; N, 4.71. Found: C, 64.59; H, 3.67; N, 4.65. ^1H NMR ($CDCl_3$) δ 7.86 (2 H, m), 7.36 (1 H, d), 6.58 (1 H, s), 2.69 (3 H, s), 2.79 (3 H, s); IR ($CHCl_3$) 1690 ($COCH_3$), 1650 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 470_s, 440 (3.95), 415 (3.95), 390_s; mass spectrum, m/e 299 (M + 2), 297 (M^+): mp 235–6 °C after recrystallization in chloroform.

1,8,13-Tricarbomethoxy-7,14-dihydrotriphenodioxazine (6a). Anal. Calcd for $C_{24}H_{18}O_8N_2$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.29; H, 3.89; N, 5.98. ^1H NMR ($CDCl_3$) δ 10.25 (1 H, s), 8.47 (1 H, s), 7.35 (2 H, m), 6.75 (1 H, d), 6.65 (1 H, d), 6.55 (2 H, t), 6.03 (1 H, s), 4.12 (3 H, s), 4.03 (3 H, s), 4.00 (3 H, s); IR ($CHCl_3$) 3340 (NH), 1720 and 1680 (un- and associated $COOCH_3$) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 462 (3.96); mass spectrum, m/e 462 (M^+), 430, 402, 370, 342; mp 202 °C.

1,8,13-Triacetyl-7,14-dihydrotriphenodioxazine (6b). Anal. Calcd for $C_{24}H_{18}O_5N_2$: C, 69.56; H, 4.38; N, 6.76. Found: C, 69.47; H, 4.37; N, 6.52. ^1H NMR ($CDCl_3$) δ 9.95 (1 H, s), 9.47 (1 H, s), 7.21 (2 H, d), 6.72 (1 H, d), 6.59 (3 H, m), 6.03 (1 H, s), 2.83 (3 H, s), 2.72 (6 H, s); IR ($CHCl_3$) 3300 (NH), 1745, 1650 (un- and associated C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 510 (3.98); mass spectrum, m/e 414 (M^+), 399; mp 253–4 °C.

3,8,13-Tricarbomethoxy-7,14-dihydroisotriphenodioxazine (6a). Anal. Calcd for $C_{24}H_{18}O_8N_2$: C, 62.34; H, 3.92; N, 6.06. Found: C, 62.25; H, 3.84; N, 5.93. ^1H NMR ($(CD_3)_2SO$) δ 9.85 (1 H, s), 9.16 (1 H, s), 7.49 (3 H, m), 6.75 (2 H, m), 5.80 (2 H, br s), 4.05 (3 H, s), 3.93 (3 H, s), 3.87 (3 H, s); IR ($CHCl_3$) 3300 (NH), 1724 ($COOCH_3$) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 462 (3.90); mass spectrum, m/e 462 (M^+), 431, 403; mp 230–2 °C.

3,8,13-Triacetyl-7,14-dihydroisotriphenodioxazine (6d). Anal. Calcd for $C_{24}H_{18}O_5N_2$: C, 69.56; H, 4.38; N, 6.76. Found: C, 69.43; H, 4.30; N, 6.60. ^1H NMR δ ($(CD_3)_2SO$) 9.80 (1 H, s), 9.20 (1 H, s), 7.50 (3 H, m), 6.73 (2 H, d), 5.9 (2 H, br s), 2.92 (3 H, s), 2.70 (6 H, s); IR ($CHCl_3$) 3300 (NH), 1680 ($COCH_3$); UV λ_{max} nm (log ϵ) 460 (3.86); mass spectrum, m/e 414 (M^+), 399, 384; mp 227–8 °C.

Photooxidation Formation of 6 from 7 by Visible Light. A sample of 10 mg of **6** was dissolved in 5 mL of chloroform and irradiated by a sunlight lamp (650 W) at 18 °C. After 30 min, 90% of **6** was transformed into **7**.

1,8,13-Tricarbomethoxytriphenodioxazine (7a). Anal. Calcd for $C_{24}H_{16}O_8N_2$ C, 62.61: H, 3.50; N, 6.90. Found: C, 62.50; H, 3.43; N, 6.02. ^1H NMR ($CDCl_3$) δ 7.44 (1 H, t), 7.28 (1 H, d), 7.19 (4 H, m), 6.62 (1 H, s), 3.94 (3 H, s), 3.82 (6 H, s); IR ($CHCl_3$) 1700 ($COOH_3$), 1690 (C=N) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 460_s, 482 (4.39), 517 (4.45); fluorescence ($CHCl_3$) λ_{max} 538, 580 nm; mass spectrum, m/e 460 (M^+), 429, 401, 370; mp 307–8 °C.

1,8,13-Triacetyltriphenodioxazine (7b).[10] Anal. Calcd for $C_{24}H_{16}O_5N_2$: C, 69.90; H, 3.91; N, 6.79. Found: C, 69.69; H, 3.88; N, 6.68. ^1H NMR ($CDCl_3$) δ 7.42 (1 H, d), 7.43 (1 H, d; J = 9 Hz; meta coupled J = 2 Hz), 7.30 (2 H, t, J = 9 Hz), 7.23 (1 H, d, J = 9 Hz; meta coupled J = 2 Hz), 7.2 (1 H, d, J = 9 Hz; meta coupled J = 2 Hz), 6.59 (1 H, s), 2.96 (3 H, s), 2.90 (3 H, s), 2.81 (3 H, s); IR ($CHCl_3$) 1690–80 (broad band, $COCH_3$ and C=N) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 460_s, 490 (4.30), 530 (4.41); fluorescence ($CHCl_3$) λ_{max} nm 545, 582; mass spectrum, m/e 412 (M^+), 382; mp 295–6 °C.

3,8,13-Tricarbomethoxyisotriphenodioxazine (7c). Anal. Calcd for $C_{24}H_{16}O_8N_2$: C, 62.61; H, 3.50; N, 6.09. Found: C, 62.45; H, 3.40; N, 6.00. ^1H NMR ($CDCl_3$) δ 7.85 (1 H, d, J = 9 Hz; meta coupled J = 2 Hz), 7.80 (1 H, d, J = 9 Hz; meta coupled J = 2 Hz), 7.78 (1 H, s, J = 9 Hz; meta coupled J = 2 Hz), 7.73 (1 H, s, meta coupled J = 2 Hz), 7.52 (1 H, d, J = 9 Hz), 7.51 (1 H, d, J = 9 Hz), 6.59 (1 H, s), 4.08 (3 H, s), 3.94 (6 H, s); IR ($CHCl_3$) 1730 ($COOCH_3$), 1680 (C=N) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 454_s, 490 (4.37), 528 (4.40); fluorescence ($CHCl_3$) λ_{max} nm 540, 590; mass spectrum, m/e 460 (M^+), 429, 401, 370; mp 230–2 °C.

3,8,13-Triacetylisotriphenodioxazine (7d). Anal. Calcd for $C_{24}H_{16}O_5N_2$: C, 69.90; H, 3.88; N, 6.68. Found: C, 69.88; H, 3.85; N, 6.70. ^1H NMR ($CDCl_3$) δ 8.11 (4 H, m), 7.86 (2 H, d), 6.55 (1 H, s), 2.85 (3 H, s), 2.61 (6 H, s); IR ($CHCl_3$) 1690–80 (broad band, $COCH_3$ and C=N) cm^{-1}; UV λ_{max} nm (log ϵ) 460_s, 495 (4.35), 530 (4.42); fluorescence ($CHCl_3$) λ_{max} nm 545, 585; mass spectrum, m/e 412 (M^+), 397, 382; mp 228–30 °C.

1,13-Dicarbomethoxy-8-acetyl-7,14-dihydrotriphenodioxazine (6e). Anal. Calcd for $C_{24}H_{18}O_7N_2$: C, 64.57; H, 4.06; N, 6.28. Found: C, 65.1; H, 4.11; N, 6.32. ^1H NMR ($CDCl_3$) δ 10.40 (1 H, s), 9.7 (1 H, s), 7.35 (1 H, d), 7.20 (1 H, d), 6.7 (1 H, d), 6.65 (1 H, d), 6.55 (2 H, t), 6.08 (1 H, s), 4.00 (3 H, s), 3.90 (3 H, s), 2.5 (3 H, s); IR ($CHCl_3$) 1720, 1690–40 (broad band C=O), 3300 (NH) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 468 (3.84); mass spectrum, m/e 446 (M^+); mp 265–6 °C.

1,13-Diacetyl-8-carbomethoxy-7,14-dihydrotriphenodioxazine (6f). Anal. Calcd for $C_{24}H_{18}O_6N_2$: C, 66.97; H, 4.22; N, 6.51. Found: C, 65.80; H, 4.27; N, 7.01. ^1H NMR ($CDCl_3$) δ 10.05 (1 H, s), 8.6 (1 H, s), 7.35 (1 H, d), 7.20 (1 H, d), 6.70 (1 H, d), 6.61 (1 H, d), 6.53 (2 H, two almost overlapping t), 5.93 (1 H, s), 3.76 (3 H, s), 2.52 (3 H, s), 2.4 (3 H, s); IR ($CHCl_3$) 3300 (NH), 1720 ($COOCH_3$), 1680–40 (C=O) cm^{-1}; UV ($CHCl_3$) λ_{max} nm (log ϵ) 491 (3.92); mass spectrum, m/e 430 (M^+); mp 266–7 °C.

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