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OXIDATIVE BEHAVIOUR OF 3-ARYL-2H-1,4-BENZOXAZINES

FRANCESCO CHIOCCARA, ERNESTO PONSIGLIONE and GIUSEPPE PROTA
Istituto di Chimica Organica dell'Università, Via Mezzocannone 16, Napoli, Italy

and

RONALD H. THOMSON*
Department of Chemistry, University of Aberdeen, Old Aberdeen AB9 2UE, Scotland

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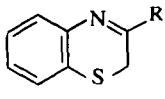
Abstract—Autoxidation of 3 - phenyl - 2H - 1,4 - benzoxazine **8** gives 2 - hydroxy - 3 - phenyl - 2H - 1,4 - benzoxazine **13**, 3 - phenyl - 2H - 1,4 - benzoxazin - 2 - one **11**, and 2 - phenylbenzoxazole **10** according to the conditions. Oxidation of **8** with DDQ in the presence of air gave mainly the bisacetal **17** but in the absence of air the major product was *trans* -$\Delta^{2,2'}$-bi-(3-phenyl-2H-1,4-benzoxazine) **21a**. Corresponding dimers were obtained from the 3-*p*-bromophenylbenzoxazine **9**. The *trans*-isomers **21a** and **22a** are photochromic and change into their *cis*-isomers on exposure in solution to direct sunlight.

In previous papers it has been shown that 3 - substituted - 2H - 1,4 - benzothiazines **1** (R = aryl) undergo oxidative coupling at C-2 to give dimeric compounds of type **2**[1] or **3**[2] according to the dehydrogenating agent used. 2H-1,4-benzothiazine itself **1** (R = H) was generated *in situ* and oxidised by air to give **3** (R = H)[3] the parent chromophore of the trichosiderin pigments[4] found in reddish hair and feathers. Parallel experiments[5] designed to prepare the oxygen analogue **3** (R = H; O in place of S) were frustrated by the formation of a more extended chromophore but we now describe the first synthesis of the $\Delta^{2,2'}$-bi-(2H-benzoxazine) ring system **3** (O in place of S).



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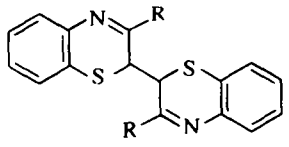

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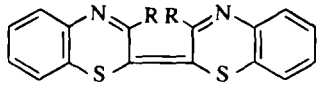
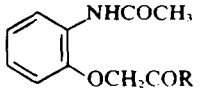
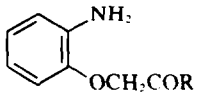


3

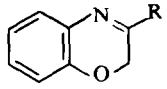
2H - 1,4 - benzoxazine has not been isolated but 3 - aryl derivatives, **8** and **9**, were obtained by a general route[6] involving cyclisation of the corresponding aminoketones **6** and **7**, generated *in situ* from the acetamides **4** and **5**, respectively, with ethanolic potassium hydroxide. In neutral solvents the 3 - arylbenzoxazines were found to be quite stable to aerial oxidation but they were readily transformed in the presence of acids or bases into various products depending upon the experimental conditions. Thus, treatment with oxygen of 3 - phenylbenzoxazine **8** in benzene solution containing a catalytic amount of trifluoroacetic acid gave many products in small amounts, two of which were identified as **10** (6%) and **11** (0.15%) by straightforward spectral analysis. A third compound, $C_{14}H_{11}NO_2$, was assigned the cyclic hemiacetal structure **13** (16%) on the basis of the following evidence. The mass spectrum showed peaks at *m/e* 225 (M^+ 28), 208(53), 197(15) and 196(100%), there is hydroxy absorption in the IR at 3500 cm^{-1}, and the UV spectrum is remarkably similar to that of **8**. The PRM spectrum (CD_3COCD_3)



4: R = Ph
5: R = *p*-BrC_6H_4

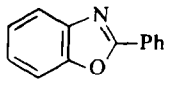


6: R = Ph
7: R = *p*-BrC_6H_4



8: R = Ph
9: R = *p*-BrC_6H_4

consists of a complex multiplet at δ 7.65 for nine aromatic protons, and a sharp 1H singlet at δ 6.40 attributable to the hemiacetal methine proton of structure **13**. This assignment was further supported by the reaction of **13** with methanol saturated with HCl which afforded the corresponding methyl derivative **14**, showing the expected spectral features. In alkaline solution the oxidation took a different course. Thus when oxygen was bubbled into a boiling solution of **8** in 3% ethanolic KOH extensive degradation occurred and, besides a trace of **13**, we isolated only the ring-contracted product **10** (13%).



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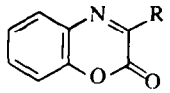
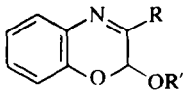


11: R = Ph
12: R = *p*-BrC_6H_4

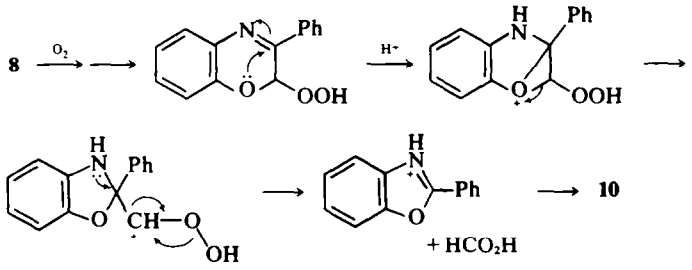


13: R = Ph; R' = H
14: R = Ph; R' = Me
15: R = *p*-BrC_6H_4; R' = H

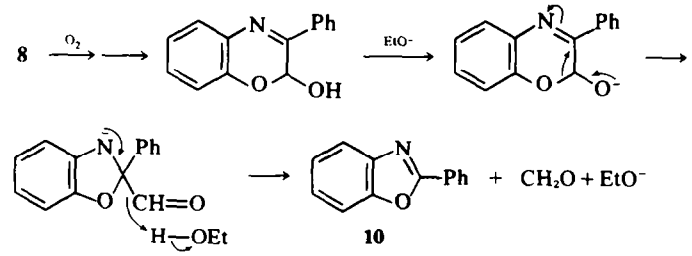
The methylene group in **8** which lies between an ether oxygen and a C=N double bond is obviously susceptible to autoxidation, and the lactone **11** and the lactol **13** must be products derived from the peroxy radical first formed.[7] As the ring contraction of **8** to 2-phenylbenzoxazole **10** requires the presence of oxygen, in acid conditions it

possibly proceeds as shown in Scheme 1, C-2 being eliminated as formic acid. In hot alkaline solution the reaction probably involves ring opening of the lactol **13** followed by ring closure as suggested in Scheme 2. We have shown in separate experiments, that the lactol **13** partially decomposes in hot ethanolic KOH to form mainly **10** but the lactone **11** gives other products.

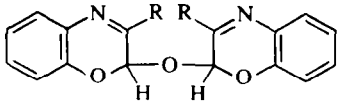
The foregoing experiments show that 3 - phenyl - 2H - 1,4-benzoxazine **8** is somewhat more sensitive to oxidation than analogous arylbenzothiazines **1** although there is no tendency to undergo dimerisation at C-2 by the action of oxygen either in acid or alkaline media. In order to effect the oxidative coupling of benzoxazines a more powerful dehydrogenating agent, DDQ, was used. When a hot dioxan solution of 8 was treated with DDQ the reaction afforded, besides a little lactone **11**, two stereo-isomers, A and B, $C_{28}H_{20}N_2O_3$, m.p. 171–3° and 185–7°, corresponding to the gross structure **17**. These two compounds have virtually identical mass spectra with very weak molecular ions, and diagnostic fragments at *m/e* 208 (base peak) and 224(2%) attributable to the ionic species **19** and **20**, respectively. The PMR spectra of the two isomers (in $CDCl_3$) differ only in the chemical shifts of the 2H singlet arising from the equivalent protons at C-2 and C-2′ of the acetal structure **17**. In isomer A these protons resonate at δ 6.32 while in isomer B they are shifted downfield to δ 6.63. We are unable to say which isomer is the *meso* and which the DL form. In agreement with the proposed structure **17**, both isomers on treatment with dilute HCl were rapidly converted into the lactol **13**, and when treated with methanolic HCl they afforded the methyl acetal **14**.



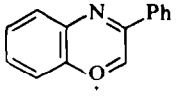
Scheme 1.



Scheme 2.



17: R = Ph
18: R = *p*-BrC_6H_4



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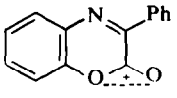


20

As expected, oxidation of 3-*p*-bromophenyl - 2H - 1,4-benzoxazine **9** with DDQ in hot dioxan proceeded similarly to give the lactol **15**, and a mixture of the two isomeric acetals **18**.

As atmospheric oxygen is implicated in the formation of these acetals (the oxidation was much faster when oxygen was bubbled through the solution) the reactions of **8** and **9** with DDQ were then carried out under anaerobic conditions in an atmosphere of very pure nitrogen. Under these conditions **8** gave mainly a mixture of two yellow–orange products **21a** and **21b** (R_f 0.68 and 0.72 on silica in C_6H_6–Et_2O, 95:5); the minor product **21b** was not isolated. That **21a** is *trans*-$\Delta^{2,2'}$-bi-(3-phenyl-2H-1,4-benzoxazine), a new heterocyclic system, follows from the molecular formula, $C_{28}H_{18}N_2O_2$, the PMR spectrum (aromatic proton resonances only), and from the characteristic UV spectrum, λ_{max} (dioxan) 244, 283 and 414 nm ($\log \epsilon$ 4.47, 4.37 and 4.01) which displayed a large reversible bathochromic shift of the visible maximum on acidification (~110 nm),† resembling that of the $\Delta^{2,2'}$ - bi - (2H - 1,4 - benzothiazine) chromophore **3**.[2,3,8] Unlike the sulphur analogue, the $\Delta^{2,2'}$-bibenzoxazine chromophore is unstable to mineral acids. Thus, for example, a dilute solution of **21** in MeOH–conc. HCl (80:20) at room temperature becomes colourless after 24 hr with formation of various products, among which the hemiacetal **13** is preponderant.

While **21a** is quite stable in the solid state, in solution it is rapidly transformed by irradiation with direct sunlight into the isomer **21b**; this is revealed by TLC and by marked changes in the UV spectrum (Fig. 1), including a bathochromic shift of the visible maximum to 430 nm. In the dark and/or on heating the process does not reverse

†In dioxan–MeOH–conc. HCl (50:34:16, v/v). The magnitude of the blue shift depends upon the nature and concentration of the acid media.

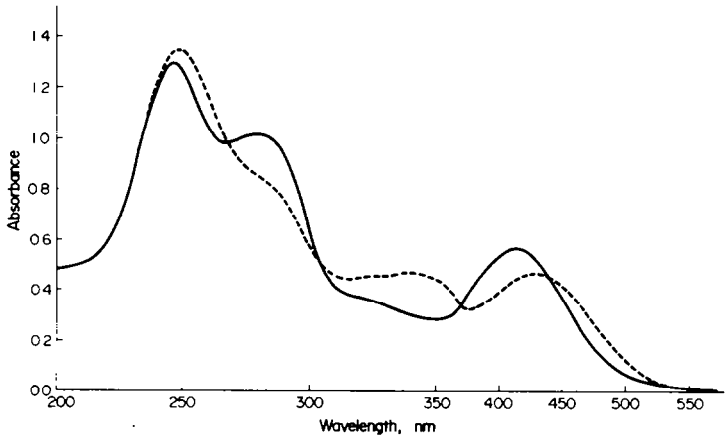
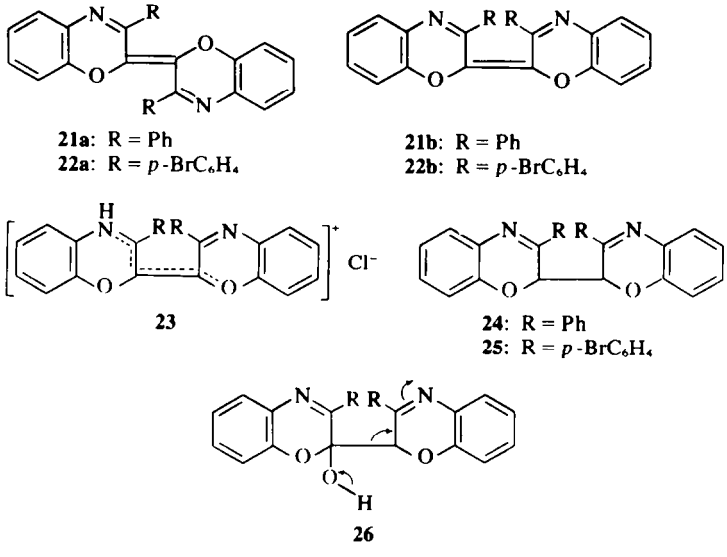


Fig. 1. UV spectra of $\Delta^{2,2'}$ - Bi - (3 - phenyl - 2H - 1,4 - benzoxazine) (**21**) in dioxan before (——) and after (---) 30 min irradiation with direct sunlight.



21a: R = Ph
22a: R = *p*-BrC_6H_4

21b: R = Ph
22b: R = *p*-BrC_6H_4

23

24: R = Ph
25: R = *p*-BrC_6H_4

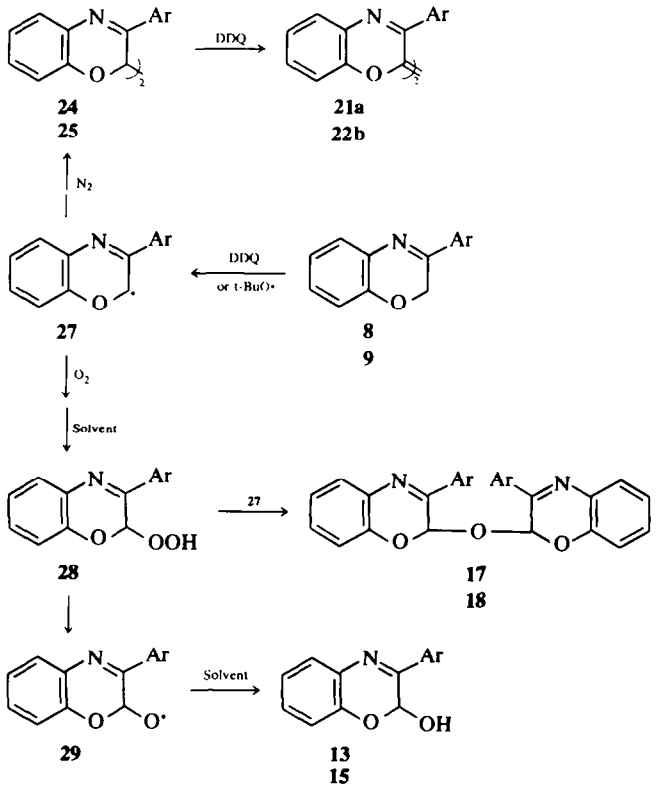
26

with an appreciable rate, but the photo-product could be rapidly transformed into the starting material **21a** by protonation with conc. HCl to give the purple mesomeric ammonium–oxonium cation **23**, from which **21a** (as well as some **21b**) was obtained by neutralisation. By analogy with the chemical and photochemical behaviour of $\Delta^{2,2'}$ - bi-(2H-1,4-benzothiazine) isomers,[3] the observed interconversion of the two $\Delta^{2,2'}$-bi-(2H-1,4-benzothiazine) derivatives, together with their relative stabilities, led us to conclude that the more stable form had the *trans* - configuration **21a** around the central C=C bond, and that its photo-product was the *cis*-form **21b**. This contrasts with the bi-benzothiazine analogue, **3** (R = Ph) where the *cis*-form is the more stable isomer as a result of the particular conformation of the two thiazine rings which favour a close van der Waals interaction between the phenyl groups at the 3- and 3'-positions.[2]

Similarly 3 - *p* - bromophenyl - 2H - 1,4 - benzoxazine **9** underwent oxidative coupling at C-2 when treated with DDQ in the absence of air, yielding mainly the *trans* - $\Delta^{2,2'}$ - bibenzoxazine **22a**, showing UV absorption and photochemical behaviour similar to that of **21a**.

The oxidation reactions of benzoxazines **8** and **9** with DDQ are summarised in Scheme 3. DDQ can abstract[9] either a hydrogen atom or hydride ion from appropriate substrates, and the formation of dimers implies that this is a radical process. In the formation of $\Delta^{2,2'}$-bibenzoxazines **21a** and **22a** by oxidation of the monomers with DDQ it was not possible to isolate the precursor dimers **24** and **25** nor could these postulated intermediates be obtained by treatment of the benzoxazines with the mild dehydrogenation agents (picric acid, nitrobenzene) used[1] successfully to prepare the corresponding dimers from benzothiazines. However when a benzene solution of **8** (or **9**) was treated with di-t-butyl peroxalate[10] the reaction proceeded smoothly as expected to give **24** (or **25**) as a mixture of diastereo-isomers (TLC evidence). Subsequent treatment of **24** with DDQ in hot dioxan under nitrogen afforded the $\Delta^{2,2'}$ - bibenzoxazine **21a** along with a small amount of the lactone **11**. Similar dehydrogenation of **25** yielded **22a** and a trace of lactone **12**. It seems likely that the lactones are formed by hydride ion abstraction from **24** and **25** followed by solvolysis by adventitious water in the "dry" dioxan to give a hemiacetal which could decompose as indicated in **26**.

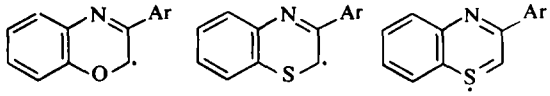
The DDQ oxidation of the benzoxazines in the presence of air resulted in autoxidation and the formation of acetals (Scheme 3) as was observed in the preliminary oxidation



Scheme 3.

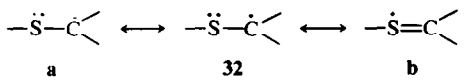
of **8** with oxygen. We showed, in separate experiments, that the bis-acetal **17** is not derived from the lactol **13** by dehydration under our conditions, and its formation in relatively good yield (~50%) is best explained by the induced decomposition of the hydroperoxide **28** by reaction with **27**, although other routes are possible (e.g. **27** + **29**). The minor product **13** probably arises by thermal decomposition of **28**, as indicated. The reaction **27** + HO· may also contribute but the lactol **13** is not formed by way of a self-reaction of a peroxy radical (the precursor of **28**) as that would also produce the lactone **11**.[11] The latter was shown to be stable under the reaction conditions but could not be detected in autoxidations which yielded **13** and **17**.

The behaviour of the benzoxazines contrasts with that of the benzothiazines which tend to dimerise rather than autoxidise. It is clear that benzothiazinyl radicals **30** have a greater thermodynamic stability then benzoxazinyl radicals **27**. This allows them to survive long enough to



27 **30** **31**

react with themselves (dimerisation) whereas benzoxazinyl radicals are rapidly scavenged by oxygen leading to the formation of the lactones, lactols, and bis-acetals. It is usually considered that α-thioalkyl radicals are relatively more stable than α-oxyalkyl radicals because the unpaired electron can be delocalised both by electron transfer **30a** and by electron sharing **30b** involving sulphur d-orbitals.[12]



a **32** **b**

A further advantage in the present case is the formation of an extended aromatic system **31**.

EXPERIMENTAL

o - *Acetylaminophenyl phenacyl ether*, **4**. To a soln of *o* - acetylaminophenol (15 g) in EtOH (400 ml) containing KOH (5.6 g), a soln of phenacyl bromide (9.8 g) in EtOH (100 ml) was added, dropwise, with stirring, and the mixture was then refluxed for 30 min. After working up the residue was crystallised from EtOH–H_2O (2:1), to give **4** (15.8 g, 59%) as needles, m.p. 105–107° (lit.,[6] 105°); *m/e* 269 (M^+, 20), 227 (32), 108(50), and 105(100%); δ (DMSO-d_6) 7.93, 7.52 and 6.85 (9H, *m*, ArH), 5.60 (2H, *s*, CH_2) and 2.10 (3H, *s*, Me). (Found: C, 71.47; H, 5.58; N, 5.03%; M^+, 269.1052. Calc. for $C_{16}H_{15}NO_3$: C, 71.33; H, 5.62; N, 5.20%; M, 269.1051).

o - *Acetylaminophenyl* p - *bromophenacyl ether*, **5**. Condensation of *o* - acetylaminophenol (2.7 g) with *p* - bromophenacyl bromide (5 g) as above gave **5** (3.9 g, 67%), as needles, m.p. 131–133° (from EtOH); *m/e* 349(10), 347(10), 307(17), 305(18), 185(32), 183(33), and 108(100%); δ ($CDCl_3$) 7.81 and 7.57 (4H, AB*q*, J = 8.8 Hz, BrC_6H_4), 6.9 (4H, *cm*, remaining ArH), 6.93 (1H, *br*, NH, removed by D-exchange), 5.30 (2H, *s*, CH_2), and 2.20 (3H, *s*, Me). (Found:† Br, 23.10; N, 3.93%; M^+, 347.0158. $C_{16}H_{14}{}^{79}BrNO_3$ requires Br, 22.99; N, 4.02%; M, 347.0157).

3 - *Phenyl* - 2H - 1,4 - *benzoxazine*, **8**. To a soln of *o* - acetylaminophenyl phenacyl ether (3 g) in 10% ethanolic KOH (12 ml), water (2.4 ml) was added, and the mixture was refluxed for 2 hr. On cooling **8** (0.92 g) separated as pale yellow plates, m.p. 111–112° (lit.,[6] 111°); *m/e* 209(M^+, 100), 208(40), 180(11) and 103(97%); δ (CD_3COCD_3) 8.1 (2H, *cm*, H-2' and H-6'), 7.3 (7H, *cm*, remaining ArH), 5.18 (2H, *s*, CH_2). (Found: C, 80.43; H, 5.22; N, 6.63%; M^+, 209.0839. Calc. for $C_{14}H_{11}NO$: C, 80.35; H, 5.30; N, 6.70%; M, 209.0840).

† a satisfactory carbon analysis could not be obtained for this compound.

3 - p - *Bromophenyl* - 2H - 1,4 - *benzoxazine*, **9**. Cyclisation of *o* - acetylaminophenyl *p*-bromophenacyl ether (1.2 g) with 10% ethanolic KOH as above, gave **9** (0.5 g) as pale yellow plates, m.p. 162–164° (from aq. EtOH); *m/e* 289(98), 288(40), 287(100), 286(25), 208(14), 183(34) and 181(32%); δ ($CDCl_3$) 7.82 and 7.57 (4H, AB*q*, J = 8.7 Hz, BrC_6H_4), 7.1 (4H, *cm*, remaining ArH), 4.99 (2H, *s*, CH_2). (Found: C, 58.27; H, 3.58; Br, 28.10; N, 5.03%; M^+, 286.9948. $C_{14}H_{10}{}^{79}BrNO$ requires: C, 58.30; H, 3.50; Br, 27.76; N, 4.86%; M, 286.9946).

Reaction of 3 - *phenyl* - 2H - 1,4 - *benzoxazine with oxygen*

(a) *In acid medium.* In a typical experiment, a stream of O_2 was bubbled through a cold soln of **8** (100 mg) in C_6H_6 (10 ml) containing TFA (0.2 ml) for 5 hr. The mixture was then washed with $NaHCO_3$ aq. and water, dried and evaporated. The residue was fractionated by PLC on silica in C_6H_6–MeOH (99 : 1) to give mainly **10**, **11** and **13**. The oxazole **10** (6%, R_f, 0.35) formed needles, m.p. 102–103° (lit.,[13] 103°) (from aq. EtOH) showing M⁺ at *m/e* 195(100%) and PMR signals at δ 8.2 (2H, *cm*, H-2′ and H-6′) and 7.5 (7H, *cm*, remaining ArH). The lactone **11** (16%, R_f, 0.45) crystallised from C_6H_6 as pale yellow prisms, m.p. 116–117° (Russian workers[6] ascribed structure **11** to a compound, m.p. 198°, obtained by an unlikely process. The only evidence provided was a nitrogen analysis); *m/e* 223 (M⁺, 36), 195(100); λ_{max} (EtOH) 235 and 334 (log ε 3.84 and 4.17); ν_{max} ($CHCl_3$) 1740 cm^{-1}; δ ($CDCl_3$) 8.3 (2H, *cm*, H-2′ and H-6′), 7.6 (7H, *cm*, remaining ArH) (Found: M⁺, 223.0633. $C_{14}H_9NO_2$ requires: M, 223.0633).

The hemiacetal **13** (0.15%, R_f 0.15) formed needles, m.p. 230–232° (from $CHCl_3$). IR, NMR and MS are discussed on p. 2033 λ_{max} (EtOH) 233, 242, 288 and 320 nm (log ε 3.96, 3.94, 4.12 and 4.05). (Found: C, 74.54; H, 4.94; N, 6.41%; M^+, 225.0786. $C_{14}H_{11}NO_2$ requires: C, 74.66; H, 4.92; N, 6.22%; M, 225.0789). Treatment of **13** (40 mg) with MeOH saturated with dry HCl for 3 hr at reflux temp. afforded, besides some unchanged starting material, the methyl acetal **14** (25 mg) which crystallised from EtOH as prisms, m.p. 227–229°; *m/e* 239 (M^-, 94), 224(45), 208(57), and 196(100%); δ ($CDCl_3$) 7.95 (2H, *cm*, H-2′ and H-6′), 7.50 and 7.15 (7H, *cm*, remaining ArH), 5.88 (1H, *s*, –OCHO–), and 3.55 (3H, *s*, –OMe).

(b) *In alkaline medium.* A stream of O_2 was bubbled through a refluxing soln of **8** (200 mg) in 3% ethanolic KOH (20 ml) for 30 min. After cooling, the mixture was concentrated to small volume, diluted with water and extracted with Et_2O(×3). Evaporation of the combined extracts gave an amorphous residue which was purified by PLC on silica in C_6H_6–MeOH (99 : 1) to give mainly **8** (30 mg) and traces of the hemiacetal **13**.

Oxidations with DDQ in the presence of air

(a) 3 - *Phenyl* - 2H - 1,4 - *benzoxazine*, **8**. A soln of **8** (1 g) and DDQ (1.5 g) in anhyd. dioxan (40 ml) was refluxed for 6 hr. The mixture was then concentrated *in vacuo* to a small volume, diluted with water and extracted with Et_2O(×3). The combined extracts were treated with $NaHSO_3$ aq., washed with NaOH aq., dried and evaporated. Crystallisation of the residue (560 mg) from EtOH afforded **17** (480 mg, 47%), as a mixture of two diastereo-isomers (A) and (B) (*meso* and racemic forms) which were separated by PLC on silica in C_6H_6–Et_2O (7 : 3). The less polar isomer (A) (R_f 0.6), formed prisms, m.p. 171–172° (from EtOH); *m/e* 432 (M^+, 2), 403(6), 224(2), and 208(100%); λ_{max} (EtOH) 235, 286 and 320 nm (log ε 4.36, 4.50 and 4.34). (Found: M^+, 432.1473. $C_{28}H_{20}N_2O_3$ requires: M, 432.1473). The other isomer (B) (R_f 0.5) had m.p. 185–187°, and UV and MS spectra identical with those of (A). (Found: M^+, 432.1472 $C_{28}H_{20}N_2O_3$ requires: M, 432.1473). For the NMR spectra of (A) and (B) see p. 2034. Fractionation of the mother liquor by PLC on silica as above afforded, besides the two diastereo-isomers **17**, 50 mg of **13**, m.p. 230–232°, identical in all respects with that obtained by reaction of 3 - phenyl - 2H - 1,4 - benzoxazine with oxygen.

The oxidation proceeded more rapidly in a stream of O_2. Thus when O_2 was bubbled through a soln of **8** (200 mg) and DDQ (300 mg) in anhydrous refluxing dioxan (8 ml) for 30 min, working up as before gave **17** (105 mg, 51%), as a mixture of diastereo-isomers, along with **11** (10 mg).

(b) 3 - p - *Bromophenyl* - 2H - 1,4 - *benzoxazine*, **9**. Similarly, treatment of **9** (200 mg) with DDQ (135 mg) in anhyd dioxan, and PLC of the oxidation mixture on silica with C_6H_6–Et_2O (7 : 3) gave three products with R_f 0.13, 0.62 and 0.71, corresponding to **15** and to the two diastereo-isomeric acetals **18** (*meso* and racemic forms), respectively. The hemiacetal **15** formed prisms, m.p. 241–243° (from CCl_4) (20 mg); δ (CD_3COCD_3) 8.04 and 7.66 (4H, AB*q*, J = 9.0 Hz, *p*-BrC_6H_4), 7.3 (4H, *cm*, remaining ArH), 6.38 (1H, *s*, –OCH–O) (Found: M^+, 302.9886. $C_{14}H_{10}{}^{79}BrNO_2$ requires: M, 302.9895). The more polar isomer **18** formed prisms, m.p. 241–243° (from C_6H_6) (20 mg); *m/e* 592(0.12), 590(0.18), 588(0.12), 563(0.16), 561(0.25), 559(0.16), 304(0.30), 302(0.30), 288(98) and 286(100%); δ ($CDCl_3$) 7.3 (16H, *cm*, ArH), and 6.34 (2H, *s*, –OCH–O–). (Found: M^+, 587.9682. $C_{28}H_{18}{}^{79}Br_2N_2O_3$ requires: M, 587.9683). The less polar isomer **18** crystallised from C_6H_6 in prisms, m.p. 291–292° (23 mg), and gave a mass spectrum identical with that given above, δ ($CDCl_3$) 7.3 (16H, *cm*, ArH) and 6.62 (2H, *s*, –OCHO–). (Found: M^-, 587.9683 $C_{28}H_{18}{}^{79}Br_2N_2O_3$ requires: M, 587.9683).

Oxidations with DDQ in the absence of air

(a) 3 - *Phenyl* - 2H - 1,4 - *benzoxazine*, **8**. A soln of **8** (200 mg) and DDQ (300 mg) in anhyd dioxan (20 ml) was refluxed for 6 hr under N_2. The mixture was then concentrated *in vacuo* to a small volume, diluted with water and extracted with $CHCl_3$(×3). The combined extracts were treated with $NaHSO_3$ aq., washed with NaOH aq., dried, and evaporated. Crystallisation of the residue from C_6H_6 gave trans $\Delta^{2,2'}$-*bi*-(3-*phenyl*-2H-1,4-*benzoxazine*) **21a**, orange needles, m.p. 321–322° (40 mg), homogeneous on TLC, insoluble in EtOH, Me_2CO and Et_2O, slightly soluble in dioxan, and $CHCl_3$; *m/e* 414(M⁺, 100), 413(10), 337(20) and 219(36%). (Found: M⁺, 414.1366. $C_{28}H_{18}N_2O_2$ requires: M, 414.1368).

TLC examination of the mother liquor on silica in C_6H_6–Et_2O (19 : 1) revealed the presence, besides **21a**, of its geometrical isomer **21b** which could not be isolated in pure form. The interconversion of the geometrical isomers is described on pp. 2034–2035.

(b) 3 - p - *Bromophenyl* - 2H - 1,4 - *benzoxazine*, **9**. Similarly, oxidation of **9** (100 mg) with DDQ (70 mg) gave trans $\Delta^{2,2'}$ - *bi*(3 - p - *bromophenyl* - 2H - 1,4 - *benzoxazine*) **22a**, red-orange prisms, dec 325° (from C_6H_6) (12 mg); *m/e* 574(46), 572(100), 570(45), 417(3), 415(3), 299(6) and 297(6%); δ ($CDCl_3$) 8.3 and 7.4 (16H, *cm*, ArH); λ_{max} (dioxan–MeOH, 7 : 3) 240, 286, 423 nm (log ε 4.46, 4.37, 4.03). On protonation the visible maximum is shifted to 530 nm (Found: M⁺, 569.9578. $C_{28}H_{16}{}^{79}Br_2N_2O_2$ requires: 569.9577). In soln **22a** exhibits marked photochromism being converted into the *cis* form **22b** on brief irradiation with direct sunlight.

Bi - 2,2′ - (3 - *phenyl* - 2H - 1,4 - *benzoxazinyl*), **24**. To a soln of **8** (300 mg) in C_6H_6 (15 ml) di - t - butyl peroxalate[16] (200 mg) was added; the mixture was heated under very pure N_2 for 3 hr at 45°, and then for 30 min at 60°. Volatile materials were removed *in vacuo*, and the residue was crystallised from CCl_4 to give **24** (92 mg, 31%), showing two distinct spots on analytical TLC (R_f 0.32 and 0.39) in C_6H_6; pale yellow needles, m.p. 263–265°; *m/e* 416 (M^+, 0.5), 208(100%), δ (CCl_4) 7.3 (18H, *cm*, ArH), 5.66 and 5.62 (*ca.* 1H each, *s*, methine protons of the *meso* and racemic forms). (Found: M^-, 416.1521. $C_{28}H_{20}N_2O_2$ requires: M, 416.1524). More (60 mg) of **24** as well as some unchanged **8**, was obtained by evaporating the mother liquor to dryness and PLC on silica in C_6H_6.

Bi - 2,2′ - (3 - p - *bromophenyl* - 2H - 1,4 - *benzoxazinyl*) **25**. By the above procedure **9** (300 mg) was treated with di - t - butyl peroxalate (250 mg) to give **25** (160 mg, 53%), as a mixture of diastereo-isomers (TLC evidence) which crystallised from C_6H_6 in pale yellow needles, m.p. 239–241°; *m/e* 576(0.2), 574(0.4), 572(0.3), 288(99) and 286(100%); δ ($CDCl_3$) 7.3 (16H, *cm*, ArH), 5.58 and 5.55 (*cm.* 1H each, *s*, methine protons of the *meso* and racemic forms). (Found: M^+, 571.9730. $C_{28}H_{18}{}^{79}Br_2N_2O_2$ requires: M, 571.9734).

$\Delta^{2,2'}$ - *Bi* - (3 - *phenyl* - 2H - 1,4 - *benzoxazine*) **21a** *from* **24**. A soln of **24** (150 mg) and DDQ (75 mg) in dioxan (7 ml) was refluxed for 6 hr. The mixture was then concentrated to a small volume, diluted with water and extracted with $CHCl_3$. The combined

extracts were treated with $NaHSO_3$ aq., washed with NaOH aq., dried, and evaporated. Crystallisation of the residue from C_6H_6 gave **21a**, m.p. 321–322° (46 mg), identical in all respects with that obtained by direct oxidation of 3 - phenyl - 2H - 1,4 - benzoxazine with DDQ in the absence of air. PLC of the mother liquor on silica in C_6H_6–MeOH (99:1) gave more $\Delta^{2,2'}$ - bi - (3 - phenyl - 2H - 1,4 - benzoxazine) as a mixture of geometrical isomers and 3 - phenyl - 2H - 1,4 - benzoxazine - 2 - one **11** (7 mg).

$\Delta^{2,2'}$ - Bi - (3 - p - bromophenyl - 2H - 1,4 - benzoxazine) from **25**. In a similar manner, **25** (250 mg) was oxidised with DDQ in dioxan to give **22a** as small orange needles, dec at 325° (40 mg), homogeneous on TLC, and identical in all respects with that obtained by direct oxidation of 3 - *p* - bromophenyl - 2H - 1,4 - benzoxazine with DDQ in the absence of air. PLC of the mother liquor on silica with C_6H_6–MeOH (99:1) gave more $\Delta^{2,2'}$ - bi - (3 - *p* - bromophenyl - 2H - 1,4 - benzoxazine) as a mixture of geometrical isomers, and **12** (5 mg) as a pale yellow amorphous solid; *m/e* 303(10), 301(7), 275(100), 273(99), 247(8) and 245(8%), ν_{max} ($CHCl_3$) 1710 cm^{-1}; δ ($CDCl_3$) 8.12 and 7.65 (each 2H, AB*q*, *p*-BrC_6H_4) and 7.4 (4H, *cm*, remaining ArH).

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