[Chem. Pharm. Bull. 31(11)3891—3896(1983)]

Rearrangement of 4-Acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one

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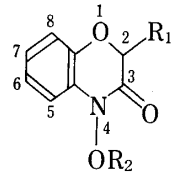
(Received March 9, 1983)

4-Acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**3**) undergoes rearrangement or nucleophilic attack to give 2-, 5-, 6-, and 7-substituted derivatives of the benzoxazinone according to the reaction conditions. The formation of 5- and 7-substituted products was interpreted in terms of nucleophilic attack on the cation (**14**) formed by the heterolysis of the N–O bond of **3**. For the formation of 6-substituted derivatives of the benzoxazinone, participation of the oxygen atom at position 1 of the benzoxazinone (that is, formation of an oxonium ion, **18**) is important. A possible mechanism for the formation of 2-substituted products also involves an oxonium ion (**19**). These novel aspects of acetoxybenzoxazinone chemistry may contribute to an understanding of the mechanism of the actions of the prohibitins in cereal plants.

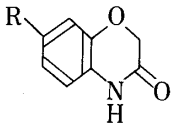
Keywords——4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one; 2,4-dihydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one; prohibitin; aryl hydroxamic acid; cyclic hydroxamic acid; acetoxy rearrangement

During recent chemical studies on the mechanism of mutagenic, antifungal and antibacterial effects of a naturally occurring unique arylhydroxamic acid, 2,4-dihydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**1**),[1-4] which is an important prohibitin found in cereal plants such as maize and wheat,[1] it was necessary to investigate the reactivity of a model compounds, 4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**2**).[5] Little information on the chemical properties of this compound (**2**) has been obtained until 1970, when Coutts and Pound reported the reaction of **2** with hydrochloric acid to give 7-chloro-2*H*-1,4-benzoxazin-3(4*H*)-one (**5**).[6] The nucleophilic attack at position 7 on the benzoxazinone by chloride is consistent with the established chemistry of arylhydroxamic acid, which suggests that positions 5 (*ortho* to the hydroxamic acid group) and 7 (*para* to the hydroxamic acid group) of **2** are the centers which are nucleophilically attacked.[7,8]

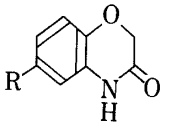
In 1971, the same authors reported another reaction of **2**: the rearrangement of 4-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**3**) in acetic acid to give 6-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**9**).[9] The reaction is unusual because the nucleophilic attack of acetate occurred at position 6, which is *meta* to the hydroxamic acid group. Coutts and Pound interpreted the



1 : R_1=OH, R_2=H
2 : R_1=H, R_2=H
3 : R_1=H, R_2=$COCH_3$



4 : R=H
5 : R=Cl
6 : R=OAc
7 : R=OMe



8 : R=Cl
9 : R=OAc
10 : R=OMe

Chart 1

unusual rearrangement in terms of an molecular mechanism (Chart 2), which seems implausible because the yield of **9** was high and no 2*H*-benzoxazin-3(4*H*)-one (**4**) or 4,6-

diacetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one was obtained. Reinvestigation of the reaction seemed necessary.

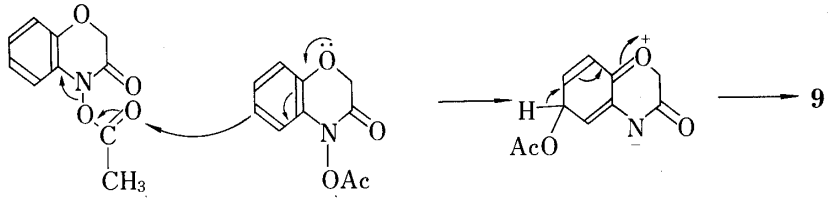


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Chart 2. Mechanism Proposed by Coutts and Pound[9]

Compound **2** was prepared by reductive cyclization[10] (using palladium on charcoal and sodium borohydride) of ethyl *o*-nitrophenoxyacetate in a yield of 64%. *O*-Acetylation of **2** was performed by the Schotten–Baumann method to give **3** in a yield of 45%. Compound **3** was stable at room temperature. Refluxing of **3** in acetic acid for 30 min gave **9** in a yield of 80%. The result is consistent with the report by Coutts and Pound.[9] For confirmation of the structure of the product (**9**), **9** was hydrolyzed with sodium hydroxide followed by methylation to give 6-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**10**), which was prepared by the reductive cyclization of ethyl 4-methoxy-2-nitrophenoxyacetate.

When **3** was refluxed in benzene for 12 h, **9** was not obtained, but rearrangement products, 2-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**12**, yield 30%) and 7-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**6**, yield 8%), were obtained. The structures were deduced from the proton nuclear magnetic resonance (^{1}H-NMR) and mass spectra, elemental analysis and infrared (IR) spectra. In addition, **6** was hydrolyzed and then methylated to give 7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**7**), and the same compound was alternatively synthesized from 5-methoxy-2-nitrophenoxyacetic acid, confirming the structure.

Other rearrangement products of **3** were obtained when **3** was treated with trifluoroacetic acid in benzene. The treatment gave **11** (yield 45%) and 5-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**13**, yield 15%).[11] The structures were deduced from the ^{1}H-NMR and mass spectra, elemental analysis and IR spectra. Compound **11** was probably formed from 6-acetoxy- or 6-trifluoroacetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one by hydrolysis during the reaction or during the work-up procedure.

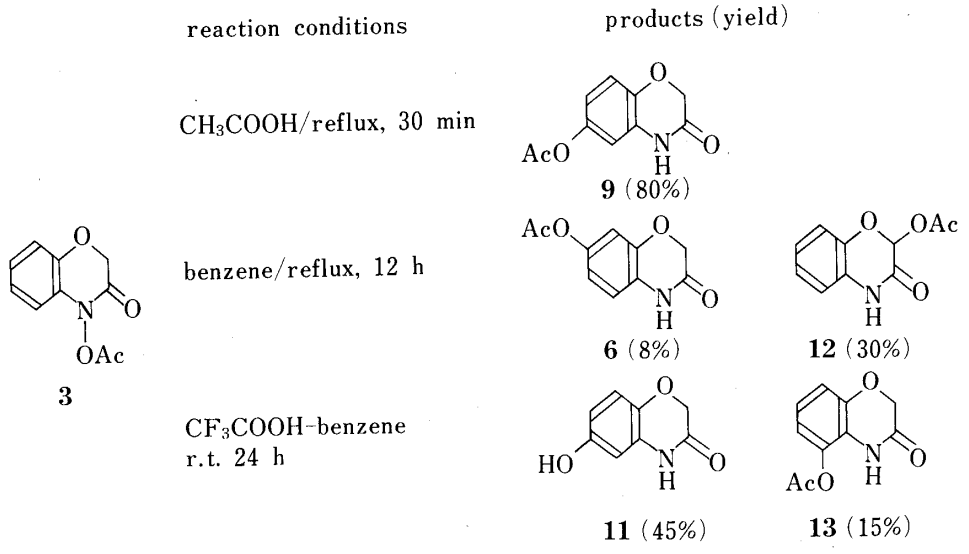
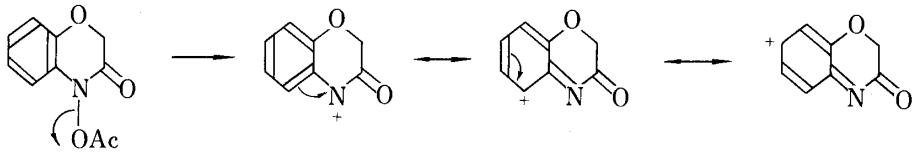


Chart 3. Rearrangement of 4-Acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**4**)

Other nucleophiles such as chloride ion also could attack compound **3**: treatment of **3** with hydrochloric acid or potassium chloride in aqueous methanol gave **5** and 6-chloro-2*H*-1,4-benzoxazin-3(4*H*)-one (**8**) in the ratio of about 1 : 3. Reaction of **2** with hydrochloric acid gave only **5** but not **8** as reported by Coutts and Pound.[6] However, treatment of **2** with acetyl chloride or *p*-toluenesulfonyl chloride gave only **8** (in yields of 21 and 39%, respectively), but not **5**. The structures of **5** and **8** were deduced from their ^{1}H-NMR and mass spectra, elemental analysis and IR spectra, and were confirmed by alternative synthesis by the reductive cyclization of 5-chloro- and 4-chloro-2-nitrophenoxyacetic acid ethyl ester followed by catalytic hydrogenation of the resulting 7-chloro-4-hydroxy- and 6-chloro-4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one, respectively.

The formation of 5- and 7-substituted benzoxazinone derivatives, **5**, **6**, and **13**, was interpreted in terms of the participation of the cations, **14b** and **14c**, formed by heterolytic cleavage of the N–O bond of **3**, as suggested from the established chemistry of arylhydroxamic acid.[7,8] The corresponding mechanism in an S_N2' manner is also possible.



3 **14a** **14b** **14c**

Chart 4

The mechanism of the rearrangement to or the reaction at positions 2 and 6 is more interesting. A contribution of the enol form (**15**) could be suggested even in the rearrangement and nucleophilic attack at position 6 of the benzoxazinone: this leads to mechanism A (Chart 5) for the formation of the 6-substituted benzoxazinone derivatives, **8** and **9**. Another possible mechanism involves a quinonium imine intermediate (mechanism B in Chart 5).

To judge the applicability of mechanism A, we investigated the reaction of 2,2-dimethyl-2*H*-1,4-benzoxazin-3(4*H*)-one (**22**, prepared by the reductive cyclization of ethyl 1-(*o*-nitrophenyl)-isobutyrate). If mechanism A applies to the rearrangement of the 4-acetoxy group to position 6, 6-acetoxy-2,2-dimethyl-2*H*-1,4-benzoxazin-3(4*H*)-one (**23**) could not be obtained from **22**, because the tautomerization to the enol form corresponding to **15** had been blocked. However, treatment of **22** with acetic anhydride in acetic acid, which should give the 6-acetoxy derivative *via* rearrangement of the 4-acetoxy derivative,[9] gave **23** in a yield of 58%. The result, formation of **23** from **22**, excluded the possibility of mechanism A for the reaction at position 6. Therefore, the more plausible mechanism is B in Chart 5, in which the oxygen atom at position 1 contributes effectively. In fact, Coutts and Pound reported that 4-acetoxy-2*H*-1,4-benzthiazin-3(4*H*)-one (**24**) gave 2-acetoxy-2*H*-1,4-benzthiazin-3(4*H*)-one (**25**), but not 6-acetoxy derivative on treatment with acetic acid.[9] In addition, 1-hydroxy-3,4-dihydrocarbostyril-2-one (**20**), obtained by the reductive cyclization of ethyl *o*-nitrophenylpropionate, did not give any 7-substituted derivative corresponding to **9** on treatment with acetic anhydride in acetic acid. Compound **20** gave only 1-acetoxy-3,4-dihydrocarbostyril-2-one (**21**). These results suggest an important contribution of the oxygen atom at position 1 of **3** in the rearrangement which yields **9**. The participation of the oxonium ion, **18**, which is a resonance structure of the ion **14a**—**c**, explains the contribution of the oxygen atom, and the nucleophilic attack at position 6 of the ion **18** (the position is *meta* to the nitrogen atom and *para* to the ether group); mechanism B. The position is a possible reaction site of quinone–imines.[12,13]

The mechanism for the reaction at position 2 could be interpreted in terms of the participation of the enol form (**15**), followed by elimination of the acetoxy group (Chart 5, A).

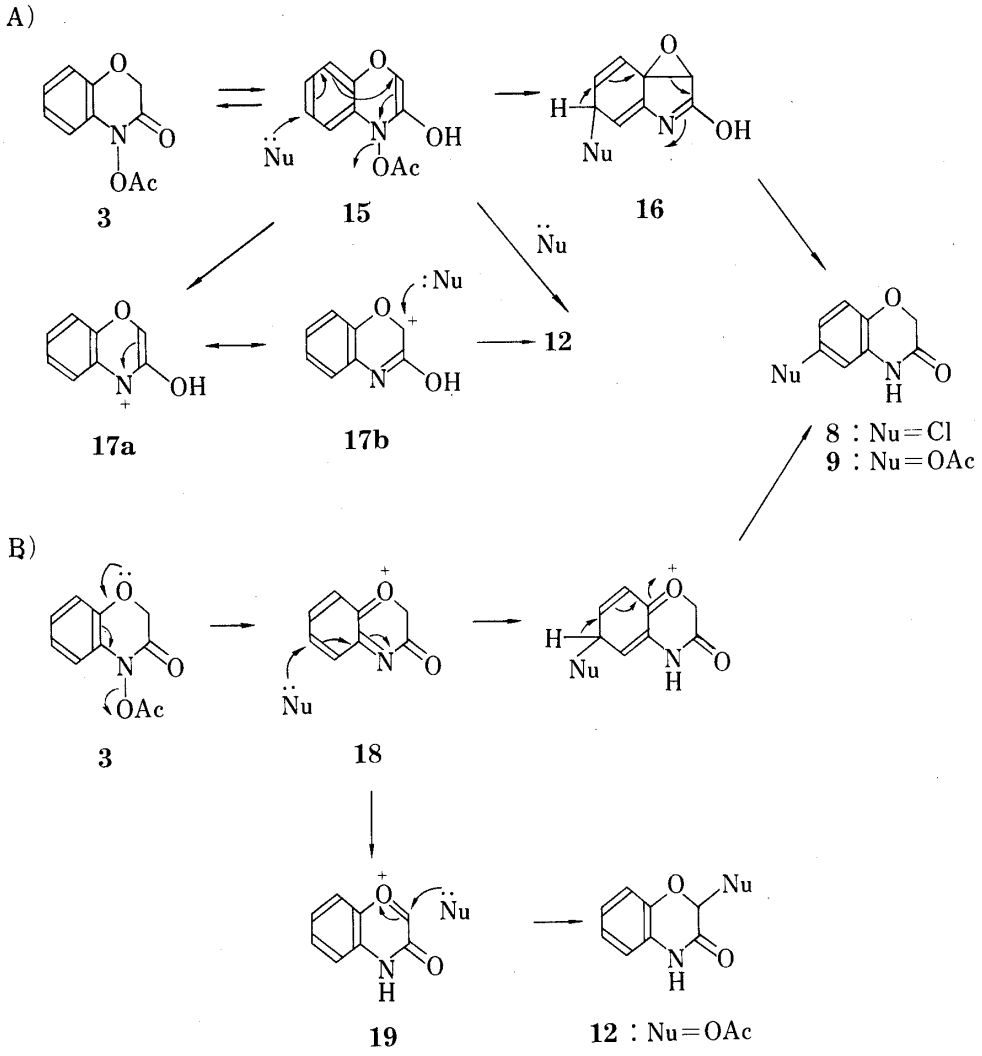


Chart 5. Possible Mechanisms of Rearrangement to the *meta* Position

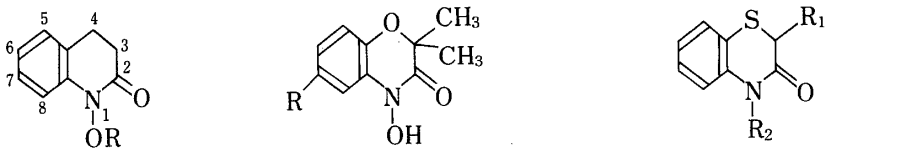


Chart 6

However, no deuterium incorporation was observed at position 2 in 2-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**12**) or in the recovered starting compound (**3**). This result excludes a rate-determining elimination of the 4-acetoxy group from the enol or the rate-determining sigmatropic acetoxy migration. Therefore, we wish to propose a mechanism which involves an oxonium ion (**19**) formed by elimination of a proton at position 2. This readily explains the formation of 2-substituted products which retain the original hydrogen atom at position 2 (Chart 5, B).

In conclusion, **3** was attacked by nucleophiles at positions 2, 5, 6, and 7, depending on the reaction conditions. A mechanism involving intermediates (or transition states), **14**, **18** and **19**,

for each pathway is proposed. The determining factors which control the reaction sites require further investigation. The present study represents a new contribution to aromatic and heteroaromatic chemistry, and may help to develop an understanding of the mechanism of the actions of prohibitins in cereal plants.

Experimental

Reductive Cyclization (General Procedure)——Reductive cyclization of ethyl *o*-nitrophenoxyacetate derivatives was performed by a modification of the method of Coutts and Pound.[10] $NaBH_4$ (4 g) was dissolved in a mixture of MeOH (40 ml) and H_2O (60 ml) under an N_2 atmosphere, and then 10% Pd-C was added. To this mixture, a solution of an ethyl *o*-nitrophenoxyacetate derivative (4 g in 120 ml of MeOH) was added dropwise in 15 min. During the addition, and for another 15 min, the mixture was vigorously stirred and N_2 was bubbled through it. Then the mixture was filtered and concentrated under reduced pressure to about 50 ml. The solution was acidified with dil. HCl, and the resulting precipitate of the corresponding 4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one derivative was collected by filtration. The products were recrystallized from aqueous MeOH.

4-Hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (2)——Ethyl *o*-nitrophenoxyacetate was reductively cyclized. Yield 64%, mp 165—169 °C, IR (KBr); 3060, 2820, 1680, 1650, 1500 cm^{-1}. *Anal.* Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.24; N, 8.48. Found: C, 58.12; H, 4.26; N, 8.32.

4-Acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (3)——One gram of **2** was dissolved in CH_2Cl_2 (40 ml) and $(CH_3CO)_2O$ (1.80 g) was added under ice-cooling. Next, 5% aqueous Na_2CO_3 (40 ml) was added and the mixture was vigorously shaken for 3—5 min under ice-cooling. The organic layer was separated, dried over Na_2SO_4, and evaporated to dryness under reduced pressure. The residue was recrystallized from CH_2Cl_2–hexane to give **3** (510 mg, yield 40%). mp 65.5—66.0 °C, (M^+) 207, NMR ($CDCl_3$): 2.50 (s, 3H), 4.85 (s, 2H), 6.80—7.20 (m, 4H). IR (KBr): 1800, 1710, 1605, 1500 cm^{-1}. *Anal.* Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.35; N, 6.76. Found: C, 58.12; H, 4.28; N, 6.55.

Rearrangement of 3——[A] Compound **3** (100 mg) was dissolved in CH_3COOH (0.7 ml) and refluxed for 30 min. The reaction mixture was poured into water and the resulting precipitate was recrystallized from benzene–MeOH to give 6-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**9**, yield 78%).[9,14] mp 164—165 °C, (M^+) 207, NMR (DMSO-d_6–$CDCl_3$): 1.90 (s, 3H), 4.28 (s, 2H), 6.60 (dd, J=2, 8 Hz, 1H), 6.64 (t, J=8 Hz, 1H), 7.70 (dd, J=2, 8 Hz, 1H), IR (KBr): 2900—3200, 1760, 1685, 1625, 1500 cm^{-1}. *Anal.* Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.35; N, 6.76. Found: C, 57.68; H, 4.27; N, 6.55. Compound **9** was suspended in 5% NaOH and stirred at room temperature for 12 h. The resulting 6-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**11**, 100 mg)[14] was suspended in 20% NaOH (25 ml) and $(CH_3O)_2SO_2$ (0.3 g) was added. The mixture was vigorously shaken for 3 h and then extracted with CH_2Cl_2. The organic layer was evaporated and the residue was recrystallized from MeOH to give 6-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**10**). mp 159 °C, IR (KBr): 3400, 1715, 1615, 1520, 1500 cm^{-1}. The same compound was obtained by reduction of 4-hydroxy-6-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one which was prepared from ethyl 4-methoxy-2-nitrophenoxyacetate by reductive cyclization.

[B] Compound **3** (100 mg) was dissolved in benzene (20 ml) and refluxed for 24 h. The reaction mixture was separated by silica gel column chromatography (CH_2Cl_2–AcOEt) to give the starting material (**3**, 31 mg, yield 31%), 2-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**12**, 30 mg, yield 30%) and 7-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**6**, 8 mg, yield 8%).[14]

Compound **12**: mp 175—176 °C, (M^+) 207, NMR ($CDCl_3$): 2.06 (s, 3H), 6.60 (s, 1H), 9.72 (br s, 1H), 6.90—7.10 (m, 4H). IR (KBr): 2850—3200, 1760, 1695, 1615, 1505 cm^{-1}. *Anal.* Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.35; N, 6.76. Found: C, 58.06; H, 4.32; N, 6.47.

Compound **6**: mp 211—216 °C, (M^+) 207, NMR ($CDCl_3$): 2.20 (s, 3H), 4.51 (s, 2H), 10.64 (br s, 1H), 6.62 (dd, J=2, 8 Hz, 1H), 6.70 (d, J=2 Hz, 1H), 6.82 (d, J=8 Hz, 1H). *Anal.* Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.35; N, 6.76. Found: C, 58.12; H, 4.41; N, 6.79.

Compound **6** was derivatized to 7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**7**) by a method similar to that described in [A]. mp 160—161 °C, (M^+) 179, NMR ($CDCl_3$): 3.82 (s, 3H), 4.70 (s, 2H), 9.63 (br s, 1H), 6.56 (dd, J=2, 8 Hz, 1H), 6.65 (d, J=2 Hz, 1H), 6.86 (d, J=8 Hz, 1H). IR (KBr): 1675, 1520, 1410 cm^{-1}. *Anal.* Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.14; H, 5.02; N, 7.76.

The same compound was obtained by reduction with H_2 in the presence of 10% Pd-C of 4-hydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one[3] which was prepared by the reductive cyclization of ethyl 5-methoxy-2-nitrophenoxyacetate.

[C] Compound **3** (300 mg) was dissolved in benzene (10 ml), and CF_3COOH (1 ml) was added. After 24 h at room temperature, the reaction mixture was evaporated under reduced pressure. The residue was separated by silica gel column chromatography (CH_2Cl_2–hexane) to give the starting material (**3**, 13.0 mg, yield 4.3%), 6-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**11**, 121 mg, yield 45%) and 5-acetoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**13**, 45.2 mg, yield 15%).

Compound **11**: mp 267—270 °C, (M^+) 165, IR (KBr): 3200, 1675, 1625, 1500 cm^{-1}. *Anal.* Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.24; N, 8.48. Found: C, 58.13; H, 4.20; N, 8.32.

Compound **13**: mp 226—227 °C, (M^+) 207, NMR (DMSO-d_6): 2.20 (s, 3H), 4.51 (s, 2H), 10.7 (br s, 1H), 6.60—7.00 (m, 3H). IR (KBr): 2800—3200, 1765, 1685, 1615, 1500 cm^{-1}. *Anal.* Calcd for $C_{10}H_9NO_4$: C, 57.97; H, 4.35; N, 6.76. Found: C, 57.91; H, 4.42; N, 6.43.

6-Acetoxy-2,2-dimethyl-2*H*-1,4-benzoxazin-3(4*H*)-one (23)——2,2-Dimethyl-4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (**22**) was prepared by reductive cyclization of ethyl 1-(*o*-nitrophenoxy)isobutyrate,[15] in a yield of 53%. Compound **22** (100 mg) was treated with CH_3COOH–$(CH_3CO)_2O$ (1—0.5 ml, refluxed for 30 min) to give the title compound (**23**) in a yield of 58%. When **22** was *O*-acetylated by the Schotten–Baumann method, 4-acetoxy-2,2-dimethyl-2*H*-1,4-benzoxazin-3(4*H*)-one was obtained (yield 65%).

Compound **23**: mp 135—137 °C, (M^+) 235, NMR ($CDCl_3$): 1.50 (s, 6H), 2.22 (s, 3H), 8.81 (br s, 1H), 6.59 (d, J = 2 Hz, 1H), 6.60 (dd, J = 8, 2 Hz, 1H), 6.90 (d, J = 8 Hz, 1H). IR (KBr): 1760, 1670 cm^{-1}. *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.28; H, 5.56; N, 5.80.

4-Acetoxy-2,2-dimethyl-2*H*-1,4-benzoxazin-3(4*H*)-one: mp 68 °C, IR (KBr): 3400, 1800, 1710, 1500, 1415 cm^{-1}. *Anal.* Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.96. Found: C, 61.10; H, 5.54; N, 5.97.

1-Acetoxy-3,4-dihydrocarbostyril-2-one (21)——1-Hydroxy-3,4-dihydrocarbostyril-2-one (**20**, mp 117—118 °C) was prepared by reductive cyclization of ethyl *o*-nitropropionate. Treatment of **20** (55 mg) with $(CH_3CO)_2O$ (0.25 ml) in CH_3COOH (0.5 ml, refluxed for 30 min) gave the title compound in a yield of 33%. Oily, (M^+) 205, NMR ($CDCl_3$): 2.32 (s, 3H), 2.60—3.10 (m, 4H), 6.70—7.30 (m, 4H). The title compound (**21**) was quantitatively recovered after being refluxed in CH_3COOH for 1 h.

Chlorination of 2——[A] Compound **2** (200 mg) was dissolved in pyridine (20 ml) and *p*-TsCl (900 mg) was added. The reaction mixture was stirred for 24 h at room temperature, and then evaporated at 40—45 °C. The residue was recrystallized from MeOH to give 6-chloro-2*H*-1,4-benzoxazin-3(4*H*)-one (**8**, 101 mg, yield 39%). mp 221 °C. (M^+) 183, NMR ($CDCl_3$): 4.40 (s, 2H), 6.70—6.80 (m, 3H), 10.40 (br s, 1H). IR (KBr): 2800—3200, 1700, 1645, 1605, 1495 cm^{-1}. *Anal.* Calcd for $C_8H_6ClNO_2$: C, 52.46; H, 3.28; N, 7.65. Found: C, 52.38; H, 3.33; N, 7.34. Treatment of **2** with CH_3COCl in benzene also gave **8** in a yield of 22%. The same compound was alternatively synthesized by reduction with Zn dust in CH_3COOH[16] of 6-chloro-4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (mp 180—182 °C) which was prepared by the reductive cyclization of ethyl 4-chloro-2-nitrophenoxyacetate.

[B] Compound **2** (300 mg) was dissolved in 2 N HCl (6 ml) and the solution was refluxed for 2.5 h. The mixture was neutralized with K_2CO_3 and then extracted with CH_2Cl_2. The organic layer was evaporated and the residue was recrystallized from MeOH to give 7-chloro-2*H*-1,4-benzoxazin-3(4*H*)-one (**5**, yield 22%).[5] mp 197—200 °C, (M^+) 183. NMR ($CDCl_3$): 4.60 (s, 2H), 6.70 (d, J = 8 Hz, 1H), 6.90 (dd, J = 2, 8 Hz, 1H), 6.95 (d, J = 2 Hz, 1H). IR (KBr): 2800—3200, 1675, 1600, 1500, 1395 cm^{-1}. *Anal.* Calcd for $C_8H_6ClNO_2$: C, 52.46; H, 3.28; N, 7.65. Found: C, 52.46; H, 3.24; N, 7.49. The same compound was alternatively synthesized by reduction with Zn dust in CH_3COOH[16] of 7-chloro-4-hydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one which was prepared by the reductive cyclization of ethyl 5-chloro-2-nitrophenoxyacetate.

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