Reactions of α,*N*-Diarylnitrones with *O*-Methyl Diphenylphosphinothioate and Oxidations of *N*-Alkylidene-2-hydroxyanilines with Silver Oxide. Preparation of Benzoxazoles

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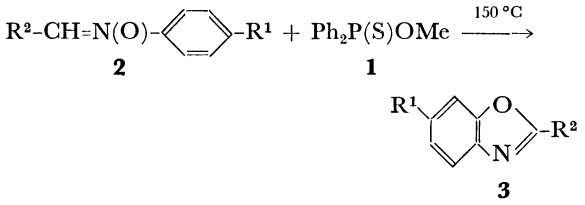
Reactions of α,*N*-diarylnitrones in the presence of *O*-methyl diphenylphosphinothioate at 150 °C gave 2-arylbenzoxazoles (**3**) in fairly good yields. Oxidation of *N*-alkylidene-2-hydroxyanilines with silver oxide afforded 2-alkenyl-, 2-alkyl-, or 2-arylbenzoxazoles (**7** and **3**) in good yields under mild reaction conditions (at room temperature). A plausible mechanism for formation of **3** and **7** has been discussed briefly.

In the previous paper,[1] we reported that reactions of α,*N*-diarylnitrones with phenylphosphonothioic dichloride gave 2-arylbenzothiazoles at room temperature in moderate yields. When *O*-methyl diphenylphosphinothioate (**1**) was used instead of phenylphosphonothioic dichloride, reactions with α,*N*-diarylnitrones (**2**) at 150 °C gave unexpectedly 2-arylbenzoxazoles (**3**).[2] Furthermore, in order to prepare **3** under mild conditions, we investigated oxidations of *N*-alkylidene-2-hydroxyanilines (**4**).[3] This paper describes these detailed results.

Reactions of α,N-*Diarylnitrones (2) with* O-*Methyl Diphenylphosphinothioate (1).* Reactions of **2** with an equimolar amount of **1** did not occur at room temperature, but gave 2-arylbenzoxazoles (**3**) at 150 °C in *o*-dichlorobenzene in fairly good yields. The results are summarized in Table 1.



As shown in Table 1, in the case of α,*N*-diphenylnitrone (**2a**), 2-phenylbenzoxazole (**3a**) was not obtained but an intractable mixture was obtained. The reason is obscure.

These reactions in the absence of **1** gave only a trace amount of **3** under similar conditions. For example, in the case of **2g**, the yield of **3g** was only 1%.

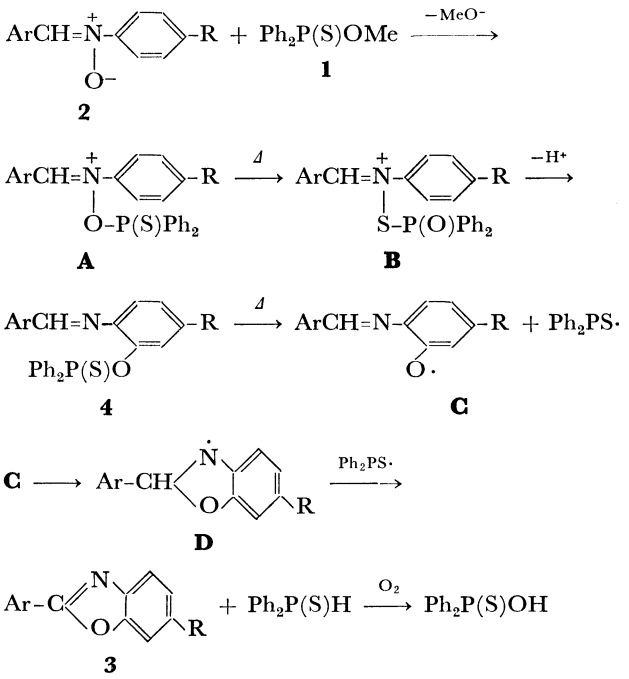
Moreover, after the reactions in the presence of **1**, about a half amount of **1** was recovered (see Table 1). The fact suggests that **1** works catalytically. In fact, in the case of **2b**, a similar reaction with a 0.1 molar amount of **1** gave **3b** in 53% yield, and the yield was nearly the same as that with an equimolar amount of **1** (61%).

Table 1. Yields of **3** from **2** and **1**

2	R¹	R²	Time/d	3 (%)	Recovery of 1/%
2a	H	C_6H_5	1	**3a** 0	a)
2b	H	*p*-$MeOC_6H_4$	2	**3b** 61	a)
2c	H	*p*-ClC_6H_4	7	**3c** 50	32
2d	Me	C_6H_5	2	**3d** 69	52
2e	Me	*p*-$MeOC_6H_4$	1	**3e** 56	33
2f	Me	*p*-ClC_6H_4	1	**3f** 47	63
2g	H	*p*-MeC_6H_4	1.75	**3g** 40	53

a) Not determined.

A plausible mechanism for formation of **3** might be as follows:



The anionic oxygen atom in the nitrone (**2**) nucleophilically attacks on the phosphorus atom in **1** to afford an intermediate (**A**) which thermally rearranges to a more stable intermediate (**B**) because P=O bond is stronger than P=S bond. Then the intermediate (**B**) is converted into *N*-benzylidene-*o*-(diphenylphosphinothioyloxy)aniline (**4**) by attack of the oxygen atom of the P=O group on the electron-deficient benzene ring. Next, **4** undergoes a homolytic cleavage to produce phenoxyl (**C**) and diphenylphosphinothioyl radicals. The radical (**C**) intramolecularly cyclizes to give a radical (**D**), and diphenylphosphinothioyl radical abstracts hydrogen atom from the radical (**D**) to afford 2-arylbenzoxazole (**3**) and diphenylphosphine sulfide. The latter compound may be oxidized to diphenylphosphinothioic acid under the reaction conditions. Since diphenylphosphinothioic acid can react with **2** to produce **A** analogously to **1**, it is considered that **1** can work catalytically even in a trace amount.

In fact, **2e** gave **3e** in the presence of 0.11 molar

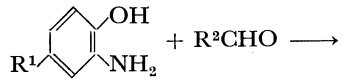
amount of diphenylphosphinothioic acid under similar conditions in 44% yield. On the other hand, **3e** was obtained in a lower yield (23%) in a similar reaction of **2e** with a 0.1 molar amount of **1** under argon atmosphere. A similar reaction of **2e** in the presence of diphenylphosphine sulfide under argon atmosphere afforded **3e** only in 7% yield. These results support the above mechanism.

It was shown in a separate experiment that **4** (Ar= *p*-$MeOC_6H_4$), prepared from diphenylphosphinothioic chloride and *N*-(4-methoxybenzylidene)-2-hydroxyaniline, gave **3b** in 52% yield (based on the Schiff's base) under similar conditions, also supporting the above mechanism.

Oxidations of N-Alkylidene-2-hydroxyanilines (5) with Silver Oxide. If phenoxyl radicals (**C**) can be generated under mild conditions in a high efficiency, it is expected from the above mechanism that 2-substituted benzoxazoles (**3** and **7**) would be produced in high yields under mild conditions.

It has been reported that **5** are oxidized with lead(IV) tetraacetate,[4] lead(IV) tetraphosphate,[5] or nickel peroxide[6] to give **3** or **7** in fairly good yields and the intermediate is phenoxyl radical (**C**),[4] supporting the above mechanism.

In this connection, other oxidizing agents were examined. *N*-(4-Methoxybenzylidene)-2-hydroxyaniline (**5b**) was oxidized with iodine and potassium iodide[7] at room temperature, but the yield of **3b** was only 11%. On the contrary, oxidation of **5b** with silver oxide[8] gave **3b** at room temperature in 92% yield. Therefore, we used silver oxide as oxidizing agent for **5**. It is considered that silver oxide can generate phenoxyl radical from **5**.



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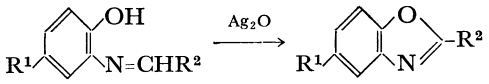
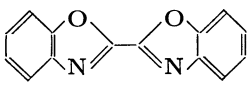


5 **3 or 7**

The Schiff's bases (**5**) are easily prepared from the corresponding aldehydes and *o*-aminophenols (**6**). Since Shiff's bases (**5k—m**) could not be purified, these were used in the oxidation reactions without further purification. The results of oxidation reactions of **5** with silver oxide are summarized in Table 2.

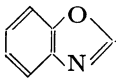
2-Alkyl- (**7f** and **7g**) and 2-alkenylbenzoxazoles (**7d**, **7h'**, and **7i**), which have not been prepared by oxidation with lead(IV) tetraacetate, were also obtained by the present method. 2,2'-Bis(benzoxazolyl) (**7j**) was prepared using glyoxal.



7j

However, in the case of butanal, the product was not 2-propylbenzoxazole, but 2-(1-ethyl-1-pentenyl)-benzoxazole (**7h**) was obtained unexpectedly, showing that an aldol-type condensation occurred at first during the preparation of the corresponding Schiff's base. **7h** was also prepared from the corresponding Schiff's base which was prepared from *o*-aminophenol and 2-ethyl-2-hexenal. 2-(1-Methyl-1-butenyl)benzoxazole (**7i**) was prepared by a similar method.

Table 2. Yields of benzoxazoles (**3** and **7**) from Schiff's bases (**5**)

5		R^2	3 or 7 R^1	Yield/%
5a	**3a**	C_6H_5	H	76
5b	**3b**	*p*-$MeOC_6H_4$	H	92
5c	**3c**	*p*-ClC_6H_4	H	81
5d	**7a**	*p*-$NO_2C_6H_4$	H	80
5e	**7b**	*p*-$MeOC_6H_4$	Me	70
5f	**7c**	*p*-$MeOC_6H_4$	Cl	69
5g	**7d**	PhCH=CH-	H	87
5h	**7e**	α-Furyl	H	45[a]
5i	**7f**	*i*-Pr	H	54[a]
5j	**7g**	*t*-Bu	H	57[a]
5k	**7h**[b]	PrCH=CEt-	H	37[a]
5k'	**7h'**	PrCH=CEt-	H	74[a]
5l	**7i**	EtCH=CMe-	H	41[a]
5m	**7j**		H	25[a]

a) Yield based on *o*-aminophenol used. b) This compound was obtained in the reaction of *o*-aminophenol with butanal followed by silver oxide oxidation (see text).

An aldol-type condensation during the preparation of the Schiff's base is supported by the fact that *N*-butylideneaniline gives *N*-(2-ethyl-2-hexenylidene)aniline through the dimerization followed by elimination of aniline.[9] Thus, we did not further apply this method to aldehydes which can undergo the corresponding reaction easily.

The benzoxazoles are usually prepared by heating *o*-aminophenols with acid anhydrides or acid halides.[10] To the best of our knowledge, yields in the present method were better and the reaction conditions employed were milder than any other methods for preparation of oxazoles. The present method is generally applicable to the 2-substituted benzoxazoles (**3** and **7**).

N-Benzylidene-2-hydroxyethylamine and -*o*-phenylenediamine did not produce the expected 4,5-dihydro-2-phenyl-1,3-oxazole and 2-phenylbenzimidazole, respectively, under similar conditions.

Experimental

All the melting points are uncorrected. The ^1H NMR spectra were measured with a Hitachi R-24 or R-20B spectrometer using TMS as an internal standard, the IR spectra were taken with a Hitachi EPI-G2 spectrophotometer, and the mass spectra were determined with a Hitachi RMU-6L spectrometer.

Materials. *O*-Methyl diphenylphosphinothioate (**1**) was prepared by reported method.[11] α,*N*-Diarylnitrones (**2a—f**) were prepared by the methods described in the previous paper.[1]

Reactions of 2 with 1. A typical procedure is described

on the reaction of **2b**.

Using an Equimolar Amount of ***1***: A solution of **2b** (252 mg, 1.11 mmol) and **1** (288 mg, 1.16 mmol) in *o*-$C_6H_4Cl_2$ (15 ml) was heated at 150 °C for 2 d. After removal of *o*-$C_6H_4Cl_2$ *in vacuo*, the residue was subjected to dry column chromatography (DCC)(SiO_2, CH_2Cl_2) to give **3b** (152 mg) in 61% yield, mp 100—101 °C (from EtOH) (lit,[12] mp 101 °C).

Using a Catalytic Amount of ***1***: A solution of **2b** (458 mg, 2.02 mmol) and **1** (50 mg, 0.2 mmol) in *o*-$C_6H_4Cl_2$ (15 ml) was heated at 150 °C for 24 h. Usual work-up gave **3b** (239 mg, 53%) and unchanged **1** (28 mg, 56%).

These results in reaction of other nitrones (**2**) were summarized in Table 1. Isolation method and mp (lit, mp) of **3** are shown below.

3c: DCC (SiO_2, CH_2Cl_2–CCl_4 (1:1)); mp 151.5—153 °C (from EtOH) (lit,[12] 150 °C). **3d**: DCC (SiO_2, CH_2Cl_2–CCl_4 (1:2)); mp 93—94 °C (from aq EtOH) (lit,[13] 92.5—93.0 °C). **3e**: DCC (SiO_2, CH_2Cl_2); mp 87—90 °C (from EtOH) (lit,[14] 91 °C). **3f**: DCC (SiO_2, CH_2Cl_2–CCl_4 (1:1)); mp 154—155 °C (from EtOH) (lit,[13] 151.5—152.0 °C). **3g**: DCC (SiO_2, CH_2Cl_2–CCl_4 (2:1)); mp 114.5—116.0 °C (from EtOH) (lit,[12] 116—117 °C).

Reaction of ***2e*** *with Diphenylphosphinothioic Acid.* A solution of **2e** (239 mg, 0.99 mmol) and diphenylphosphinothioic acid (27 mg, 0.11 mmol) in *o*-$C_6H_4Cl_2$ (7 ml) was heated at 150 °C for 24 h. After twice DCC (Al_2O_3, CCl_4 and then SiO_2, C_6H_6), **3e** was obtained in 44% yield (105 mg).

Formation of ***3b*** *from* ***4*** *(Ar=*p*-$MeOC_6H_4$).* To a solution of *N*-(4-methoxybenzylidene)-2-hydroxyaniline[15] (1.142 g, 5.03 mmol) in *o*-$C_6H_4Cl_2$ (10 ml) were added triethylamine (0.7 ml, 5.0 mmol) and then diphenylphosphinothioic chloride (1.2 ml, 5.2 mmol) at 0 °C. After stirring at 0 °C for 30 min and then at 20 °C for 3 h, the resulting precipitates (1.65 g) were filtered off and a yellow oil (3.008 g) was obtained as the residue after removal of the solvent from the filtrate *in vacuo*; ^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H) and 6.5—8.5 (m, 19H); MS (FD): *m/e* 443 (M^+). A solution of the yellow oil (0.271 g) in *o*-$C_6H_4Cl_2$ (10 ml) was heated at 150 °C for 4 d. After removal of the solvent *in vacuo*, the residue was subjected to DCC (Al_2O_3, CCl_4 and then SiO_2, $CHCl_3$) to give **3b** (53.3 mg), yield 52% based on the starting Schiff's base, mp 102—103 °C (from EtOH).

Oxidations of ***5*** *with Silver Oxide.* The following Schiff's bases were prepared by reported methods: **5a**,[15] **5b**,[15] **5c**,[4] **5d**,[6] **5e**,[16] **5f**,[17] and **5g**.[4]

General procedure of oxidation is as follows. A mixture of **5** (1 mmol) and Ag_2O (1.1—1.3 mmol) in CH_2Cl_2 (20—40 ml) was stirred at room temperature for 2—5 h and an insoluble material was filtered off. The filtrate was evaporated and the residue was purified by recrystallization (recryst) or DCC to give pure **7**. The results were shown in Table 2.

Isolation method and mp (lit, mp) of **3** and **7** are shown below.

3a: DCC (SiO_2, CH_2Cl_2); mp 103—105 °C (from EtOH) (lit,[4] 102 °C). **3b**: DCC (SiO_2, CH_2Cl_2); mp 101—102 °C (from aq EtOH) (lit,[12] 101 °C). **3c**: DCC (SiO_2, CH_2Cl_2–CCl_4 (1:1)); mp 151—152 °C (from aq EtOH) (lit,[4] 151—152 °C). **7a**: recryst from xylene; mp 266.5—268.0 °C (lit,[4] 268 °C). **7b**: DCC (SiO_2, CCl_4); mp 109—111 °C (from EtOH) (lit,[18] 98—100 °C). **7c**: DCC (Al_2O_3, CH_2Cl_2–CCl_4 (1:1)); mp 155—156 °C (from EtOH) (lit,[17] 153—154 °C). **7d**: DCC (Al_2O_3, CCl_4); mp 83—85 °C (from aq EtOH) (lit,[4] 83 °C).

Preparation of ***7e*** *from Furfural.* A mixture of *o*-aminophenol (294 mg, 2.7 mmol), furfural (0.2 ml, 2.2 mmol), and anhydrous sodium sulfate (2 g) in benzene (20 ml) was stirred for 20 h at room temperature and filtered. The residual oil (325 mg) (^{1}H NMR ($CDCl_3$): δ 6.45 (q, J=2 Hz, 1H), 6.83—7.3 (m, 6H), 7.52 (d, J=2 Hz, 1H), and 8.4 (s, 1H)) from the filtrate was stirred with Ag_2O (461 mg, 2 mmol) in CH_2Cl_2 (20 ml) overnight and the reaction mixture was subjected to DCC (Al_2O_3, CCl_4) to give **7e** (225 mg, 45%), mp 88—89 °C (from aq EtOH) (lit,[6] 86.0—86.5 °C).

Preparation of ***7f*** *from 2-Methylpropanal.* A mixture of *o*-aminophenol (272 mg, 2.49 mmol), 2-methylpropanal (0.3 ml, 3.31 mmol), and anhydrous sodium sulfate (2 g) in benzene (30 ml) was stirred for 30 min at 0 °C and then for 3 h at room temperature and filtered. The residue (376 mg) from the filtrate was stirred with Ag_2O (769 mg, 3.31 mmol) in CH_2Cl_2 (20 ml) at 0—10 °C overnight and the reaction mixture was subjected to DCC (Al_2O_3, CCl_4) to give oily **7f** (217 mg, 54%) (lit,[19] bp 109—111 °C/10 mmHg, 1 mmHg=133.322 Pa); ^{1}H NMR ($CDCl_3$): δ 1.42 (d, J=7 Hz, 6H), 3.2 (m, 1H), and 7.1—7.85 (m, 4H); MS: *m/e* 161 (M^+, 34%) and 146 (100).

Preparation of ***7g*** *from 2,2-Dimethylpropanal.* A mixture of *o*-aminophenol (253 mg, 2.32 mmol), 2,2-dimethylpropanal (0.3 ml, 2.8 mmol) in benzene (20 ml) was refluxed using Dean-Stark apparatus for 3.5 h, the reaction mixture was concentrated to remove unchange *o*-aminophenol (36 mg), and then evaporated. The residue (360 mg) was stirred with Ag_2O (568 mg, 2.45 mmol) in CH_2Cl_2 (20 ml) at room temperature overnight, and the reaction mixture was subjected to DCC (Al_2O_3, CCl_4) to give oily **7g** (231 mg, 57%) (lit,[20] bp 124 °C/17 mmHg); ^{1}H NMR ($CDCl_3$): δ 1.5 (s, 9H) and 7.15—7.8 (m, 4H); MS: *m/e* 175 (M^+, 32%), 160 (100), and 133 (43).

Preparation of ***7h***. *From Butanal*: A mixture of *o*-aminophenol (259 mg, 2.37 mmol), butanal (0.5 ml, 5.67 mmol), and anhydrous sodium sulfate (2 g) in toluene (15 ml) was stirred at 0 °C for 6 h and filtered. The residue (558 mg) from the filtrate was stirred with Ag_2O (600 mg, 2.58 mmol) in CH_2Cl_2 (20 ml) at 0 °C overnight and the reaction mixture was subjected to DCC (Al_2O_3, CCl_4) to give oily **7h** (191 mg, 37%); ^{1}H NMR ($CDCl_3$): δ 1.0 (t, J=7 Hz, 3H), 1.2 (t, J=7 Hz, 3H), 1.3—1.8 (m, 2H), 2.3 (q, J=7 Hz, 2H), 2.7 (q, J=7 Hz, 2H), 6.71 (t, J=7 Hz, 1H), and 7.1—7.8 (m, 4H); MS: *m/e* 215 (M^+, 41%), 200 (100), 186 (40), 133 (47), and 120 (38).

Found: C, 77.90; H, 8.06; N, 6.75%. Calcd for $C_{14}H_{17}NO$: C, 78.14; H, 7.91; N, 6.51%.

From 2-Ethyl-2-hexenal: A mixture of *o*-aminophenol (275 mg, 2.52 mmol), 2-ethyl-2-hexenal[21] (500 μl), and anhydrous sodium sulfate (2 g) in benzene (50 ml) was refluxed overnight and filtered. The residue from the filtrate (527 mg) was stirred with Ag_2O (570 mg, 2.46 mmol) in CH_2Cl_2 (20 ml) at 0 °C overnight and the reaction mixture was subjected to DCC (Al_2O_3, CCl_4) to give **7h′** (=**7h**) (401 mg, 74%).

Preparation of ***7i*** *from 2-Methyl-2-pentenal.* A mixture of *o*-aminophenol (275 mg, 2.52 mmol) and 2-methyl-2-pentenal (452 mg, 4.61 mmol) in benzene (20 ml) was refluxed for 6 h using Dean-Stark apparatus and evaporated to give a residue (498 mg); ^{1}H NMR ($CDCl_3$): δ 1.1 (t, J=6 Hz, 3H), 2.0 (s, 3H), 2.4 (m, 2H), 6.2 (t, J=7 Hz, 1H), 6.8—7.3 (m, 4H), and 8.2 (s, 3H).

The residue was stirred with Ag_2O (781 mg, 3.37 mmol) in CH_2Cl_2 (20 ml) at room temperature overnight and the reaction mixture was subjected to DCC (Al_2O_3, CCl_4) to give oily **7i** (191 mg, 41%); ^{1}H NMR ($CDCl_3$): δ 1.1 (t,

J=7 Hz, 3H), 2.1 (s, 3H), 2.0—2.5 (m, 2H), 6.8 (t, J= 7 Hz, 1H), 7.3 (m, 3H), and 7.65 (m, 2H).

Found: C, 77.15; H, 7.06; N, 7.57%. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%.

Preparation of ***7j*** *from Glyoxal.* A mixture of *o*-aminophenol (1.50 g, 13.8 mmol), 40% aq glyoxal (1.0 g, 6.9 mmol), and anhydrous sodium sulfate (10 g) in benzene (40 ml) was stirred at room temperature overnight and filtered. The solvent was removed, $CHCl_3$ (50 ml) was added and an insoluble part was filtered off. After removal of $CHCl_3$, the residue (849 mg) was stirred with Ag_2O (1.677 g, 7.23 mmol) in CH_2Cl_2 (50 ml) at room temperature overnight, and the reaction mixture was filtered through Celite. After evaporation of the filtrate, the residue was subjected to DCC (Al_2O_3, $CHCl_3$) to give **7j** (404 mg, 1.71 mmol, 25%), mp 262—263 °C (from EtOH) (lit,[22] 255—257 °C); MS: *m/e* 236 (M^+, 100%).

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