On the Structure of Condensation Products of o-Aminophenols with α-Dicarbonyl Compounds. II

By Ichiro MURASE

(Received June 1, 1959)

It has been reported in the previous paper[1] that 2,2′-bibenzoxazoline and its 2,2′-dimethyl derivative were formed by the condensation of *o*-aminophenol (2 mol.) with glyoxal (1 mol.) and with diacetyl (1 mol.), respectively.

Now, condensation of skeletal derivatives of *o*-aminophenol with several kinds of α-dicarbonyl compounds was studied and the structures of these condensation products were determined.

The condensation reaction proceeded generally in the same way as in the case of 2,2′-bibenzoxazoline previously reported. However it was found that the products were classified into two groups according to the molar ratio of the reactants.

The following investigation led to the conclusion that the compounds of the first group were the condensation products of two moles of *o*-aminophenols with one mole of α-dicarbonyl compounds and the structures proved to be 2,2′-bibenzoxazoline derivatives as in the case previously reported. The second group was equimolar condensation products of each component and the structures proved to be 2-hydroxy 2,3-disubstituted 1,4-benzoxazine derivatives. The structures of these two groups are summarized in Tables I and II, respectively, together with their infrared and ultraviolet absorption spectra. The melting points and analytical data of both groups are listed in Tables III and IV, respectively.

It was found that the more bulky the alkyl groups in the dicarbonyl compounds were, the poorer the yield of the condensation product became. In some cases, such bulky groups affected only benzoxazine type products as the single ones. Acetylisobutylyl reacted only with 4-nitro-2-aminophenol to give a benzoxazine type condensation product. On the other hand, it proved that phenylglyoxal reacted with all *o*-aminophenols examined to give products of the same type in good yields. It was exceptional that acetylbenzoyl despite the bulky groups and though it did not react with any other skeletal derivatives, condensed with two moles of *o*-aminophenol to give a bibenzoxazoline type product. Benzil did not react at all with any of *o*-aminophenols examined.

5-Nitro-2-aminophenol and picrylamine did not react with any α-dicarbonyl compounds examined, while 4-nitro-2-aminophenol was very reactive.

Thus, the ease and the type of the condensation are affected by the basicity of the amino group and the acidity of the hydroxyl group of the *o*-aminophenols and further by the steric factor of the α-dicarbonyl compounds.

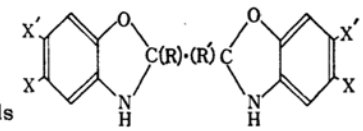
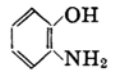
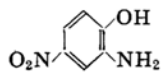
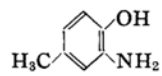
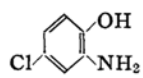
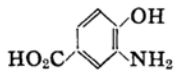
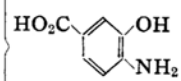
It is interesting to note that in place of methylglyoxal and diacetyl, their monoximes reacted with *o*-aminophenol and 4-nitro-2-aminophenol with elimination of the oximino groups to produce the same condensation products as those obtained from the mother dicarbonyl compounds. But dimethyl glyoxime did not react with them.

The 2,2′-bibenzoxazoline structures were established by means of their infrared and ultraviolet absorption spectra; the sharp NH band and the anilino band were present in each infrared spectrum, which were the same as those of an authentic 2,2′-bibenzoxazoline, and the features of the ultraviolet spectra excellently agreed with each other regarding those of the compounds derived from the same aminophenols (refer to Table I).

Among these bibenzoxazoline derivatives, those which were derived from glyoxal, methylglyoxal and diacetyl were stable toward the cold dilute solution of both mineral acid and aqueous alkali, while higher homologues were more sensitive to these reagents and were hydrolyzed gradually on standing at room temperature. The carboxylic derivatives dissolved in sodium hydrogen carbonate solution to give a colorless solution, and in sodium hydroxide solution with orange coloration.

1) I. Murase, This Bulletin, 32, 827 (1959).

TABLE I. 2,2′-BIBENZOXAZOLINE DERIVATIVES AND THEIR INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA; THOSE OF 2,2′-BIBENZOXAZOLINE AND 2,2′-DIMETHYL-2,2′-BIBENZOXAZOLINE ARE LISTED FOR COMPARISON PURPOSES

No.	Components: α-Dicarbonyl compounds	Components: o-Aminophenols	 R	R′	X	X′	UV-spectra (in ethanol) mμ: λ_{max}	ε	IR-spectra (Nujol mull) cm^{-1}: NH-band	Anilino band
—	CHOCHO		H	H	H	H	236 294	14340 9880	3378	1613
—	$CH_3COCOCH_3$		CH_3	CH_3	H	H	236 293	13200 9880	3358	1613
1	CH_3COCHO		CH_3	H	H	H	236 294	12140 8798		
2	$CH_3COCOC_2H_5$		CH_3	C_2H_5	H	H	236 293	12620 9273		
3	$C_2H_5COCOC_2H_5$		C_2H_5	C_2H_5	H	H	236 294	11880 8908		
4	$C_6H_5COCOCH_3$		C_6H_5	CH_3	H	H	240 292	12380 9981	3390	1613
5	CHOCHO		H	H	NO_2	H	225 261 305 365	22930 27600 11540 10070	3448 3390	1623
6	CH_3COCHO		CH_3	H	NO_2	H	225 261 306 367	23600 24250 10071 9184		
7	$CH_3COCOCH_3$		CH_3	CH_3	NO_2	H	225 262 306 369	23210 27090 11420 10860		
8	$CH_3COCOC_2H_5$		CH_3	C_2H_5	NO_2	H	225 261 306 366	23610 27850 11960 11100		
9	$C_2H_5COCOC_2H_5$		C_2H_5	C_2H_5	NO_2	H	225 262 306 371	23310 27370 12050 10800		
10	CHOCHO		H	H	CH_3	H	238 298	12250 9866	3413	1621
11	$CH_3COCOCH_3$		CH_3	CH_3	CH_3	H	237 298	11160 10280		
12	CHOCHO		H	H	Cl	H	242 303	11860 10880	3390	1608
13	CHOCHO		H	H	CO_2H	H	235 261 315	55910 16670 10480	3425	1616
14	CHOCHO		H	H	H	CO_2H	insoluble		3401	1613
15	$CH_3COCOCH_3$		CH_3	CH_3	H	CO_2H	234 277 309	29480 21720 26050	3378	1616
16	$CH_3COCOC_2H_5$		CH_3	C_2H_5	H	CO_2H	235 278 310	29010 22000 26630		
17	$C_2H_5COCOC_2H_5$		C_2H_5	C_2H_5	H	CO_2H	234 278 310	27150 21770 26510		

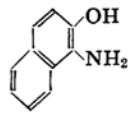
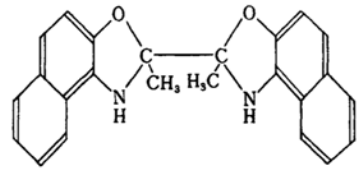
18	$CH_3COCOCH_3$			234 255 311 346	43080 79130 6534 9118	3460	1626

TABLE II. 2-HYDROXY-1,4-BENZOXAZINE DERIVATIVES AND THEIR INFRARED AND ULTRAVIOLET ABSORPTION SPECTRA

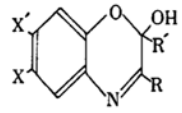
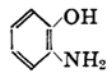
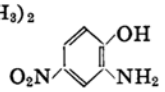
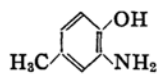
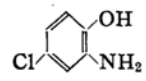
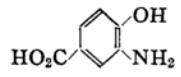
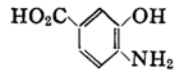
No.	Components: *α*-Dicarbonyl compounds	Components: *o*-Aminophenols	 R	R′	X	X′	UV-spectra (in ethanol) mμ λ_{max}	ε	IR-spectra (Nujol mull) 3000 cm^{-1} region (broad)	1600 cm^{-1} region
19	C_6H_5COCHO		H	C_6H_5	H	H	234 281 310	9924 14450 12340	3300～2600	1610 1592 1563
20	$CH_3COCOCH(CH_3)_2$		CH_3	$CH(CH_3)_2$	NO_2	H	220 260 310	17890 12200 7516	3400～2700	1639 1608 1600
21	C_6H_5COCHO		H	C_6H_5	NO_2	H	224 286	17960 30170	3200～2500	1623 1592 1567
22	$CH_3COCOC_2H_5$		CH_3	C_2H_5	CH_3	H	217 262 311	20960 5000 2552	3200～2500	1634 1618 1592
23	$C_2H_5COCOC_2H_5$		C_2H_5	C_2H_5	CH_3	H	219 261 305	21060 5148 2756	3200～2500	1629 1618 1592
24	C_6H_5COCHO		H	C_6H_5	CH_3	H	249 287 320	11400 15530 10800	3200～2500	1616 1613 1575
25	$CH_3COCOCH_3$		CH_3	CH_3	Cl	H	251 305	4678 2708	3300～2700	1639 1600 1582
26	$CH_3COCOC_2H_5$		CH_3	C_2H_5	Cl	H	222 256 311	29630 4406 2632	3300～2700	1629 1597 1582
27	C_6H_5COCHO		H	C_6H_5	Cl	H	220 245 285 330	17720 12860 17480 10430	3300～2600	1621 1595 1570
28	C_6H_5COCHO		H	C_6H_5	CO_2H	H	219 255 295	19910 28780 16340	3200～2500	1618 1608 1597 1585 1570
29	C_6H_5COCHO		H	C_6H_5	H	CO_2H	297	20420	3300～2500	1623 1592 1585 1570

TABLE III. MELTING POINTS AND ANALYTICAL DATA OF 2,2'-BIBENZOXAZOLINE DERIVATIVES LISTED IN TABLE I

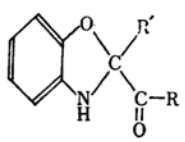
No.	Formula	m. p. °C	Anal. Found C%	Found H%	Found N%	Calcd. C%	Calcd. H%	Calcd. N%
1	$C_{15}H_{14}N_2O_2$	220	70.69	5.62	10.93	70.85	5.55	11.02
2	$C_{17}H_{18}N_2O_2$	142	72.39	6.45	9.84	72.32	6.43	9.92
3	$C_{18}H_{20}N_2O_2$	154	73.14	6.78	9.51	72.95	6.80	9.45
4	$C_{21}H_{18}N_2O_2$	218	76.44	5.58	8.48	76.34	5.49	8.48
5	$C_{14}H_{10}N_4O_6$	225	50.54	3.25	16.60	50.91	3.05	16.97
6	$C_{15}H_{12}N_4O_6$	216	52.25	3.64	16.35	52.33	3.51	16.28
7	$C_{16}H_{14}N_4O_6$	252	53.47	3.91	15.42	53.63	3.94	15.64
8	$C_{17}H_{16}N_4O_6$	238	55.07	4.52	14.98	54.84	4.33	15.05
9	$C_{18}H_{18}N_4O_6$	199	55.99	4.82	14.68	55.95	4.70	14.50
10	$C_{16}H_{16}N_2O_2$	215	71.47	6.19	10.51	71.62	6.01	10.44
11	$C_{18}H_{20}N_2O_2$	237	72.80	6.86	9.33	72.95	6.80	9.45
12	$C_{14}H_{10}N_2O_2Cl_2$	208	54.50	3.49	8.64	54.39	3.26	9.06
13	$C_{16}H_{12}N_2O_6$	237.5	58.35	3.73	8.38	58.54	3.68	8.53
14	$C_{16}H_{12}N_2O_6$	286	58.52	3.66	8.22	58.54	3.68	8.53
15	$C_{18}H_{16}N_2O_6 \cdot 2H_2O$	241	55.08	5.02	6.86	55.10	5.14	7.14
16	$C_{19}H_{18}N_2O_6 \cdot 2H_2O$	221	55.95	5.53	6.58	56.15	5.46	6.89
17	$C_{20}H_{20}N_2O_6 \cdot 2H_2O$	219	56.78	6.07	6.43	57.13	5.75	6.66
18	$C_{24}H_{20}N_2O_2$	204	78.28	5.42	7.62	78.24	5.47	7.60

TABLE IV. MELTING POINTS AND ANALYTICAL DATA OF 2-HYDROXY-1,4-BENZOXAZINE DERIVATIVES LISTED IN TABLE II

No.	Formula	m. p. °C	Anal. Found C%	Found H%	Found N%	Calcd. C%	Calcd. H%	Calcd. N%
19	$C_{14}H_{11}NO_2$	228	74.85	4.93	6.42	74.65	4.92	6.22
20	$C_{12}H_{14}N_2O_4$	131	57.90	5.68	11.31	57.59	5.64	11.20
21	$C_{14}H_{10}N_2O_4$	235	62.36	3.78	10.28	62.22	3.73	10.37
22	$C_{12}H_{15}NO_2$	151	70.58	7.46	6.77	70.22	7.37	6.82
23	$C_{13}H_{17}NO_2$	133	70.92	8.16	6.38	71.20	7.81	6.39
24	$C_{15}H_{13}NO_2$	196	75.22	5.25	5.72	75.29	5.48	5.85
25	$C_{10}H_{10}NO_2Cl$	172	56.72	4.89	6.40	56.75	4.76	6.62
26	$C_{11}H_{12}NO_2Cl$	131	58.61	5.45	6.46	58.54	5.36	6.21
27	$C_{14}H_{10}NO_2Cl$	216	64.55	4.01	5.08	64.75	3.88	5.39
28	$C_{15}H_{11}NO_4$	241	67.02	3.90	5.41	66.91	4.12	5.20
29	$C_{15}H_{11}NO_4$	238	67.24	4.04	5.30	66.91	4.12	5.20

It is apparent that they were tautomerized to Schiff bases in the latter case as indicated in the previous paper[1].

Concerning the equimolar condensation products (the second group), benzoxazoline structure A was considered at first, since the compounds of this group were insoluble in aqueous alkali except carboxylic derivatives.



(A)

The broad infrared absorption bands found near 3000 cm^{-1} in all spectra indicate the presence of hydrogen bonded OH or NH groups. However carbonyl absorption, the presence of which was expected from formula A, was not found in any spectra, and instead comparatively weak absorptions were present in the 1600 cm^{-1} region. Further, the fact that, in the case of α-iminoketones such as $C_6H_5NHCH_2COCH_3$ and $C_6H_5NHC(CH_3)_2COCH_3$, the sharp NH band at 3413 cm^{-1} in the both compounds and the strong C=O band at 1706 cm^{-1} in the former and at 1709 cm^{-1} in the latter existed, excluded the possibility of α-iminoketonic formula A.

Therefore, the author proposed the 1,4-benzoxazine structure C and the mode of the reaction indicated.

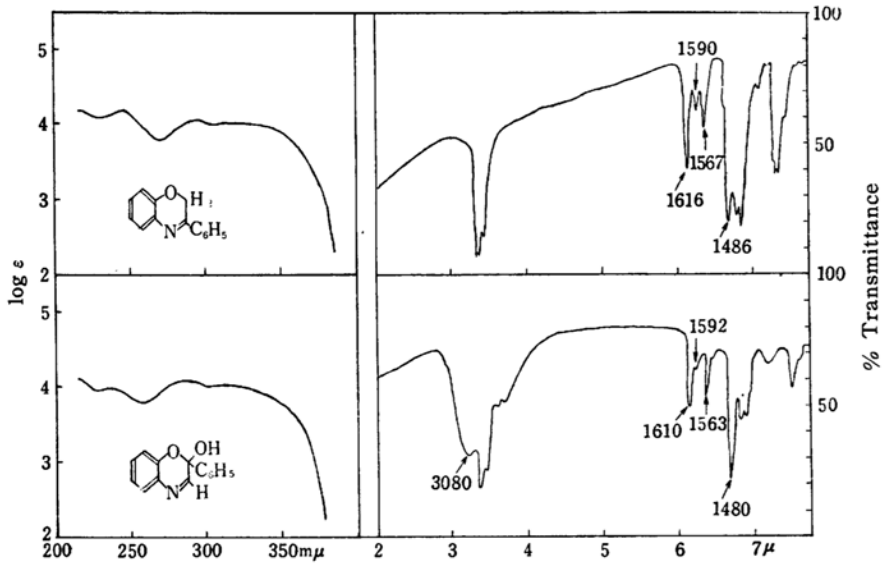
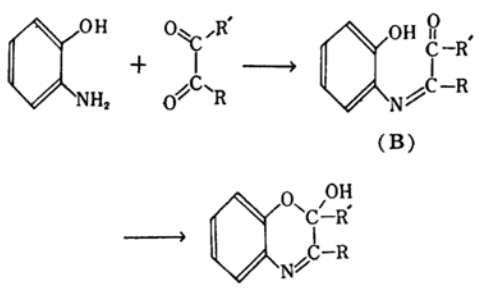


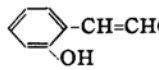
Fig. 1. Ultraviolet (in ethanol) and infrared (Nujol mull) spectra of 19 (bottom) and 3-phenyl-1,4-benzoxazine (top).

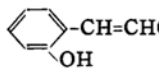


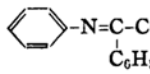
(B)

(C)

The intermediate Schiff base structure B was also excluded because the C=O absorption was absent in their infrared spectra and they were insoluble in alkali. This was further supported by the fact that the following compounds of which structures were closely related to B, showed very strong C=O absorptions:


1645 cm^{-1}

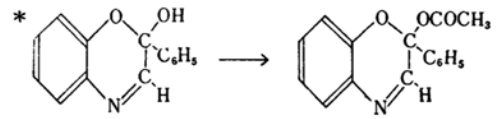

1642 cm^{-1}


1667 cm^{-1}

(1645 cm^{-1}, C=N)

Thus, the 1,4-benzoxazine structure C carrying no carbonyl group is most favorable and is further supported by the comparison with the known 1,4-benzoxazine structure. While such 2-hydroxyl substituted 1,4-benzoxazines as C have not been reported in literatures so far, 3-phenyl-1,4-benzoxazine is known[2] as one of a few 1,4-benzoxazine compounds and it was found that the condensation product of *o*-aminophenol with phenylglyoxal (19) resembled 3-phenyl-1,4-benzoxazine in the infrared and ultraviolet spectra as shown in Fig. 1.

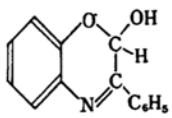
Acetylation of 19 with acetic anhydride gave the acetyl derivative (19a), m. p. 92°C, and the catalytic hydrogenation of 19a afforded the dihydro derivative (19b), m. p. 147°C, one mole of hydrogen being absorbed. The reaction can be explained as follows and the structures of the resulting compounds were consistent with their infrared spectra shown in Fig. 2.



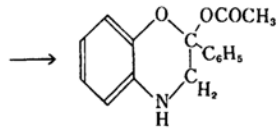
(19) (19a)

2) E. Lellmann and A. Donner, *Ber.*, 23, 173 (1890).

* In the case of the condensation of *o*-aminophenol with phenylgyoxal, if the amino group reacts with the ketonic carbonyl group to form a Schiff base type product in the first step, and then it undergoes ring-closure to form benzoxazine, the structure should be given as follows:



This isomeric strcuture of 19 was excluded, however, because on potassium permanganate oxidation in boiling acetone, 19 was recovered and the 2-hydroxyl group proved to be attached to a tertiary carbon atom as indicated in the scheme.



(19b)

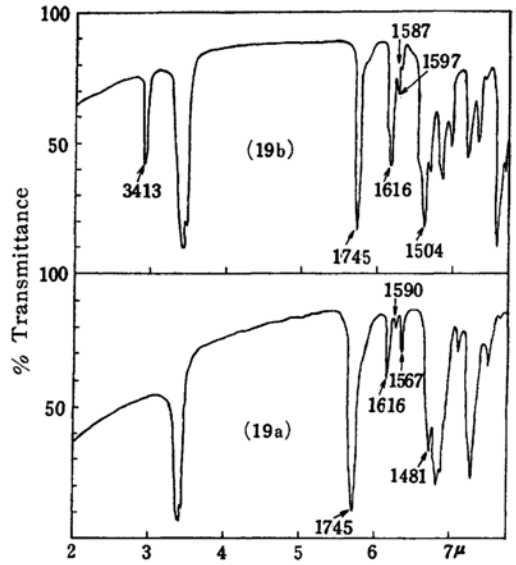
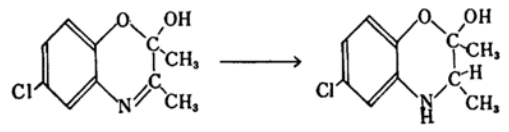


Fig. 2. Infrared spectra of 19a and 19b (Nujol mull).



(25) (25a)

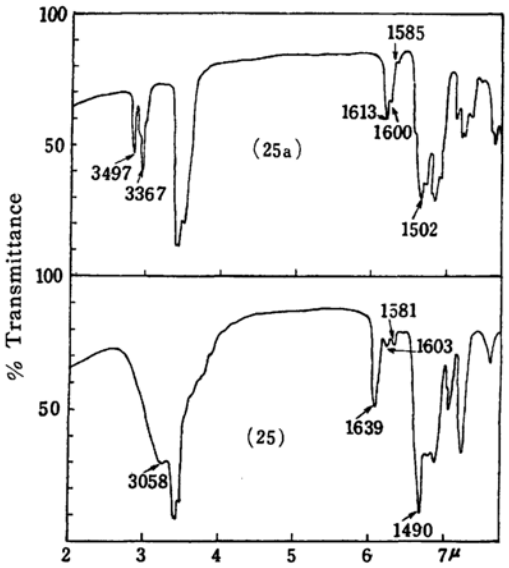


Fig. 3. Infrared spectra of 25 and 25a (Nujol mull).

Definite assignment of C=N absorptions of these 1,4-benzoxazines has remained unsolved, because phenyl ring absorptions were overlapped by other bands in this region, however the bands which were commonly observed in 1,4-benzoxazine derivatives at 1567 cm^{-1} (3-phenyl-1,4-benzoxazine, Fig. 1), 1563 cm^{-1} (19, Fig. 1) and 1567 cm^{-1} (19a, Fig. 2) disappeared by hydrogenation (19b, Fig. 2), and thus the author tentatively assigned these bands to C=N absorptions and other bands in this region which remained even after hydrogenation to phenyl ring absorptions (refer to Table II).

Further, the broad absorption bands in the 3000 cm^{-1} region (19, Fig. 1) should be due to intermolecular hydrogen bond of the hydroxyl group**, because it disappeared by acetylation and the *O*-acetate carbonyl band appeared at 1745 cm^{-1} (19a, Fig. 2).

In the case of the condensation product of 4-chloro-2-aminophenol with diacetyl (25), catalytic hydrogenation was conducted and dihydro derivative (25a), m.p. 135°C, was obtained.

** Because the solubility of 19 in the suitable solvent was very small, it could not be confirmed by taking the infrared spectra with a dilution method.

The structures of 25 and 25a were also consistent with features of their infrared absorption spectra shown in Fig. 3.

Since the others of this second group gave quite similar infrared spectra concerning the 3000 cm^{-1} and the 1600 cm^{-1} regions as shown in Table II, it can be recognized that they should also have the benzoxazine structures.

Thus, it has been concluded that the compounds resulting from the condensation of equimolar *o*-aminophenols and α-dicarbonyl compounds have the structure of 2-hydroxy-1,4-benzoxazine derivatives.

The condensation products of asymmetric α-diketones such as acetylpropionyl and acetylisobutylyl (20, 22, 26) have not been worked out as regards the position 2- or 3- of the alkyl group in 1,4-benzoxazine. The author tentatively proposed the 3-methyl substituted structure, considering that the carbonyl attached to the methyl group is more reactive than others and reacts with the amino group at first, as shown in the above scheme proposed.

The 2-phenyl derivatives were stable toward 6 N hydrochloric acid at 100°C and dilute alkali at room tempreature, but in the case of 19 it was hydrolyzed to *o*-aminophenol by boiling with 10% sodium

hydroxide solution. On the other hand, 2,3-dialkyl homologues were sensitive to acid and alkali and hydrolyzed gradually even at room temperature.

On applying semicarbazide to 25 and phenylhydrazine to 19, diacetyl disemicarbazone and phenylglyoxal phenylosazone were obtained respectively. Hydrolysis must have occurred in these cases.

Experimental

General Procedure of the Condensation Reaction of o-Aminophenols with α-Dicarbonyl Compounds. —The procedure was equally conducted both in the bibenzoxazoline type and the benzoxazine type condensations.

Freshly prepared *o*-aminophenols were dissolved in a large amount of distilled water which was previously boiled and cooled at 80°C. To this solution, a slight excess of calculated amount of α-dicarbonyl compounds dissolved in a little amount of water was added and mixture was held at this temperature with occasionally shaking for about 1 hr. Precipitates were soon or gradually formed. After cooling, they were filtered and washed with water. Recrystallization from alcohol or dilute alcohol using a Norit gave pure crystalls.

2-Methyl-2'-ethyl-2, 2'-bibenzoxazoline (2). — A mixture of *o*-aminophenol (2 g.) and acetylpropionyl (1.5 g.) dissolved in a little amount of alcohol was boiled for 3 hr. The solvent was then distilled off and the remaining tarrish residue was extracted several times with petroleum benzine (80~120°C). The combined extract was decolorized using a Norit and concentrated to form crystals. Recrystallization from dilute alcohol gave prisms, m. p. 142°C.

2-Methyl-2'-phenyl-2, 2'-bibenzoxazoline (4). — A solution of *o*-aminophenol (1 g.) and acetylbenzoyl (1.5 g.) in dioxane (15 ml.) was boiled for 2 hr. and then the solvent was distilled off under reduced pressure. The remaining oil soon solidified and was recrystallized from alcohol to give long needles, m. p. 218°C. Mol. wt. (Rast), Found: 329, Calcd.: 330.

2-Hydroxy-2-isopropyl-3-methyl-7-nitro-1, 4-benzoxazine (20). — An equivalent portion of 4-nitro-2-aminophenol and acetylisobutylyl was well mixed and heated on a hot plate about at 120°C for 20 min. On cooling, the oily product solidified which was pressed on a clay plate and recrystallized from benzene to give needles, m. p. 131°C.

Condensation of o-Aminophenol with Isonitrosoacetone; 2-Methyl-2,2'-bibenzoxazoline (1).—To a solution of *o*-aminophenol (1 g.) in hot water (50 ml.), isonitrosoacetone (1 g.) was added and the mixture was boiled for 1 hr. Precipitates gradually formed and they were recrystallized from alcohol to give fine needles, m. p. 220°C.

The condensations of isonitrosoacetone with 4-nitro-2-aminophenol and diacetyl monoxime with *o*-aminophenol were carried out in the same manner and 5,5'-dinitro-2'-methyl-2,2'-bibenzoxazoline (6) and 2,2'-dimethyl-2,2'-bibenzoxazoline were obtained respectively.

2-Acetoxy-2-phenyl-1, 4-benzoxazine (19a). — A solution of 2-hydroxy-2-phenyl-1,4-benzoxazine (19) (1 g.) in acetic anhydride (60 ml.) was boiled for 2 hr. and then the solution was concentrated under reduced pressure. The remaining oily product solidified on standing and was recrystallized from dilute alcohol to give fine prisms, m. p. 92.3°C.

Anal. Found: C, 72.12; H, 5.01; N, 5.37. Calcd. for $C_{16}H_{13}NO_3$: C, 72.01; H, 4.88; N, 5.22%.

Hyrogenation of 19a: 2-Acetoxy-3-phenyl-3,4-dihydro-1,4-benzoxazine (19b).—A solution of 19a (0.5 g.) in acetic acid (25 ml.) was hydrogenated using Adams calalyst at atmospheric pressure and room temperature. A slightly excessive amount of hydrogen was absorbed after 3 hr. The solvent was removed under reduced pressure and the residue was recrystallized from alcohol to give colorless needles, m. p. 147°C.

Anal. Found: C, 71.29; H, 5.71; N, 5.47. Calcd. for $C_{16}H_{15}NO_3$: C, 71.38; H, 5.58; N, 5.20%.

Action of Phenylhydrazine on 19: Phenylglyoxal Phenylosazone.—To a suspension of 19 in a little amount of acetic acid, an excess of phenylhydrazine was added and the mixture was heated on water bath, the contents being gradually dissolved. After 30 min., water was added and the resulting precipitates were recrystallized from alcohol. Yellow prisms, m. p. 150~151°C; showed no depression with an authentic phenylglyoxal phenylosazone, m. p. 151°C.

Hydrogenation of 25: 2-Hydroxy-2,3-dimethyl-6-chloro-3, 4-dihydro-1, 4-benzoxazine (25a). — A solution of 25 (1 g.) in alcohol (60 ml.) was hydrogenated using Adams catalyst at atmospheric pressure and room temperature. A slightly excessive amount of hydrogen was absorbed after 5 hr. The resulting colorless solution was concentrated under reduced pressure and then water was added. The crystals obtained on cooling of the mixture in an ice box were recrystallized several times from dilute alcohol to give fine plates, m. p. 135°C.

Anal. Found: C, 55.92; H, 5.23; N, 6.56. Calcd. for $C_{10}H_{12}NO_2Cl$: C, 56.21; H, 5.62; N, 6.56%.

Alkali Hydrolysis of 19.—A suspension of 19 in 5% sodium hydroxide solution was boiled for 20 min., the contents were gradually dissolved and reddish brown solution was obtained. To this solution an excess of acetic anhydride was added and the mixture was evaporated to dryness on a water bath. The resulting residue was washed with water and recrystallized from hot water. Needles, m. p. 201°C, showed no depression with *N*-acetyl-2-aminophenol, m. p. 201°C.

Action of Semicarbazide on 25: Diacetyl Disemicarbazone.—To a warm solution of 25 (0.35 g.), semicarbazide hydrochloride (0.3 g.) dissolved in water (1 g.) containing 0.3 g. of sodium acetate was added and the mixture was allowed to stand at room temperature. White precipitates soon formed and they were filtered and well washed

with alcohol. The white crystals, m. p. 279°C, which were almost insoluble in most organic solvents showed no depression with an authentic diacetyl disemicarbazone, m. p. 279°C.

The author wishes to express his thanks to Professor Tokuichi Tsumaki and Professor Takeichi Nishikawa for their exceedingly kind directions to this work. The author also thanks Dr. Yo Ueda and Mr. Hiroshige Yano of the Department of Pharmacy for their measurement of infrared spectra and Mr. Michio Shido and Miss Sachiko Indo for microanalysis. The cost of this research was partly defrayed from the Research Grant of the Ministry of Education, to which the author's thanks are also due.

General Education Department
Kyushu University
Otsubo-machi, Fukuoka