

J. Petridou-Fischer and E. P. Papadopoulos

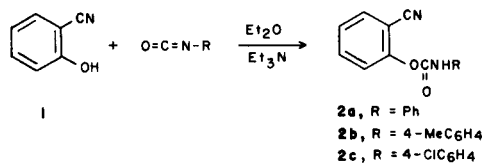
Department of Chemistry, University of New Mexico,
Albuquerque, NM 87131
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Triethylamine catalyzes the reaction of 2-hydroxybenzonnitrile (**1**) with aryl isocyanates to form the corresponding carbamates **2a-c**, as well as the cyclization of the latter compounds to either 4-[*N*-(*N*-arylcarbamoyl)imino]-3-aryl-2*H*-1,3-benzoxazin-2-ones **4a-c**, or 4-arylamino-2*H*-1,3-benzoxazin-2-ones **7a-c**, depending on the reaction temperature. Under analogous conditions, the carbamates obtained from **1** and 2-chloroethyl isocyanate, 3-chloropropyl isocyanate and ethyl isocyanatoacetate undergo a double cyclization yielding imidazo- and pyrimido[1,2-*c*][1,3]benzoxazinones **13a,b,17**. Upon heating in phenyl ether, compounds **7a-c**, rearrange to 2-(2-hydroxyphenyl)-4(3*H*)-quinazolinones **10a-c**.

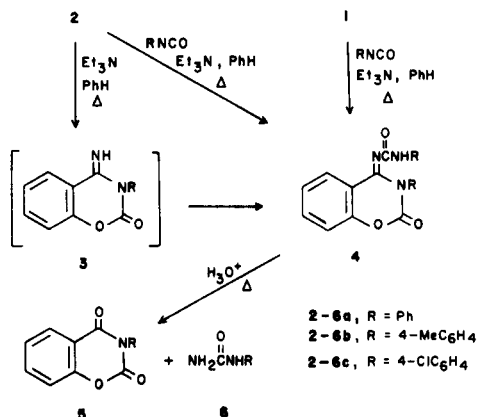
J. Heterocyclic Chem., **20**, 1159 (1983).

Whereas the reactions of 2-aminobenzonnitrile with isocyanates have been investigated extensively and have been found to lead to a variety of heterocyclic systems [1-4], the analogous reactions of 2-hydroxybenzonnitrile (**1**) have not attracted much attention [5,6]. In this paper, we report the results of an investigation of the reactions of **1** with isocyanates.

Treatment of an ethyl ether solution of **1** with an aromatic isocyanate, in the presence of triethylamine, yields readily the anticipated carbamate **2** in excellent yield. When,

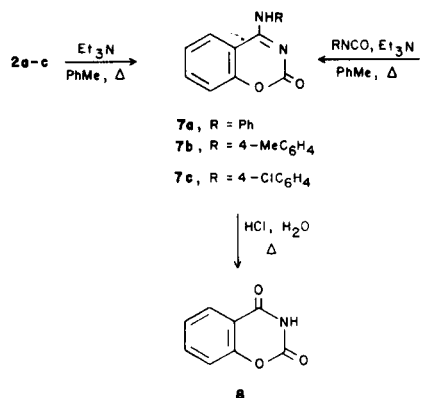


in analogy with the behavior of the corresponding adduct of 2-aminobenzonnitrile [1,2], cyclization of **2a** is attempted by the action of triethylamine in refluxing benzene, the carbamoylimino derivative **4a** is obtained instead of the expected simple iminobenzoxazinone **3a**. In a similar manner, carbamates **2b** and **2c** are converted into carbamoylimino derivatives **4b** and **4c**, respectively. It thus appears that the isocyanate which results from partial decomposition of **2** [6] reacts with intermediate **3** to form the



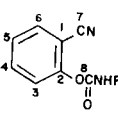
isolated product. Somewhat surprisingly, there is no improvement in the yield of **4** when **2** is refluxed in benzene with an equivalent amount of isocyanate in the presence of triethylamine. The carbamoylimino derivatives **4a-c** are also obtained, under the same reaction conditions, directly from 2-hydroxybenzonnitrile (**1**) and the corresponding isocyanate. Once again, no improvement in yield is observed when 2 equivalents of isocyanate are used. In no case were we able to isolate the presumed intermediate iminobenzoxazinone **3**. Structures **4a-c** are consistent with the infrared, as well as proton and carbon-13 nmr spectra of the products and are further supported by their hydrolytic cleavage to the corresponding 3-aryl-2*H*-1,3-benzoxazine-2,4(3*H*)-diones **5** and arylureas **6**.

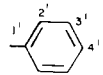
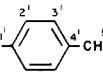
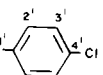
The substitution of toluene for benzene as the solvent alters the outcome of the cyclization reactions of **2a-c**. The products which are obtained in high yield under these conditions are *N*-aryl-4-amino-2*H*-1,3-benzoxazin-2-ones **7** and indicate that the higher reaction temperature causes a Dimroth rearrangement of intermediate **3** to take place.



Compounds **7a-c** are also obtained when carbamates **2a-c** are heated at temperatures higher than their melting points and when a mixture of 2-hydroxybenzonnitrile (**1**), the corresponding isocyanate, and triethylamine is refluxed in toluene. The structures of compounds **7a-c** are sup-

Table I
¹³C Chemical Shifts of 2-[(*N*-Substituted)aminocarbonyloxy]benzonitriles (a) (b)

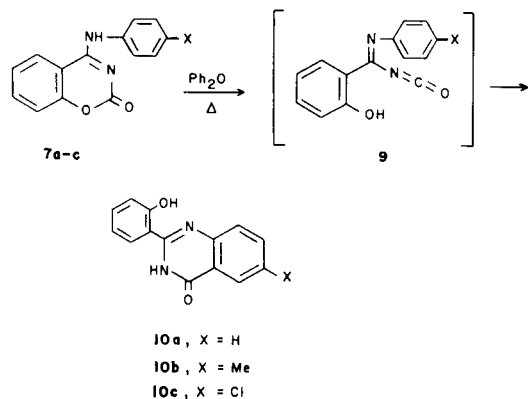


Compound No.	R	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-1'	C-2'	C-3'	C-4'	C-5'
2a		106.7	152.2 (c)	123.0	133.8 (d)	125.7	133.0 (d)	115.1	150.1 (c)	136.7	119.3	128.9	124.2	
2b		106.7	152.2 (c)	123.1	133.8 (d)	125.7	133.1 (d)	115.2	150.0 (c)	134.0	119.3	129.6	134.0	20.5
2c		106.6	152.0 (c)	123.0	134.0 (d)	125.9	133.1 (d)	115.2	149.9 (c)	135.3	120.4	129.0	128.9	
11a	1' 2' -CH ₂ CH ₂ Cl	106.7	152.4 (c)	123.0	133.8 (d)	125.6	132.9 (d)	115.0	152.8 (c)	43.0	43.0			
11b	1' 2' 3' -CH ₂ CH ₂ CH ₂ Cl	106.7	152.5 (c)	123.0	133.7 (d)	125.5	132.8 (d)	115.1	152.9 (c)	38.7	31.9	41.8		
15	1' 2' 3' 4' -CH ₂ COOCH ₂ CH ₃	106.3	152.1 (c)	122.7	133.5 (d)	125.4	132.7 (d)	114.7	152.8 (c)	42.6	169.0	61.2	13.6	

(a) In deuteriochloroform. (b) Model compounds: 2-hydroxybenzonitrile [9], ethyl *N*-phenylcarbamate [10a], 4-pyridylmethyl *N*-(4-methylphenyl)carbamate [10b], ethyl *N*-(4-chlorophenyl)carbamate [10c], ethoxycarbonylmethylurea [10d]. (c) (d) These values may be interchanged.

ported by their ir, proton nmr, and C-13 nmr spectra as well as by their hydrolytic cleavage to 2*H*-1,3-benzoxazine-2,4(3*H*)-dione (**8**).

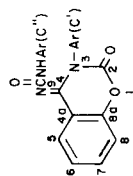
At this point in our investigation, we became aware of a recent publication [6] describing the preparation of **2a** and



its conversion into **7a** by a method different from ours. The same paper indicates that **7a** rearranges to 2-(2-hydroxyphenyl)-4(3*H*)-quinazolinone (**10a**) when heated at 250° in a sealed, evacuated tube. We confirmed this thermal rearrangement of **7a** to **10a** by running the reaction in refluxing phenyl ether and extended it to compounds **7b** and **7c** to obtain quinazolinones **10b** and **10c**, respectively. As in the case of the thermal cyclization of *N*-ethoxycarbonylamidines to form 2-substituted quinazolinones [7], it is very likely that the present reaction proceeds through the intermediate formation of an imidoyl isocyanate **9**.

The reactions of 2-aminobenzonitrile with 2-chloroethyl isocyanate and ethyl isocyanatoacetate were recently shown to allow a convenient synthesis of the imidazo-[1,2-*c*]quinazoline ring system [3,4]. Analogous reactions of 2-hydroxybenzonitrile (**1**) have now been found to lead in a

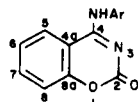
Table II
¹³C Chemical Shifts of 4-[(N-Arylcabamoyl)imino]-3-aryl-2H-1,3-benzoxazin-2-ones (a) (b)



Compound No.	Ar	C-2	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-9	C-1'	C-2'	C-3'	C-4'	C-5'	C-1''	C-2''	C-3''	C-4''	C-5''		
4a		150.9	157.4	112.9	126.7 (c)	125.2 (c)	135.1	117.1	146.9	145.2	136.5	129.0 (e)	128.8 (e)	128.4 (e)	128.9	118.9	128.6 (e)	122.7				
4b		150.9	157.4	113.0	126.7 (c)	125.1 (c)	135.0	117.0	147.0	144.9	133.8	128.9 (e)	129.3 (e)	137.9 (d)	20.6 (d)	136.4	118.8	128.7 (e)	131.6	20.3 (d)		
4c		151.1	157.3	113.2	126.8 (c)	125.4 (c)	135.4	117.1	146.9	145.0	135.2	131.2	129.0	133.6	138.0	120.3	128.6	126.6				

(a) In hexadeuteriodimethylsulfoxide. (b) Model compounds: *N,N'*-diphenylurea [10e], *N,N'*-di(4-methylphenyl)urea [11], *N,N'*-di(4-chlorophenyl)urea [11], 3-phenyl-, 3-(4-methylphenyl)-, and 3-(4-chlorophenyl)-2,4(1*H*,3*H*)-quinazolin-2,4-dione [12], 2*H*-1,3-benzoxazine-2,4-dione [11], 3-phenyl-, 3-(4-methylphenyl)- and 3-(4-chlorophenyl)-1,3-benzoxazine-2,4-dione [11]. (c) (d) (e) These values may be interchanged.

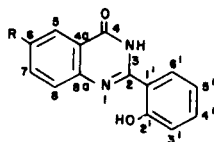
Table III

¹³C Chemical Shifts of 4-(Arylamino)-2*H*-1,3-benzoxazin-2-ones (a) (b)

Compound No.	Ar	C-2	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-1'	C-2'	C-3'	C-4'	C-5'
7a		155.6	160.4	110.1	124.0 (c)	123.7 (c)	135.2	116.5	151.4	137.3	124.1	128.5	125.6	
7b		155.6	160.3	110.1	124.1 (c)	123.7 (c)	135.2	116.5	151.3	134.7 (d)	124.0	128.9	134.9 (d)	20.5
7c		155.7	160.1	110.2	124.3 (c)	123.9 (c)	135.5	116.7	151.2	136.6	125.6	128.5	129.6	

(a) In hexadeuteriodimethylsulfoxide. (b) Model compounds: phenyl carbamate [10f], 2-hydroxybenzamide [10g], 1,3-benzoxazine-2,4-dione [11], 2,4-(1*H*,3*H*)-quinazolin-2-one [12], and 3-β-D-ribofuranosyl-2,7-dioxypyrido[2,3-*d*]pyrimidine [13]. (c) (d) These values may be interchanged.

Table IV

¹³C Chemical Shifts of 2-(2-Hydroxyphenyl)-4-(3*H*)-quinazolinones (a) (b)

Compound No.	R	C-2	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-1'	C-2'	C-3'	C-4'	C-5'	C-6'	R
10a	H	159.7	161.1	120.5	127.5	126.5	134.5	125.7 (c)	145.9	113.7	153.5	117.5	133.3	118.5	125.5 (c)	
10b	CH ₃	159.5	160.9	120.2	127.3	136.3	135.6	125.3 (c)	143.8	113.7	152.6	117.4	132.9	118.4	125.1 (c)	20.3
10c	Cl	159.2	160.0	121.6	127.7	130.6	134.3	127.7	144.9	114.0	153.7	117.4	133.2	118.5	124.6	

(a) In hexadeuteriodimethylsulfoxide. (b) Model compounds: 2-benzyl-4(3*H*)-quinazolinone [14], 3-amino-4-ethoxycarbonylamino-5-(2-hydroxyphenyl)-4*H*-1,2,4-triazole [10h]. (c) These values may be interchanged.

simple manner to the imidazo- and pyrimido[1,2-*c*]-1,3-benzoxazine system. Thus, treatment of **1** with 2-chloroethyl isocyanate in ethyl ether, with or without added triethylamine, yields the expected carbamate **11a** in high yield. When the same reagents, however, are allowed to react in refluxing toluene, in the presence of an equivalent amount of triethylamine, 2,3-dihydro-5*H*-imidazo[1,2-*c*]-1,3-benzoxazin-5-one (**13a**) is obtained as product. The same compound is isolated as product when carbamate **11a** and triethylamine are refluxed in toluene. The analogous reactions of **1** with 3-chloropropyl isocyanate lead to the homologous carbamate **11b** and pyrimido[1,2-*c*][1,3]-benzoxazin-6-one (**13b**). Apparently in these cases, the presumed imino intermediates **12** undergo a further cycliza-

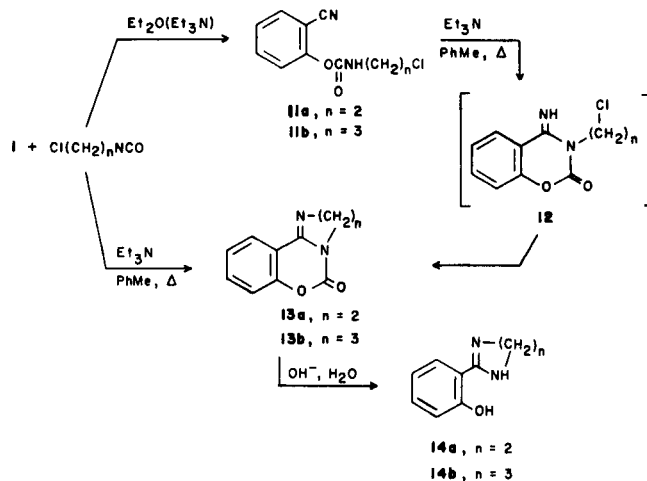
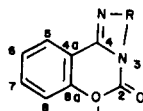


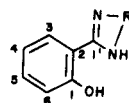
Table V

¹³C Chemical Shifts of Compounds **13a**, **13b**, and **17** (a)

Compound No.	R	Solvent	C-2	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	C-1'	C-2'	C-3'
13a	^{1'} ^{2'} (-N)CH ₂ CH ₂ (N=)	DMSO-d ₆	149.9	152.3	111.8	125.4 (b)	124.9 (b)	133.9	116.3	144.7	53.54	44.2	
13b	^{1'} ^{2'} ^{3'} (-N)CH ₂ CH ₂ CH ₂ (N=)	DMSO-d ₆	146.8	150.1	116.0	125.0 (b)	124.7 (b)	132.7	115.9	141.9	43.5	19.8	42.0
17	^{1'} ^{2'} CH ₂ CO	CF ₃ COOD	155.7	167.0	103.6	128.1	128.1	143.7	118.0	140.3	broad	168.4	

(a) Model compounds: 2-(2-hydroxyphenyl)benzoxazole [10i], 3-phenyloxazolidin-2-one [10j], 3-amino-4-ethoxycarbonylamino-5-(2-hydroxyphenyl)-4H-1,2,4-triazole [10h]. (b) These values may be interchanged.

Table VI

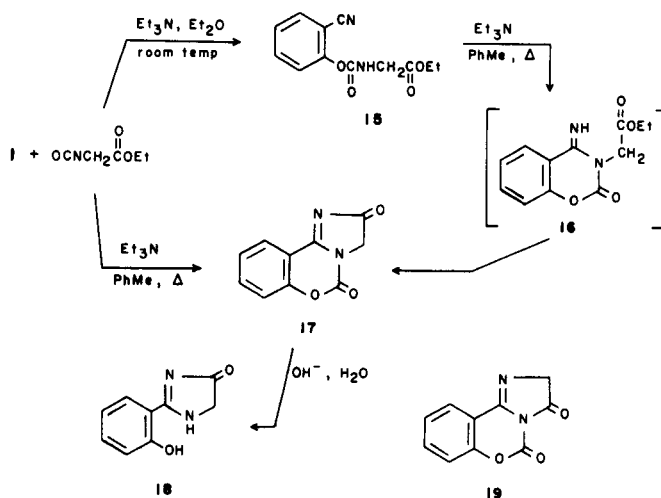
¹³C Chemical Shifts of Compounds **14a**, **b** and **18** (a)

Compound No.	R	Solvent	C-1	C-2	C-3	C-4	C-5	C-6	C-1'	C-2'	C-3'	C-4'
14a	^{2'} ^{3'} (HN)CH ₂ CH ₂ (N)	DMSO-d ₆	163.0	110.6	127.3	117.8 (b)	132.4	115.7 (b)	166.1	46.8	46.8	
14b	^{2'} ^{3'} ^{4'} (HN)CH ₂ CH ₂ CH ₂ (N)	CH ₃ OD	160.1	110.2	125.4	123.6	134.2	113.5	171.7	38.4	19.1	38.4
18	^{2'} ^{3'} CH ₂ CO	DMSO-d ₆	160.3	110.7	127.5	118.6 (b)	133.7	117.2 (b)	167.4	55.3	182.0	

(a) Model compounds: As in Table V. (b) These values may be interchanged.

tion to form the tricyclic products **13** with elimination of hydrogen chloride. The structures assigned to compounds **13a** and **13b** are supported by their melting points and their ir and nmr spectra, as well as by their hydrolysis to 4,5-dihydro-2-(2-hydroxyphenyl)-1H-imidazole (**14a**) and 1,4,5,6-tetrahydro-2-(2-hydroxyphenyl)pyrimidine (**14b**), respectively.

In a similar manner carbamate **15** and imidazo[1,2-c]-[1,3]benzoxazin-2,5(3H)-dione (**17**) are obtained from 2-hydroxybenzonitrile (**1**) and ethyl isocyanatoacetate. For the cyclization of **15** into **17**, however, a catalytic amount of triethylamine does not seem to be adequate and best results are obtained when one-half to one equivalent of triethylamine is used. Hydrolysis of **17** yields 1,5-dihydro-2-(2-hydroxyphenyl)imidazol-3-one (**18**).



The fact that the yields in which benzoxazinones **13a**, **13b**, and **17** are obtained are not as good as for the analogous quinazolinones [3,4] is very likely due to the tendency of carbamates such as **11a**, **11b**, and **15** to partially decompose upon heating to their precursor phenol and isocyanate [6].

Since compounds **7a-c** are believed to be formed by a Dimroth rearrangement of the initial cyclization products **3**, under the same reaction conditions which lead to the formation of compounds **13a,b**, and **17** (*i.e.*, refluxing with triethylamine in toluene), the question arises whether a similar rearrangement precedes the cyclization of intermediates **12** and **16**. In the case of **12**, the structure of the product must be the same (**13**) whether a rearrangement takes place or not. In the case of intermediate **16**, however, a Dimroth rearrangement before cyclization would result in the formation of **19**, instead of **18**. In view of the fact that in our experience and that of others [2,6], such rearrangements have been found to require fairly high temperatures, the observation that compound **17** can be obtained by a prolonged, room temperature treatment of **1** with ethyl isocyanatoacetate and triethylamine in toluene argues against a rearrangement of **16** prior to cyclization when the reaction is run in refluxing toluene.

EXPERIMENTAL

Melting points were determined in capillaries with a Thomas-Hoover Uni-Melt apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer using mineral oil mulls. Proton nmr spectra were obtained on a Varian EM360 and a Varian FT80A spectrometer using solutions in the indicated solvents and tetramethylsilane as internal standard.

The ^{13}C -nmr spectra were recorded at 80-100° for compounds **10a-c** and at 30-35° for all other compounds using 5 mm tubes and concentrations of 5-6% w/w. The measurement conditions were as follows: frequency 20 MHz, tip angle 44°, pulse repetition time 0.5 sec, spectral width 5,000 Hz, and 1600 points for the Fourier transform. Chemical shift assignments were based on calculated values using substituent parameters [8] and on the comparison of the recorded spectra with each other and with the spectra of model compounds (see Tables I-VI). The multiplicity of signals in the off-resonance decoupled spectra, and the relative peak intensities, as affected by nuclear Overhauser enhancements, and the equivalence of aromatic ring carbon atoms, were also taken into consideration in making these assignments. All chemical shifts are reported in ppm downfield from tetramethylsilane using the solvent as internal standard.

2-Hydroxybenzoxazinone (**1**).

A literature procedure [15] was modified with regard to product isolation, in order to improve the yield of pure product. This procedure was followed up to the point of extraction of the product with ethyl ether from inorganic materials. After the ether solution had been successively washed with dilute hydrochloric acid and with water, it was extracted with several portions of 10% aqueous sodium hydroxide to yield a basic solution, which was chilled and acidified with dilute hydrochloric acid. The resulting semisolid precipitate was extracted with benzene to give a solution, which was washed successively with dilute hydrochloric acid and with water. After it had been dried with anhydrous magnesium sulfate, the benzene solution was concentrated to give a solid, which was recrystallized from benzene to afford **1** as colorless crystals, mp 92-96° (lit [15] 94-95°), in 55-58% yield.

2-(Phenylaminocarbonyloxy)benzoxazinone (**2a**).

To 1.2 g (10 mmoles) of 2-hydroxybenzoxazinone in 3 ml of anhydrous ethyl ether were added 1.2 g (10 mmoles) of phenyl isocyanate in 0.50 ml of ethyl ether and 3 drops of triethylamine. An exothermic reaction took place and a solid started being formed within an hour. The mixture was allowed to stand overnight to yield 2.6 g (95%) of **2a**, mp 96-102°. Recrystallization from benzene yielded the pure compound as colorless crystals, mp 103-104.5° (lit [6] mp 105-106°); ir: 3360 (N-H), 2225 (C≡N), 1760 (C=O) cm^{-1} ; ^1H -nmr (DMSO- d_6): δ 6.9-8.0 (m, 9, ArH), 10.5 (s, 1, NH); ^{13}C -nmr: see Table I.

Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.56; H, 4.34; N, 11.95.

2-[(4-Methylphenyl)aminocarbonyloxy]benzoxazinone (**2b**).

To 1.2 g (10 mmoles) of 2-hydroxybenzoxazinone in 3 ml of anhydrous ethyl ether were added 1.3 g (10 mmoles) of 4-methylphenyl isocyanate in 2 ml of ethyl ether and 2 drops of triethylamine. An exothermic reaction yielded within a few minutes 2.5 g (99%) of **2b**, mp 128.5-132°. Recrystallization from toluene gave the pure compound as a colorless solid, mp 130.5-133.5°; ir: 3325 (N-H), 2150-2230 (br, C≡N), 1720 (C=O) cm^{-1} ; ^1H -nmr (deuteriochloroform): δ 2.3 (s, 3, CH_3), 6.9-8.1 (m, 8, ArH), 10.5 (s, 1, NH); ^{13}C -nmr: see Table I.

Anal. Calcd. for $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}_2$: C, 71.41; H, 4.80; N, 11.11. Found: C, 71.52; H, 4.93; N, 11.20.

2-[(4-Chlorophenyl)aminocarbonyloxy]benzoxazinone (**2c**).

To 1.5 g (10 mmoles) of 4-chlorophenyl isocyanate dissolved in 10 ml of anhydrous ethyl ether was added 1.2 g (10 mmoles) of 2-hydroxybenzoxazinone and 5 drops of triethylamine. An immediate, exothermic reaction yielded within 5 minutes 2.5 g (91%) of **2c**, mp 130-131.5°. The pure compound was obtained by recrystallization from toluene as colorless crystals, mp 133.5-135°; ir: 3300 (N-H), 2220 (C≡N), 1770 (C=O) cm^{-1} ; ^1H -nmr (DMSO- d_6): δ 6.9-8.0 (m, 8, ArH), 10.7 (s, 1, NH); ^{13}C -nmr: see Table I.

Anal. Calcd. for $\text{C}_{14}\text{H}_9\text{ClN}_2\text{O}_2$: C, 61.66; H, 3.33; N, 10.27. Found: C, 61.65; H, 3.54; N, 10.13.

4-[N-(N-Phenylcarbamoyl)imino]-3-phenyl-2H-1,3-benzoxazin-2-one (**4a**).

A solution of 1.2 g (10 mmoles) of 2-hydroxybenzoxazinone, 1.2 g (10 mmoles) of phenyl isocyanate, and 4 drops of triethylamine in 5 ml of benzene was refluxed for 8 hours to yield 1.4 g of crude **4a**, mp 174-180°. Recrystallization from acetonitrile gave 0.90 g (50%) of a colorless product, mp 198-199°, and further recrystallization yielded the pure compound, mp 202.5-205°; ir: 3340 (N-H), 1750 (C=O), 1660 (C=O), 1640 (C=N) cm^{-1} ; ^1H -nmr (DMSO- d_6): δ 6.9-8.0 (m, 14, ArH), 9.5 (s, 1, NH) ppm; ^{13}C -nmr: see Table II.

Anal. Calcd. for $\text{C}_{22}\text{H}_{15}\text{N}_3\text{O}_3$: C, 70.61; H, 4.23; N, 11.76. Found: C, 70.33; H, 4.25; N, 11.82.

B.

A solution of 1.2 g (10 mmoles) of **1**, 2.4 g (20 mmoles) of phenyl isocyanate, and 4 drops of triethylamine in 5 ml of benzene was refluxed for 21 hours to yield 2.1 g (57%) of **4a**, mp 199-202°.

C.

A mixture of 1.0 g (4.2 mmoles) of **2a**, 6 ml of benzene and 4 drops of triethylamine was refluxed overnight to yield 0.51 g of a crude product, mp 171-181°, recrystallization of which from acetonitrile afforded 0.30 g (40%) of **4a**, mp 202.5-205°.

D.

After a mixture of 1.2 g (4.9 mmoles) of **2a**, 0.60 g (5.0 mmoles) of phenyl isocyanate, 5 ml of benzene, and 3 drops of triethylamine had been refluxed for 24 hours, there was obtained 0.73 g (42%) of **4a**, mp 196-197.5°.

Hydrolysis of **4a** to 3-Phenyl-2H-1,3-benzoxazine-2,4(3H)-dione (**5a**).

A mixture of 0.20 g (0.56 mmole) of **4a**, 3 ml of ethanol, and 0.5 ml of concentrated hydrochloric acid was refluxed for 3 hours to yield 0.12 g (90%) of **5a**, mp 242-243°. Recrystallization from benzene gave the pure compound as colorless crystals, mp 242.5-243.5° (lit [16] mp 246-247°), identical in all respects with an authentic sample [16].

4-[*N*-[*N*-(4-Methylphenyl)carbamoyl]imino]-3-(4-methylphenyl)-2*H*-1,3-benzoxazin-2-one (**4b**).

A.

To 0.60 g (5.0 mmoles) of **1** dissolved in 3 ml of benzene were added successively a solution of 0.67 g (5.0 mmoles) of 4-methylphenyl isocyanate in 2 ml of benzene and 5 drops of triethylamine. The resulting mixture was refluxed for 13 hours to yield 0.80 g (83%) of **4b**, mp 199-203°. Recrystallization from acetonitrile gave the pure compound as colorless crystals, mp 205.5-207°; ir: 3280 (N-H), 1770 (C=O), 1660 (C=O), 1640 (C=N) cm⁻¹; ¹H-nmr (DMSO-d₆): δ 2.2 (s, 3, CH₃), 2.3 (s, 3, CH₃), 6.9-8.1 (m, 12, ArH), 9.4 (s, 1, NH); ¹³C-nmr: see Table II.

Anal. Calcd. for C₂₃H₁₈N₃O₃: C, 71.68; H, 4.97; N, 10.90. Found: C, 71.49; H, 4.94; N, 10.90.

B.

A mixture of 1.2 g (10 mmoles) of **1**, 5 ml of benzene, 3 drops of triethylamine, and 2.7 g (20 mmoles) of 4-methylphenyl isocyanate was refluxed for 12 hours to yield 2.5 g (65%) of **4b**, mp 203-207°.

C.

When a mixture of 0.60 g (2.4 mmoles) of **2b**, 3 ml of benzene, and 4 drops of triethylamine had been refluxed for 5 hours, there was obtained 0.32 g of a crude product, mp 191-196°, recrystallization of which from acetonitrile gave 0.20 g (44%) of **4b**, mp 201-203°.

D.

A mixture of 1.0 g (4.0 mmoles) of **2b**, 0.53 g (4.1 mmoles) of 4-methylphenyl isocyanate, 6 ml of benzene, and 3 drops of triethylamine was refluxed for 17 hours to yield 0.80 g (52%) of **4b**, mp 193-200°.

Hydrolysis of **4b** to 3-(4-Methylphenyl)-2*H*-1,3-benzoxazine-2,4(3*H*)-dione (**5b**).

A mixture of 0.50 g (1.3 mmoles) of **4b**, 5 ml of ethanol, and 2 ml of concentrated hydrochloric acid was refluxed for 14 hours to give 0.25 g (76%) of **5b**, mp 220.5-222°. Recrystallization from ethanol gave the pure compound, mp 222-224.5° (lit [17] mp 226-227°), identical in all respects with an authentic sample [15]. When the filtrate from the isolation of **5b** was partially evaporated, there was obtained 0.05 g of (4-methylphenyl)urea, mp 178-182° (lit [18] mp 182°), identical with a sample prepared from 4-methylphenyl isocyanate and ethanolic ammonia.

4-[*N*-[*N*-(4-Chlorophenyl)carbamoyl]imino]-3-(4-chlorophenyl)-2*H*-1,3-benzoxazin-2-one (**4c**).

A.

A mixture of 1.2 g (10 mmoles) of **1**, 10 ml of benzene, 1.5 g (10 mmoles) of 4-chlorophenyl isocyanate, and 6 drops of triethylamine was refluxed for 3 hours and then filtered while hot to yield 1.2 g (56%) of **4c**, mp 201-203°. Recrystallization of this material from acetonitrile gave the pure compound as colorless crystals, mp 214-215°; ir: 3280 (N-H), 1750 (C=O), 1670 (C=O), 1630 (C=N) cm⁻¹; ¹H-nmr (DMSO-d₆): δ 6.9-8.0 (m, 12, ArH), 9.6 (s, 1, NH).

Anal. Calcd. for C₂₁H₁₃Cl₂N₃O₃: C, 59.17; H, 3.07; Cl, 16.63; N, 9.86. Found: C, 59.56; H, 3.36; Cl, 16.79; N, 10.18.

B.

A mixture of 1.2 g (10 mmoles) of **1**, 3.1 g (20 mmoles) of 4-chlorophenyl isocyanate, 10 ml of benzene, and 5 drops of triethylamine was refluxed for 17 hours and then it was cooled and filtered to yield 1.9 g (45%) of **4c**, mp 206-208°.

C.

A mixture of 1.0 g (3.7 mmoles) of **2c**, 5 ml of benzene, and 5 drops of triethylamine was refluxed for 10 hours and then it was filtered while hot. After the precipitate had been washed with a small amount of acetonitrile, there was obtained 0.50 g (62%) of **4c**, mp 201-203°.

D.

After a mixture of 1.4 g (5.1 mmoles) of **2c**, 0.80 g (5.1 mmoles) of 4-chlorophenyl isocyanate, 12 ml of benzene, and 5 drops of triethylamine had been refluxed for 69 hours, there was obtained 1.6 g of a crude product, mp 182-204°. Recrystallization of this material from acetonitrile gave 0.80 g (37%) of **4c**, mp 198.5-204°.

Hydrolysis of **4c** to 3-(4-Chlorophenyl)-2*H*-1,3-benzoxazine-2,4(3*H*)-dione (**5c**).

A mixture of 0.53 g (1.2 mmoles) of **4c**, 5 ml of ethanol, and 3 ml of concentrated hydrochloric acid was stirred and refluxed for 7 hours. Upon standing overnight at room temperature, there precipitated 0.30 g (91%) of **5c**, mp 220-230°, raised to 236-238° by recrystallization from ethyl acetate (lit [17] mp 243-244°). Partial evaporation of the filtrate from the initial isolation of **5c** yielded a further small amount of impure **5c**, and neutralization of the new filtrate with aqueous ammonia precipitated 0.050 g of a solid identified as impure 4-chlorophenylurea by comparison of its ir and nmr spectra with those of an authentic sample.

4-(Phenylamino)-2*H*-1,3-benzoxazin-2-one (**7a**).

A.

To a solution of 2.4 g (20 mmoles) of **1** in 10 ml of toluene were added 2.4 g (20 mmoles) of phenyl isocyanate and 3 drops of triethylamine. The resulting mixture was heated under reflux for 19 hours to yield 4.2 g (87%) of **7a**, mp 240-245°. Recrystallization from acetonitrile gave the pure compound as colorless crystals, mp 244-245° (lit [6] mp 240-241°); ir: 3270 (N-H), 1690 (C=O) cm⁻¹; ¹H-nmr (DMSO-d₆): δ 7.2-8.0 (m, 8, ArH), 8.4 (m, 1, ArH), 10.4 (s, 1, NH); ¹³C-nmr: see Table III.

Anal. Calcd. for C₁₄H₁₀N₂O₂: C, 70.58; H, 4.23; N, 11.76. Found: C, 70.63; H, 4.23; N, 11.68.

B.

A mixture of 1.0 g (4.2 mmoles) of **2a**, 6 ml of toluene and 3 drops of triethylamine was refluxed overnight to yield 0.70 g (70%) of **7a**, mp 243-246°.

C.

Compound **2a** (0.30 g, 1.3 mmoles) was heated in an oil bath at 150-170° until the initial melt had resolidified (5 hours). The crude product (0.25 g), mp 170-220°, had an infrared spectrum identical with that of the products of the two previous reactions. Recrystallization from acetonitrile gave 0.13 g (43%) of pure **7a**, mp 244-245°.

Hydrolysis of **7a** to 2*H*-Benzoxazine-2,4(3*H*)-dione (**8**).

After a mixture of 0.50 g (2.1 mmoles) of **7a**, 10 ml of ethanol, and 3.5 ml of concentrated hydrochloric acid had been heated on a steam bath for 15 minutes, it was allowed to stand at room temperature for 2 days to yield 0.14 g (41%) of **8**, mp 224-225°. The pure compound was obtained by recrystallization from ethanol, mp 226-228° (lit [19] mp 227.5-228.5°), identical in all respects with an authentic sample [19].

4-[(4-Methylphenyl)amino]-2*H*-1,3-benzoxazin-2-one (**7b**).

A.

A mixture of 2.4 g (20 mmoles) of **1**, 10 ml of toluene, 2.7 g (20 mmoles) of 4-methylphenyl isocyanate, and 3 drops of triethylamine was refluxed for 19 hours to yield 4.2 g (82%) of **7b**, mp 237-242°. Recrystallization of the crude product from acetonitrile gave the pure compound in the form of colorless crystals, mp 243-245°; ir: 3300 (N-H), 1690 (C=O), 1590 (C=N) cm⁻¹; ¹H-nmr (DMSO-d₆): δ 2.4 (s, 3, CH₃), 7.1-8.0 (m, 7, ArH), 8.5 (m, 1, ArH), 10.4 (s, 1, NH); ¹³C-nmr: see Table III.

Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.41; H, 4.80; N, 11.11. Found: C, 71.49; H, 4.91; N, 11.13.

B.

A mixture of 1.0 g (3.9 mmoles) of **2b**, 5 ml of toluene, and 3 drops of triethylamine was refluxed for 20 hours to yield 0.59 g (59%) of **7b**, mp 240-244°.

C.

When **4b** (0.50 g, 2.0 mmoles) was heated in an oil bath at 150-190° until the initial melt had resolidified, there was obtained 0.40 g of crude **7b**, mp 194-230°.

Hydrolysis of **7b** to 2*H*-Benzoxazine-2,4(3*H*)-dione (**8**).

After a mixture of 0.50 g (2.0 mmoles) of **7b**, 10 ml of ethanol, and 2.5 ml of concentrated hydrochloric acid had been refluxed for 17 hours, it was concentrated to one-half its volume to yield 0.12 g (36%) of **8**, mp 220-225°.

4-[(4-Chlorophenyl)amino]-2*H*-1,3-benzoxazin-2-one (**7c**).

A.

A mixture of 1.2 g (10 mmoles) of **1**, 1.5 g (10 mmoles) of 4-chlorophenyl isocyanate, 6 ml of toluene, and 5 drops of triethylamine was stirred and heated under reflux for 6 hours to yield 2.0 g (74%) of **7c**, mp 295-297.5°. The pure compound was obtained by recrystallization from *N,N*-dimethylformamide as colorless crystals, mp 302.5-303°; ir: 3250 (N-H), 1680 (C=O) cm^{-1} ; ¹H-nmr (DMSO-*d*₆): δ 7.2-7.9 (m, 7, ArH), 8.4 (m, 1, ArH).

Anal. Calcd. for $C_{14}H_9ClN_2O_2$: C, 61.66; H, 3.33; N, 10.27. Found: C, 61.88; H, 3.29; N, 10.48.

B.

A mixture of 1.0 g (3.7 mmoles) of **2c**, 5 ml of toluene, and 3 drops of triethylamine was stirred and heated under reflux for 46 hours to yield 0.75 g (75%) of **7c**, mp 295-297°.

Hydrolysis of **7c** to 2*H*-Benzoxazine-2,4(3*H*)-dione (**8**).

After a mixture of 0.30 g (1.1 mmoles) of **7c**, 10 ml of ethanol, and 2 ml of concentrated hydrochloric acid had been refluxed for 1.5 hours, it was allowed to stand at room temperature for 2 days to give 0.080 g (44%) of **8**, mp 226-227.5°.

2-(2-Hydroxyphenyl)-4(3*H*)-quinazolinone (**10a**).

A solution of 0.37 g (1.6 mmoles) of **7a** in 3.5 ml of phenyl ether was heated in an oil bath at 160-170° for 1 hour. Upon cooling and dilution with petroleum ether (bp 63-75°) there was obtained 0.34 g (92%) of **10a**, mp 297-298°. Recrystallization of this material from 1-butanol gave the pure compound as yellow crystals, mp 297.5-298° (lit [6] mp 301-302°); ir: 3250-3050 (O-H, N-H), 1660 (C=O) cm^{-1} ; ¹H-nmr (DMSO-*d*₆): δ 6.8-8.3 (m, 8, ArH), 12.4, 13.7 (broad signals, 2, NH, OH); ¹³C-nmr: see Table IV.

2-(2-Hydroxyphenyl)-6-methyl-4(3*H*)-quinazolinone (**10b**).

A solution of 0.30 g (1.2 mmoles) of **7b** in 3 ml of phenyl ether was heated under reflux for 2 hours and then it was cooled and diluted with petroleum ether to yield 0.27 g (98%) of **10b**, mp 322-328°. The pure compound was obtained by recrystallization from 1-butanol as yellow crystals, mp 322.5-324°; ir: 3200-3100 (O-H, N-H), 1680 (C=O) cm^{-1} ; ¹H-nmr (DMSO-*d*₆): δ 2.5 (s, 3, CH₃), 6.8-8.3 (m, 7, ArH); ¹³C-nmr: see Table IV.

Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.41; H, 4.80; N, 11.11. Found: C, 71.61; H, 4.98; N, 10.94.

6-Chloro-2-(2-hydroxyphenyl)-4(3*H*)-quinazolinone (**10c**).

A solution of 0.5 g (1.8 mmoles) of **7c** in 4 ml of phenyl ether was refluxed for 6 hours. The cooled solution was diluted with petroleum ether to yield 0.44 g (88%) of **10c**, mp 328-331°. Recrystallization from *N,N*-dimethylformamide gave the pure compound as yellow crystals, mp 334-335°; ir: 3200-3100 (O-H, N-H), 1670 (C=O) cm^{-1} ; ¹H-nmr (DMSO-*d*₆):

δ 6.8-8.3 (m, 7, ArH).

Anal. Calcd. for $C_{14}H_9ClN_2O_2$: C, 61.66; H, 3.33; N, 10.27. Found: C, 61.75; H, 3.10; N, 10.47.

2-[(2-Chloroethyl)aminocarbonyloxy]benzonitrile (**11a**).

A.

The mixture obtained from the addition of 2-chloroethyl isocyanate (2.1 g, 20 mmoles) to a solution of **1** (2.4 g, 20 mmoles) in 10 ml of anhydrous ethyl ether was swirled and allowed to stand. An exothermic reaction yielded 4.4 g (96%) of **11a**, mp 108-111°, recrystallization of which from benzene afforded the pure compound as colorless crystals, mp 111.5-113.5°; ir 3310 (N-H), 2220-2150 (C≡N), 1710 (C=O) cm^{-1} ; ¹H-nmr (deuteriochloroform): δ 3.5-3.7 (m, 4, CH₂CH₂), 5.8 (br, s, 1, NH), 7.2-7.7 (m, 4, ArH); ¹³C-nmr: see Table I.

Anal. Calcd. for $C_{10}H_9ClN_2O_2$: C, 53.47; H, 4.04; N, 12.47. Found: C, 53.58; H, 4.06; N, 12.27.

B.

To a solution of **1** (1.2 g, 10 mmoles) in 3 ml of anhydrous ethyl ether was added 2-chloroethyl isocyanate (1.1 g, 10 mmoles) in 0.5 ml of the same solvent. Upon further addition of 4 drops of triethylamine, an exothermic reaction took place which yielded 2.2 g (96%) of **11a**, mp 101-106°.

2-[(3-Chloropropyl)aminocarbonyloxy]benzonitrile (**11b**).

To a solution of 1.2 g (10 mmoles) of **1** in 10 ml of anhydrous ethyl ether were added successively 1.2 g (10 mmoles) of 3-chloropropyl isocyanate [20] and 3 drops of triethylamine. The resulting mixture was swirled and allowed to stand at room temperature for 2 hours. Filtration yielded 1.8 g of **11b**, mp 76-80°, and concentration of the filtrate afforded an additional 0.40 g product, mp 74-76° (total yield: 92%). The pure compound was obtained in the form of colorless crystals by recrystallization from benzene/cyclohexane, mp 76-78°; ir: 3330 (N-H), 2220 (C≡N), 1720 (C=O) cm^{-1} ; ¹H-nmr (deuteriochloroform): δ 2.1 (m, 2, CH₂CH₂CH₂), 3.4 (t, 2, NCH₂), 3.7 (t, 2, CH₂Cl), 5.7 (br s, 1, NH), 7.2-7.8 (m, 4, ArH); ¹³C-nmr: see Table I.

Anal. Calcd. for $C_{11}H_{11}ClN_2O_2$: C, 55.35; H, 4.65; N, 11.74. Found: C, 55.43; H, 4.85; N, 11.52.

2,3-Dihydro-5*H*-imidazo[1,2-*c*][1,3]benzoxazin-5-one (**13a**).

A.

A mixture of **1** (1.2 g, 10 mmoles), toluene (6 ml), 2-chloroethyl isocyanate (1.1 g, 10 mmoles), and triethylamine, (1.0 g, 10 mmoles) was refluxed for 24 hours. Filtration of the cooled reaction mixture and washing of the dried precipitate with water yielded 1.2 g (64%) of **13a**, mp 129-133°. The pure compound was obtained by recrystallization from petroleum ether (bp 63-75°) as colorless crystals, mp 133-135° (lit [21] mp 135-137°); ir: 1745 (C=O), 1655 (C=N) cm^{-1} ; ¹H-nmr (DMSO-*d*₆): δ 3.9 (m, 4, CH₂CH₂), 7.2-7.9 (m, 4, ArH); ¹³C-nmr: see Table V.

B.

A solution of **11a** (2.0 g, 8.9 mmoles) and triethylamine (0.9 g, 8.9 mmoles) in 7 ml of toluene was refluxed for 18 hours to yield a colorless solid. This was dried, washed with water, and recrystallized from petroleum ether (bp 63-75°) to give 0.85 g (51%) of **13a**, mp 133-135°.

Hydrolysis of **13a** to 4,5-Dihydro-2-(2-hydroxyphenyl)-1*H*-imidazole (**14a**).

A mixture of 0.80 g (4.2 mmoles) of **13a** and 10 ml of 10% aqueous potassium hydroxide was heated on a steam bath to effect dissolution, and the resulting solution was cooled and filtered. Neutralization of the filtrate with 2*N* hydrochloric acid to pH 8 gave 0.40 g (60%) of **14a**, mp 202-206°, raised to 203-207° by recrystallization from 1-propanol (lit [21] mp 206-208°); ¹H-nmr (DMSO-*d*₆): δ 3.7 (s, 4, CH₂CH₂), 6.6-7.7 (m, 4, ArH); ¹³C-nmr: see Table VI.

3,4-Dihydro-2*H*,6*H*-pyrimido[1,2-*c*][1,3]benzoxazin-6-one (**13b**).

A.

A mixture of 1.2 g (10 mmoles) of **1**, 6 ml of toluene, 1.2 g (10 mmoles) of 3-chloropropyl isocyanate [20], and 1.0 g (10 mmoles) of triethylamine was refluxed for 17 hours. The resulting solid material was washed with water to afford 1.4 g (67%) of **13b**, mp 143-147°. Recrystallization from cyclohexane gave the pure compound as colorless crystals, mp 144-147° (lit [21] mp 143-145°); ir: 1725 (C=O), 1645 (C=N) cm^{-1} ; $^1\text{H-nmr}$ (deuteriochloroform): δ 2.0 (m, 2, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.7 (t, 2, $\text{CH}_2\text{CH}_2\text{CH}_2$), 4.0 (t, 2, $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.0-7.6 (m, 3, ArH), 8.0 (m, 1, ArH); $^{13}\text{C-nmr}$: see Table V. B.

A mixture of 1.0 g (4.2 mmoles) of **11b**, 5 ml of toluene, and 0.42 g (4.2 mmoles) of triethylamine was refluxed for 18 hours to yield 0.50 g (59%) of **13b**, mp 142-145.5°.

Hydrolysis of **13b** to 1,4,5,6-Tetrahydro-2-(2-hydroxyphenyl)pyrimidine (**14b**).

A mixture of 0.50 g (2.5 mmoles) of **13b** and 10 ml of 10% aqueous potassium hydroxide was stirred at room temperature for 18 hours and then neutralized with 2*N* hydrochloric acid. There was obtained 0.25 g (58%) of **14b**, mp 247-251°, raised to 248-251.5° by recrystallization from 1-butanol (lit [21] mp 252-254°); ir: 3300-3150 (N-H, O-H), 1625 (C=N) cm^{-1} ; $^1\text{H-nmr}$ (methanol- d_4): δ 1.7-2.3 (m, 2, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.8 (t, 4, $\text{CH}_2\text{CH}_2\text{CH}_2$), 6.3-7.0 (m, 2, ArH), 7.0-7.7 (m, 2, ArH); $^{13}\text{C-nmr}$: see Table VI.

2-[(Ethoxycarbonylmethyl)aminocarbonyloxy]benzonitrile (**15**).

A.

Addition of 2 drops of triethylamine to a mixture of 0.60 g (5.0 mmoles) of **1**, 5 ml of anhydrous ethyl ether, and 0.65 g (5.0 mmoles) of ethyl isocyanatoacetate caused an exothermic reaction to occur. After one-half of the ether had been evaporated, there was obtained 1.2 g (96%) of **15**, mp 67-72°. Recrystallization from toluene gave the pure compound as colorless crystals, mp 71-75°; ir: 3360 (N-H), 2220 (C≡N), 1760, 1720 (C=O) cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): δ 1.2 (t, 3, CH_3), 3.9 (d, 2, NCH_2), 4.1 (q, 2, CH_2CH_3), 7.3-8.0 (m, 4, ArH), 8.6 (t, 1, NH); $^{13}\text{C-nmr}$: see Table I.

Anal. Calcd. for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}_4$: C, 58.06; H, 4.87; N, 11.29. Found: C, 58.24; H, 5.03; N, 11.31.

B.

A mixture of **1** (1.2 g, 10 mmoles), toluene (10 ml), ethyl isocyanatoacetate (1.3 g, 10 mmoles), and triethylamine (3 drops) was refluxed for 24 hours and then allowed to stand overnight. There was obtained 2.2 g (87%) of **15**, mp 70-75°.

Imidazo[1,2-*c*][1,3]benzoxazine-2,5(3*H*)-dione (**17**).

A.

A mixture of 1.2 g (10 mmoles) of **1**, 7 ml of toluene, 1.3 g (10 mmoles) of ethyl isocyanatoacetate, and 0.5 g (5 mmoles) of triethylamine was refluxed for 3 hours to yield 1.1 g of crude **17**, mp 279-283°. Recrystallization from acetonitrile gave 0.99 g (49%) of the pure compound as yellow crystals, mp 301-302°; ir: 1760, 1745 (C=O) cm^{-1} ; $^1\text{H-nmr}$ (trifluoroacetic acid): δ 5.1 (s, 2, CH_2), 7.8 (t, 2, ArH), 8.3 (t, 2, ArH); $^{13}\text{C-nmr}$: see Table V.

Anal. Calcd. for $\text{C}_{10}\text{H}_6\text{N}_2\text{O}_3$: C, 59.41; H, 2.99; N, 13.86. Found: C, 59.31; H, 3.06; N, 14.07.

B.

A mixture of 1.2 g (10 mmoles) of **1**, 10 ml of toluene, 1.3 g (10 mmoles) of ethyl isocyanatoacetate, and 1.1 g (11 mmoles) of triethylamine was stirred at room temperature for 4.5 days. Recrystallization of the crude,

solid product from acetonitrile gave 0.50 g (25%) of **17**, mp 293-300°.

C.

A mixture of 0.60 g (2.4 mmoles) of **15**, 5 ml of toluene, and 0.25 g (2.5 mmoles) of triethylamine was refluxed for half an hour to yield 0.20 g (41%) of **17**, mp 279-282°.

Hydrolysis of **17** to 1,5-Dihydro-2-(2-hydroxyphenyl)imidazol-3-one (**18**).

Treatment of 2.7 g (13 mmoles) of **17** with 21 ml of 10% aqueous potassium hydroxide yielded a solution which was filtered and then neutralized with acetic acid to afford 2.1 g (87%) of **18**, mp 189-197° dec. The pure compound was obtained by recrystallization from 1-propanol as orange crystals, mp 197-200.5°; ir: 3200-3100 (O-H, NH), 1710 (C=O), 1625 (C=N) cm^{-1} ; $^1\text{H-nmr}$ (DMSO- d_6): δ 4.4 (s, 2, CH_2), 6.8-7.9 (m, 4, ArH), 9.5-11.5 (br, 2, NH, OH); $^{13}\text{C-nmr}$: see Table VI.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{N}_2\text{O}_2$: C, 61.36; H, 4.57; N, 15.89. Found: C, 61.25; H, 4.72; N, 15.92.

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