thoxy-3-oxazoline (VI, R = $CH_3$), was separated by preparative gas chromatography and obtained as a colorless solid: mp 30°, infrared at 5.95 $\mu$. The proton nmr spectrum showed a singlet at $\tau$ 5.81 (in $CDCl_3$) with a width at a half-height of 0.8 cps. The $F^{19}$ nmr spectrum showed two septets centered at 73.9 and 78.5 ppm.

*Anal.* Calcd for $C_8H_3F_{12}NO_2$: C, 25.75; H, 0.81; F, 61.11; N, 3.78. Found: C, 25.61; H, 1.15; F, 60.49; N, 3.69.

The less abundant component was identified as 2,2,5,5-tetrakis(trifluoromethyl)-3-methyl-4-hydroxyoxazolidone by comparison of its infrared spectrum and gas chromatographic retention time with those of an authentic sample.

**2,2,5,5-Tetrakis(trifluoromethyl)-3-ethyl-4-oxazolidone (VII, R = Et) and 2,2,5,5-Tetrakis(trifluoromethyl)-4-ethoxy-3-oxazoline (VI, R = Et).**—Hexafluoroacetone (125 ml at −78°, 1.2 moles) was distilled over a period of 30 min into a stirred suspension of 30 g (0.6 mole) of sodium cyanide in 500 ml of acetonitrile. The reaction mixture warmed to 50° during the addition. The mixture was cooled to 25°, 150 g of diethyl sulfate was added, and the resulting mixture was stirred for 18 hr. Water was added to dissolve the precipitated salts, and the organic layer was separated, washed with 5% sodium bicarbonate solution and then with water, and dried over anhydrous magnesium sulfate. Distillation gave 147 g (61%) of a colorless oil: bp 140–141°, $n^{25}D$ 1.3234.

*Anal.* Calcd for $C_9H_5F_{12}NO_2$: C, 27.93; H, 1.30; F, 58.88; N, 3.62. Found: C, 28.42; H, 1.59; F, 58.71; N, 3.78.

Gas chromatographic analysis indicated the product was a mixture of two components in the ratio of 47:53. The components were separated by preparative gas chromatography for further characterization.

2,2,5,5-Tetrakis(trifluoromethyl)-4-ethoxy-3-oxazoline, the minor component, was obtained as a colorless oil: bp 136°, $n^{25}D$ 1.3178, infrared at 5.98 $\mu$. The proton nmr spectrum showed a quartet ($J$ = 7 cps) at $\tau$ 5.38 of area 2 and a triplet ($J$ = 7 cps) at 8.57 of area 3. The $F^{19}$ nmr spectrum showed two septets centered at 73.9 and 78.4 ppm.

*Anal.* Found: C, 28.03; H, 1.50; F, 58.72; N, 3.75.

2,2,5,5-Tetrakis(trifluoromethyl)-3-ethyl-4-oxazolidone, the major component, was obtained as a colorless oil: bp 142°, $n^{25}D$ 1.3263, infrared at 5.65 $\mu$. The proton nmr spectrum showed a quartet ($J$ = 7 cps) at $\tau$ 6.28 of area 2 and a triplet ($J$ = 7 cps) at 8.65 of area 3. The $F^{19}$ nmr spectrum showed two septets centered at 74.6 and 77.1 ppm.

*Anal.* Found: C, 28.08; H, 1.55; F, 58.78; N, 3.75.

**Reaction of Silver Salt of 2,2,5,5-Tetrakis(trifluoromethyl)-4-oxazolidone with Ethyl Iodide.**—Hexafluoroacetone (21 ml at −78°, 0.1 mole) was distilled into a stirred suspension of 4.9 g (0.1 mole) of sodium cyanide in 100 ml of acetonitrile. A solution of 17.0 g (0.1 mole) of silver nitrate in 25 ml of acetonitrile was added, and the sodium nitrate that precipitated was collected on a filter. Ethyl iodide (15.6 g, 0.1 mole) was added to the solution of the silver salt. An exothermic reaction ensued, and a precipitate formed. The reaction mixture was allowed to stand for 20 hr and then filtered. Distillation of the filtrate gave 25 g of a colorless oil: bp 140–141°, $n^{25}D$ 1.3280. Infrared, proton nmr, and gas chromatographic analyses showed this product to consist of an approximately 50:50 mixture of 2,2,5,5-tetrakis(trifluoromethyl)-3-ethyl-4-oxazolidone and 2,2,5,5-tetrakis(trifluoromethyl)-4-ethoxy-3-oxazoline.

**Sodium Salt of 2,2,5,5-Tetrakis(trifluoromethyl)-4-oxazolidone (III).**[7]—Hexafluoroacetone (42 ml at −78°, *ca.* 0.4 mole) was slowly distilled into a stirred suspension of 9.8 g (0.2 mole) of sodium cyanide in 200 ml of acetonitrile. The reaction mixture was cooled to 25° and filtered. The filtrate was evaporated to dryness under reduced pressure. There was obtained 72 g of the sodium salt of 2,2,5,5-tetrakis(trifluoromethyl)-4-oxazolidone as a white powder, mp 165–175° dec, infrared at 6.0 $\mu$.

*Anal.* Calcd for $C_7F_{12}NNaO_2$: Na, 6.30. Found: Na, 6.36.

**Registry No.**—Hexafluoroacetone, 684-16-2; sodium cyanide, 143-33-9; II, 7770-94-7; 3,3,3-trifluoro-2-methoxy-2-trifluoromethylpropionamide, 7775-62-4; IV, 7730-28-1; V, 7730-29-2; 2,2,5,5-tetrakis(trifluoromethyl)-3-methyl-4-hydroxyoxazolidone, 7730-31-6; VI, R = $CH_3$, 7730-32-7; VI, R = Et, 7730-33-8; VII, R = $CH_3$, 7730-30-5; VII, R = Et, 7730-34-9; sodium salt of 2,2,5,5-tetrakis(trifluoromethyl)-4-oxazolidone, 7770-95-8.

(7) J. D. Warnell has found that potassium cyanide reacts with excess hexafluoroacetone in the absence of solvent, even at −78°, to give the potassium salt of the oxazolidone.

# The Reaction of Isocyanates with *o*-Hydroxy Aromatic Aldehydes. Condensations of 3,4-Dihydro-4-hydroxy-3-alkyl-2H-1,3-benzoxazin-2-ones with Compounds Having Active Hydrogen

GEORGE BOBOWSKI AND JOHN SHAVEL, JR.

*Department of Organic Chemistry, Warner-Lambert Research Institute, Morris Plains, New Jersey*

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3,4-Dihydro-3-alkyl-2H-1,3-benzoxazin-2-ones (type **1**), 4,4′-oxobis(3,4-dihydro-3-alkyl-2H-benzoxazin-2-ones) (type **3**), and 1-(3,4-dihydro-3-alkyl-2-oxo-2H-1,3-benzoxazin-4-yl-1,3-dialkylureas (type **2**) were obtained by the condensation of *o*-hydroxy aromatic aldehydes with alkyl isocyanates. Type **1** condenses readily with compounds having active hydrogen to give 4-substituted 3,4-dihydro-3-alkyl-2H-1,3-benzoxazin-2-ones (type **8**). Ring opening to carbamates and other chemical transformations of compounds of type **8** (borohydride reduction of ketones, condensation of diketones with diamines to give quinoxalines) are described.

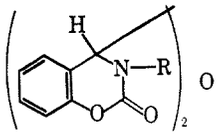
The base-catalyzed condensation of *o*-hydroxy aromatic aldehydes with equimolar quantities of aliphatic isocyanates in ether has been reported[1] to give compounds of type **1a**, and with 2 moles of isocyanate to give type **1b**. In the case of aromatic isocyanates, only type **1b** was obtained (see Chart I).

As part of a basic research program to develop new syntheses of novel heterocyclic compounds, we have independently studied this reaction (generally under somewhat different conditions) and found that condensation of *o*-hydroxy aromatic aldehydes with 2 moles of aliphatic isocyanates in tetrahydrofuran or benzene at refluxing temperature gave compounds of type **1a** (*ca.* 15%), **2** (*ca.* 30%), and a dimeric material (**3**), the latter being a major product (*ca.* 45–50%). Under similar reaction conditions, phenyl isocyanate gave the N-phenyl analog of **3** in 50% yield. Compounds of type **3** prepared by this method are listed in Table I. The structure of type **3** compounds was based on elemental analyses, Rast molecular weight determinations, infrared, and proton magnetic resonance spectral studies, plus additional chemical evidence discussed below.

The infrared absorption spectra (Nujol mulls) of these compounds show absence of OH and NH func-

(1) R. E. Strube and F. A. MacKellar, *Rec. Trav. Chim.*, **83**, 1191 (1964).

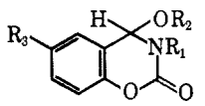
TABLE I
3-N-SUBSTITUTED 4,4'-OXOBIS(3,4-DIHYDRO-2H-1,3-BENZOXAZIN-2-ONES)



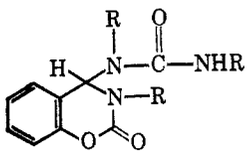
| Compd | R | Mp, °C | Yield, % | Formula | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|---|
| 3 | $CH_3$ | 210–211[a] | 48 | $C_{18}H_{16}N_2O_5$ | 63.52 | 4.74 | 8.23 | 63.71 | 4.89 | 8.29 |
| 39 |  | 241–242[a] | 53 | $C_{28}H_{20}N_2O_5$ | 72.40 | 4.34 | 6.03 | 72.23 | 4.39 | 6.32 |
| 40 | $C_2H_5$ | 163–164 | 52 | $C_{20}H_{20}N_2O_5$ | 65.21 | 5.47 | 7.61 | 65.51 | 5.62 | 7.62 |
| 41 |  | 235–236[a] | 48 | $C_{28}H_{32}N_2O_5$ | 70.57 | 6.77 | 5.88 | 70.51 | 6.91 | 5.64 |

[a] Melts with decomposition.

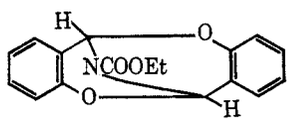
CHART I



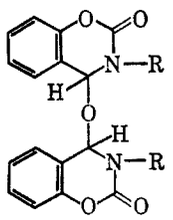
**1a**, $R_2$ = H; $R_1$ = $CH_3$; $R_3$ = H or $NO_2$
**b**, $R_2$ = CONHR; $R_1$ = $CH_3$ or $C_6H_5$; $R_3$ = H or $NO_2$



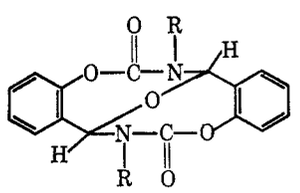
**2**, R = $CH_3$



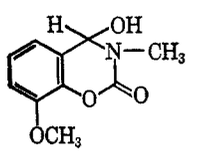
**4**



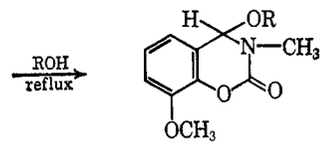
**3**, R = $CH_3$



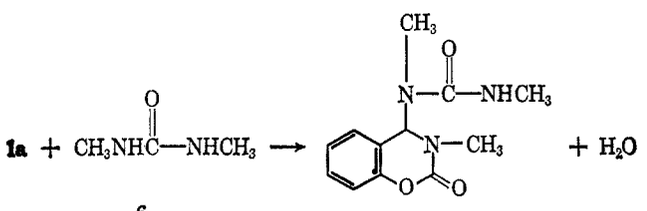
**3x**



**1g**

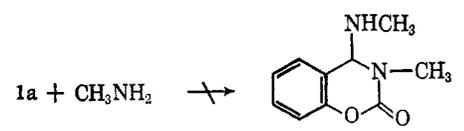


**5c**, R = $CH_3$
**d**, R = $C_2H_5$



**6**

**2**



**7**

tions and exhibit strong bands in the 1715–1725 and 940–970-$cm^{-1}$ regions. The nmr spectrum of the N-ethyl analog of **3** (Figure 1) determined in deuteriochloroform shows two benzylic protons as a singlet at $\delta$ = 5.73 ppm and two methyl groups as a triplet at 1.13 ppm with a coupling constant ($J_{CH_3,CH_2}$) of 7.0 cps. The methylene protons resonate as two sextets centered at 3.10 and 3.78 ppm with an apparent coupling constant of 7.0 cps. In order to explain this pattern, nonequivalency of the N-methylene protons must be assumed, presumably as a result of the proximity of the asymmetric benzylic carbon.[2] The sextet pattern is explained by a geminal coupling constant of 14 cps[3] and vicinal $J$ of 7.0 cps.[4] The nmr spectrum of **3** (R = $CH_3$) determined in deuteriochloroform displays a signal of the methyl groups at $\delta$ = 2.71 ppm as a five-proton singlet and two half-proton singlets at 3.12 and 3.24 ppm. The benzylic protons resonate as a singlet at 5.62 ppm. When determined in deuterated dimethyl sulfoxide, the spectrum exhibits a singlet corresponding to the five methyl protons at 2.92 and a one methyl proton singlet at 3.09 ppm; the benzylic protons appear as two nearly equal peaks at 6.08 and 6.15 ppm. Temperature variations in the 30–135° range did not cause any change in the spectrum.[5]

The possibility that compound **3** might, in fact, have structure **3x** (compatible with the spectral evidence) was considered on the basis of a possible analogy with the product of reaction of salicylaldehyde with ethyl carbamate, known[6] to have structure **4**. Structure **3x** was ruled out on the basis of the following facts. (a) Compound **3** may be produced by treatment of **1a**

(2) (a) A. H. Lewin, J. Lipowitz, and T. Cohen, *Tetrahedron Letters*, No. 18, 1241 (1965); (b) P. L. Southwick, J. A. Fitzgerald, and G. E. Milliman, *ibid.*, **18**, 1247 (1965); (c) R. K. Hill and Tak-Hang Chan, *Tetrahedron*, **21**, 2015 (1965); (d) K. M. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965.

(3) The coupling constant of the geminal protons is usually found in the range 12–15 cps which is approximately twice that of the vicinal protons: L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1964, p 85.

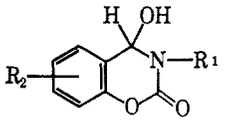
(4) The coupling constants were read from a spectrum recorded at 100 Mcps; so the first-order treatment is fairly justified.

(5) The reason for the multiplicity of the $CH_3$ protons (in either $CDCl_3$ or DMSO-*d*) and of the benzylic protons (in DMSO-*d*) is not entirely clear but may point to the existence of an equilibrium between the two possible diastereoisomers of **3** and/or less likely the alternate structure **3x**.

(6) R. Merten and G. Mueller, *Ber.*, **97**, 682 (1964).

TABLE II

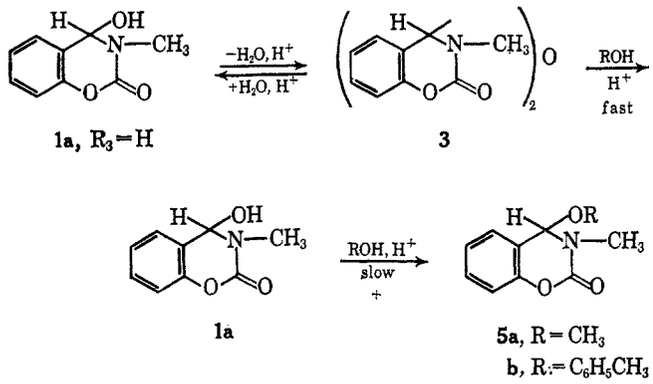
3,4-DIHYDRO-4-HYDROXY-3-ALKYL-2H-1,3-BENZOXAZIN-2-ONES



| Compd | $R_1$ | $R_2$ | Mp, °C | Yield, % | Formula | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1a | $CH_3$ | H | 127–128[a,b] | 83 | $C_9H_9NO_3$ | 60.33 | 5.06 | 7.82 | 60.55 | 5.06 | 7.58 |
| 1b | $C_2H_5$ | H | 100–101 | 63 | $C_{10}H_{11}NO_3$ | 62.16 | 5.74 | 7.25 | 62.28 | 5.89 | 7.34 |
| 1c | $CH_2CH=CH_2$ | H | 107–108 | 56 | $C_{11}H_{11}NO_3$ | 64.38 | 5.40 | 6.83 | 64.58 | 5.54 | 6.63 |
| 1d | $CH_2CH=CH_2$ | 6-Cl | 143–144[b] | 60 | $C_{11}H_{10}ClNO_3$ | 55.13 | 4.21 | 5.84 | 55.17 | 4.20 | 5.74 |
| 1e | $CH_2CH=CH_2$ | 8-$OCH_3$ | 112–114 | 79 | $C_{12}H_{13}NO_4$ | 61.27 | 5.57 | 5.96 | 61.26 | 5.58 | 5.98 |
| 1f | $CH_2CH=CH_2$ | 7-OCONHCH$_3$ | 100.5–102 | 58 | $C_{13}H_{14}N_2O_5$ | 59.20 | 5.30 | 9.21 | 58.92 | 5.44 | 9.30 |
| 1g | $CH_3$ | 8-$OCH_3$ | 162–163[a] | 62 | $C_{10}H_{11}NO_4$ | | | | | | |
| 1h |  | H | 141.5–143[b] | 38[c] | $C_{14}H_{17}NO_3$ | 67.99 | 6.93 | 5.66 | 67.75 | 6.82 | 5.79 |
| 1i | $CH_2COOC_2H_5$ | H | 103.5–105 | 61 | $C_{12}H_{13}NO_5$ | 57.37 | 5.22 | 5.58 | 57.22 | 5.27 | 5.86 |

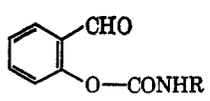
[a] The preparation of **1a** (mp 123°) and **1g** (mp 156–158°) has been described by R. E. Strube and F. A. MacKellar.[1] [b] Melts with decomposition. [c] The low yield is due to the concurrent formation of type **3** compound.

($R_3$ = H) with acid[7] and is reconverted to **1a** by treatment with aqueous solvents in the presence of acids. (b) Structure **3** is analogous to that of compounds **5a** and **5b** obtained by treatment of **1a** with methanol or benzyl alcohol, respectively, and to that of compounds **5c** and **5d** similarly obtained by treatment of the 8-methoxy analog (**1g**) of **1a** with methanol or ethanol. (c) Treatment of **3** with methanol or benzyl alcohol and a trace of acid gives a mixture of equimolar quantities of **1a** and its methyl (**5a**) or benzyl (**5b**) ethers, respectively. Only upon prolonged refluxing is the entire material converted to the ethers (**5a** and **5b**). This finding is readily rationalized as a nucleophilic attack of the alcohol on protonated **3**; it cannot be rationalized on the basis of reasonable transformations starting with dimer structure **3x**.




The infrared spectrum (Nujol mull) of compound **2** (R = $CH_3$) exhibits a sharp NH peak at 3320, a strong band at 1735 (cyclic carbamate), a strong urea carbonyl band at 1626, and a strong NH deformation absorption band of HNC=O at 1540 $cm^{-1}$.

(7) If the ring structure of **1a** ($R_3$ = H) stays intact during dimerization, it is hard to see how the dimer can be anything other than **3**. However, the possibility exists that **1** is in tautomeric equilibrium with a very small amount (≪1%) of the open aldehyde structure



This structure could dimerize to **3**, which is thus not totally excluded by this particular line of evidence.

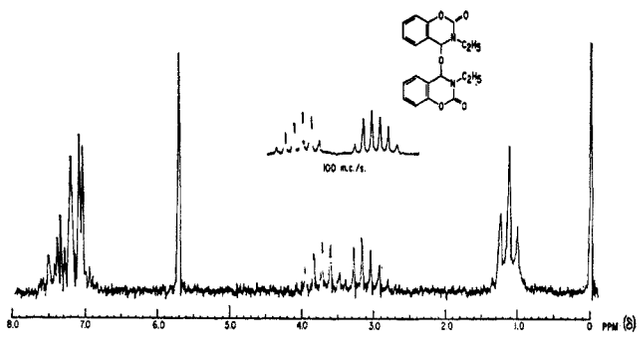


Figure 1.—Nmr spectrum of 4,4′-oxobis(3,4-dihydro-3-ethyl-2H-benzoxazin-2-one).

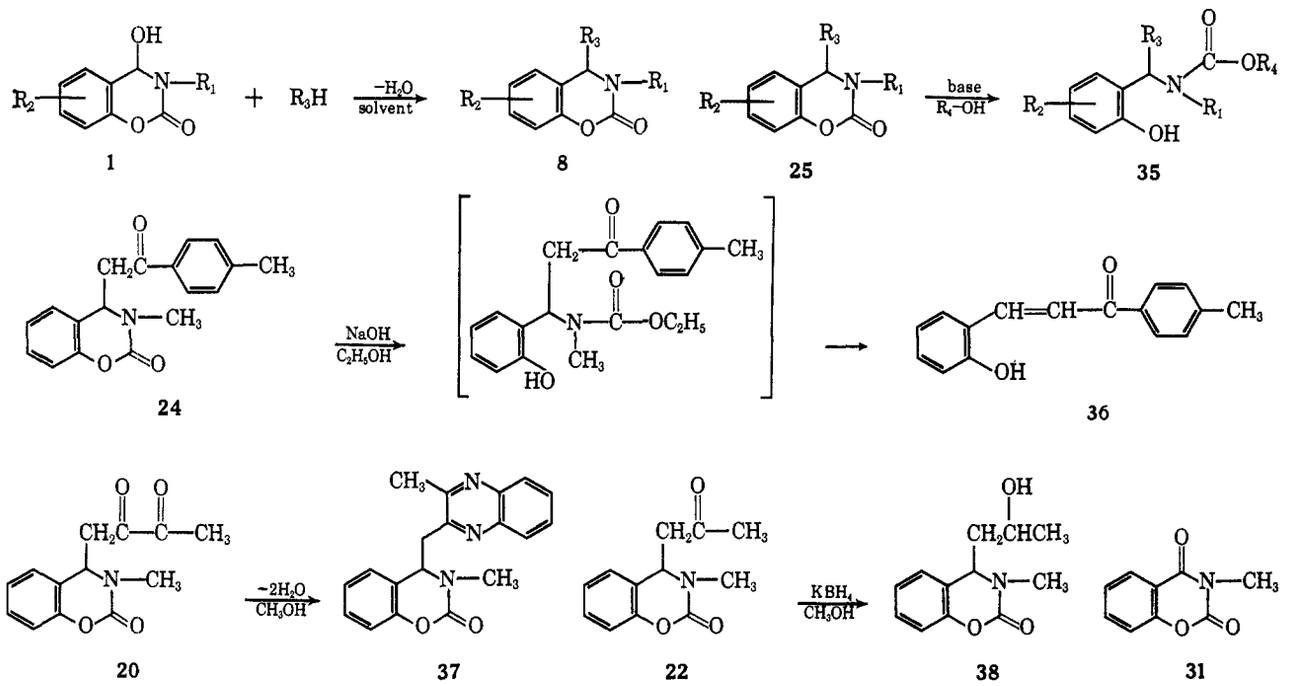
The nmr spectrum ($CDCl_3$) shows a singlet of the benzylic proton at 7.01, a quartet of a NH proton at 5.83 ($J_{NH,CH_3}$ = 4.5 cps), a singlet of methyl protons (cyclic carbamate) at 3.06, a doublet of the terminal methyl at 2.91 ($J_{NH,CH_3}$ = 4.5 cps), and a singlet of $CH_3N$ at 2.58 ppm. The structure of **2** was proved by an independent synthesis consisting of condensation of **1a** with 1,3-dimethylurea. The urea derivative **2** was also formed in *ca.* 45% yield when **1a** was allowed to react with methyl isocyanate in tetrahydrofuran at room temperature. However, when compound **1a** and excess methyl isocyanate were refluxed in benzene solution, compound **2** was obtained in only *ca.* 30% yield, while compound **3a** was the major product (50%). Formation of **3a** in this reaction can be attributed to the dehydrating properties of the isocyanate.

A possible mechanism of the formation of **2** is the reaction of methyl isocyanate with traces of water to form 1,3-dimethylurea (**6**) which, as indicated above, will condense with **1a** to give **2** and more water.

As an alternate mechanism, one might have considered the reaction of methyl isocyanate with traces of water to form methylamine which on reaction with **1a** might have led to methylamino derivative **7**, which upon addition of methyl isocyanate would lead to **2**. However, reaction of **1a** with methylamine failed to give **7**, but returned **1a** unchanged; thus this mechanism is excluded.

Reaction of a variety of ring-substituted *o*-hydroxy aromatic aldehydes with equimolar quantities of various aliphatic isocyanates in ether at room temperature in

CHART II



accordance with the previous work[1] yielded a series of compounds of type **1a** listed in Table II.[8]

It was found that compounds of type **1a**, which may be considered as analogs of the methylolamines ($R_2NCH_2OH$) believed to be intermediates in the formation of Mannich bases, are very useful and versatile intermediates which react with compounds having active hydrogen according to the scheme shown at the top of Chart II (**1** → **8**).

Mineral acids, such as HCl or toluenesulfonic acid catalyze the reaction, although in some cases (*e.g.*, when $R_3H$ is dimedone or benzenesulfonamide) no catalyst is required. Azeotropic removal of water in water-immiscible solvents accelerates the reaction so as to lead to completion within 0.5 to 2 hr. The products are isolated in 75–95% yields. Compounds of type **8** prepared by the above scheme are listed in Table III.

Some of the compounds with active hydrogen required prolonged refluxing to condense with **1a**. In such cases 3-methyl-2H-1,3-benzoxazine-2,4(3H)-dione (**31**)[9] was also isolated as a by-product which apparently resulted from the air oxidation of the hydroxyl function of **1a**.

Several compounds of type **8** have been cleaved by strong inorganic bases at room temperature in the presence of methanol or ethanol to give open-chain carbamic acid derivatives (Table IV). The transformation of **25** to **35** (Chart II) is an example.

In some cases, fission of the benzoxazine ring is also followed by $\beta$ elimination of the carbamate moiety to give an $\alpha,\beta$-unsaturated ketone as is illustrated by the transformation of **24** to **36**.[10]

Compounds of type **8** are, in general, unaffected by organic bases. $\alpha$-Dicarbonyl derivatives may be condensed with $\beta$-diamines to the corresponding dihydropyrazines or quinoxalines. For example, compound **20** condenses with *o*-phenylenediamine to give quinoxaline derivative **37** in good yield (Chart II).

Carbonyl derivatives can be reduced by $KBH_4$ to the corresponding aminoalkanol, as typified by the conversion of **22** to **38**.

It is clear that a wide variety of functionally different compounds may be synthesized from the condensation products of *o*-hydroxy aromatic aldehydes and isocyanates. The utilization of these products for the elaboration of a wide variety of heterocyclic compounds will be the subject of a series of forthcoming papers.

## Experimental Section

Physical constants, yields, and analytical values for the compounds below are reported in Tables I–IV. Melting points were determined using a Thomas–Hoover capillary melting point apparatus which was calibrated against known standards. The ultraviolet and infrared spectra were obtained, respectively, with a Beckman DK-1 spectrophotometer and a Baird Model 455 double-beam spectrograph. Unless otherwise stated, the former were determined as solution in 95% ethanol and the latter as Nujol mulls. The nmr spectra were recorded on a Varian A-60 spectrometer with tetramethylsilane as an internal reference. Thin layer chromatography was carried out on silica gel G (Stahl) using acetone, benzene, and heptane in varying proportions, as the eluent. The chromatograms were developed by spraying with iodine solution in ethanol.

**Preparation of N-Substituted 4,4′-Oxobis(3,4-dihydro-2H-1,3-benzoxazin-2-ones). Type 3 Compounds (Table I). 4,4′-Oxobis(3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one (3). Method A.**—A solution of 22.8 g (0.4 mole) of methyl isocyanate in 25 ml of anhydrous benzene was added with stirring to a solution of 24.4 g (0.2 mole) of salicylaldehyde and 0.2 ml of triethylamine in 25 ml of benzene over a period of 30 min. The reaction was exothermic, causing the solution to reflux and white crystals to form immediately. After the reaction mixture was cooled

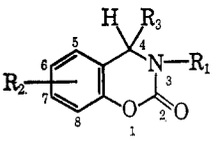
(8) When the reaction of salicylaldehyde and methyl or cyclohexyl isocyanate was carried out in benzene at reflux temperature, compounds **2** and **3** were shown (by infrared and tlc evidence) to be formed in addition to **1**. Compound **2** was isolated in 11% yield for R = $CH_3$ and 4% yield for R = $C_6H_{11}$. These results may explain why the earlier workers[1] were able to obtain **1a** (R = $CH_3$) in only 56% yield when operating in refluxing ether.

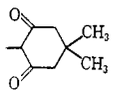
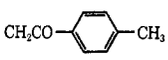
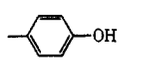
(9) A. Einhorn and C. Mettler, *Ber.*, **38**, 3651 (1905).

(10) Compound **36**, mp 152°, was first reported by S. von Kostanecki and J. Tambor, *ibid.*, **29**, 239 (1896).

TABLE III

4-SUBSTITUTED 3,4-DIHYDRO-3-ALKYL-2H-1,3-BENZOXAZIN-2-ONES



| Compd | $R_1$ | $R_2$ | $R_3$ | Mp, °C | Yield, % | Formula | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | $CH_3$ | H | $CH_3NCONHCH_3$ | 156–157 | 79 | $C_{12}H_{15}N_3O_3$ | 58.14 | 6.19 | 16.61 | 57.82 | 6.07 | 16.86 |
| 8 | $CH_3$ | H | $NHCOOC_2H_5$ | 167–168 | 80 | $C_{12}H_{14}N_2O_4$ | 57.59 | 5.64 | 11.20 | 57.63 | 5.69 | 11.11 |
| 9 | $CH_3$ | 6-Cl | $NHCOOC_2H_5$ | 190–191[a] | 91 | $C_{12}H_{13}ClNO_4$ | 50.63 | 4.60 | 9.84 | 50.61 | 4.75 | 9.97 |
| 10 | $CH_3$ | 7-$OCONHCH_3$ | $NHCOOC_2H_5$ | 175–178[a] | 68 | $C_{14}H_{17}N_3O_6$ | 52.01 | 5.30 | 13.00 | 52.00 | 5.34 | 13.20 |
| 11 | $CH_3$ | 8-$OCH_3$ | $NHCOOC_2H_5$ | 166–167 | 92 | $C_{13}H_{16}N_2O_5$ | 55.71 | 5.75 | 10.00 | 55.75 | 5.80 | 9.72 |
| 12 | $CH_2CH{=}CH_2$ | H | $NHCOOC_2H_5$ | 113–114 | 80 | $C_{14}H_{16}N_2O_4$ | 60.86 | 5.84 | 10.14 | 60.97 | 5.84 | 10.36 |
| 13 | $CH_3$ | H | $N(CH_3)COOC_2H_5$ | 49.5–51 | 50 | $C_{13}H_{16}N_2O_4$ | 59.08 | 6.10 | 10.60 | 59.15 | 6.14 | 10.36 |
| 14 | $CH_3$ | H | $NHSO_2C_6H_5$ | 203–204.5[a] | 97 | $C_{15}H_{14}N_2O_4S$ | 56.59 | 4.43 | 8.80 | 56.50 | 4.39 | 8.91 |
| 15 | $CH_3$ | H |  | 181–182 | 73 | $C_{13}H_{12}N_2O_4$ | 59.99 | 4.65 | 10.77 | 59.70 | 4.92 | 10.68 |
| 16 | $CH_3$ | H |  | 196–197[a] | 97 | $C_{17}H_{19}NO_4$ | 67.76 | 6.36 | 4.65 | 68.06 | 6.51 | 4.89 |
| 17 | $CH_3$ | H | $CH_3COCHCOCH_3$ | 136–138 | 92 | $C_{14}H_{15}NO_4$ | 64.36 | 5.79 | 5.36 | 64.34 | 5.91 | 5.27 |
| 18 | $CH_3$ | H | $CH_3COCHCOOC_2H_5$ | 140–141 | 88 | $C_{15}H_{17}NO_5$ | 61.85 | 5.88 | 4.81 | 61.85 | 6.02 | 5.00 |
| 19 | $CH_3$ | H | $CH_3COCHCOC_6H_5$ | 163–165[a] | 60 | $C_{19}H_{17}NO_4$ | 70.57 | 5.30 | 4.33 | 70.44 | 5.40 | 4.55 |
| 20[b] | $CH_3$ | H | $CH_2COCOCH_3$ | 143–144.5[a] | 45 | $C_{13}H_{13}NO_4$ | 63.15 | 5.30 | 5.67 | 63.21 | 5.59 | 5.57 |
| 21 | $CH_3$ | H | $CH_3COCC_6H_5CN$ | 160–161 | 91 | $C_{19}H_{16}N_2O_3$ | 71.24 | 5.03 | 8.75 | 70.95 | 5.32 | 8.50 |
| 22 | $CH_3$ | H | $CH_2COCH_3$ | 95–96.5 | 86 | $C_{12}H_{13}NO_3$ | 65.74 | 5.98 | 6.39 | 65.72 | 6.02 | 6.47 |
| 23 | $CH_3$ | H | $CH_2COCH_2Cl$ | 162–164[a] | 35 | $C_{12}H_{12}ClNO_3$ | 56.82 | 4.77 | 5.52 | 57.09 | 4.92 | 5.59 |
| 24 | $CH_3$ | H |  | 153–154 | 88 | $C_{18}H_{17}NO_3$ | 73.20 | 5.80 | 4.74 | 73.35 | 5.91 | 4.61 |
| 25 | $CH_3$ | H |  | 151.5–153 | 86 | $C_{15}H_{17}NO_3$ | 69.48 | 6.61 | 5.40 | 69.56 | 6.81 | 5.16 |
| 26 | $CH_3$ | H |  | 123–124 | 94 | $C_{13}H_{11}NO_3$ | 68.11 | 4.84 | 6.11 | 68.38 | 5.02 | 6.16 |
| 27 | $CH_3$ | H |  | 130–131.5 | 90 | $C_{14}H_{13}NO_3$ | 69.12 | 5.39 | 5.76 | 69.24 | 5.42 | 5.59 |
| 28 | $CH_3$ | H |  | 136–137 | 82 | $C_{13}H_{11}NO_2S$ | 63.65 | 4.52 | 5.71 | 63.91 | 4.57 | 5.83 |
| 29 | $CH_3$ | H |  | 219–220 | 67 | $C_{15}H_{13}NO_3$ | 70.58 | 5.13 | 5.49 | 70.88 | 5.34 | 5.21 |
| 30 | $CH_2CH{=}CH_2$ | 6-Cl | $NHCOOC_2H_5$ | 156–158[a] | 89 | $C_{14}H_{15}Cl_2O_4$ | 54.11 | 4.87 | 9.01 | 54.35 | 4.97 | 8.82 |

[a] Melts with decomposition. [b] Yellow crystals.

to room temperature and allowed to stand overnight, 19.2 g of white crystals was collected, mp 204–206° dec. Recrystallization from benzene and then from acetonitrile gave analytically pure white crystals: mp 220–221° dec; $\lambda_{max}$ 266.5 mμ (ε 2370), 273.5 mμ (ε 2200); $\nu_{max}^{CHCl_3}$ 1730 (cyclic carbamate), 978 (ether) $cm^{-1}$. The Nujol mull spectrum resembled the chloroform solution spectrum closely, which makes unlikely the existence of an equilibrium such as **3** ⇄ **3x**.

**Method B.**—A solution of 3.0 g (0.068 mole) of 3,4-dihydro-4-hydroxy-3-methyl-2H-1,3-benzoxazin-2-one (**1a**) and 0.01 g of *p*-toluenesulfonic acid monohydrate in 60 ml of anhydrous benzene was refluxed for 2 hr, and 0.15 ml of water separated in a Dean–Stark trap. Concentration of the solution to *ca.* 30 ml and cooling gave 1.7 g of white crystals which melted with decomposition at 207–209°. Recrystallization from benzene gave pure **3**, mp 220–221° dec. A mixture melting point with the sample obtained by method A was not depressed.

**Method C.**—A solution of 5.0 g (0.028 mole) of **1a** and 3.2 g (2 equiv) of methyl isocyanate in 100 ml of anhydrous benzene was refluxed for 1 hr. Concentration of the solution to *ca.* 50 ml and cooling gave 2.4 g of **3**, mp 217–219° dec. Evaporation of the mother liquor and trituration of the residue with ethyl acetate gave 1.6 g of 1-(3,4-dihydro-3-methyl-2-oxo-2H-1,3-benzoxazin-4-yl)-1,3-dimethylurea (**2**), mp 152–154°.

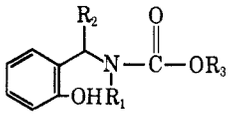
Applying the same general procedure (method A), compounds listed in Table I were prepared. In some cases (**39**) tetrahydrofuran instead of benzene was used. The products were recrystallized from tetrahydrofuran–dimethylformamide (**39**), ethanol (**40**), and ethyl acetate (**41**). The purity of products, besides the elemental analyses, was also checked by thin layer chromatography (tlc).

Chromatography of the original mother liquor (from the preparation of **3**, method A) over 160 g of magnesium silicate (Florisil, 100–200 mesh) using benzene and chloroform, consecutively as eluents, gave 12.2 g of crude 1-(3,4-dihydro-3-methyl-2-oxo-2H-1,3-benzoxazin-4-yl)-1,3-dimethylurea (**2**), mp 145–150°, and 5.1 g of 3,4-dihydro-4-hydroxy-3-methyl-1,3-benzoxazin-2-one (**1a**), mp 125–127°.

**Cleavage of 4,4′-Oxobis(3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one) (3) to Give 1a. A. In Aqueous Ethanol.**—Compound **3** (2.0 g, 0.0059 mole) in 40 ml of 80% aqueous ethanol containing 0.01 g of *p*-toluenesulfonic acid monohydrate was re-

TABLE IV

SOLVOLYSIS PRODUCTS OF 4-SUBSTITUTED 3,4-DIHYDRO-3-ALKYL-2H-1,3-BENZOXAZIN-2-ONES



| Compd | $R_1$ | $R_2$ | $R_3$ | Mp, °C | Yield, % | Formula | Calcd, % C | Calcd, % H | Calcd, % N | Found, % C | Found, % H | Found, % N |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 32 | $CH_3$ |  | $CH_3$ | 140–141[a] | 71 | $C_{14}H_{15}NO_4$ | 64.36 | 5.79 | 5.36 | 64.61 | 5.89 | 6.44 |
| 33 | $CH_3$ |  | $C_2H_5$ | 104.5–106 | 79 | $C_{15}H_{17}NO_4$ | 65.44 | 6.22 | 5.09 | 65.36 | 6.27 | 4.96 |
| 34 | $CH_3$ |  | $CH_3$ | 100–101[a] | 88 | $C_{15}H_{17}NO_4$ | 65.44 | 6.22 | 5.09 | 65.14 | 6.25 | 5.26 |
| 35 | $CH_3$ |  | $C_2H_5$ | 248–249[a] | 64 | $C_{17}H_{23}NO_4$ | 66.86 | 7.59 | 4.59 | 66.77 | 7.63 | 4.46 |

[a] Melts with decomposition.

fluxed for 30 min when the solution became clear. Subsequent thin layer chromatography (silica gel G; acetone–benzene–heptane, 2:2:1) showed absence of **3**, the new product having identical mobility with **1a**, $R_f$ 0.26. The solvent was evaporated and the residue triturated with isopropyl ether–ethyl acetate to give 1.4 g of white crystals, mp 125–127° dec. Recrystallization from ethyl acetate gave pure 3,4-dihydro-4-hydroxy-3-methyl-2H-1,3-benzoxazin-2-one (**1a**), mp 127–128° dec. A mixture melting point with an analytically pure **1a** was not depressed.

**B.**—Essentially the same result was obtained in aqueous tetrahydrofuran.

**C. Direct Conversion of Compound 3 to 4-Alkoxy Derivatives. 3,4-Dihydro-4-methoxy-3-methyl-2H-1,3-benzoxazin-2-one (5a).**—To a refluxing suspension of 8 g (0.0275 mole) of 4,4′-oxobis(3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one) (**3**) in 100 ml of absolute methanol was added 0.01 g of *p*-toluenesulfonic acid monohydrate, and the solution became complete within 2 min. At this point thin layer chromatography (the same system as in the previous experiment) showed a 1:1 mixture of **1a** ($R_f$ 0.26) and **5a** ($R_f$ 0.58), the starting material **3** ($R_f$ 0.3) being absent. After the solution was refluxed for 5 hr the conversion to **5a** ($R_f$ 0.58) was complete. The solvent was removed and the colorless oily residue was vacuum distilled to give two fractions, 0.7 g, bp 132–135° (0.20 mm), and 5.1 g of analytically pure colorless oil: bp 135–136° (0.20 mm); $\lambda_{max}$ 266 mμ (ε 1040), 274 mμ (ε 980); $\nu_{max}^{CHCl_3}$ 1725 (cyclic carbamate), 1060 (ether) cm$^{-1}$; δ 2.98 ($NCH_3$), 3.16 ($OCH_3$), 5.74 (benzylic proton).

*Anal.* Calcd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 61.95; H, 5.92; N, 7.43.

**D. 4-(Benzyloxy)-3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one (5b).**—To a refluxing mixture of 5 g (0.0147 mole) of 4,4′-oxobis(3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one) (**3**) and 10 g of benzyl alcohol in 30 ml of dry tetrahydrofuran was added 0.01 g of *p*-toluenesulfonic acid monohydrate and the solution became complete within 1 min. Subsequent thin layer chromatography showed a 1:1 mixture of **1a** ($R_f$ 0.26) and **5b** ($R_f$ 0.60). After the refluxing was continued for 6 hr the conversion to **5b** ($R_f$ 0.60) was complete. Evaporation of the solvent and excess benzyl alcohol gave a nearly colorless semisolid which on trituration with isopropyl ether–cyclohexane (2:1) yielded 5.1 g (68%) of 4-benzyloxy-3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one (**5b**) as white crystals, mp 94–95°. Recrystallization from isopropyl ether gave analytically pure product: mp 95–96°; $\lambda_{max}$ 266 mμ (ε 1600), 273 mμ (ε 1400); $\nu_{max}^{CHCl_3}$ 1727, 1718 (cyclic carbamate), 1040, 1020 (ether) cm$^{-1}$.

The methylene part of the benzyl group was seen as an AB pattern of two slightly nonequivalent protons, owing to the proximity of the asymmetric center in the heteroring (see discussion in text regarding the similar situation with respect to the spectrum shown in Figure 1).

*Anal.* Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.44; H, 5.72; N, 5.16.

**Transformation of 5a into 5b.**—A solution of 2.5 g (0.0137 mole) of **5a**, 5g of benzyl alcohol, and 0.005 g of *p*-toluenesulfonic acid monohydrate was heated on a steam bath for 1 hr, after which time the conversion to **5b** was complete. The excess benzyl alcohol was removed *in vacuo* and the nearly colorless semisolid was triturated with isopropyl ether to give 2.3 g (66%) of pure **5b**, mp 95–96°.

**3,4-Dihydro-4,8-dimethoxy-3-methyl-2H-1,3-benzoxazin-2-one (5c).**—3,4-Dihydro-4-hydroxy-8-methoxy-3-methyl-2H-1,3-benzoxazin-2-one[1] (3.0 g, 0.0145 mole) in 60 ml of anhydrous methanol was refluxed for 72 hr. Concentration of the solution to *ca.* 10 ml and cooling gave 1.5 g of white crystals, mp 87–89°. Evaporation of the mother liquor and trituration of the residue with cyclohexane–ether gave an additional crop of 0.45 g of crystalline material, mp 85–88°. Recrystallization of the first crop from ethanol gave an analytically pure product: mp 88–90°; $\lambda_{max}$ 223 mμ (ε 5850), 274 (1720), 280 (1660); $\nu_{max}^{CHCl_3}$ 1730 (cyclic carbamate), 1270 (aromatic ether), 1130 (aliphatic ether), 1062 (aliphatic ether) cm$^{-1}$; δ 2.98 ($NCH_3$), 3.17 (4-$OCH_3$), 3.90 (8-$OCH_3$), 5.73 (benzylic proton).

*Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.44; H, 5.95; N, 6.40.

**3,4-Dihydro-4-ethoxy-8-methoxy-3-methyl-2H-1,3-benzoxazin-2-one (5d).**—Following the above procedure 1g[1] (8.0 g, 0.0387 mole) was refluxed in absolute ethanol for 3 days. After the removal of solvent, the residue was crystallized from isopropyl ether to give 6.8 g of nearly white, crystalline material, mp 68–70°. Recrystallization from ethyl ether–isopropyl ether (1:1) gave analytically pure, white crystals, mp 69.5–71°.

*Anal.* Calcd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.75; H, 6.41; N, 5.63.

**Preparation of 3,4-Dihydro-4-hydroxy-3-alkyl-2H-1,3-benzoxazin-2-ones. Type 1 Compounds (Table II). General Procedure.**—Equimolar quantities of an *o*-hydroxy aromatic aldehyde and an isocyanate in ether solution, containing a catalytic amount of triethylamine, was allowed to stand at room temperature for 1 to 5 days. The crystalline precipitate was filtered off and the filtrate was concentrated to give an additional amount of the product. Those aldehydes which are insufficiently soluble in ether were first dissolved in anhydrous tetrahydrofuran and then diluted with ether. Single recrystallization from ethyl acetate usually gave analytically pure products.

**Preparation of 4-Substituted 3,4-Dihydro-3-alkyl-2H-1,3-benzoxazin-2-ones (Table III). General Procedure.**—Equimolar quantities of 3,4-dihydro-3-alkyl-4-hydroxy-2H-1,3-benzoxazin-2-one (type 1), a compound having active hydrogen, and a catalytic amount of *p*-toluenesulfonic acid in benzene or chloroform solution were refluxed for 0.5 to 2 hr with azeotropic removal of water. After removal of solvent, the residue was recrystallized from ethanol (compounds **9**, **17**, **18**, **20**, **25**, **27**, and **28**), methanol (**19**, **24**, and **29**), isopropyl alcohol (**10** and **11**), ethyl acetate (**2**, **14**, **16**, and **23**), or combination of solvents (cyclohexane–ethyl acetate, **12**; ethanol–ethyl acetate, **26**; eth-

anol–ether, 21). In some cases the analytically pure products were obtained on concentration of the reaction solution (13 and 15).

The above general procedure is illustrated by the following detailed description of the preparation of compound 2 (method A).

**1-(3,4-Dihydro-3-methyl-2-oxo-2H-1,3-benzoxazin-4-yl)-1,3-dimethylurea (2). Method A.**—A solution of 8.0 g (0.0446 mole) of 3,4-dihydro-4-hydroxy-3-methyl-2H-1,3-benzoxazin-2-one (1a), 4.3 g (0.05 mole) of 1,3-dimethylurea, and 0.01 g of *p*-toluenesulfonic acid monohydrate in 180 ml of anhydrous benzene was refluxed for 0.5 hr, while 0.8 ml of water separated in a Dean–Stark trap. Concentration of the solution to *ca.* 80 ml gave 8.7 g of white crystals, mp 154–156°. Recrystallization from ethyl acetate gave an analytically pure product: mp 156–157°; $\lambda_{max}$ 267 mμ (ε 1190), 274 mμ (ε 1150); $\nu_{max}$ 3320 (NH), 1733 (cyclic carbamate), 1626 (urea C=O), 1540 (NH-C=O, deformation) cm$^{-1}$.

**Method B.**—A solution of 4.0 g (0.0223 mole) of 1a, 3.54 g (0.062 mole) of methyl isocyanate, and 0.2 g of triethylamine in 30 ml of tetrahydrofuran was allowed to stand for 3 days at room temperature. The resulting white, crystalline material (1.8 g) was collected by filtration, mp 153–155°. Evaporation of the mother liquor *in vacuo* and trituration of the residue with ethyl acetate gave an additional crop of white crystals, mp 152–155°. The recrystallized product was identical in all respects with 2 obtained by method A.

**3,4-Dihydro-2,4-dioxo-3-methyl-2H-1,3-benzoxazine (31).**—A solution of 5.0 g (0.028 mole) of 3,4-dihydro-4-hydroxy-3-methyl-2H-1,3-benzoxazin-2-one (1a), 10.0 g (0.116 mole) of diacetyl, and 0.02 g of *p*-toluenesulfonic acid monohydrate in 150 ml of anhydrous benzene was refluxed for 3 hr while 0.45 ml of water separated in a Dean–Stark trap. After the solvent was removed *in vacuo*, the orange residue was crystallized from ethanol to give 3.1 g of 1-(3,4-dihydro-3-methyl-2-oxo-2H-1,3-benzoxazin-4-yl)-2,3-butanedione (20, Table III), as yellow crystals. The mother liquor was evaporated to dryness. The residue was refluxed with 100 ml of ether for 1 hr and the hot mixture was filtered to give an additional amount of crude 20. The filtrate was evaporated and triturated with ethanol to give 0.7 g of crystals, mp 145–147°. Recrystallization from ethanol gave analytically pure, white crystals, mp 147–148° (lit.[9] mp 146°).

*Anal.* Calcd for $C_9H_7NO_3$: C, 61.02; H, 3.98; N, 7.91. Found: C, 61.23; H, 4.09; N, 7.72.

**Solvolysis Products of 4-Substituted 3,4-Dihydro-3-alkyl-2H-1,3-benzoxazin-2-ones (Table IV). General Procedure.**—A compound of type 8 and 2 equiv of sodium hydroxide pellets were stirred in an anhydrous alcohol for 0.5 hr and the resulting, clear solution was allowed to stand for 1 to 3 hr at room temperature. The solvent was removed *in vacuo* below 30° and the residue was dissolved in a small amount of water. The resulting solution was adjusted to pH 5.0 with acetic acid and extracted with chloroform. The extracts were dried over sodium sulfate and the solvent was evaporated *in vacuo*. The residue was recrystallized from methanol (compound 32), cyclohexane (33), ether–cyclohexane (34), and ethyl acetate (35). When compound 24 was treated with sodium hydroxide in ethanol and worked up according to the above general procedure, the resulting solvolysis product underwent β elimination of carbamate group to give *p*-tolyl (2-oxystyryl) ketone (36) in 79% yield as yellow crystals: mp 162–163° dec;[10] $\lambda_{max}$ 256 mμ sh (ε 8000), 300 (18,000) 354 (15,500); $\nu_{max}^{CHCl_3}$ 3580 (free OH), 3230 (associated OH), 1658 (C=O), 1608 (conjugated C=C), 1586 (conjugated aromatic ring), 1330 (deformation, CO) cm$^{-1}$.

*Anal.* Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.85; H, 5.88.

**2-(3,4-Dihydro-3-methyl-2-oxo-2H-1,3-benzoxazin-4-ylmethyl)-3-methylquinoxaline (37).**—A solution of 3.0 g (0.0121 mole) of 1-(3,4-dihydro-3-methyl-2-oxo-2H-1,3-benzoxazin-4-yl)-2,3-butanedione (20), and 1.3 g (0.0121 mole) of *o*-phenylenediamine in 25 ml of methanol was refluxed for 3 hr. Concentration of the solution to a low volume and cooling gave 2.7 g of an off-white, crystalline product, mp 137–139°. Recrystallization from ethanol gave analytically pure, white crystals: mp 139–140°; $\lambda_{max}$ 237 mμ (ε 29,000), 261–276 plateau (3200), 319 (8350); $\nu_{max}$ 1710 (cyclic carbamate) cm$^{-1}$.

*Anal.* Calcd for $C_{19}H_{17}N_3O_2$: C, 71.45; H, 5.37; N, 13.16. Found: C, 71.31; H, 5.44; N, 13.27.

**3,4-Dihydro-4-(2-hydroxypropyl)-3-methyl-1,3-benzoxazin-2-one (38).**—A mixture of 2.0 g (0.0091 mole) of 4-(1-acetonyl)-3,4-dihydro-3-methyl-2H-1,3-benzoxazin-2-one (22) and 0.8 g (0.0145 mole) of $KBH_4$ in 25 ml methanol was stirred until a clear solution resulted. After an additional 2 hr at room temperature, the solvent was removed *in vacuo* at 25°. The residue was taken up with water and extracted twice with 25 ml of ethyl acetate. The combined extracts were dried over sodium sulfate and concentrated to a low volume to give 1.5 g of off-white crystals, mp 240–243°. Recrystallization from ethyl acetate gave an analytically pure white product: mp 245.5–247°; $\lambda_{max}$ 215 mμ (ε 7400), 274 (2870), 280 sh (2550); $\nu_{max}$ 3040 (associated OH), 1664 (H-bonded cyclic carbamate), 1250, 1078 (CO) cm$^{-1}$.

*Anal.* Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.84; H, 6.84; N, 6.36.

**Registry No.**—**3,** 7690-99-5; **2,** 7688-15-5; **1a,** 941-88-8; **5a,** 7687-90-3; **5b,** 7687-91-4; **5c,** 7687-92-5; **5d,** 7687-93-6; **31,** 1672-01-1; **36,** 7645-95-6; **37,** 7645-96-7; **38,** 7645-97-8; **39,** 7645-98-9; **40,** 7645-99-0; **41,** 7646-00-6; **1b,** 7646-01-7; **1c,** 7646-02-8; **1d,** 7646-03-9; **1e,** 7646-04-0; **1f,** 7646-05-1; **1g,** 947-71-7; **1h,** 7646-07-3; **1i,** 7646-08-4; **8,** 7646-09-5; **9,** 7646-10-8; **10,** 7678-08-2; **11,** 7687-94-7; **12,** 7646-11-9; **13,** 7646-12-0; **14,** 7646-13-1; **15,** 7646-14-2; **16,** 7646-15-3; **17,** 7646-16-4; **18,** 7646-17-5; **19,** 7646-18-6; **20,** 7646-19-7; **21,** 7646-20-0; **22,** 7646-21-5; **23,** 7646-22-2; **24,** 7678-09-3; **25,** 7646-23-3; **26,** 7646-24-4; **27,** 7646-25-5; **28,** 7646-26-6; **29,** 7646-27-7; **30,** 7646-28-8; **32,** 7646-29-9; **33,** 7646-30-2; **34,** 7646-31-3; **35,** 7678-10-6.

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