ersity) and to the Science and Engineering Research Council (SERC) for the provision of the 400-MHz NMR spectra; to K. C. Farrow (Aston University, U.K.), Dr. J. A. Ballantine (University College, Swansea, U.K.), the Physico Chemical Measurements Unit (Harwell, U.K.), and the SERC for the electron impact and FAB mass spectra; to Dr. T. A. Baillie and Dr. P. G. Pearson (University of Washington) for LSIMS and FAB mass spectra; and to Glaxo Group Research, Ltd., for provision of the polarimeter. Thanks are also due to J. Zuilhof for technical assistance. Generous financial support for this work was provided by the Cancer Research Campaign of Great Britain and by NATO.

Registry No. **2a**, 120033-44-5; **3a**, 120033-45-6; **3b**, 120033-68-3; **4a**, 120033-46-7; **4b**, 120033-69-4; **4c**, 120033-70-7; **5c**, 120033-71-8; **6**, 616-91-1; **7**, 120033-47-8; **8**, 18598-63-5; **9**, 55757-46-5; **10**, 20887-95-0; **11a**, 120033-48-9; **11b**, 120144-33-4; **12**, 120033-49-0; **13**, 34592-47-7; **14**, 96402-64-1; **14**·$(i\text{-Pr})_2$NH, 120033-72-9; **15**, 120033-50-3; **16**, 120033-51-4; **17**, 120033-52-5; **18**, 51077-16-8; **19**, 120033-53-6; **20**, 120033-54-7; **22**, 120033-55-8; **23**, 120033-56-9; **24**, 120033-57-0; **25**, 120033-58-1; **26a**, 30044-61-2; **26b**, 10389-65-8; **26c**, 6968-11-2; **27**, 120033-59-2; **28a**, 120033-60-5; **28b**, 120033-73-0; **29a**, 120033-61-6; **29b**, 120033-74-1; **29c**, 24948-53-6; **30**, 58036-46-7; **31a**, 120033-62-7; **31b**, 120033-75-2; **32**, 120033-63-8; **33**, 82152-24-7; **34**, 120033-64-9; **35**, 120033-65-0; **36**, 120033-66-1; **37**, 118448-76-3; **38**, 120033-67-2; MeNCO, 624-83-9; H-Cys-OH·HCl, 52-89-1; EtNCO, 109-90-0; Me_2NCOCl, 79-44-7; $PhCH_2OCOCl$, 501-53-1; H-Gly-OCH_2Ph·TsOH, 1738-76-7; H-Gly-OMe·HCl, 5680-79-5; H-Gly-OBu-*t*·HCl, 27532-96-3; H-Cys(SBu-*t*)-Gly-OH·DCl, 120033-76-3; *t*-BuSH, 75-66-1.

A New Synthetic Method for the 2-Substitution of N-Unsubstituted Benzimidazoles: Formaldehyde as a Versatile Protecting Agent for Heterocyclic NH[1]

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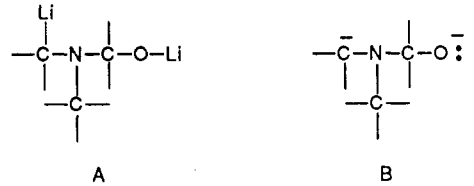
N-Unsubstituted benzimidazoles **1** are readily converted in a one-pot sequence into 2-substituted derivatives **2** with good overall yields. N-Protection with formaldehyde and lithiation with lithium *N,N*-diisopropylamide (LDA), *n*-butyllithium, or *tert*-butyllithium gives the dilithiohemiaminals **6**, which readily react with a range of electrophiles at the 2-carbon. The 2-substituted 1-(lithioxymethyl)benzimidazoles **7** undergo smooth acid-catalyzed dehydroxymethylation under mild conditions to give N-unsubstituted 2-substituted benzimidazoles **2**.

In connection with our investigations of methodologies for the protection of amines and alcohols during functionalization using carbon dioxide as the source of protecting group,[2] we have been seeking alternative protecting groups that satisfy our criterion that both protection and deprotection should work well under conditions mild enough not to damage sensitive functionalities. We focused our search for a group that could be used for systems when the carbon dioxide method failed, as for heterocyclic NH in rings containing more than one heteroatom.[3] We now report a solution to this problem.

Hemiaminals are well known as unstable intermediates in the reactions of aldehydes and ketones with amines and some are stable enough to isolate.[4] Most stable hemiaminals contain electron-withdrawing groups attached to the nitrogen atom as in those derived from benzotriazole,[5] phthalimide,[6] and succinimide.[7] The chemistry of hemiaminals is for the most part unexplored although recent publications from our laboratory have described a series of benzotriazole hemiaminals.[8]

We anticipated that hemiaminal formation could provide potential protection for the functionalization of certain NH compounds since some hemiaminals are readily prepared from the nitrogen compound and aldehyde and are readily converted back into the NH derivative under mild acidic conditions at low temperature.[9] Provided a formal hemiaminal oxyanion could survive in the presence of a strong base such as *n*-butyllithium, it seems likely that the subsequent lithiation would occur to afford A, which should be stable, cf. B. Although elimination might be



A B

(1) Paper 1 of our new series Formaldehyde: A Reagent for the Simultaneous Protection of Nucleophilic Centers and the Activation and Stabilization of Alternative Locations to Electrophilic Attack.

(2) Cf. our series Carbon Dioxide: A Reagent for the Simultaneous Protection of Nucleophilic Centers and the Activation of Alternative Locations to Electrophilic Attack. (a) Part 1: Katritzky, A. R.; Akutagawa, K. *Tetrahedron Lett.* **1985**, *26*, 5935. Part 2: Katritzky, A. R.; Akutagawa, K. *Tetrahedron* **1986**, *42*, 2571. Part 3: Katritzky, A. R.; Fan, W.; Akutagawa, K. *Tetrahedron* **1986**, *42*, 4027. Part 4: Katritzky, A. R.; Fan, W.; Akutagawa, K. *Synthesis* **1987**, 415. Part 5: Katritzky, A. R.; Akutagawa, K. *J. Am. Chem. Soc.* **1986**, *108*, 6808 and subsequent papers.

(3) E.g., for benzimidazole, the expected carbamic acid lithium salt is formed by the successive action of *n*-butyllithium and carbon dioxide, but on further treatment with strong base does not undergo 2-metalation, probably because of alkyllithium attack on the carbonyl group of the carbamic anion.

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Table I. Preparation of (*N*-Unsubstituted-benzimidazol-2-yl)phenylcarbinol[a]

entry	CH_2O source	lithiating agent[b]	time (min)[c]	electrophile[d]	2-substituent	yield,[e] %
1	1.0 CH_2O/H_2O	2.5 *t*-BuLi	30	PhCHO	CH(OH)Ph	45
2	1.0 CH_2O/H_2O	2.5 *n*-BuLi	60[f]	PhCHO	CH(OH)Ph	<10
3	1.0 CH_2O/H_2O	2.5 *n*-BuLi	60[f]	Ph_2CO	$C(OH)Ph_2$	<10
4	1.0 CH_2O/H_2O	2.5 *n*-BuLi	20	PhCHO	CH(OH)Ph	46
5	1.0 CH_2O/H_2O	2.5 *n*-BuLi	40	PhCHO	CH(OH)Ph	44
6	1.0 CH_2O/H_2O	2.5 *n*-BuLi	60	PhCHO	CH(OH)Ph	40
7	1.0 CH_2O/H_2O	2.0 *n*-BuLi	30	PhCHO	CH(OH)Ph	65
8	1.0 CH_2O/H_2O	2.1 *n*-BuLi	30	PhCHO	CH(OH)Ph	56
9	1.0 CH_2O/H_2O	2.2 *n*-BuLi	30	PhCHO	CH(OH)Ph	52
10	3.0 $(CH_2O)_n$	2.0 *n*-BuLi	30	PhCHO	CH(OH)Ph	42
11	2.0 $(CH_2O)_n$	2.0 *n*-BuLi	30	PhCHO	CH(OH)Ph	38
12	1.0 $(CH_2O)_n$	2.0 *n*-BuLi	30	PhCHO	CH(OH)Ph	56
13	1.0 CH_2O/H_2O	2.0 LDA	30	PhCHO	CH(OH)Ph	72
14[g]		2.0 *n*-BuLi	60	PhCHO	CH(OH)Ph	62[h]
15[g]		2.0 *s*-BuLi	60	PhCHO	CH(OH)Ph	37[h]
16[g]		2.0 *t*-BuLi	60	PhCHO	CH(OH)Ph	68[h]
17[g]		2.0 LDA	60	PhCHO	CH(OH)Ph	75[h]
18	1.0 CH_2O/H_2O	2.0 *t*-BuLi[i]	50	PhCHO	CH(OH)Ph	50

[a] mp 207.0–209.0 °C, mp (lit.[16a] 208 °C. [b] Lithiating agent added at −78 °C. [c] Time (min) for aging at −20 °C. [d] Electrophile (1.0 to 1.1 equiv) was added at −78 °C. [e] Overall isolated yields after recrystallization of 2-(phenylhydroxymethyl)benzimidazole on the basis of benzimidazole. [f] Time (min) for aging at −50 °C. [g] Prepurified 1-(hydroxymethyl)benzimidazole was used. [h] Overall isolated yields after recrystallization of 2-(phenylhydroxymethyl)benzimidazole on the basis of 1-(hydroxymethyl)benzimidazole. [i] After aging the solution at −20 °C for 50 min, 1.0 equiv of $MgBr_2{\cdot}Et_2O$ was added at −78 °C. The solution was kept at −20 °C for 30 min, and then benzaldehyde was added.

expected at the formal monooxyanion stage, especially with a good leaving group as is found in stable hemiaminals, the reluctance of formaldehyde to exist in the monomeric form[10] was promising. No previous paper has been found in the literature that discusses the possibility of protection as a hemiaminal to enable dimetalation.

We now report the first examples of the dilithiation (second lithiation at the carbon α to nitrogen) of a hemiaminal[11] and demonstrate the synthetic applications of the sequence, using 1-(hydroxymethyl)benzimidazole[6,7,12] as a model. The dilithiation of an N-unsubstituted benzimidazole has not been achieved to our knowledge.[13]

Results and Discussion

Our new reaction sequence consists of three stages: (1) protection; (2) lithiation and substitution; (3) workup and deprotection.

Protection. 1-(Hydroxymethyl)benzimidazole (**3**) was formed[6,7,12,14] by the reaction of benzimidazole (**1**) with a formaldehyde source, CH_2O/H_2O, or paraformaldehyde at 20 °C.

Lithiation and Substitution. Two equivalents of a lithiating agent were then added at −78 °C. We found that *n*-butyllithium, *sec*-butyllithium, *tert*-butyllithium, or LDA all produced the dilithiated benzimidazole **6** smoothly in tetrahydrofuran at −20 °C in less than 30 min. Organometallic **6** was then trapped by the addition of an electrophile at −78 °C, followed by allowing the solution to warm to 20 °C to give the 2-substituted 1-(lithioxymethyl)benzimidazole **7**.

Workup and Deprotection. The reaction mixture was then quenched with aqueous ammonium chloride, diluted with diethyl ether, and extracted with dilute hydrochloric acid. Under these conditions, the hemiaminal **4** suffered spontaneous fission and the desired products **2** were obtained in acceptable overall yields [based on N-unsubstituted benzimidazole **1**]. The results of applying the method to a variety of electrophiles are listed in Table II.

The synthetic method described above is a one-pot method. We have also investigated the dilithiation reaction of prepurified 1-(hydroxymethyl)benzimidazole as a starting material and found that this gave similar results (entries 14, 15, 16, and 17 of Table I and entry 10 of Table II).

The reaction conditions were optimized by using benzaldehyde as the electrophile (Table I). *n*-Butyllithium, *sec*-butyllithium, *tert*-butyllithium, and LDA all gave the desired products in fair to good yields after aging the solution at −20 °C, followed by the reaction with benzaldehyde. The second lithiation at the 2-carbon proceeds slowly at −50 °C (entries 2 and 3) but is completed in less than 30 min in tetrahydrofuran at −20 °C (entries 4, 5, and 6). Excess of the lithiating agent causes lower yields (entries 4, 5, 6, and 9). Paraformaldehyde could be used as the source of formal monomeric formaldehyde, whereas trioxane gave unsatisfactory results in the protection stage. One, two, and three equivalents of paraformaldehyde gave similar results (entries 10, 11, and 12).

As is well known,[15] N-substituted benzimidazoles and imidazoles are generally lithiated at the 2-carbon, and numerous procedures have been suggested for N-protecting groups to enable the lithiation of NH benzimidazoles or imidazoles,[16] most recently a procedure utilizing *N*-[(dialkylamino)methyl] protection from our own group.[17]

(10) Cf. the usual occurrence as metaformaldehyde or paraformaldehyde.

(11) Ortho-lithiation (γ-lithiation to the nitrogen) of α-alkoxidobenzylamines; see: "Heteroatom-Facilitated Lithiations"; Gschwend, H. W., Rodriguez, H. R. *Org. React.* **1979**, *26*, 52–53. Barsky, L.; Gschwend, H. W.; McKenna, J.; Rodriguez, H. R. *J. Org. Chem.* **1976**, *41*, 3651.

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(14) See Experimental Section.

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Table II. One-Pot Preparation of *N*-Unsubstituted-2-substituted-benzimidazoles from Benzimidazole

entry	CH_2O[a] source	lithiating[b] agent	time (min)[c] aging at −20 °C	electrophile[d]	2-substituent	yield,[e] %	mp, °C	lit. mp, °C
0	*f*	*f*	*f*	C_6H_5CHO	$CH(OH)C_6H_5$	38–72	207.0–209.0	208[16a]
1	CH_2O/H_2O	LDA	60	4-CH_3-C_6H_4CHO	$CH(OH)C_6H_4$-CH_3-4	50	78.0–79.0[g] 155.0–157.0	135[16a]
2	CH_2O/H_2O	LDA	55	4-Cl-C_6H_4CHO	$CH(OH)C_6H_4$-Cl-4	55	85.0–89.0,[h] 151.0–152.0	145[16a]
3	CH_2O/H_2O	*t*-BuLi	40	4-Cl-C_6H_4CHO	$CH(OH)C_6H_4$-Cl-4	52	85.0–89.0,[h] 151.0–152.0	145[16a]
4	CH_2O/H_2O	*t*-BuLi	55	3,4$(MeO)_2$-C_6H_3CHO	$CH(OH)C_6H_3$-$(OMe)_2$-3,4	59	214.0–218.0	
5	CH_2O/H_2O	*t*-BuLi	50	2-furaldehyde	$CH(OH)(C_4H_3O)$	54	182.0–183.0	185[16a]
6	CH_2O/H_2O	LDA	55	$(C_6H_5)_2CO$	$C(OH)(C_6H_5)_2$	46	231.0–231.5	218[16a]
7	CH_2O/H_2O	*n*-BuLi	30	$(C_6H_5)_2CO$	$C(OH)(C_6H_5)_2$	38	231.0–231.5	218[16a]
8	CH_2O/H_2O	LDA	55	9-fluorenone	9-hydroxyfluorenyl	45	240.0–241.0	187–188[16a]
9	CH_2O/H_2O	LDA	30	cyclohexanone	$\overline{C(OH)(CH_2)_4CH_2}$	50	261.0–263.0	263[16a]
10[i]		LDA	60	$(CH_3S)_2$	SCH_3	58[j]	202.5–203.5	203[18]
11	CH_2O/H_2O	*t*-BuLi	50	$(C_6H_5CH_2S)_2$	$SCH_2C_6H_5$	53	183.0–185.0	180–182[19]
12	$(CH_2O)_n$	*t*-BuLi	60	$(C_6H_5CH_2S)_2$	$SCH_2C_6H_5$	45	183.0–185.0	180–182[19]
13	CH_2O/H_2O	LDA	55	$(C_6H_5S)_2$	SC_6H_5	46	201.5–202.5	201[20]

[a] 1.0 equiv of formaldehyde source was used. [b] 2.0 equiv of lithiating agent was added at −78 °C. [c] The solution was aged at −20 °C. [d] 1.0 to 1.1 equiv of electrophile was added at −78 °C. [e] Overall isolated yields after recrystallization of the 2-substituted benzimidazoles on the basis from benzimidazole. [f] See Table I. [g] When the product was purified from ethyl acetate–ethanol, the crystals, mp 78.0–79.0 °C, contained 1 mol of ethanol (^1H NMR evidence). On heating, gas came off, new crystals gradually appeared, and then melted again at 155.0–157.0 °C. [h] When the product was purified from ethyl acetate–ethanol, the crystals, mp 85.0–89.0 °C, contained 1 mol of ethanol (^1H NMR). On heating, gas came off, new crystals gradually appeared, and then melted again at 151.0–152.0 °C. [i] 1-(Hydroxymethyl)benzimidazole was used as a starting material. [j] Overall isolated yield after recrystallization of the 2-substituted benzimidazoles on the basis from 1-(hydroxymethyl)benzimidazole.

However, all of these methods possess at least one of the following disadvantages from the synthetic point of view:

1. Many of the protection steps require severe conditions, special reagents, special solvents, high temperature, and/or long reaction times.
2. The protected benzimidazole *must* be purified before the main reaction.
3. Some protecting groups are partially cleaved or rearranged during the main reaction. In particular, electron-withdrawing protecting groups tend to do this even at low temperature. The electrophilic assistance of a metallo species on the benzimidazole imino nitrogen prompts deprotection during the lithiation, and some newly introduced functionality can cause ejection of the protecting group because the substituted benzimidazole becomes a better leaving group.
4. Some protecting groups are lithiated in competition with the 2-hydrogen.
5. Sterically bulky protecting groups restrict reaction with large electrophiles.
6. Some protecting groups stabilize the intermediate N-protected 2-lithiobenzimidazole so much that the reactivity toward electrophiles decreases, lowering product yields.
7. Some deprotections are difficult or impossible without destroying the benzimidazole ring or require severe conditions that could damage other functionalities.
8. 2-Lithio N-protected species can react with the N-protected benzimidazole to give self-condensation products.

Our one-pot hemiaminal method for the 2-functionalization of benzimidazole has the following advantages over previously reported procedures:

1. The protecting group is readily introduced under mild conditons; in particular, neither an acid nor a Lewis catalyst acid is required. No purification step is needed. Two different formaldehyde sources, 37% aqueous formaldehyde and paraformaldehyde, are commercially available and cheap.
2. A variety of readily available lithiating agents, (*n*-butyllithium, *sec*-butyllithium, *tert*-butyllithium, or LDA) provides 2-lithio-*N*-(lithioxymethyl)benzimidazole efficiently under mild conditions. No chelating agent such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) or hexamethylphosphoramide (HMPA) is required, and thus the reaction mixture remains uncontaminated, and the workup and purification are simplified.
3. Deprotection is readily accomplished by *shaking* with 2 N aqueous hydrochloric acid solution at 20 °C.
4. The whole procedure is a one-pot method with a good overall yield.

In summary, 2-substituted benzimidazoles were synthesized in one-pot sequences in the key step of which lithium *N*-(2-lithiobenzimidazole) hemiaminal was successfully reacted with a variety of lithiating agents. The particular ease of introduction and of removal that characterize our use of formaldehyde as a protecting group offer considerable advantages over the N substituents that have previously been applied for this purpose.

Experimental Section

General. Melting points of the products were measured by a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR spectra were obtained with a Varian EM 360 L spectrophotometer using tetramethylsilane as an internal standard. Commercial benzimidazole (Aldrich) was purified by recrystallization from tetrahydrofuran and dried under vacuum. *n*-Butyllithium (Aldrich), *sec*-butyllithium (Aldrich), and *tert*-butyllithium (Aldrich) were used without further purification. LDA was freshly prepared from *N,N*-diisopropylamine (dried with calcium hydride and distilled) and *n*-butyllithium immediately before each run. Tetrahydrofuran (reagent grade from Fisher Chemical Co.) was dried with calcium hydride (Eastman Kodak) and then with liquid potassium (Aldrich) or sodium–benzophenone and used directly after distillation under dry argon. Formaldehyde (37% aqueous solution, Fisher Scientific Co.) and paraformaldehyde (Fisher Scientific Co.) were used without further purification. Electrophiles were purified by standard methods before use. Processes were carried out under dry argon.

2-Functionalization of Benzimidazole: One-Pot Preparation of 2-Substituted Benzimidazoles. Protection A:

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Preparation of the Hemiaminal Using 37% Aqueous Formaldehyde. Benzimidazole (1.57 g, 13.3 mmol) was placed in a two-necked flask. Tetrahydrofuran (40.0 mL) was added at 20 °C to give a suspension. To this was added formaldehyde (1.0 mL, 1.0 equiv, 37% water solution), at 20 °C to give a homogeneous solution. After 5 min, TLC (silica gel and ethyl acetate) showed that benzimidazole was consumed and 1-(hydroxymethyl)benzimidazole was formed. The solvent was removed under reduced pressure with a rotary evaporator, and the residue was dried in vacuo for 24 h.

Protection B: Preparation of the Hemiaminal Using Paraformaldehyde. Benzimidazole (1.57 g, 13.3 mmol) and paraformaldehyde (420 mg, 1.0 equiv) were placed in a two-necked flask. The interior of the flask was evacuated and flushed with dry argon three times. Tetrahydrofuran (60.0 mL) was added to give a suspension. The whole was kept stirring at 20 °C for 10 h to give a homogeneous solution. TLC showed only 1-(hydroxymethyl)benzimidazole.

Dilithiation of the Hemiaminal. (Protection method A requires the following additional procedure to a main reaction. The interior of the flask was evacuated and flushed with dry argon three times. Tetrahydrofuran (60.0 mL) was added to give a suspension. The solution was allowed to warm up to make a homogeneous solution.) The solution (from protection method A or protection method B) was cooled to −78 °C to give a precipitate, and freshly prepared LDA [2.0 equiv, from diisopropylamine (26.5 mmol, 3.73 mL) and *n*-butyllithium (26.5 mmol, 10.6 mL of 2.5 M hexane solution)] or *n*-butyllithium (26.5 mmol, 10.6 mL of a 2.5 M hexane solution) or *tert*-butyllithium (26.5 mmol, 15.6 mL of a 1.7 M pentane solution) was slowly added at −78 °C. The cooling bath was removed to allow the solution to warm to −20 °C. The solution was aged at −20 °C for 30–60 min with efficient stirring to give a homogeneous yellow to orange solution. The solution was cooled to −78 °C and quenched with an electrophile (1.0–1.1 equiv) at −78 °C. The solution was kept at −78 °C for 2 h and was then allowed to warm to 20 °C within 6 h.

Deprotection: Acid Dehydroxymethylation. The solution at 0 °C was quenched with aqueous ammonium chloride (20 mL), diluted with diethyl ether (100 mL), and carefully extracted with 2 N aqueous hydrochloric acid four times.

Workup. The aqueous acidic extracts were combined and basified with aqueous ammonium hydroxide or sodium carbonate with efficient stirring at 0 °C, giving a precipitate that was filtered off, dried first on the filter pump and then under vacuum for 24 h to give a solid that was washed with an appropriate solvent and recrystallized to give the desired product. The organic layer was extracted with diethyl ether or ethyl acetate when a precipitate was not formed. The solvent was removed on a rotary evaporator under reduced pressure to give the crude product, which was purified by recrystallization. The overall yield was 38–72% on the basis of benzimidazole.

(2-Benzimidazolyl)phenylcarbinol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 6.08 (s, 1 H, C*H*), 6.75 (bs, 1 H, O*H*), 7.12–7.77 (m, 9 H, aromatic protons), and 12.62 (bs, 1 H, N*H*).

(2-Benzimidazolyl)(4′-methylphenyl)carbinol–ethanol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 1.12 (t, 3 H, CH_3CH_2OH), 2.28 (s, 3 H, 4-$CH_3C_6H_4$), 3.55 (q, 2 H, CH_3CH_2OH), 4.48 (bs, 1 H, CH_3CH_2OH), 6.03 (s, 1 H, C*H*), 6.61 (bs, 1 H, O*H*), 7.12–7.65 (m, 8 H, aromatic protons), and 12.52 ppm (bs, 1 H, N*H*).

(2-Benzimidazolyl)(4′-chlorophenyl)carbinol–ethanol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 1.12 (t, 3 H, CH_3CH_2OH), 3.57 (q, 2 H, CH_3CH_2OH), 4.55 (bs, 1 H, CH_3CH_2OH), 6.10 (s, 1 H, C*H*), 6.93 (bs, 1 H, O*H*), 7.12–7.78 (m, 8 H, aromatic protons), and 12.67 ppm (bs, 1 H, N*H*). Anal. Calcd: C, 63.05; H, 5.62; N, 9.19. Found: C, 63.53; H, 5.64; N, 9.52.

(2-Benzimidazolyl)(3′,4′-dimethoxyphenyl)carbinol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 3.83 (s, 6 H, OCH_3), 6.03 (s, 1 H, C*H*), 6.47 (bs, 1 H, O*H*), 6.83–7.70 (m, 7 H, aromatic protons), and 12.20 ppm (bs, 1 H, N*H*). Anal. Calcd: C, 67.59; H, 5.67; N, 9.85. Found: C, 67.59; H, 5.72; N, 10.13.

(2-Benzimidazolyl)-2′-furylcarbinol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 6.10 (s, 1 H, C*H*), 6.33 (bs, 2 H, furyl-*H*), 7.13–7.70 (m, 5 H, aromatic protons and furyl protons), 8.53 (bs, 1 H, O*H*), and 11.20 ppm (bs, 1 H, N*H*).

(2-Benzimidazolyl)diphenylcarbinol: ^{1}H NMR ($CDCl_3$, DMSO-d_6, TMS) 6.95 (s, 1 H, O*H*), 7.12–7.75 (m, 14 H, aromatic protons), and 12.37 ppm (bs, 1 H, N*H*).

9-(2-Benzimidazolyl)fluoren-9-ol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 6.80 (s, 1 H, O*H*), 6.93–7.80 (m, 12 H, aromatic protons), and 12.80 ppm (bs, 1 H, N*H*).

(2-Benzimidazolyl)cyclohexanol: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 1.60–1.93 (m, 10 H, -$(CH_2)_5$-), 5.30 (bs, 1 H, O*H*), and 7.13–7.73 ppm (m, 4 H, aromatic protons).

2-(Methylthio)benzimidazole: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 2.78 (s, 3 H, SCH_3), 7.35–7.68 (m, 4 H, aromatic protons), and 12.72 ppm (bs, 1 H, N*H*).

2-(Benzylthio)benzimidazole: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 4.63 (s, 2 H, CH_2), 7.13–7.70 ppm (m, 9 H, aromatic protons), and 12.47 ppm (bs, 1 H, N*H*).

2-(Phenylthio)benzimidazole: ^{1}H NMR (DMSO-d_6, $CDCl_3$, TMS) 7.15–7.68 (m, 9 H, aromatic protons), and 12.75 ppm (bs, 1 H, N*H*).

Registry No. 1, 51-17-2; 3, 19541-99-2; PhCHO, 100-52-7; Ph_2CO, 119-61-9; 4-$CH_3C_6H_4CHO$, 104-87-0; 4-ClC_6H_4CHO, 104-88-1; 3,4-$(MeO)_2C_6H_3CHO$, 120-14-9; $(CH_3S)_2$, 624-92-0; $(C_6H_5CH_2S)_2$, 150-60-7; $(C_6H_5S)_2$, 882-33-7; formaldehyde, 50-00-0; 2-furaldehyde, 98-01-1; 9-fluorenone, 486-25-9; cyclohexanone, 108-94-1; (2-benzimidazolyl)phenylcarbinol, 50-97-5; (2-benzimidazolyl)(4′-methylphenyl)carbinol, 56969-29-0; (2-benzimidazolyl)(4′-chlorophenyl)carbinol, 5028-38-6; (2-benzimidazolyl)(3′,4′-dimethoxyphenyl)carbinol, 120496-42-6; (2-benzimidazolyl)-2′-furylcarbinol, 24898-47-3; (2-benzimidazolyl)diphenylcarbinol, 1235-28-5; 9-(2-benzimidazolyl)-fluoren-9-ol, 85330-60-5; (2-benzimidazolyl)cyclohexanol, 5805-32-3; 2-(methylthio)benzimidazole, 7152-24-1; 2-(benzylthio)-benzimidazole, 51290-77-8; 2-(phenylthio)benzimidazole, 2360-29-4; paraformaldehyde, 30525-89-4.