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Studies on Benzimidazoles and Related Compounds. IV.[1] Reactivity of 2-Azido-1-methylbenzimidazole

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Reactions of 2-azido-1-methylbenzimidazole (I) with such reagents as aluminum chloride in toluene, thiobenzophenone, hydrogen bromide, and acetic anhydride were investigated and compared with those of phenyl azide. In reaction of I with acetic anhydride, 3-acetyl-1-methyl-2-benzimidazolinone (VI) and 6-acetoxy-2-diacetylamino-1-methylbenzimidazole (VII) were obtained and its reaction mechanism was discussed.

Bromination of 2-amino-1-methylbenzimidazole (IIIa) with bromine in glacial acetic acid selectively occurred at C_6-position and this selectivity was also discussed.

2-Azidobenzimidazole and certain of its derivatives are known to exist as azide form rather than isomeric tetrazole by means of infrared (IR) and ultraviolet (UV) absorption spectra[3] and to react with triphenylphosphine to give a stable adduct which decomposes thermally to the corresponding phosphinimine.[4] On the other hand, it was reported that N-[(2-azido-1-benzimidazolyl)carbonyl] glycine isopropyl ester did not react with benzyne which was known to react readily with organic azides and might not be a typical azide because of interaction between the azide group and the heterocyclic nitrogen atom.[5] From these facts described above, it was expected that 2-azido-1-methylbenzimidazole (I) might be possible as a precursor of the iminonitrene system which was proposed as a potential 1,3-dipole without octet-stabilization by Huisgen and co-workers.[6] Therefore, it will be of great interest to examine reactivity of the azide (I) in comparison with that of phenyl azide. The present paper describes the reactions of the azide (I) with such reagents as aluminum chloride in toluene,[7] thiobenzophenone,[8] hydrogen bromide,[9] and acetic anhydride.[10]

Reaction of I[11] with aluminum chloride in toluene at the reflux temperature gave a mixture of 1-methyl-2-(*p*-toluidino) benzimidazole (II), 2-amino-1-methylbenzimidazole (IIIa), and neutral products (Chart 1). The products, II and IIIa, were anticipated from the reaction of phenyl azide with aluminum chloride in toluene[7] and identified with a sample prepared from 2-chloro-1-methylbenzimidazole[11] and *p*-toluidine and an authentic sample[12] of IIIa, respectively. For the neutral products showed three spots on thin-layer chromatogrum (TLC), no attempt was made to investigate the each component.

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[1] Part III: S. Ishiwata and Y. Shiokawa, *Chem. Pharm. Bull.* (Tokyo), **18**, 1245 (1970).

[2] Location: *Women's Division, Ueno Sakuragi 1-10-19, Daito-ku, Tokyo.*

[3] *a*) G.A. Reynolds, J.A. VanAllan, and J.F. Tinker, *J. Org. Chem.*, **24**, 1205 (1959); *b*) G.A. Reynolds and J.A. VanAllan, *ibid.*, **24**, 1478 (1959).

[4] G.A. Reynolds and J.A. VanAllan, *J. Heterocyclic Chem.*, **5**, 471 (1968).

[5] G.A. Reynolds, *J. Org. Chem.*, **29**, 3733 (1964).

[6] R. Huisgen, R. Grashey, and J. Sauer, "Cycloaddition Reactions of Alkenes" in "The Chemistry of Alkenes," ed. by S. Patai, Interscience Publishers, Inc., New York, N.Y., 1964, p. 739.

[7] W. Borsche and H. Hahn, *Chem. Ber.*, **82**, 260 (1949).

[8] A. Schönberg and W. Urban, *J. Chem. Soc.*, **1935**, 530.

[9] P.A.S. Smith and B.B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951).

[10] R.K. Smalley and H. Suschitzky, *J. Chem. Soc.*, **1963**, 5571.

[11] N.P. Bednyagina and I.Y. Pastovskii, *Zhur. Obshchei. Khim.*, **30**, 1431 (1960) [*C.A.*, **55**, 1586h (1961)].

[12] A.M. Simonov and N.D. Vitkevich, *Zhur. Obshchei. Khim.*, **30**, 590 (1960) [*C.A.*, **54**, 24677i (1960)].

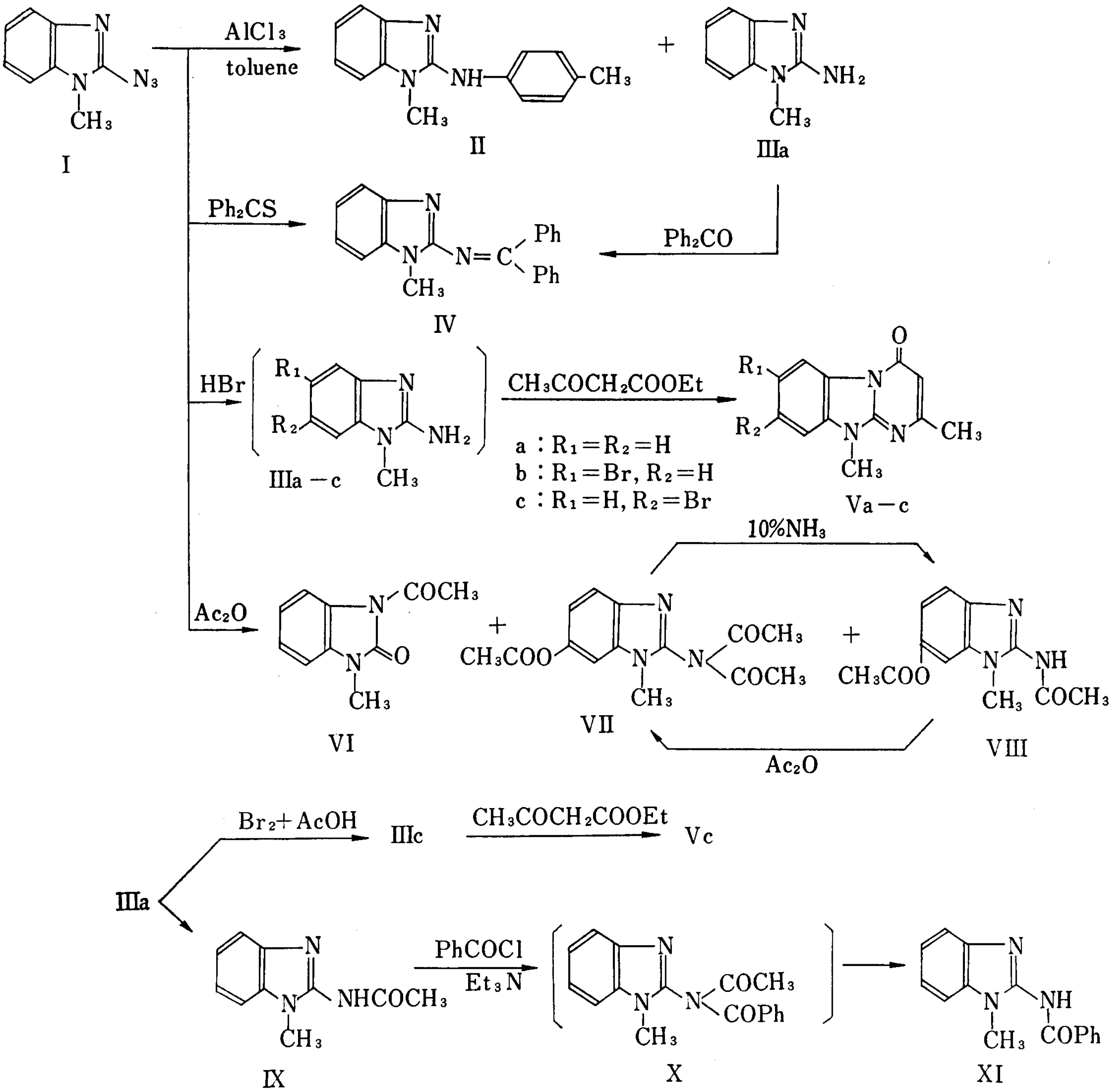

Chart 1

When I was heated with thiobenzophenone at 130° in a stream of nitrogen, the Schiff base (IV) and unreacted I were obtained. About mechanism of the Schiff base formation, Schönberg and Urban[8] suggested two possible intermediates produced from 1,3-dipolar cycloaddition of the azide and addition of the nitrene to the thioketone. The Schiff base (IV) obtained was identified with a sample prepared from IIIa and benzophenone by mixed melting point determination and IR spectral comparison.

I was treated with a 30% solution of hydrogen bromide in acetic acid at 80° and gave rise to a mixture of the amines (IIIa—c) with and without bromination. Since separation of the mixture into the each amine and determination of the brominated position were difficult in this stage, the mixture was converted by treatment with ethyl acetoacetate[13] into a mixture of pyrimido[1,2-*a*]benzimidazol-4(10*H*)-one derivatives (Va—c) which was separated into each component by repeated silica gel column chromatography. In nuclear magnetic resonance (MNR) spectra (Table I) of Va—c in deuteriochloroform, C_6-proton was greatly

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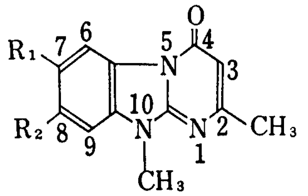
[13] H. Antaki and V. Petrow, *J. Chem. Soc.*, **1951**, 551.

TABLE I. Chemical Shifts (τ) in $CDCl_3$

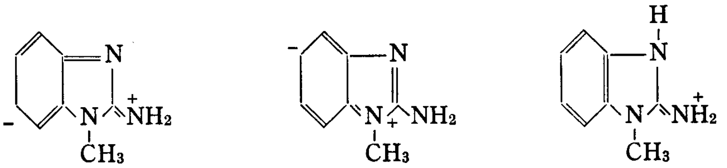


		C_2-CH_3	N-CH_3	C_3-H	C_6-H	C_7-H	C_8-H	C_9-H
Va	$R_1=R_2=H$	7.64	6.28	4.03	1.43 (d-d, $J=8.5$ and 2Hz)	2.56——2.83 (m)		
Vb	$R_1=Br$, $R_2=H$	7.64	6.28	4.01	1.25 (d, $J=2$Hz)	—	2.46 (d-d, $J=9$ and 2Hz)	2.87 (d, $J=9$Hz)
Vc	$R_1=H$, $R_2=Br$	7.64	6.30	4.00	1.57 (d, $J=9$Hz)	2.50—2.65 (m)	—	2.50—2.65 (m)

affected by the paramagnetic anisotropy of the carbonyl group at C_4-position as was expected and its signal was shifted to a lower magnetic field. From the splitting and coupling constant in signal due to C_6-proton, structures of Va, Vb, and Vc were confirmed to be 2,10-dimethylpyrimido[1,2-*a*]benzimidazol-4(10*H*)-one, its 7-bromo, and 8-bromo compound, respectively.

According to the mechanism suggested by Smith and Brown,⁹⁾ azide was reduced to the corresponding amine with loss of nitrogen by hydrogen bromide and then bromination of the amine with free bromine occurred. Reaction of IIIa with bromine in glacial acetic acid at room temperature selectively gave 2-amino-6-bromo-1-methylbenzimidazole (IIIc). IIIc was converted into Vc by treatment with ethyl acetoacetate.

It is well known that nitration of 1,2-substituted benzimidazole derivatives gives a mixture of 5- and 6-nitro compounds.¹⁴⁾ This fact may be explained easily in terms of resonance forms in benzimidazole. In case of IIIa, it may be considered that XIIa predominates as compared with XIIb because of strong electron-donating effect of the amino group at C_2-position and that bromination selectively occurs at C_6-position (Chart 2). In the presence of strong acid such as hydrogen bromide, however, difference in reactivity between at C_5- and C_6-position may be expected to diminish by contribution of XIIc protonated at $N_{(3)}$-position. In fact, bromination of IIIa in the presence of hydrogen bromide gave a mixture of IIIb and IIIc.



XIIa XIIb XIIc

Chart 2

Reaction of I with acetic anhydride provided a mixture consisted of three components, VI (mp 122—123°), VII (mp 151.5—152.5° (decomp.)), and VIII (np 224.5—226.0° (decomp.)). This mixture was separated into each component by column chromatography over silica gel. The structure of VI was supported by IR (in KBr) and NMR (in $CDCl_3$) spectra respectively showed a very strong, broad absorption for carbonyl groups at 1720 cm^{-1} and signals at 6.56τ (3H, singlet, N-CH_3) and 7.19τ (3H, singlet, $COCH_3$) and concluded to be 3-acetyl-1-

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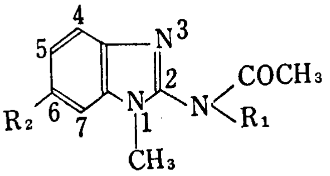
14) M.T. Le Bris and H. Wahl, *Rev. Textile-tiba*, **57**, 164 (1958) [*C.A.*, **53**, 2208e (1959)].

methyl-2-benzimidazolinone by identification with a sample obtained from the reaction of 1-methyl-2-benzimidazolinone[15] with acetic anhydride.

IR spectrum (in KBr) of VII exhibits absorptions of three carbonyl groups at 1765, 1740, and 1720 cm^{-1} and its NMR spectrum (in $CDCl_3$) indicates signals at 7.65τ (9H, singlet, $2COCH_3$ and $OCOCH_3$), 6.40τ (3H, singlet, N-CH_3), 2.91τ (1H, doublet–doublet, J=2 and 8 Hz, C_5-H), 2.77τ (1H, doublet, J=2Hz, C_7-H), and 2.19τ (1H, doublet, J=8Hz, C_4-H). And, these spectroscopic data of VII correspond with those (Table II) of 2-diacetylamino-1-methylbenzimidazole[16] prepared from IIIa and acetic anhydride. The assignment of the signal at 2.19τ to the proton at C_4-position may be reasonable from that its signal is expected to be shifted to a lower magnetic field by the deshielding due to the nonbonded electron pair of nitrogen atom at $N_{(3)}$-position. On the basis of splitting and coupling constant in the signal attributed to C_4-proton, the substituted position of acetoxy group was determined to be at C_6-position. Therefore, the structure of VII was confirmed to be 6-acetoxy-2-diacetylamino-1-methylbenzimidazole.

TABLE II. Data in NMR, IR, and UV Spectra



	Chemical shifts (τ) in $CDCl_3$						
	R_1	R_2	N-$COCH_3$	N-CH_3	C_7-H	C_5-H	C_4-H
R_1=$COCH_3$, R_2=H	7.66	2.58 (bs)	7.66	6.39	2.58 (bs)	2.58 (bs)	2.15 (m)
R_1=$COCH_3$, R_2=$OCOCH_3$	7.65	7.65	7.65	6.40	2.77 (d, J=2Hz)	2.91 (d–d, J=8 and 2Hz)	2.19 (d, J=8Hz)
R_1=H, R_2=$OCOCH_3$	1.14 (bs)	7.75 (or 7.70)	7.70 (or 7.75)	6.42	3.00 (d, J=2Hz)	3.08 (d–d, J=8 and 2Hz)	2.68 (d, J=8Hz)

	IR cm^{-1} (KBr): ν_{CO}			UV λ_{max}^{EtOH} mμ			
R_1=$COCH_3$, R_2=H		1745	1720	255	269	276	284
R_1=$COCH_3$, R_2=$OCOCH_3$	1765	1740	1720	256		279	286

For the third component (VIII), its structure was determined to be 6-acetoxy-2-acetylamino-1-methylbenzimidazole by the following methods. VIII showed absorptions for free and associated amino group at 3150—2700 cm^{-1} and two carbonyl groups at 1760 and 1710 cm^{-1} in IR spectrum (in KBr) and signals at 7.75τ (3H, singlet, $OCOCH_3$ (or $COCH_3$)), 7.70τ (3H, singlet, $COCH_3$ (or $OCOCH_3$)), 6.42τ (3H, singlet, N–CH_3), 3.08τ (1H, doublet–doublet, J=8 and 2Hz, C_5–H), 3.00τ (1H, doublet, J=2Hz, C_7–H), 2.68τ (1H, doublet, J=8Hz, C_4–H), and 1.14τ (1H, singlet, NH) in NMR spectrum (in $CDCl_3$). From these spectroscopic data, VIII was deduced to be 2-acetylamino-1-methylbenzimidazole derivative substituted by acetoxy group and assumed to be the secondary product drived from VII. This assumption was justified by the fact that VIII was obtained by treatmrnt of VII with ammonia

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[15] A. Hunger, J. Kebrle, A. Rossi, and K. Hoffmann, *Helv. Chim. Acta*, **44**, 1273 (1961).
[16] P.N. Craig and J.R.E. Hoover, Brit. Patent 1111957 (1968) [*C.A.*, **69**, 96721j (1968)].

under the same condition. Also, VIII was converted into VII by treatment with acetic anhydride.

From the fact that decomposition of phenyl azide in acetic anhydried gave a mixture of acetylated *o*-aminophenol, aniline, and azobenzene, Smalley and Suschitzky proposed to the mechanism involved intramolecular rearrangement of O,N-diacetylphenylhydroxylamine, which arised by interaction of phenylnitrene with acetic anhydride.[10] For rearrangement of the intermediate (XIII), both acetyl and acetoxy groups may possibly be rearranged and the following mechanism is suggested (Chart 3). Formation of VI and VII may respectively be explained migration of the former, followed by hydrolysis of the imino ester (XIV) (path A) and migration of the latter, followed by acetylation of XV (path B).

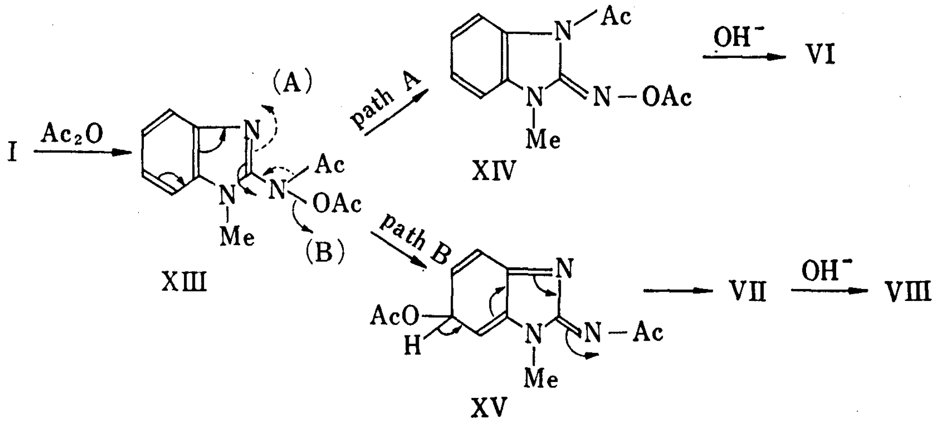

Chart 3

For reactions of benzimidazolium salt and benzimidazole 3-oxide derivatives with potassium cyanide and phenyl isocyanate, Takahashi and Kano suggested the quinoid form intermediate analogous to XV.[17]

UV absorption spectrum of VIII is similar to that of 2-acetylamino-1-methylbenzimidazole (IX), whereas its IR spectrum considerably differs as described below. That is, IR spectra (in KBr) of 2-ethoxycarbamido-, 2-benzamido-1-methylbenzimidazole (XI), and IX respectively showed absorptions for carbonyl groups at 1635, 1600, and 1580 cm^{-1} and amino groups at 3380, 3230, and 3250 cm^{-1}. In case of 2-acetylamino-6-bromo-1-methylbenzimidazole prepared from IIIc and acetic anhydride, however, its IR spectrum (in KBr) showed absorptions for free and associated amino group at 3125—2650 and carbonyl group at 1700 cm^{-1} and was similar to that of VIII. Although the difference obserbed in IR spectra (in KBr) may be considered to be due to the presence of C$_6$-substituent, its effect is not obvious.

Reaction of IX with benzoyl chloride in the presence of triethylamine gave XI instead of 2-(N-acetyl-N-benzoylamino)-1-methylbenzimidazole (X), which could not be isolated from the reaction mixture. Before the treatment of the reaction mixture, that is, its TLC indicated the presence of a spot corresponding to X. However, X was converted into the mixture of X and XI by treatment of the reaction mixture with water. Even in silica gel column or in air, the similar conversion partially occurred. The structure of X was assumed from NMR spectrum (in CDCl$_3$), showed signals at 6.31 τ (singlet, N–CH$_3$ of XI), 6.39 τ (singlet, N–CH$_3$ of X), and 7.54τ (singlet, COCH$_3$ of X), of the mixture of X and XI.

From the present experiments, the reactions of I with aluminum chloride in toluene, thiobenzophenone, and hydrogen bromide need more drastic conditions than those of phenyl azide with the reagents. Also, I is stable toward concentrated sulfuric acid.

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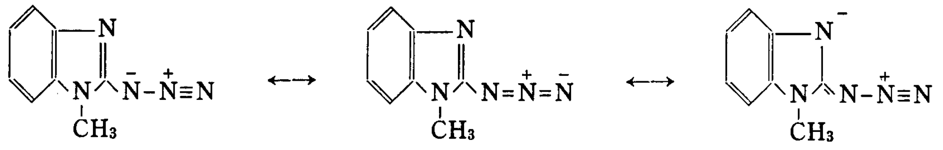
17) *a*) S. Takahashi and H. Kano, *Chem. Pharm. Bull.* (Tokyo), **14**, 375 (1966); *b*) *Idem*, *ibid*, **14**, 1219 (1966).



Ia Ib Ic

Chart 4

On the hypothesis that I exists as a typical azide, the chemical behaviour of that is considered on the basis of the resonance stabilization of the azide group[18] as follows. In addition to the two octet resonance contributors (Ia and Ib) of the azide group, it may be expected that Ic due to conjugation between the C=N bond and the azide group makes a contribution to the resonance stabilization of I (Chart 4) and that the doublet-bond character of the N–N_2 bond which breaks is decreased. Therefore, I is considered to be unstable than phenyl azide, but it contradicts with the experimental results. As suggested by Reynolds,[5] it is concluded that I may not be a typical azide because of interaction between the azide group and the heterocyclic nitrogen atom.

Experimental[19]

Reaction of 2-Azido-1-methylbenzimidazole (I) with Aluminum Chloride in Toluene——To a solution of I (0.1 g) in toluene (10 ml) $AlCl_3$ (0.3 g) was added, the mixture was heated under reflux for 2 hr, and evaporated *in vacuo*. The residue was made alkaline with conc. NH_4OH under ice-cooling, extracted with $CHCl_3$, the extract was washed with H_2O, dried over anhyd. K_2CO_3, and evaporated *in vacuo*. The residue was dissolved in $CHCl_3$ and the solution was chromatographed on a silica gel (3 g) column. The neutral fraction eluated with the same solvent was evaporated *in vacuo* and the residue showed three spots on a TLC (silica gel, C_6H_6–*n*-hexane, 1:1). For neutral products, no attempt was made to investigate the each component.

Next, 0.035 g (25.6%) of II was obtained and recrystallized from benzene, mp 174.5—175.5°. *Anal.* Calcd. for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.79; H, 6.61; N, 16.99. IR cm^{-1} (KBr): ν_{NH} 3250, 3130; $\nu_{NH \cdots N}$ 3050—2850. NMR (in $CDCl_3$) τ: 6.32 (N–CH_3, s), 7.74 (C–CH_3, s).

The fraction eluated with $CHCl_3$–MeOH (30:1) was evaporated *in vacuo* and the residue was recrystallized from dil. EtOH to give 0.016 g (18.8%) of IIIa, mp 209.5—211°. *Anal.* Calcd. for $C_8H_9N_3$: C, 65.28; H, 6.16; N, 28.55. Found: C, 65.11; H, 6.14; N, 29.19. IR cm^{-1} (KBr): ν_{NH_2} 3450, 3350; $\nu_{NH \cdots N}$ 3200—2800.

The products, II and IIIa, were respectively identified with a sample prepared by a method described below and an authentic sample[12] of IIIa by mixed melting point determination and IR spectral comparison.

1-Methyl-2-(*p*-toluidino)benzimidazole (II)——A mixture of 2-chloro-1-methylbenzimidazole[11] (0.3 g) and *p*-toluidine (0.288 g) in diglyme (12 ml) was heated under reflux for 1 hr. The starting material dissolved in the solution and then a crystalline product precipitated. After cooling, the product was collected by filtration, washed with $CHCl_3$, and recrystallized from H_2O to give 0.29 g of II–HCl, mp 202—207°. II–HCl was dissolved in a small amount of hot H_2O, the solution was made alkaline with conc. NH_4OH, the precipitate was collected by filtration, and recrystallized from benzene to give 0.22 g (52%) of II, mp 174.5—175.5°.

Reaction of I with Thiobenzophenone——A mixture of I (0.57 g) and the thioketone (0.65 g) was heated at 130° for 3 hr in a stream of nitrogen. Further, 0.65 g of the thioketone was added and the mixture was heated for 3 hr under the same conditions. After cooling, the mixture was dissolved in a small amount of benzene and the solution was chromatographed on a silica gel (6 g) column. Unreacted I (0.075 g) was recovered from the fraction eluated with benzene.

The fraction eluated with $CHCl_3$ was evaporated *in vacuo* and the residue was recrystallized from benzene–*n*-hexane to give 0.235 g (26%) of IV, mp 146—147°. *Anal.* Calcd. for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.50. Found: C, 81.10; H, 5.50; N, 13.27. IR cm^{-1} (KBr): $\nu_{C=N}$ 1605. UV λ_{max}^{EtOH} mμ: 261, 281, 364. NMR (in $CDCl_3$) τ: 6.40 (N–CH_3, s).

The Schiff base (IV) was identified with a sample prepared by a method described below by mixed melting point determination and IR spectral comparison.

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[18] G. L'abbé, *Chem. Rev.*, **69**, 345 (1969).

[19] Melting points were measured on a Yanagimoto Micro Melting Point Apparatus and uncorrected. NMR spectra were taken on a JNM-4H-100 spectrometer in $CDCl_3$ with tetramethylsilane as internal standard.

The Schiff Base (IV)——A mixture of IIIa (0.1 g) and benzophenone (0.124 g) in anhyd. xylene (4 ml) was heated under reflux for 30 hr. H_2O formed was made to distill off outside the reaction system as an azeotropic mixture with xylene. The reaction mixture was filtered to remove unreacted IIIa (0.029 g), the filtrate was evaporated *in vacuo*, the residue was dissolved in benzene, and the solution was chromatographed on a silica gel (3 g) column. Unreacted benzophenone was recovered from the fraction eluated with benzene.

The fraction eluated with $CHCl_3$ was evaporated *in vacuo* and the residue was recrystallized from benzene–*n*-hexane to give 0.087 g (52%) of IV, mp 146—147°.

Reaction of I with Hydrogen Bromide in Acetic Acid——To a solution of I (0.2 g) in acetic acid (5 ml) a 30% solution (5 ml) of hydrogen bromide in acetic acid was added, the solution was heated at 80° for 7 hr, and evaporated *in vacuo*. The residue was dissolved in a small amount of H_2O, the solution was made alkaline with conc. NH_4OH under ice-cooling, and the precipitate was collected by filtration.

A mixture of the precipitate and ethyl acetoacetate (0.5 ml) was heated at 140° for 0.5 hr and recrystallized from EtOH to give 0.107 g of a mixture of Va—c. The mixture was separated into each component by column chromatography over silica gel (3 g). The first fraction eluated with benzene–AcOEt (30:1) mixture was evaporated *in vacuo* and the residue was recrystallized from MeOH to give 0.022 g (6.5%) of Vc, mp 224—225.5°. *Anal.* Calcd. for $C_{12}H_{10}ON_3Br$: C, 49.33; H, 3.46; N, 14.39. Found: C, 49.30; H, 3.55; N, 14.15. IR cm^{-1} (KBr): $\nu_{C=O}$ 1680. NMR: (see Table I).

The next fraction eluated with the same solvent was evaporated *in vacuo* and the residue was recrystallized from MeOH to give 0.012 g (3.5%) of Vb, mp 261.5—263.5°. *Anal.* Calcd. for $C_{12}H_{10}ON_3Br$: C, 49.33; H, 3.46; N, 14.39. Found: C, 49.45; H, 3.39; N, 14.58. IR cm^{-1} (KBr): $\nu_{C=O}$ 1680. NMR: (see Table I).

The last fraction eluated with the same solvent was evaporated *in vacuo* and the residue was recrystallized from MeOH to give 0.051 g (20.5%) of Va, mp 231.5—232.5°. *Anal.* Calcd. for $C_{12}H_{11}ON_3$: C, 67.59; H, 5.20; N, 19.71. Found: C, 67.48; H, 5.20; N, 19.77. IR cm^{-1} (KBr): $\nu_{C=O}$ 1685. NMR: (see Table I).

This compound was identified with a sample prepared from IIIa and ethyl acetoacetate by mixed melting point determination and IR spectral comparison.

2-Amino-6-bromo-1-methylbenzimidazole (IIIc)——To a solution of IIIa (0.1 g) in glacial acetic acid (4 ml) bromine (0.05 ml) was added and the solution was stirred for 3 hr at room temperature. After addition of ether (20 ml), the mixture was kept in a refrigerator overnight. The precipitate was collected by filtration, dissolved in a small amount of H_2O, and the solution was made alkaline with conc. NH_4OH under ice-cooling. Recrystallization of the precipitate from dil. EtOH gave 0.062 g (40.5%) of colorless crystals, mp 275.5—277.5° (decomp.). *Anal.* Calcd. for $C_8H_8N_3Br$: C, 42.49; H, 3.57; N, 18.59. Found: C, 42.40; H, 3.58; N, 18.39. IR cm^{-1} (KBr): ν_{NH_2} 3440, 3270; $\nu_{NH\cdots H}$ 3180—2750.

This compound was converted into Vc by treatment with ethyl acetoacetate and the brominated position was determined from NMR spectrum of Vc.

Reaction of I with Acetic Anhydride——A solution of I (0.2 g) in acetic anhydride (6 ml) was heated under reflux for 2 hr and evaporated *in vacuo*. The residue was dissolved in $CHCl_3$, the solution was made alkaline with 10% NH_4OH under ice-cooling, $CHCl_3$ layer was separated from H_2O layer, washed with H_2O, dried over anhyd. K_2CO_3, and evaporated *in vacuo*. The residue was dissolved in $CHCl_3$ and the solution was chromatographed on a silica gel (3 g) column. The first fraction eluated with the same solvent was evaporated *in vacuo* and the residue was recrystallized from iso-PrOH to give 0.053 g (24.1%) of VI, mp 122—123°. *Anal.* Calcd. for $C_{10}H_{10}O_2N_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.03; H, 5.25; N, 14.67. IR cm^{-1} (KBr): $\nu_{C=O}$ 1720 (broad). UV λ_{max}^{EtOH} mμ: 256, 279, 286 (shoulder). NMR (in $CDCl_3$) τ: 7.19 ($COCH_3$, s), 6.56 (N–CH_3, s), 2.96 (C_7-H, d–d, $J=7.5$ and 2 Hz), 2.62—2.78 (C_5-H and C_6-H, m,) 1.70 (C_4-H, d–d, $J=7.5$ and 2 Hz).

This compound was identified with a sample prepared from 1-methyl-2-benzimidazolinone[15] and acetic anhydride by mixed melting point determination and IR spectral comparison.

The second fraction eluated with the same solvent was evaporated *in vacuo* and the residue was recrystallized from ether to give 0.092 g (27.5%) of VII, mp 151.5—152.5° (decomp.). *Anal.* Calcd. for $C_{14}H_{15}O_4N_3$: C, 58.12; H, 5.23; N, 14.53. Found: C, 58.44; H, 5.08; N, 14.39. IR cm^{-1} (KBr): $\nu_{C=O}$ 1765, 1740, 1720. UV λ_{max}^{EtOH} mμ: 256, 279, 286. NMR: (see Table II).

This product was identified with a sample obtained from acetylation of VIII with acetic anhydride.

The last fraction eluated with $CHCl_3$–MeOH (30:1) was evaporated *in vacuo* and the residue was recrystallized from acetone to give 0.045 g (18.9%) of VIII, mp 224.5—226.0° (decomp.). *Anal.* Calcd. for $C_{12}H_{13}O_3N_3$: C, 58.29; H, 5.30; N, 17.00. Found: C, 58.22; H, 5.34; N, 17.06. IR cm^{-1} (KBr): $\nu_{C=O}$ 1760, 1710; ν_{NH} 3150, 3060; $\nu_{associated NH}$ 3000—2700. UV λ_{max}^{EtOH} mμ: 249, 288, 297 (shoulder), 310. NMR: (see Table II).

This product was identified with a sample obtained from treatment of VII with 10% NH_4OH.

Treatment of VII with 10% NH_4OH——To a solution of VII (0.05 g) in glacial acetic acid (1 ml) H_2O (2 ml) was added and the solution was made alkaline with 10% NH_4OH under ice-cooling. The precipitate was collected by filtration, washed with H_2O, and recrystallized from acetone to give 0.026 g (73%) of VIII, mp 224.5—226.0° (decomp.).

Acetylation of VIII with Acetic Anhydride——A mixture of VIII (0.03 g) and acetic anhydride (2 ml) was refluxed for 30 min, evaporated *in vacuo*, the residue was dissolved in benzene, and the solution was chromatographed on a silica gel (2 g) column. VII obtained from the fraction eluated with $CHCl_3$ was recrystallized from ether to give 0.028 g (80%), mp 151.5—152.5° (decomp.).

Reaction of IX with Benzoyl Chloride——A mixture of IX (0.222 g), Et_3N (0.119 g), and benzoyl chloride (0.165 g) in anhyd. benzene (4 ml) was heated under reflux for 0.5 hr and evaporated *in vacuo*. The residue was extracted with $CHCl_3$, the extract was washed with H_2O, dried over anhyd. Na_2SO_4, and evaporated *in vacuo*. The residue showed two spots on a TLC. Separation of X from the residue by column chromatography was unsuccessful and only XI was purely obtained. Yield, 0.166 g (64%), mp 160—161°.

XI was identified with an authentic sample[20] by IR spectral comparison.

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