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Reaction of Guanidines with α-Diketones. Syntheses of 4,5-Disubstituted-2-aminoimidazoles and 2,6-Unsymmetrically Substituted Imidazo[4,5-*d*]imidazoles[1]

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2-Amino-4,5-diaryl-4-hydroxy-4*H*-imidazoles were obtained by the reaction of substituted benzils with guanidine in methanol at room temperature. Catalytic hydrogenation of the 4-hydroxy-4*H*-imidazoles produced 2-amino-4,5-diarylimidazoles in excellent yields. In the case of 1-phenyl-1,2-propanedione and butane-2,3-dione, the intermediate 4-hydroxy-4*H*-imidazoles could not be isolated and the reaction mixtures were hydrogenated directly to yield the corresponding 2-aminoimidazoles. 1,1-Dimethylguanidine and benzils also produced the corresponding 4*H*-imidazoles in excellent yields. These compounds were quantitatively converted to 2-(dimethylamino)-5,5-diarylimidazolin-4-ones by heating. 1-Amidino-3,5-dimethylpyrazole did not give the corresponding 4*H*-imidazoles, but produced the 2,6-unsymmetrically substituted imidazo[4,5-*d*]imidazoles. Probable mechanisms for the formation of these products are discussed.

It is well known that the base-catalyzed reaction of benzil with guanidine produces 2-amino-5,5-diphenylimidazolin-4-one and 2,6-diamino-4,8-diphenylimidazo[4,5-*d*]imidazole,[2-5] while that with 1,1-disubstituted guanidines gives only 2-(disubstituted amino)-5,5-diphenylimidazolin-4-ones.[6] However, our previous results[7,8] suggested the possibility of also obtaining 4-hydroxy-4*H*-imidazoles or 4,5-dihydroxyimidazolines in this condensation reaction. In this paper, we report the successful syntheses of 4-hydroxy-4*H*-imidazoles by the reaction of α-diketones with guanidine and 1,1-dimethylguanidine, a new route to 2-amino-4,5-disubstituted imidazoles, and the reaction of 1-amidino-3,5-dimethylpyrazole with α-diketones to form unsymmetrical imidazo[4,5-*d*]imidazoles.

Results and Discussion

Reaction of α-Diketones with Guanidine. Lempert-Sréter et al.[5] have reported that benzil (**1a**) and guanidine (**2**) gave 2,6-diamino-4,8-diphenylimidazo[4,5-*d*]imidazole (**3**) with a small amount of 2-amino-5,5-diphenylimidazolin-4-one (**4**) when the reaction was carried out in methanol at room temperature either in the presence or absence of a small amount of alkali.

When we substituted dioxane for methanol in this reaction, colorless needles, mp 212 °C, were obtained. IR, NMR, MS and elemental analysis of this product were inconsistent with the desired 2-amino-4*H*-imidazole or 4,5-dihydroxyimidazoline. Since recrystallization from methanol and ether gave imidazo[4,5-*d*]imidazole **3** and its NMR spectrum showed a signal assignable to the *O*-methylene protons of dioxane, this material was identified as **3** containing one molecule of dioxane as the solvent of crystallization. The yield of **3** was 74% based on **2**. When 2 equiv of **2** were used, the yield of **3** was reduced to 31% and, furthermore, **4** was obtained in 53% yield. This result can be explained by the report of Lempert-Sréter et al.[5] that higher alkali concentration increased the yield of **4** compared to that of **3**. However, by stirring a suspension of **1a** and **2** in a smaller amount of methanol than that reported by Lempert-Sréter et al. at room temperature, we succeeded in isolating the desired 2-amino-4,5-diphenyl-4-hydroxy-4*H*-imidazole (**5a**) in 85% yield.

When 4-hydroxy-4*H*-imidazole **5a** was refluxed in methanol in the presence of NaOH, imidazolin-4-one **4** was obtained in 92% yield. Treatment of **5a** with concentrated HCl in an attempt to prepare the HCl salt gave the unstable 2-amino-4,5-dihydroxy-4,5-diphenylimidazoline (**6**) hydrochloride by addition of water to the 1,5 C=N bond. In another attempt to obtain **5a**·HCl, treatment of **5a** with methanol containing a slight excess of HCl yielded 2-amino-4,5-dimethoxy-4,5-diphenylimidazoline (**7**) hydrochloride. The only other reported examples of this type of compound are 4,5-dimethoxyimidazolin-2-ones, which were obtained by photosensitized oxidation of imidazoles in methanol.[9]

It is interesting to note that although **5a** decomposed to unidentified products when dissolved in untreated THF, imidazo[4,5-*d*]imidazole **3** precipitated in 72% yield when **5a** was dissolved in sodium-dried and distilled THF at room temperature.

Hydrogenation of 4*H*-imidazole **5a** in methanol with palladium on charcoal gave 2-amino-4,5-diphenylimidazole (**8a**) in 84% yield, and the nitrate salt in 90% yield after acidification with nitric acid. Thus, we attempted to apply this syn-

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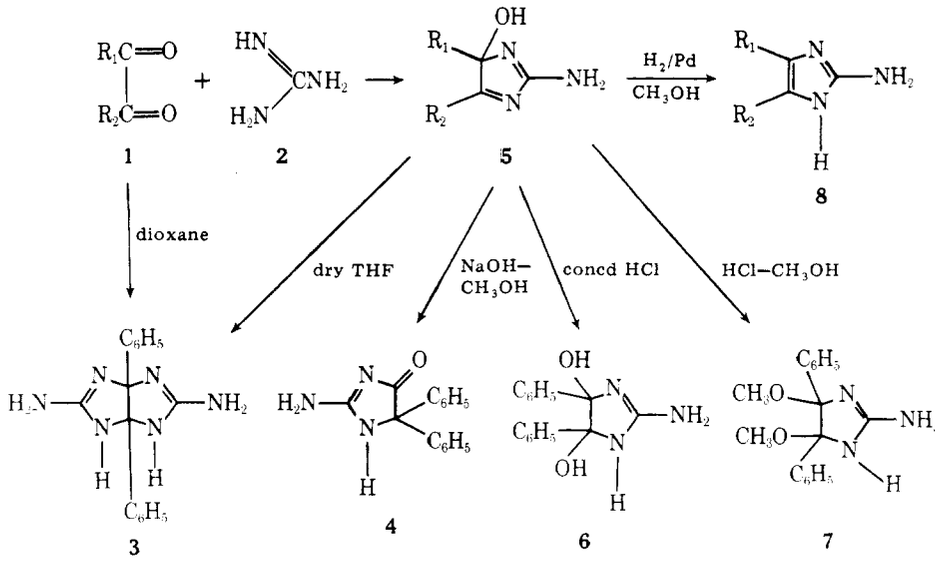


a, $R_1 = C_6H_5$, $R_2 = C_6H_5$; b, $R_1 = p\text{-}CH_3OC_6H_4$, $p\text{-}CH_3OC_6H_4$; c, $R_1 = p\text{-}ClC_6H_4$, $R_2 = p\text{-}ClC_6H_4$; d, $R_1 = p\text{-}CH_3C_6H_4$, $R_2 = p\text{-}CH_3C_6H_4$; e, $R_1 = CH_3$, $R_2 = CH_3$; f, $R_1 = CH_3$, $R_2 = C_6H_5$

thetic method of 2-aminoimidazoles to other α-diketones. 4,4′-Dichloro- (**1c**) and 4,4′-dimethylbenzils (**1d**) gave the corresponding 4*H*-imidazoles **5c** and **5d** in 91 and 83% yields, respectively. However, 4,4′-dimethoxybenzil (**1b**) failed to react, probably because of the reduced reactivity of the carbonyl group due to the electron-donating methoxy groups.

Hydrogenation of **5c** and **5d** yielded the corresponding 2-aminoimidazoles **8c** and **8d** in good yields. In the case of 2,3-butanedione (**1e**) and 1-phenyl-1,2-propanedione (**1f**), the corresponding 4*H*-imidazoles were very unstable and quickly became tinged with red or violet.[10] Thus, the solutions obtained by reacting **1e** or **1f** with guanidine at −10 °C were directly subjected to Pt-catalyzed hydrogenation at 0–5 °C to give the corresponding 2-aminoimidazoles **8e** and **8f** as the nitrate salts in 47 and 55% yields, respectively.

Since 2-aminoimidazoles have been prepared previously only by the reduction of 2,2-azoimidazoles[11] and the reaction of cyanamide with α-aminocarbonyl compounds,[12] our method deserves consideration as a new route for the synthesis of 2-aminoimidazoles.

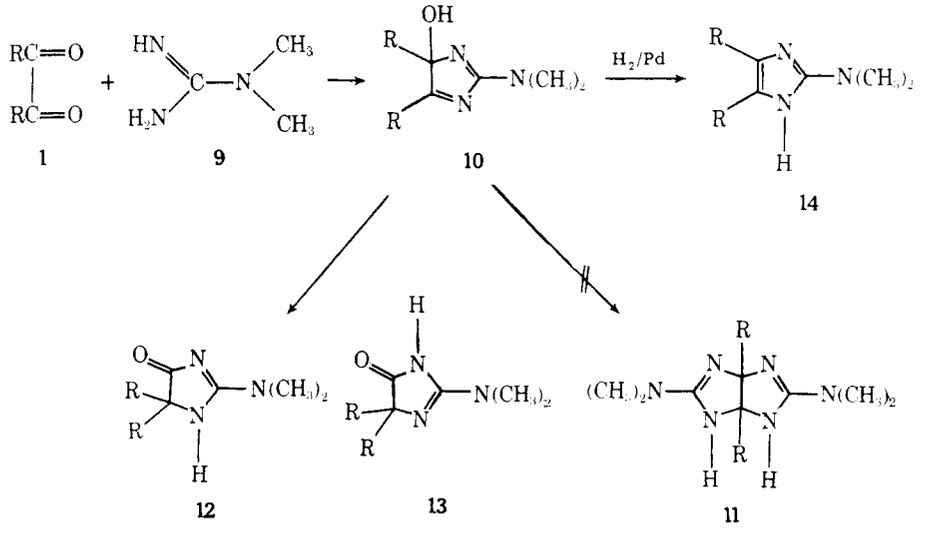
Reaction of Benzils with 1,1-Dimethylguanidine. Reaction of benzil (**1a**) with 1,1-dimethylguanidine (**9**) in methanol at room temperature produced 2-(dimethylamino)-4-hydroxy-4,5-diphenyl-4*H*-imidazole (**10a**) in 80% yield. Similarly 4,4′-dimethoxy- (**1b**) and 4,4′-dichlorobenzils (**1c**) gave the corresponding 4*H*-imidazoles **10b** and **10c** in 91 and 85% yields, respectively. The corresponding 2,6-bis(dimethylamino)imidazo[4,5-*d*]imidazoles (**11**) were not obtained in these experiments.

Quantitative conversion of 4*H*-imidazole **10a** to 2-(dimethylamino)-5,5-diphenylimidazolin-4-one (**12a**), mp >315 °C, occurred upon heating at 140 °C without solvent. The color change from yellow to white at 133 °C suggests that **10a** rearranges into **12a** at this temperature. The yield of **12a** was also quantitative when **10a** was heated in DMF at 140 °C or refluxed in ethanol for 4 h. Methoxy- (**10b**) and chlorophenyl-4*H*-imidazoles (**10c**) were similarly converted to the corresponding imidazolinones **12b** and **12c** in excellent yields.

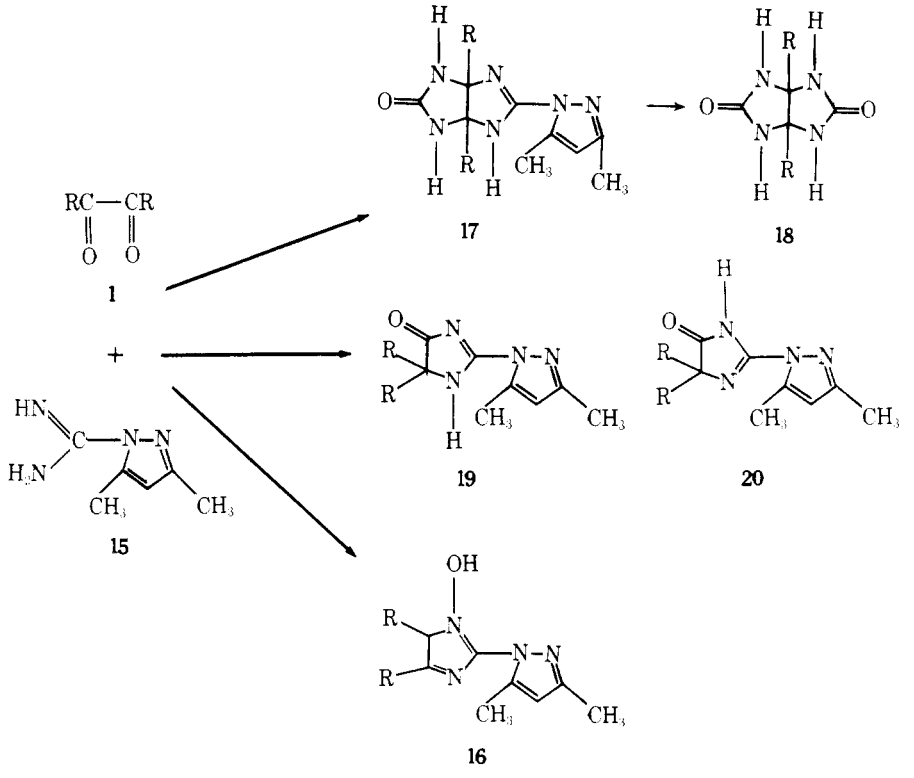
All of the imidazolinones obtained above exhibited an IR band at 1680 cm^{-1} assignable to C=O stretching vibrations, indicating that they exist as the imidazolin-4-one **12** rather than the other tautomeric form **13** in the solid state.[13]

Hydrogenation of 2-(dimethylamino)-4*H*-imidazoles **10** was facile and gave the corresponding new 2-(dimethylamino)-imidazoles **14a, 14b,** and **14c** hydrochlorides in 72, 66, and 82% yields, respectively.

Reaction of α-Diketones with 1-Amidino-3,5-dimethylpyrazole. In the reaction of benzil (**1a**) with 1-amidino-3,5-dimethylpyrazole (**15**), attempts to obtain the corresponding 4*H*-imidazole **16a** under various conditions failed.



a, $R = C_6H_5$; b, $R = p\text{-}CH_3OC_6H_4$; c, $R = p\text{-}ClC_6H_4$



a, R = C_6H_5; b, R = *p*-$CH_3OC_6H_4$; c, R = *p*-ClC_6H_4; d, R = *p*-$CH_3C_6H_4$; e, R = CH_3

However, an interesting imidazo[4,5-*d*]imidazole **17a** having different substituents at the 2 and 6 positions was obtained in 74% yield, based on **15**, by heating **1a** and **15** in ethanol at 80 °C. The structure of **17** was determined by IR, MS, NMR and elemental analysis. This structure was further confirmed by coincidence of the IR spectrum of an acid hydrolysis product of **17a** with that of glycoluril **18** obtained by the reaction of benzil with urea.[14] When the theoretically required ratio of **1a**/**15** of 1:2 was employed, the yield of **17a** decreased to 51%, as with the reaction between **1a** and **2**. Similarly, 4,4′-dichlorobenzil (**1c**) and 2,3-butanedione (**1e**) gave the corresponding imidazoimidazoles **17c** and **17e** in 57 and 40% yields, respectively.

As for the stereochemistry of imidazoimidazoles **3** and **17**, their cis configuration is most probable, since the greater strain[15] involved in trans compared to cis fusion of two five-membered rings and the cis geometry of **18** have been established.[16]

2-(3,5-Dimethyl-1-pyrazolyl)imidazolinones **19** were obtained in excellent yields by refluxing **1** and **15** nitrate in ethanol in the presence of NaOH and then acidifying the reaction mixture. The (methoxy- and chlorophenyl)imidazolinones **19b** and **19c** showed C=O stretching vibrations at 1760 and 1750 cm^{-1} and C=N stretching vibrations at 1660 and 1650 cm^{-1}, respectively, while these bands were found at 1705 and 1700 cm^{-1} and at 1550 and 1550 cm^{-1} for the unsubstituted **19a** and tolylimidazolinones **19d**. Therefore, **19a** and **19d** exist as conjugated 5*H*-imidazolin-4-ones **19**, and **19b** and **19c** as nonconjugated 4*H*-imidazolin-5-ones **20** in the solid state.[13]

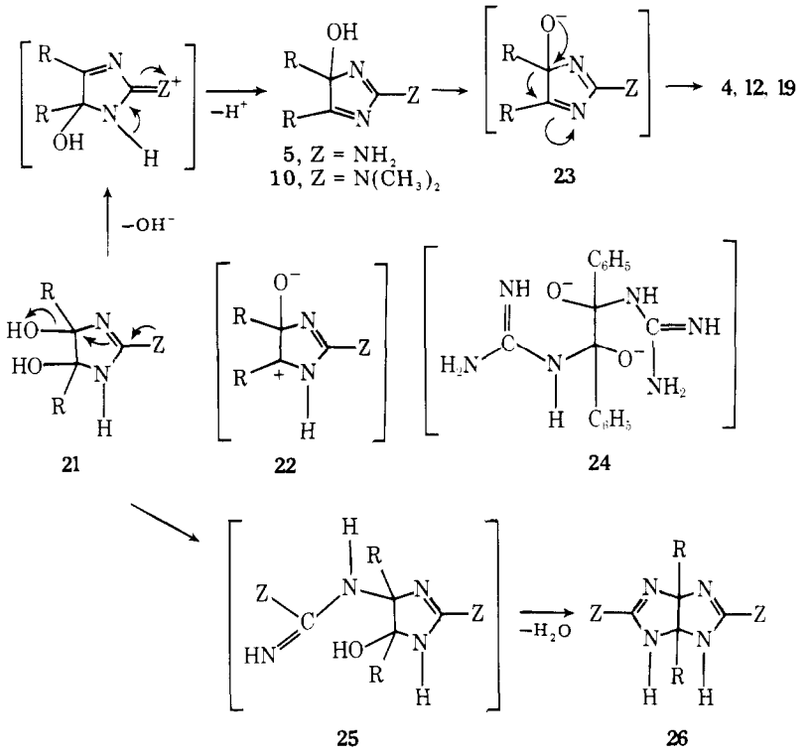
Discussion

It is well documented that the reaction of amidines with α-diketones gives 4,5-dihydroxyimidazolines.[17] According to a recent investigation by Imbach,[17k] 4,5-dihydroxyimidazolines, but not uncyclized intermediates, were detected by IR and NMR spectroscopy in the reaction mixtures of amidines with α-diketones. In view of these facts, the relatively stable 4,5-dihydroxyimidazolines **21** are probably formed initially in the condensation of benzils with guanidines. As the mechanism for formation of 2-(disubstituted amino)imidazolinones, Furukawa and his collaborators[6] proposed anionotropic migration of a phenyl group in the carbonium ions **22** formed from **21**. However, when Z in **21** is an electron-donating substituent such as amino or dimethylamino, dehydration takes place easily to form the 4*H*-imidazoles (**5** and **10**) rather than the carbonium ion intermediate **22**. 2-(Dimethylamino)-4-hydroxy-4*H*-imidazoles (**10**) quantitatively produced the corresponding imidazolinones (**12**) upon heating, presumably via anion **23**.

When Z in **21** is a 3,5-dimethylpyrazolyl group, the dehydration of **21** into the corresponding 4*H*-imidazoles is difficult because of the insufficient electron-donating character of the pyrazolyl group to release hydroxy ion from **21**. However, under alkaline conditions imidazolinones **19** are probably formed by the same mechanism as in the case where Z is dimethylamino or amino. The possibility of the intermediacy of 4-hydroxy-4*H*-imidazoles for the formation of imidazolinones is substantiated by a recent kinetic study of the reaction of ureas with benzils to form 5,5-diphenylhydantoins.[18]

Lempert[5] proposed the dianion **24** as the precursor in the formation of imidazo[4,5-*d*]imidazole **3**. We consider dehydrative cyclization of intermediates **25** produced by condensation of dihydroxyimidazolines **21** with guanidines to be a plausible mechanism for this reaction. When Z is a dimethylamino group, the 4-hydroxy-4*H*-imidazoles **10** are considerably more stable and thus **25** would not be formed. This might be the reason why 2,6-bis(dimethylamino)-imidazo[4,5-*d*]imidazoles **11** were not obtained in the reaction of 1,1-dimethylguanidine with α-diketones. On the other hand, when Z is an amino group, 4-hydroxy-4*H*-imidazoles **5** are suspected to be somewhat unstable in solution, since slight decomposition of **5a** into the starting materials was detectable on TLC. Thus, dihydroxyimidazolines (**21**) which must be formed in the course of the decomposition of **5** may be utilized as precursors of the imidazoimidazoles **26**.

However, the dehydrative cyclization mechanism described



above cannot explain the formation of unsymmetrical imidazoimidazoles **17** obtained in the case of amidinopyrazole **15**. The mechanism for formation of **17** is under investigation.

Experimental Section

Melting points were determined in capillary tubes and are uncorrected. IR spectra were obtained on a Hitachi recording spectrophotometer EPI-G2 as KBr tablets. NMR spectra were recorded on a Hitachi R-24 (60 MHz) spectrometer in the solvents indicated, and chemical shifts are given in parts per million relative to tetramethylsilane as an internal standard. The mass spectra were determined on a Japan Electron Optics JMS-OIS high-resolution spectrometer operating with an ionizing energy of 70 eV by the direct inlet procedure.

4,4′-Dichlorobenzil (1c) was prepared according to ref 19.

Guanidine (2). **2** carbonate (1.08 g, 6 mmol) was suspended in a solution of NaOH (0.44 g, 11 mmol) in methanol (15 mL), the mixture stirred for 1 h, and the resulting precipitate filtered off. The filtrate was evaporated to dryness under reduced pressure, and the residue was extracted with ethanol (10 mL). The extract was concentrated to dryness under reduced pressure, and the residue was dried over P_2O_5 in vacuo overnight to give 0.63 g (97%) of a semicrystalline mush.

1,1-Dimethylguanidine (9). By a similar procedure, **9** hydrogen sulfate (2.09 g, 15.4 mmol) yielded 1.08 g (89%) of white powder, mp 148–153 °C.

1-Amidino-3,5-dimethylpyrazole (15). A suspension of **15** nitrate (2.00 g, 10 mmol) in methanol (20 mL) containing NaOH (0.44 g, 11 mmol) was stirred for 30 min. After removing precipitated $NaNO_3$, the filtrate was concentrated at room temperature under reduced pressure and the remaining oily residue was extracted with ether (20 mL × 3). Drying over anhydrous Na_2SO_4 and evaporation of the extract gave 1.24 g (90%) of colorless oil.

2,6-Diamino-4,8-diphenylimidazo[4,5-*d*]imidazole (3). Method A. To a solution of benzil (**1a**; 2.10 g, 10 mmol) in dioxane (100 mL) was added a solution of **2** (0.59 g, 10 mmol) in methanol (10 mL) at room temperature, and the mixture was allowed to stand for 28 h. The resulting crystals were collected and washed with dioxane (2 mL × 3) to give 1.42 g (74%) of **3**·$C_4H_8O_2$ (dioxane solvate) as colorless needles, mp 221–222 °C dec. An analytical sample was obtained by dissolving in ethanol followed by addition of dioxane: mp 212 °C dec; IR (KBr) 3350, 3050, 1655, 1600, 1495, 1120, 900, 870, 700 cm^{-1}; NMR (Me_2SO-d_6) δ 3.58 (8 H, s, $C_4H_8O_2$), 6.80–7.30 (10 H, m, phenyl ring protons); MS *m/e* (rel intensity) 292 (3, M^+), 249 (13), 235 (10), 188 (7), 104 (13), 88 (100), 57 (80), 42 (37). Anal. Calcd for $C_{16}H_{16}N_6$·$C_4H_8O_2$: C, 63.14; H, 6.36; N, 22.09. Found: C, 63.05; H, 6.28; N, 22.24.

The dioxane solvate of **3** was dissolved in methanol and precipitated by the addition of ether to give colorless plates of dioxane-free **3**: mp 227 °C dec (lit.[5] mp 235 °C dec); IR (KBr) 3500–2900 (brd), 1650, 1455, 1240, 780, 700 cm^{-1}; MS *m/e* (rel intensity) 292 (9, M^+), 249 (20), 235 (41), 233 (38), 188 (12), 165 (15), 130 (33), 104 (45), 103 (100), 77 (52).

Method B. A solution of 2-amino-4,5-diphenyl-4-hydroxy-4*H*-imidazole (**5a**·CH_3OH: 0.50 g, 1.8 mmol) in sodium-dried and distilled THF (10 mL) was allowed to stand at room temperature for 4 h to give 0.21 g (72%) of colorless needles: mp 200–201 °C dec; IR was identical with that of **3**.

2-Amino-5,5-diphenylimidazolin-4-one (4). Method A. To a suspension of **5a**·CH_3OH (2.83 g, 10 mmol) in methanol (40 mL) was added a solution of NaOH (0.80 g, 20 mmol) in water (4 mL). The mixture was heated at 65 °C for 5 min and then allowed to stand at room temperature to give 2.32 g (92%) of colorless prisms: mp >290 °C (lit.[5] mp 360 °C); IR (KBr) 3340, 3020, 1720 (m, νC=O), 1660, 1500, 1450, 1280, 760, 700 cm^{-1}; MS *m/e* (rel intensity) 251 (85, M^+), 223 (32), 222 (100), 182 (41), 180 (42), 165 (44), 146 (27), 120 (32), 103 (85). IR and mass spectra were identical with those of an authentic sample obtained by the procedure in ref 5.

Method B. To a solution of **1a** (2.10 g, 10 mmol) in dioxane (200 mL) was added a solution of **2** (1.18 g, 20 mmol) in methanol (20 mL) at room temperature, and the mixture was allowed to stand for 28 h, during which time **3**·$C_4H_8O_2$ (1.20 g, 31%), mp 222–224 °C dec, precipitated. After filtration, the filtrate was allowed to stand for 27 h at room temperature, giving 1.34 g (46%) of **4**.

2-Amino-4-hydroxy-4,5-diphenyl-4*H*-imidazole (5a·CH_3OH). To a solution of **2** (3.07 g, 52 mmol) in methanol (75 mL) was added **1a** (10.92 g, 52 mmol) at room temperature, and the mixture was stirred for 30 min. The precipitated solid was collected and washed with methanol (10 mL × 2) and then with ether (10 mL × 2) to give 12.45 g (85%) of pale yellow microcrystalline solid: mp 99–100 °C sinter, decomposed at about 220 °C (dependent upon rate of heating). A 1-g amount of the crude product was dissolved in methanol (32 mL) at 70 °C, and the solution was filtered hot. The filtrate was allowed to stand at room temperature for 7 h to give 0.19 g of pure **5a**·CH_3OH: mp about 247 °C dec (dependent upon rate of heating); IR (KBr) 3350, 3180, 2700 (brd), 1610, 1590, 1575, 1450, 1400, 1160, 1015, 750, 700 cm^{-1}; NMR (Me_2SO-d_6) δ 3.31 (3 H, s, CH_3OH), 3.6–4.3 (about 1 H, brd, disappeared on addition of D_2O, OH of the 4-hydroxy group or the solvated methanol), 6.5–7.6 (about 1 H, brd, disappeared on addition of D_2O, OH of the 4-hydroxy group or the solvated methanol), 6.84 (2 H, brd s, disappeared on addition of D_2O, NH_2), 7.20–7.60 (3 H, m, H_{3-5} of 5-C_6H_5), 7.90–8.20 (2 H, m, $H_{2,6}$ of 5-C_6H_5); MS *m/e* (rel intensity) 251 (13, M^+), 235 (11), 222 (15), 148 (29), 147 (32), 105

(100), 104 (23), 103 (13), 77 (60), 51 (24). Anal. Calcd for $C_{15}H_{13}N_3O \cdot CH_3OH$: C, 67.83; H, 6.05; N, 14.83. Found: C, 67.53; H, 6.07; N, 15.09.

Other 4*H*-imidazoles were prepared in a similar manner except for the 2-dimethylamino compounds (**12**), in which case 3–4 mL of methanol/mmol of **11** and a reaction period of 24 h at room temperature were employed.

Since 4*H*-imidazoles (**5, 10**) are transformed easily into imidazolinones (**4, 12**) in hot solution, it is very difficult to obtain high recoveries of the pure materials by recrystallization. However, the crude products showed no sign of impurities in their NMR spectra, and were used in the next steps, giving the desired reaction products in high yields.

2-Amino-4-hydroxy-4,5-bis(4-chlorophenyl)-4*H*-imidazole (5c). A 1-h reaction period gave a pale yellowish green powder in 91% yield: mp 172 °C sinter, 182–201 °C dec; IR (KBr) 3460, 3330, 3160, 1670, 1610, 1585, 1500, 1390, 1170, 1010, 840, 760 cm^{-1}. Further purification was unsuccessful.

2-Amino-4-hydroxy-4,5-bis(4-methylphenyl)-4*H*-imidazole (5d·CH$_3$OH): 83% yield of yellowish microcrystals; mp 104–107 °C eff. Pure **5d**·CH_3OH (from methanol): yellow prisms; mp 132 °C sinter, 275 °C dec (gradual darkening ≥170 °C); IR (KBr) 3470, 3330, 3160, 1670, 1610, 1580, 1560, 1520, 1390, 1335, 1195, 1170, 1015, 830, 750 cm^{-1}; NMR (Me_2SO-d_6) δ 2.19 (3 H, s, 4-$C_6H_4CH_3$), 2.26 (3 H, s, 5-$C_6H_4CH_3$), 3.14 (3 H, s, CH_3OH), 3.5–4.4 (about 1 H, brd, disappeared on addition of D_2O, OH of the 4-hydroxy group or the solvated methanol), 6.20 (about 1 H, brd, disappeared on addition of D_2O, OH of the 4-hydroxy group or the solvated methanol), 6.63 (2 H, brd s, disappeared on addition of D_2O, NH_2), 7.02 (4 H, s, 4-$C_6H_4CH_3$), 7.10 (2 H, d, J = 8.0 Hz, $H_{3,5}$ of 5-$C_6H_4CH_3$), 7.78 (2 H, d, J = 8.0 Hz, $H_{2,6}$ of 5-$C_6H_4CH_3$). Anal. Calcd for $C_{17}H_{17}N_3O \cdot CH_3OH$: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.22; H, 6.72; N, 13.56.

2-(Dimethylamino)-4-hydroxy-4,5-diphenyl-4*H*-imidazole (10a): 80% of yellow prisms; mp 140 °C color change, >300 °C. Pure **10a** (from methanol): mp 133.5–134 °C color change, >300 °C; IR (KBr) 3050, 3010, 1640, 1615, 1430, 1405, 1185, 1150, 700 cm^{-1}; NMR ($CDCl_3$) δ 3.22 (6 H, s, NCH_3), 3.8–4.8 (1 H, brd, disappeared on addition of D_2O, OH), 7.12–7.55 (8 H, m, 4-C_6H_5 and H_{3-5} of 5-C_6H_5), 8.02–8.25 (2 H, m, $H_{2,6}$ of 5-C_6H_5). Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.09; H, 6.13; N, 15.04. Found: C, 72.75; H, 6.00; N, 14.90.

2-(Dimethylamino)-4-hydroxy-4,5-bis(4-methoxyphenyl)-4*H*-imidazole (10b): 91% yield of yellow prisms; mp 163–165 °C color change, 268–271 °C dec. Pure **10b** (from methanol): mp 163 °C color change, 267–270 °C dec; IR (KBr) 2950, 2840, 1635, 1625, 1520, 1400, 1270, 1175, 1150, 1035, 850 cm^{-1}; NMR ($CDCl_3$) δ 3.16 (6 H, s, NCH_3), 3.60 (1 H, brd s, disappeared on addition of D_2O, OH), 3.71 (3 H, s, 4-$C_6H_4OCH_3$), 3.78 (3 H, s, 5-$C_6H_4OCH_3$), 6.68 (2 H, d, J = 9.0 Hz, $H_{3,5}$ of 4-$C_6H_4OCH_3$), 6.79 (2 H, d, J = 9.0 Hz, $H_{3,5}$ of 5-$C_6H_4OCH_3$), 7.22 (2 H, d, J = 9.0 Hz, $H_{2,6}$ of 4-$C_6H_4OCH_3$), 8.02 (2 H, d, J = 9.0 Hz, $H_{2,6}$ of 5-$C_6H_4OCH_3$). Anal. Calcd for $C_{19}H_{21}N_3O_2$: C, 67.23; H, 6.23; N, 12.38. Found: C, 67.16; H, 6.20; N, 12.51.

2-(Dimethylamino)-4-hydroxy-4,5-bis(4-chlorophenyl)-4*H*-imidazole (10c): 85% yield of yellowish powder; mp 178–180 °C color change, 269–275 °C. Pure **10c** (from DMF): yellow prisms; mp 175–189 °C color change, 272–276 °C; IR (KBr) 2720 (brd), 1640, 1600, 1495, 1430, 1410, 1160, 1100, 1020, 840, 750 cm^{-1}; NMR (Me_2SO-d_6) δ 3.18 (6 H, s, NCH_3), 6.90 (1 H, s, disappeared on addition of D_2O, OH), 7.25 (4 H, s, 4-C_6H_4Cl), 7.45 (2 H, d, J = 9.0 Hz, $H_{3,5}$ of 5-C_6H_4Cl), 7.93 (2 H, d, J = 9.0 Hz, $H_{2,6}$ of 5-C_6H_4Cl). Anal. Calcd for $C_{17}H_{15}N_3OCl$: C, 58.63; H, 4.37; N, 12.07. Found: C, 58.51; H, 4.38; N, 12.14.

2-Amino-4,5-dihydroxy-4,5-diphenylimidazoline (6) Hydrochloride. A suspension of 4*H*-imidazole **5a**·CH_3OH (0.27 g, 0.9 mmol) in concentrated HCl (5 mL) was allowed to stand for 2.5 h at room temperature. Filtration and washing with concentrated HCl (1 mL × 2) and then with ether (20 mL) of the resulting precipitate gave 0.13 g (45%) of colorless needles: mp 115–116 °C dec; IR (KBr) 3130 (brd), 1685, 1560, 1455, 1220, 1100, 1060, 780, 700 cm^{-1}; MS m/e (rel intensity) 210 (4), 105 (100), 77 (34). Purification of this material was unsuccessful because of its liability to decompose to **1a** and **2**.

2-Amino-4,5-dimethoxy-4,5-diphenylimidazoline (7) Hydrochloride 0.5 H$_2$O·0.5 CH$_3$OH. 4*H*-Imidazole **5a**·CH_3OH (4.36 g, 15.4 mmol) was dissolved in methanol (48 mL) containing concentrated HCl (2 mL), and the solution was evaporated to dryness at room temperature. The residue was dissolved in hot methanol (5 mL), and ether (33 mL) was added to the solution. After standing overnight, the resulting precipitates were collected and washed with ether (5 mL × 2) to give 3.84 g (71%) of colorless needles, mp 153–154 °C eff. Concentration of the filtrate and addition of ether afforded an additional 0.8 g (total yield was 82%) of the desired imidazoline, mp 143 °C eff. Three recrystallizations from methanol–ether yielded colorless needles: mp 144.5 °C eff; IR (KBr) 3110 (brd), 1695, 1560, 1460, 1260, 1105, 1050, 780, 700 cm^{-1}; NMR (Me_2SO-d_6) δ 2.90 (6 H, s, OCH_3), 3.20 (1.5 H, s, CH_3OH), 7.45 (10 H, m, C_6H_5); MS m/e (rel intensity) 265 (8, $M^+ - CH_3OH$), 251 (10), 235 (17), 180 (18), 165 (24), 162 (61), 161 (55), 148 (63), 105 (100), 77 (77). Anal. Calcd for $C_{17}H_{19}N_3O_2 \cdot 0.5H_2O \cdot 0.5CH_3OH$: C, 58.57; H, 6.46; N, 11.71. Found: C, 58.51; H, 6.16; N, 12.04.

2-Amino-4,5-diphenylimidazole (8a). A suspension of **5a**·CH_3OH (2.83 g, 10 mmol) and 5% Pd/C (0.60 g) in methanol (20 mL) was hydrogenated at room temperature and under atmospheric pressure. Hydrogen uptake ceased after 8 h, amounting to about 350 mL (1.5 times the theoretical amount) of hydrogen. The catalyst was then filtered off and the filtrate evaporated to dryness under reduced pressure. To the crystalline residue was added ethanol (4 mL), and the mixture was allowed to stand overnight at room temperature. The resulting crystals were collected by filtration and washed with ethanol (1 mL × 2) to give 1.99 g (84%) of pale yellow prisms, mp 231–235 °C dec. Recrystallization from ethanol yielded pale yellow prisms, mp 233–235 °C dec (lit.[11a] mp 233–234 °C dec).

8a Nitrate. A solution of **5a**·CH_3OH (2.83 g, 10 mmol) in methanol (20 mL) was hydrogenated according to the same procedure as above, and the catalyst was filtered off. To the filtrate was added 61% HNO_3 (0.75 mL), and the solution was allowed to sit overnight. Filtration and washing with methanol (1 mL × 2) of the precipitated crystals afforded 1.94 g (65%) of colorless needles, mp 163–164 °C dec. Concentration of the filtrate to one-quarter of its volume and addition of ether (40 mL) gave a second crop (0.64 g, total 86%) of the desired product, mp 159–161 °C dec. Recrystallization from methanol afforded pure **8a**·HNO_3: mp 167 °C dec; IR (KBr) 3400, 3170, 3050, 1700 (vs, νC=N), 1400 (vs, NO_3^-), 1340, 770, 700 cm^{-1}; MS m/e (rel intensity) 235 (100, M^+), 193 (10), 165 (23), 105 (51), 104 (27), 103 (16), 77 (33). Anal. Calcd for $C_{15}H_{13}N_3 \cdot HNO_3$: C, 60.39; H, 4.73; N, 18.78. Found: C, 60.34; H, 4.78; N, 19.07.

2-Amino-4,5-bis(4-chlorophenyl)imidazole (8c) Hydrochloride. According to the procedure described for the preparation of **8a**, a solution of **5c** (1.60 g, 5 mmol) in methanol (30 mL) was hydrogenated in the presence of 5% Pd/C (0.40 g). After hydrogen uptake was complete (about 180 mL of hydrogen absorbed), concentrated HCl was added to the reaction mixture and the catalyst was filtered off. The filtrate was concentrated to dryness under reduced pressure, and drying over P_2O_5 and KOH in vacuo gave 1.62 g (95%) of white powder, mp 111 °C sinter, 238 °C dec, which was pure enough to be utilized in the next step without purification. The crude product was recrystallized by dissolution in hot ethanol (14.5 mL) followed by addition of ether (10 mL) to give 0.36 g of colorless needles; mp 250–253 °C dec. Workup of the filtrate and washings yielded 0.33 g of **8c**·HCl, mp 247–253 °C dec, the total yield being 41%. Further recrystallization from ethanol afforded an analytical sample: mp 268–269 °C dec; IR (KBr) 3150 (brd), 1700, 1680, 1510, 1100, 850, 830 cm^{-1}. Anal. Calcd for $C_{15}H_{11}N_3Cl_2 \cdot HCl$: C, 52.89; H, 3.55; N, 12.33. Found: C, 52.85; H, 3.85; N, 12.57.

8c Nitrate. In the same procedure as employed in the preparation of **8a**·HCl, 61% HNO_3 (0.4 mL) was replaced by concentrated HCl. The reaction mixture was concentrated to about 5 mL under reduced pressure and ethanol (2 mL) was added. Complete drying up should be avoided because it gives a brown intractable residue. The mixture was kept in a refrigerator overnight to yield 0.54 g of colorless needles, mp 157–159 °C dec. Concentration of the filtrate to about 2 mL and addition of ether (6 mL) gave a second crop (0.73 g), mp 139 °C dec. The total yield was 69%. Recrystallization from ethanol provided an analytical sample: colorless plate; mp 160 °C dec; IR (KBr) 3200 (brd), 1720, 1690, 1400 (NO_3^-), 1330, 1100, 830 cm^{-1}; MS m/e (rel intensity) 305 (64, M^+), 303 (100, M^+), 141 (30), 140 (19), 139 (100), 138 (30), 111 (36). Anal. Calcd for $C_{15}H_{11}N_3Cl_2 \cdot HNO_3$: C, 49.06; H, 3.29; N, 15.26. Found: C, 49.08; H, 3.33; N, 15.25.

2-Amino-4,5-bis(4-methylphenyl)imidazole (8d) Hydrochloride. In the same manner as in **8c**·HCl, a residue obtained from **5d**·CH_3OH (3.11 g, 10 mmol), methanol (50 mL), 5% Pd/C (1.20 g), and concentrated HCl (6.4 mL) was dissolved in hot methanol (6 mL), and the solution was allowed to stand overnight to give 2.40 g (78%) of pale yellow prisms, mp 244–255 °C dec. Recrystallization from methanol afforded pale yellow prisms, mp 255–259 °C dec. Anal. Calcd for $C_{17}H_{17}N_3 \cdot HCl \cdot 0.5H_2O$: C, 66.12; H, 6.20; N, 13.60. Found: C, 66.23; H, 6.18; N, 13.71.

8d Nitrate. In the same procedure as employed in the preparation of **10d**·HCl, 61% HNO_3 (0.75 mL) was used in place of concentrated HCl. Concentration of the reaction mixture to about 5 mL and keeping it overnight in a refrigerator gave 3.04 g (93%) of pale yellowish green prisms, mp 202 °C dec. Recrystallization from ethanol afforded pure

8d·HNO_3: pale yellow needles; mp 186 °C dec; IR (KBr) 3150 (brd), 1710, 1700, 1390 (NO_3^-), 1335, 820 cm^{-1}; MS *m/e* (rel intensity) 263 (100, M^+), 188 (16). Anal. Calcd for $C_{17}H_{17}N_3 \cdot HNO_3$: C, 62.56; H, 5.56; N, 17.17. Found: C, 62.62; H, 5.63; N, 17.19.

2-Amino-4,5-dimethylimidazole (8e) Nitrate. Butane-2,3-dione (**1e**; 1.72 g, 20 mmol) was added dropwise with stirring to a solution of **2** (1.18 g, 20 mmol) in methanol (40 mL) cooled at −10 °C. After 5 min, the solution was hydrogenated under atmospheric pressure in the presence of PtO_2 while cooling at 0–5 °C with ice water. Hydrogen uptake ceased after 4 h, amounting to 630 mL (1.4 times the theoretical amount). The reaction mixture was acidified with 61% HNO_3 (1.50 mL) and the catalyst was filtered off. The filtrate was concentrated to about 5 mL under reduced pressure at 40 °C. To the yellowish brown viscous concentrate was added ether (8 mL), and the solution was allowed to stand overnight in a refrigerator. The resulting solid was filtered and washed with 1:1 ethanol–ether (4 mL × 2) to yield 1.63 g (47%) of pale yellow powder, mp 175–210 °C dec (gradual darkening ≥140 °C). Recrystallization from water afforded pale brown needles: mp ~248 °C dec without melting; IR (KBr) 3450, 3200, 1695, 1680, 1395 (NO_3^-) cm^{-1}; MS *m/e* (rel intensity) 111 (100, M^+), 110 (88), 96 (20), 68 (38), 43 (44), 42 (61), 41 (29). Calcd for $C_5H_{10}N_3 \cdot HNO_3$: C, 34.48; H, 5.78; N, 32.17. Found: C, 34.60; H, 5.63; N, 32.38.

2-Amino-4(5)-methyl-5(4)-phenylimidazole (8f) Nitrate. In the same manner as employed in the preparation of **8e·HNO_3**, a mixture of 1-phenyl-1,2-propanedione (**1f**; 1.52 g, 10.3 mmol), **2** (0.61 g, 10.3 mmol), PtO_2 (0.25 g), and methanol (20 mL) was allowed to absorb 380 mL of hydrogen (1.6 times the theoretical amount). The catalyst was removed by filtration and the crystals began to precipitate immediately after addition of 61% HNO_3 (0.75 mL) to the filtrate. After standing overnight in a refrigerator, 0.59 g (25%) of the pale pink needles, mp 200–206 °C dec, was collected by filtration. Concentration of the filtrate, washings, and addition of ethanol (4 mL) yielded an additional 0.71 g (total 55%) of **8f·HNO_3**, mp 175–181 °C dec. Two recrystallizations from methanol afforded analytically pure **8f·HNO_3**: pale pink flaked crystals; mp 211–214 °C dec; IR (KBr) 3370, 3150 (brd), 1710, 1680, 1390 (NO_3^-), 1340, 740, 700 cm^{-1}; MS *m/e* (rel intensity) 173 (100, M^+), 172 (52), 104 (25), 103 (25). Anal. Calcd for $C_{10}H_{11}N_3 \cdot HNO_3$: C, 50.84; H, 5.12; N, 23.72. Found: C, 50.61; H, 5.13; N, 24.02.

2-(Dimethylamino)-4,5-diphenylimidazole (14a) Hydrochloride. A suspension of 4*H*-imidazole **10a** (1.40 g, 5 mmol) and PtO_2 (0.15 g) in 150 mL of methanol was hydrogenated at room temperature and under atmospheric pressure. Hydrogen uptake ceased after 1.5 h, amounting to about 180 mL (1.6 times the theoretical amount) of hydrogen. Concentrated HCl (0.7 mL) was then added to the reaction mixture, and the catalyst was filtered off. The filtrate was concentrated to dryness under reduced pressure, and the residue was recrystallized from ethanol (27 mL) to give 0.76 g of colorless prisms, mp 261–271 °C dec. An additional 0.32 g (total 72%), mp 278–283 °C dec, of **14a**·HCl was obtained by evaporation of the mother liquor and recrystallization of the residue. An analytical sample was prepared by two recrystallizations from ethanol: colorless prisms; mp 283 °C dec; IR (KBr) 2940, 2750, 2680, 1680, 1650, 1460, 925, 770, 700 cm^{-1}; MS *m/e* (rel intensity) 263 (100, M^+), 248 (33), 234 (31), 193 (20), 178 (15). Anal. Calcd for $C_{17}H_{17}N_3$·HCl: C, 68.11; H, 6.05; N, 14.02. Found: C, 68.06; H, 6.26; N, 14.07.

The following 2-(dimethylamino)imidazoles were prepared in a similar manner.

2-(Dimethylamino)-4,5-bis(4-methoxyphenyl)imidazole (14b) Hydrochloride: 82% yield of pale yellow microcrystals; mp 234–240 °C dec. Pure **14b**·HCl (from ethanol): colorless needles; mp 239–241 °C dec; IR (KBr) 2920 (brd), 2250, 2160, 1675, 1610, 1530, 1515, 1460, 1300, 1260, 1180, 1035, 920, 835 cm^{-1}; MS *m/e* (rel intensity) 323 (100, M^+), 308 (51). Anal. Calcd for $C_{19}H_{21}N_3O_2$·HCl: C, 63.42; H, 6.16; N, 11.68. Found: C, 63.44; H, 6.42; N, 11.94.

2-(Dimethylamino)-4,5-bis(4-chlorophenyl)imidazole (14c) Hydrochloride: 66% yield of colorless granular crystals; mp >303 °C; IR (KBr) 2940, 2750, 2660, 1685, 1640, 1495, 1460, 1100, 1020, 920, 830 cm^{-1}; MS *m/e* (rel intensity) 333 (64, M^+), 331 (100, M^+), 316 (34), 302 (24), 261 (12), 246 (14). Anal. Calcd for $C_{17}H_{15}N_3Cl_2$·HCl: C, 55.38; H, 4.37; N, 11.40. Found: C, 55.12; H, 4.39; N, 11.49.

2-(Dimethylamino)-5,5-diphenylimidazolin-4-one (12a). Method A. 4*H*-Imidazole **10a** (0.10 g, 0.3 mmol) was refluxed in ethanol (20 mL) for 4 h and allowed to stand overnight in a refrigerator to give 0.07 g (70%) of colorless prisms: mp >315 °C (lit.[8] mp 357 °C); IR (KBr) 3050, 1680, (νC=O), 1620 (νC=N), 1590, 1450, 1420, 1305, 770, 710, 700 cm^{-1}; MS *m/e* (rel intensity) 279 (100, M^+), 250 (29), 180 (17), 165 (22), 147 (17), 112 (20), 104 (17), 83 (27), 77 (21), 71 (68), 70 (21).

Method B. Heating finely powdered **10a** (0.1 g, 0.3 mmol) without solvent for 20 min at 140–150 °C (oil bath temperature) yielded **12a** in quantitative yield. Its IR spectrum was identical with that of **12a** obtained in method A.

Method C. Immediately after dissolution of **10a** (2.79 g, 10 mmol) in 35 mL of DMF at 140 °C, the solution was allowed to sit for 5 h at room temperature. Precipitated crystals were filtered, washed with ethanol (2 mL × 3), and air-dried to afford colorless needles (2.37 g, 85%), mp >315 °C. Its IR spectrum was identical with that of **12a** prepared in method A.

12a Hydrochloride. Imidazolinone **12a** (1.30 g) was dissolved in 2% HCl (26 mL) at 80 °C. After standing overnight at room temperature, the collected solid was washed with acetone (3 mL × 3) to afford 1.31 g (86%) of colorless prisms, mp 175 °C sinter, 187–193 °C eff (dependent upon rate of heating). Recrystallization from 2% HCl yielded pure **12a**·HCl: colorless prisms; mp 178 °C sinter, 183–185 °C eff (dependent upon rate of heating); IR (KBr) 3350 (brd), 2920, 2790, 2700, 1780 (νC=O), 1720, 1505, 1450, 1260, 700 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N_3O$·HCl·0.5H_2O: C, 62.86; H, 5.89; N, 12.93. Found: C, 62.93; H, 6.05; N, 13.03.

The following 2-(dimethylamino)imidazolinones were prepared in a similar manner.

2-(Dimethylamino)-5,5-bis(4-methoxyphenyl)imidazolin-4-one (12b). A. An 83% yield of pale yellow prisms was obtained, mp 265–271 °C. **B.** Heating at 170–180 °C gave a 100% yield of white powder, mp 267–270 °C. **C.** Dissolving **10b** (2.00 g, 5.9 mmol) in DMF (4 mL) at 160 °C yielded 1.96 g (98%) of a white powder, mp 263–270 °C. An analytical sample (from ethanol) showed the following: colorless prisms; mp 270–271 °C; IR (KBr) 3150 (brd), 1680 (νC=O), 1610, 1590, 1515, 1450, 1310, 1260, 1180, 1040, 835 cm^{-1}; NMR (CD_3OD) δ 3.75 (6 H, s, $C_6H_4OC\mathbf{H}_3$), 7.02 (8 H, m, $C_6\mathbf{H}_4OCH_3$); MS *m/e* (rel intensity) 339 (100, M^+), 310 (34), 227 (25), 134 (16), 117 (18), 83 (23), 71 (25), 70 (20). Anal. Calcd for $C_{19}H_{21}N_3O_3$: C, 67.29; H, 6.24; N, 12.38. Found: C, 67.41; H, 6.24; N, 12.39.

12b Hydrochloride: 78% yield of colorless needles; mp 183 °C eff; IR (KBr) 3400 (brd), 2950, 2840, 1780 (νC=O), 1720, 1620, 1520, 1260, 1180, 1040, 840 cm^{-1}. Anal. Calcd for $C_{19}H_{21}N_3O_3$·HCl: C, 57.93; H, 6.14; N, 10.67. Found: C, 57.88; H, 6.06; N, 10.68.

2-(Dimethylamino)-5,5-bis(4-chlorophenyl)imidazolin-4-one (12c). A. A 60% yield of colorless crystals was obtained, mp 261–263 °C. **B.** Heating at 180 °C gave a 100% yield of white powder, mp 258–271 °C. Its NMR spectrum was identical with that of **12c** obtained in A. **C.** Heating of **10c** (1.39 g, 4 mmol) in 2.5 mL of DMF at 150–155 °C for 20 min, addition of ether (10 mL) to the cooled solution, and standing overnight at room temperature yielded 1.25 g (90%) of colorless crystals, mp 260–262 °C. Pure **12c** (from ethanol): mp 261–263 °C; IR (KBr) 3220, 1685 (νC=O), 1620, 1500, 1445, 1310, 1100, 1020, 830 cm^{-1}; NMR (Me_2SO-d_6) δ 3.07 (6 H, s, NCH_3), 7.30 (8 H, s, C_6H_4Cl), 9.00 (1 H, brd s, disappeared on addition of D_2O, NH); MS *m/e* (rel intensity) 349 (47, M^+), 347 (74, M^+), 320 (24), 318 (35), 181 (43), 138 (20), 112 (26), 98 (25), 83 (33), 71 (100), 70 (65).

12c Hydrochloride. A hot solution of **12c** (1.05 g, 3 mmol) in acidic ethanol (5 mL of ethanol + 0.4 mL of concentrated HCl) was stripped on a rotary evaporator, and the residue was crystallized from ethanol–ether to give 1.03 g (90%) of colorless needles, mp 191 °C sinter, 200 °C. Recrystallization from ethanol–ether produced pure **12c**·HCl: colorless needles; mp 188 °C sinter, 206 °C; IR (KBr) 2770, 2660, 1785 (νC=O), 1720, 1500, 1100, 1020, 890, 830 cm^{-1}. Anal. Calcd for $C_{17}H_{15}N_3OCl_2$·HCl·0.5H_2O: C, 51.86; H, 4.35; N, 10.67. Found: C, 51.90; H, 4.33; N, 10.68.

6-(3,5-Dimethylpyrazol-1-yl)-4,8-diphenyl-2,3-dihydroimidazo[4,5-*d*]imidazol-2-one (17a). A mixture of **1a** (1.06 g, 5 mmol) and 1-amidino-3,5-dimethylpyrazole (**15**; 0.69 g, 5 mmol) in ethanol (1.5 mL) was heated at 80 °C for a few minutes and then immediately cooled to room temperature. After addition of ether, the solution was allowed to sit overnight at room temperature. The resulting precipitates were collected and washed well with ether to give 0.69 g (74% based on **15**) of colorless prisms, mp 272–275 °C dec. Dissolution in DMF and addition of methanol yielded pure **17a**: mp 276 °C dec; IR (KBr) 3400, 3180, 3070, 1705 (νC=O), 1630, 1510, 1450, 970, 700 cm^{-1}; NMR (CF_3CO_2D) δ 2.42 and 2.75 (3 H, and 3 H, s, CCH_3), 6.45 (1 H, s, =CH–), 7.20 (10 H, s, C_6H_5); MS *m/e* (rel intensity) 372 (64, M^+), 329 (19), 328 (32), 277 (16), 276 (16), 268 (19), 273 (29), 123 (7), 104 (100), 97 (42), 95 (5), 77 (48). Anal. Calcd for $C_{21}H_{20}N_6O$: C, 67.72; H, 5.41; N, 22.57. Found: C, 67.22; H, 5.50; N, 22.33.

6-(3,5-Dimethylpyrazol-1-yl)-4,8-bis(4-chlorophenyl)-2,3-dihydroimidazo[4,5-*d*]imidazol-2-one (17c). To a solution of **1c** (1.39 g, 5 mmol) in ethanol (10 mL) + benzene (25 mL) was added a solution of **15** (1.38 g, 10 mmol) in benzene (10 mL). After refluxing for 2 h, the resulting precipitates were filtered, washed with $CHCl_3$

(3 mL × 3), and air-dried to give 1.25 g (57%) of white powder, mp 256–257 °C dec. Recrystallization from ethanol yielded colorless prisms: mp 259 °C dec; IR (KBr) 3230 (brd), 1710 (νC=O), 1640, 1510, 1500, 1400, 1100, 1020, 840 cm^{-1}; MS *m/e* (rel intensity) 442 (28, M^+), 440 (35, M^+), 398 (18), 396 (20), 345 (18), 309 (13), 302 (28), 207 (23), 138 (100), 97 (42), 95 (20). Anal. Calcd for $C_{21}H_{18}N_6OCl_2 \cdot 0.5C_2H_5OH \cdot 0.5H_2O$: C, 55.82; H, 4.67; N, 17.76. Found: C, 55.42; H, 4.82; N, 17.70.

6-(3,5-Dimethylpyrazol-1-yl)-4,8-dimethyl-2,3-dihydroimidazo[4,5-*d*]imidazol-2-one (17e). Refluxing **1e** (0.43 g, 5 mmol) and **15** (1.38 g, 10 mmol) in methanol (7 mL) for 2 h gave 0.50 g (40%) of colorless plates, mp 222–224 °C dec. Recrystallization from methanol afforded colorless plates: mp 227 °C dec; IR (KBr) 3250, 1710 (νC=O), 1625, 1510, 1410, 1160, 1110 cm^{-1}; MS *m/e* (rel intensity) 248 (94, M^+), 204 (42), 190 (17), 165 (16), 164 (35), 163 (32), 153 (42), 152 (23), 123 (70), 112 (25), 111 (30), 97 (89), 96 (82), 95 (38), 84 (39), 83 (45), 42 (100). Anal. Calcd for $C_{11}H_{16}N_6O \cdot 0.5H_2O$: C, 51.34; H, 6.66; N, 32.67. Found: C, 51.55; H, 6.51; N, 33.06.

Hydrolysis of 17a to 3a,6a-Diphenylglycoluril (18). A suspension of **17a** (0.20 g, 0.5 mmol) in 10% HCl (4 mL) was heated at 95 °C for 3 h and then allowed to sit overnight at room temperature. The resulting precipitates were filtered, washed with water and then with methanol, and dried to yield 0.11 g (70%) of white powder, mp >310 °C (lit.[14] mp 330 °C). Its IR spectrum was identical with that of an authentic sample prepared according to ref 14.

2-(3,5-Dimethylpyrazol-1-yl)-5,5-diphenyl-5*H*-imidazolin-4-one (19a). Refluxing **15**·HNO_3 (2.00 g, 10 mmol) and **1a** (2.10 g, 10 mmol) in methanol (50 mL) containing NaOH for 2 h, acidifying with concentrated HCl, adding H_2O (100 mL), and standing overnight at room temperature gave precipitates which were filtered, washed well with water, and dried over P_2O_5 under reduced pressure overnight to give 3.16 g (91%) of white powder, mp 195–204 °C. Recrystallization from methanol yielded colorless prisms (55% recovery): mp 212–213 °C; IR (KBr) 3200, 1705 (νC=O), 1600, 1550 (νC=N), 1505, 1450, 1250, 1150, 975, 740, 700 cm^{-1}; MS *m/e* (rel intensity) 330 (44, M^+), 301 (13), 234 (100), 206 (29), 165 (44), 150 (45), 104 (21), 103 (36), 77 (26). Anal. Calcd for $C_{20}H_{18}N_4O$: C, 72.70; H, 5.49; N, 16.96. Found: C, 72.53; H, 5.54; N, 17.11.

The following imidazolinones **19** were prepared in a similar manner.

2-(3,5-Dimethylpyrazol-1-yl)-5,5-bis(4-methylphenyl)-5*H*-imidazolin-4-one (19b). A 94% yield of white powder was obtained, mp 66–91 °C. Recrystallization from ethanol–petroleum ether afforded colorless plates (67% recovery): mp 132–135 °C; IR (KBr) 3300, 1760 (νC=O), 1660 (νC=N), 1520, 1470, 1260, 1180, 1040, 840 cm^{-1}; MS *m/e* (rel intensity) 390 (41, M^+), 361 (11), 294 (100), 266 (29), 235 (17), 225 (23), 211 (13), 159 (12), 134 (26), 113 (16). Anal. Calcd for $C_{22}H_{22}N_4O_3$: C, 67.67; H, 5.68; N, 14.55. Found: C, 67.80; H, 5.68; N, 14.52.

2-(3,5-Dimethylpyrazol-1-yl)-5,5-bis(4-chlorophenyl)-5*H*-imidazolin-4-one (19c). A 94% yield of pale yellow powder was obtained, mp 75 °C sinter, 156–165 °C. Recrystallization from ethanol gave colorless prisms (71% recovery): mp 171 °C; IR (KBr) 3150 (brd), 1750 (νC=O), 1650 (νC=N), 1500, 1460, 1440, 1095, 1020, 830 cm^{-1}; MS *m/e* (rel intensity) 400 (24, M^+), 398 (45, M^+), 396 (10), 304 (37), 302 (53), 269 (37), 267 (100), 239 (34), 199 (31), 150 (77), 97 (37), 96 (28), 95 (23). Anal. Calcd for $C_{20}H_{16}N_4OCl$: C, 60.16; H, 4.04; N, 14.03. Found: C, 59.99; H, 4.09; N, 14.19.

2-(3,5-Dimethylpyrazol-1-yl)-5,5-bis(4-methylphenyl)-5*H*-imidazolin-4-one (19d). A 96% yield of pale yellow powder was obtained, mp 73 °C sinter, 102–106 °C. Recrystallization from 50% ethanol yielded pale yellow prisms (85% recovery): mp 132–136 °C; IR (KBr) 3230, 1700 (νC=O), 1600, 1550 (νC=N), 1510, 1370, 1240, 1140, 970, 820, 740 cm^{-1}; MS *m/e* (rel intensity) 358 (46, M^+), 329 (14), 262 (100), 234 (24), 219 (28), 193 (18), 179 (18), 150 (49), 118 (31), 117 (24), 96 (15), 91 (20). Anal. Calcd for $C_{22}H_{22}N_4O$: C, 73.72; H, 6.19; N, 15.63. Found: C, 73.89; H, 6.27; N, 15.75.

Registry No.—**1a,** 134-81-6; **1c,** 3457-46-3; **1e,** 431-03-8; **1f,** 579-07-7; **2,** 113-00-8; **2** carbonate, 3425-08-9; **3,** 68212-59-9; **4,** 26975-70-2; **5a,** 68212-60-2; **5c,** 68212-61-3; **5d,** 68212-62-4; **6**·HCl, 68212-63-5; **7**·HCl, 68212-64-6; **8a,** 37980-29-3; **8a** nitrate, 68212-65-7; **8c**·HCl, 68212-66-8; **8c** nitrate, 68212-68-0; **8d**·HCl, 68212-69-1; **8d** nitrate, 68212-71-5; **8e** nitrate, 68212-72-6; **8f** nitrate, 68212-73-7; **9,** 6145-42-2; **9** hydrogen sulfate, 311-77-3; **10a,** 68212-74-8; **10b,** 68212-75-9; **10c,** 68212-76-0; **12a,** 16459-73-7; **12a**·HCl, 68212-77-1; **12b,** 68212-78-2; **12b**·HCl, 68212-79-3; **12c,** 68212-80-6; **12c**·HCl, 68212-81-7; **14a**·HCl, 68238-01-7; **14b**·HCl, 68212-82-8; **14c**·HCl, 68212-83-9; **15,** 22906-75-8; **15** nitrate, 38184-47-3; **17a,** 68212-84-0; **17c,** 68212-85-1; **17e,** 68212-86-2; **18,** 5157-15-3; **19a,** 68212-87-3; **19b,** 68212-88-4; **19c,** 68212-89-5; **19d,** 68238-02-8.

References and Notes

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