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Syntheses and Characterization of Aromatic Secondary and Tertiary Amines and a New Imidazolone from Dicyanoimidazole

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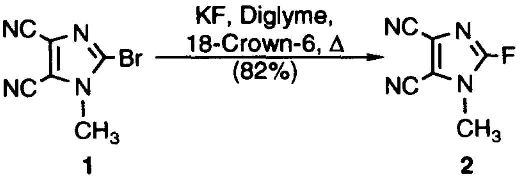
Abstract: Aromatic primary amines substituted with electron donating groups such as methoxy and methyl at the para position undergo nucleophilic aromatic substitution (S_NAr) reactions on 4,5-dicyano-2-fluoro-1-methylimidazole(**2**) in dimethyl sulfoxide at room temperature to give secondary amines substituted with dicyanoimidazolyl groups. Aromatic primary diamines and hydrazine similarly react with **2** to give new secondary diamines. Aromatic primary amines substituted with electron withdrawing group such as nitro group and also secondary amines such as carbazole react with **2** only after activation of the amine by deprotonation using sodium hydride. The electrophilicity of **2** is high enough to react with oxyanions such as nitrite and carbonate anions and also polar aprotic solvents via O-attack at 60 °C to give a new imidazolone, 4,5-dicyano-1-methyl-3-(4,5-dicyano-1-methyl-2-imidazolyl)-2-imidazolone(**10a**). UV-Vis spectra of the newly synthesized compounds are described.

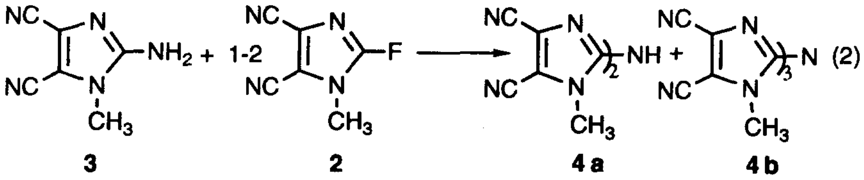
INTRODUCTION

Nucleophilic aromatic substitution (S_NAr) reaction is an important method for bond formation between a carbon atom and a heteroatom in synthetic organic chemistry.[1] S_NAr reactions generally proceed by an ionic mechanism (S_N2) or a free radical ($S_{RN}1$)[2] mechanism. The radical mechanism is thought to be predominant in many heterocyclic systems.[3] Imidazole is among those heterocycles for which S_NAr reactions have been extensively studied.[4] For years our group has been interested in the chemistry of dicyanoimidazoles for the synthesis of thermally stable materials,[5] charge-transfer complexes[6] and negatively dopable polymers[7]. Apen and Rasmussen[8] reported the derivatization of dicyanoimidazoles by the S_NAr reactions of 2-bromo-4,5-dicyano-1-methylimidazole(**1**) with aliphatic amines. Aromatic amines such as aniline and diphenylamine generally do not react with **1** due to their poor nucleophilicity. The electrophilicity of the 2-carbon in **1** was markedly enhanced by transhalogenation to the fluorine derivative using spray-dried potassium fluoride (eq 1).[9]



(1)

Recently, we reported the syntheses and properties of secondary and tertiary amines by the S_NAr reaction of **2** with a weaker amine such as 2-amino-4,5-dicyano-1-methylimidazole(**3**) giving rise to bis and tris(4,5-dicyano-1-methyl-2-imidazolyl)amines (**4a** and **4b**, eq 2).[10]

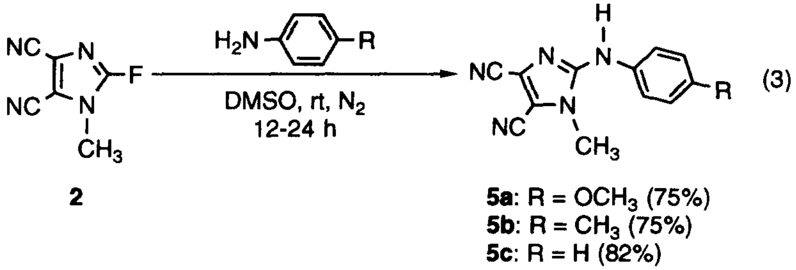


In this paper, the S$_N$Ar reactions of various aromatic primary amines and diamines, carbazole and oxyanions such as carbonate and nitrite anions will be described. UV-Vis spectra of these new compounds are also described.

S$_N$Ar REACTIONS ON 4,5-DICYANO-2-FLUORO-1-METHYLIMIDAZOLE (2)

Reactions with Aromatic primary amines

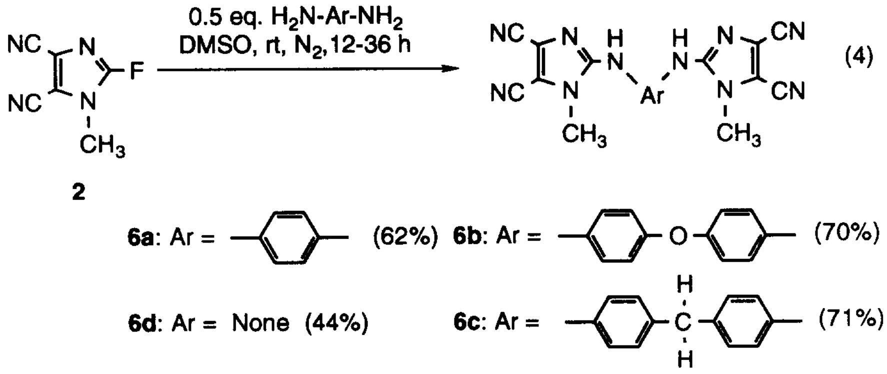
S$_N$Ar reactions of the bromodicyanoimidazole **1** with amines require high temperatures (70-90 °C) and the presence of a proton scavenger such as potassium carbonate.[7,8] The fluorodicyanoimidazole **2**, on the other hand, reacts with anilines at room temperature in dimethylsulfoxide(DMSO) and in the absence of potassium carbonate giving rise to various secondary amines (eq 3).



The anisole(**5a**) and anisidine(**5b**) derivatives crystallized as colorless flakes whereas the aniline derivative **5c** crystallized in the form of colorless cubes. There is precedence for the room temperature S$_N$Ar reactions in DMSO involving various primary amines with 1-alkylamino-2,4-dinitronaphthalenes.[11] In the reaction involving **2**, potassium carbonate needs to be avoided due to its reaction with **2** giving rise to imidazolones(**10a** and **10b**) which will be discussed below. The formation of the imidazolones was also observed upon reaction of **2** with DMSO and other polar aprotic solvents at higher temperatures.

Reactions of 2 with Aromatic Primary Diamines

As an extension of the S$_N$Ar reactions discussed above, we allowed **2** to react with several diamines such as 1,4-phenylenediamine, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylmethane and hydrazine under similar reaction conditions (eq 4).

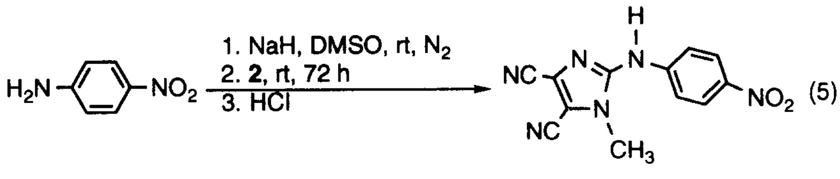


(4)

The 1,4-phenylenediamine derivative **6a** was quite insoluble in polar solvents such as acetone, methanol and DMSO. The product **6a** was a colorless solid which turned red upon crystallization from large excess of water and acetone. Although the color may be associated with oxidation giving traces of quinonoidal derivatives, their presence was not detected in the infrared spectrum.

Reaction of 2 with 4-Nitroaniline

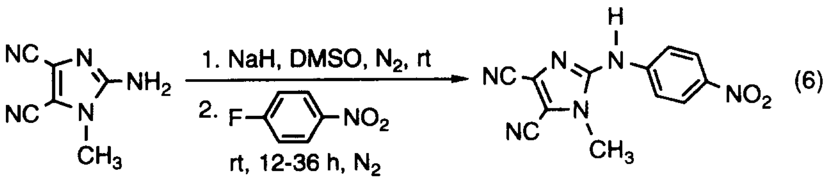
Aromatic amines substituted with electron withdrawing groups such as nitro group at the para position did not react with **2** under typical reaction conditions due to their poor nucleophilicity. Similarly, 2-amino-4,5-dicyano-1-methylimidazole(**3**) also did not react with **2** at room temperature.[10] However, the reactivity of 4-nitroaniline can be enhanced by deprotonation to give the anion of the amine which undergoes S_NAr reaction with **2** at room temperature to give the secondary amine **7** (eq 5).



(5)

7 (30%)

The anion of **7** was bright red whereas the neutral form was yellow. Alternatively, **7** was synthesized in higher yields by the S_NAr reaction of the amine anion of **3** with 4-fluoronitrobenzene (eq 6).

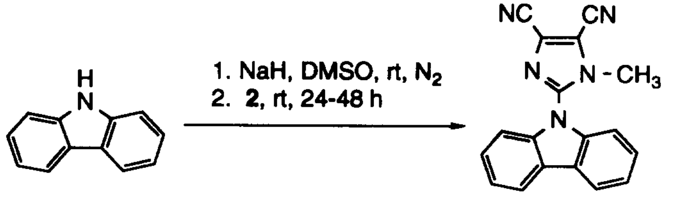


(6)

3 **7** (71%)

Reaction of 2 with Carbazole

The secondary amines synthesized, **5a-c**, **6a-d** and **7**, do not further react with **2** at room temperature due to their poor nucleophilicity. On the other hand, the reaction of **3** with **2** gave the secondary amine **4a** along with the tertiary amine **4b** as the secondary amine(**4a**) is quite acidic (pKa ≈ 4.2) and undergoes deprotonation in the reaction medium.[10] Attempts to synthesize the tertiary amines from the secondary amines, **5a-c** and **7**, by reaction with **2** after deprotonation using NaH, however, did not give clean reactions. Alternately, carbazole(**8**), a secondary amine, was allowed to react with **2**. Carbazole itself did not react with **2** but the anion of carbazole reacts with **2** at room temperature to give the N-substituted carbazole derivative (**9**, eq 7).



(7)

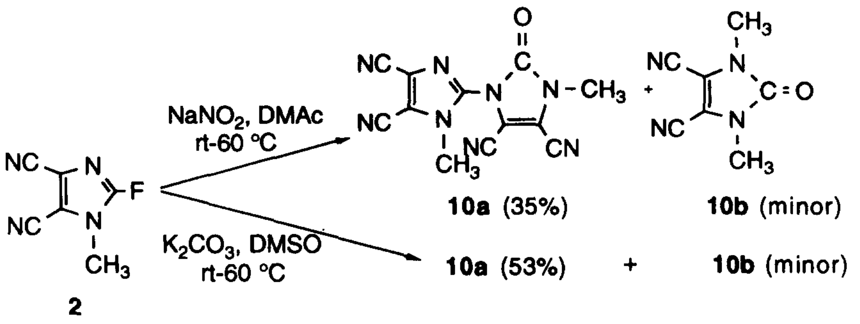
8 **9** (38%)

Reactions of 2 with K_2CO_3 and $NaNO_2$

The reaction of **2** with amines was always carried out at room temperature and in the absence of potassium carbonate because potassium carbonate reacts with **2** at 50-60 °C to give a white solid precipitate. We were also intersted in the possibility of synthesizing the 2-nitro derivative of dicyanoimidazole by the S_NAr reaction of sodium nitrite with **2**. Sodium nitrite is an ambivalent anion that can react through oxygen or nitrogen as a nucleophile in the S_NAr reactions.[12] When **2** was heated with sodium nitrite in acetonitrile or N,N-dimethylacetamide(DMAc) from rt-60 °C, a white solid precipitated. GC/MS analysis of the reaction mixture showed two products, a major product with $M^+ = 278$ (**10a**) and a minor product with a $M^+ = 162$ (**10b**). No compound corresponding to the 2-nitro or 2-nitrito derivative with a molecular ion peak of $M^+ = 177$ was detected in the GC/MS analyses.

The component with $M^+ = 278$ precipitated out of the reaction mixture. The infrared spectrum of the reaction mixture showed strong $\nu_{C=O}$ in the 1740-1760 cm^{-1} region. The precipitate **10a** was recrystallized from water/acetonitrile to give long, colorless, needles. The ^1H and ^{13}C NMR spectra and the elemental analysis data confirmed the structure of **10a** to be the imidazolone, 4,5-dicyano-3-(4,5-dicyano-1-methyl-2-imidazolyl)-1-methyl-2-imidazolone (eq 8).

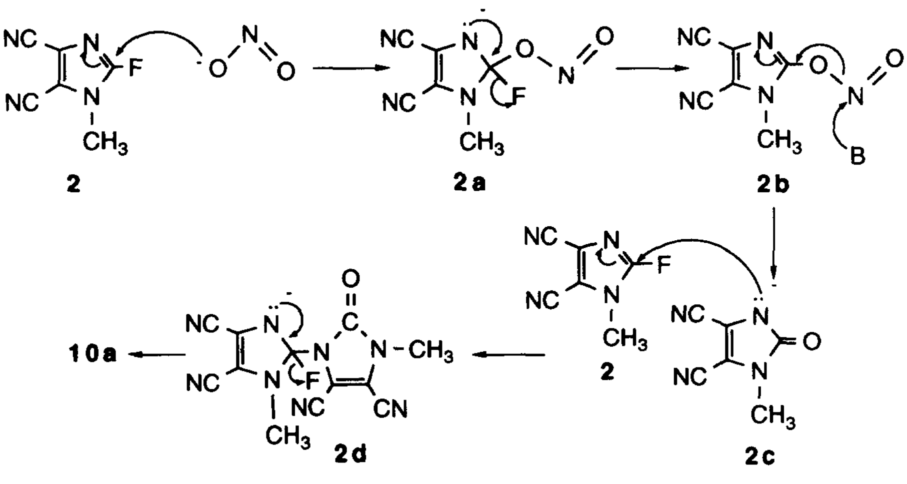
The products of the reaction of **2** with potassium carbonate was also found to be **10a** and **10b** by GC/MS analysis. As in the reaction of sodium nitrite with **2**, only **10a** could be isolated. The product **10b** with $M^+ = 162$ is assigned to be 4,5-dicyano-1,3-dimethyl-2-imidazolone (**10b**) which was not be isolated however, due to its low yield in both reactions.[13] It was also found that polar aprotic solvents such as DMSO, DMAc and N,N-dimethylformamide(DMF) react with **2** at elevated temperatures to give the imidazolone **10a**.



(8)

Previously, 4,5-dicyano-2-imidazolone has been synthesized from diamonomaleonitrile(DAMN) or diiminosuccinonitrile(DISN).[14] Mitsuhashi et al.[15] reported the syntheses of bicyclic and tricyclic imidazolones by the reaction of 4,5-dicyanoimidazole with alkyl and aryl isocyanates.

An ionic mechanism may be postulated for the formation of the imidazolone(**10a**) as shown below. The electrophilicity of the 2-carbon is high, and the electrophilicity will increase further if the nitrogen of the nitrite anion reacts by the S_NAr reaction at the 2-carbon to give a 2-nitro derivative. However, an O-attack from the nitrite anion will give a nitrito derivative **2b** in which the electrophilicity of the 2-carbon is significantly reduced by resonance. Therefore O-attack at the 2-carbon predominates over N-attack. The O-attack from the nitrite anion is in agreement with the observations by Miller and Furin[16] on the reaction of pentafluorobenzenes substituted with nitro, cyano or ester groups giving rise to p-hydroxytetrafluorobenzene derivatives. Similarly, Broxton et al.[17] reported preferential O-attack of the nitrite anion on fluoronitrobenzenes compared to the chloro, bromo and iodonitrobenzenes.



The nitrito derivative **2b** may be readily cleaved at the N-O bond by any weak nucleophile(B) to generate the oxide anion at the 2-carbon. The oxide anion generated at the 2-carbon resonates with the imidazolone type anion at the 3-nitrogen (**2c**) to give the stable imidazolone intermediate. The anion at the 3-nitrogen is more nucleophilic than the oxide anion. A second S_NAr reaction of the 3-anion(**2c**) with another mole of **2** gives the imidazolone **10a**. A similar mechanism may be postulated for the reaction of carbonate dianion with **2**.

The product **10b** might be formed if the 3-anion(**2c**) undergoes transmethylation with another mole of **2** or with the solvent DMAc. Generally, higher temperatures (150-200 °C) are required for effective transmethylations and demethylations in dicyanoimidazole systems.[6,9] Therefore, the transmethylation observed in this reaction might have come from the solvent DMAc. When the reaction was performed in acetonitrile, the amount of **10b** formed was negligible according to GC/MS analysis.

Since **10a** was obtained readily from the fluoro derivative **2**, this reaction was also examined with the bromo derivative **1** in DMAc and in acetonitrile. When sodium nitrite was allowed to react with **1** in DMAc, no **10a** was isolated but traces of **10b** was detected by GC/MS analysis along with unreacted starting material. No reaction took place when acetonitrile was used as the solvent. The progress of the reaction, in both solvents, appeared to be much slower for **1**.

UV-VISIBLE SPECTROSCOPY

The UV-Vis spectra of several derivatives of dicyanoimidazoles have been reported.[6-10] The absorption maxima for the amines substituted with dicyanoimidazolyl groups is generally around 300 nm in acetonitrile and N,N-dimethylformamide (DMF). The UV-Vis spectra of the amino derivatives and the imidazolone synthesized have been recorded and the λ_{max} values are listed in Table 1 along with the corresponding molar absorptivity coefficients (ε).

Table 1. UV-Vis Spectral Data for Amines and Imidazolone

Compound	λ_{max} (nm) (ε)
5a†	311 (11,650), 255 (32,000)
5b†	314 (14,900), 258 (45,700)
5c†	309 (20,000), 258 (43,700)
6a*	329 (37,300), 282 (76,800)
6b*	318 (13,000), 273 (30,300)
6c*	319 (6,000), 271 (14,350)
6d†	285 (16,900)
7*	348 (60,600)
9†	321 (22,600), 309 (25,700), 285 (68,300), 278 (54,000)
10a†	285 (17,400), 212 (23,600)

*c=0.01-1.00 mM in DMF

†c=0.01-1.00 mM in CH_3CN

When the 2-position of the dicyanoimidazolyl group is substituted by aromatic secondary amines (**5a-c** and **7**), generally two wavelengths of absorption are observed which may be explained on the basis of the delocalization of non-bonded electrons from the nitrogen to the two different aromatic groups by n-π* transitions. When the two groups are same, for example bis(4,5-dicyano-1-methyl-2-imidazolyl)amine(**4a**), only one absorption maximum was noticed.[10] This is also true for the hydrazine derivative **6d**. The wavelengths of absorption for the carbazole derivative **9** and the imidazolone **10a** may be attributed to various π-π* and n-π* transitions of the aromatic groups.

SUMMARY AND CONCLUSIONS

S_NAr reactions of aniline, p-toluidine, p-anisidine with 4,5-dicyano-2-fluoro-1-methylimidazole(**2**) have been carried out, under the mild conditions of room temperature in DMSO, giving rise to new secondary amines in high yields. 4-Nitroaniline undergoes S_NAr reaction with **2** only after deprotonation of the amine using sodium hydride. Secondary amine such as carbazole similarly reacts with **2** only after activation by deprotonation of the amine. 4,5-Dicyano-2-fluoro-1-methylimidazole(**2**) also reacts with potassium carbonate, which has often been used as a proton scavenger in S_NAr reactions, to give a new imidazolone, 4,5-dicyano-3-(4,5-dicyano-1-methyl-2-imidazolyl)-1-methyl-2-imidazolone(**10a**). Compound **10a** was also obtained by the reaction of **2** with sodium nitrite and also with polar aprotic solvents at higher temperatures. The UV-vis spectra of the newly synthesized secondary amines generally showed two wavelengths of absorption due to n-π* transitions involving the amine nitrogen and the two aromatic systems.

EXPERIMENTAL SECTION

Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Thin layer chromatography was accomplished on Eastman Kodak silica gel sheets containing fluorescent indicator. Infrared spectra were recorded using a Nicolet 5-DX FTIR spectrophotometer. ^1H NMR and ^{13}C NMR were recorded using Bruker AM-300 or AM-360 or AC-200 spectrometers. Chemical shift values are reported relative to appropriate solvents. All ^{13}C NMR spectra were done using broad band proton decoupling. Nominal mass spectra were recorded on a Finnigan model 4021 mass spectrometer. High resolution mass spectra were recorded on a VG analytical model 70-250S mass spectrometer. Elemental analyses were performed at University of Michigan on a Perkin-Elmer 2400 CHN analyzer or by Oneida Research Services, Inc., Whitesboro, N.Y. UV-Vis spectra were recorded on Shimadzu UV-2101PC or Shimadzu UV-160U UV-visible spectrophotometers. All solvents were purified and distilled under nitrogen prior to use.

4,5-Dicyano-2-fluoro-1-methylimidazole(2)[9]

2-Bromo-4,5-dicyano-1-methylimidazole (**1**, 25.01 g, 0.119 mol), spray-dried potassium fluoride (8.78 g, 0.151 mol) and a catalytic amount of 18-crown-6 were weighed inside a glove box and was suspended in freshly distilled diglyme (25 mL) under nitrogen. The reaction mixture was refluxed for 12 h. The reaction mixture turned yellow-brown. The reaction mixture was filtered and the filtered salt was washed with acetone. The filtrate and the acetone wash were combined and the acetone was removed using rotary evaporation. The diglyme was removed by distillation under vacuum when a brown, viscous oil was obtained. The oil obtained was distilled twice under vacuum (0.02 mM Hg) to give the product as a white, waxy solid. Yield: 14.67 g (82%). M.p. 46-48 °C; TLC(EtOAc) R_f 0.64; IR(KBr) 2243, 1595, 1512, 1411, 1174 cm^{-1}; ^1H NMR($CDCl_3$) δ

3.73(s, 3H); ^{13}C NMR($CDCl_3$) δ 150.01 (d, J=252.1 Hz), 117.34(d, J=12.7 Hz), 110.72, 110.45(d, J=3.9 Hz), 107.01, 31.44; MS(EI/70eV) m/z 151(M+1, 8), 150(M^+, 100%), 149(20), 135(2), 122(5), 109(5); Anal. calcd for $C_6H_3N_4F$: C, 48.02, H, 2.00, N, 37.33; found: C, 47.96, H, 1.85, N, 37.15.

SYNTHESES OF SECONDARY AMINES: GENERAL PROCEDURE (5a-c, 6a-d)

4,5-Dicyano-2-fluoro-1-methylimidazole(**2**) and the primary amine were dissolved in DMSO (0.5 mL) under N_2 and the solution was stirred at rt for 18 h. If a solid precipitated, then additional 1-2 mL DMSO was added to redissolve the precipitate. The reaction is generally over in 18-24 h according to thin layer chromatography. The reaction mixture was poured into excess water (30-40 mL) when the product precipitated. The aqueous suspension was stirred for 20 min and was filtered. The solid obtained was crystallized from water/acetone (2:1) and was dried in vacuum at 100 °C for 12 h.

4,5-Dicyano-2-(4-methoxyphenyl)amino-1-methylimidazole(5a)

Reagents: 4,5-Dicyano-2-fluoro-1-methylimidazole (**2**, 0.275g, 1.833 mmol) and p-anisidine (0.229 g, 1.862 mmol). Yield: 0.347 g (75%). M.p. 205-206 °C; TLC(2:1 Hexane/EtOAc) R_f 0.15; IR(KBr) 3358, 2234, 2227, 1620, 1581, 1543, 1510, 1458, 1443, 1421, 1382, 1319, 1305, 1244, 1215, 1193, 1178, 1117, 1051, 1030, 830, 778, 730, 715, 676, 548, 528, 517, 504, 482, 470 cm^{-1}; ^{1}H NMR(acetone-d_6) δ 8.35(s, 1H), 7.50(d, 2H), 6.88(d, 2H), 3.76(s, 3H), 3.72(s, 3H); ^{13}C NMR(acetone-d_6) δ 156.46, 133.42, 121.18, 121.09, 119.73, 114.81, 113.65, 110.12, 109.80, 55.63, 31.95; MS(EI/70eV) m/z 253(M^+), 238(100%), 210, 195, 121, 63, 40. Anal. calcd for $C_{13}H_{17}N_5O$: C, 61.65, H, 4.38, N, 27.65; found: C, 61.07, H, 4.21, N, 27.37.

4,5-Dicyano-1-methyl-2-N-(4-methylphenyl)aminoimidazole(5b)

Reagents: p-toluidine (0.138 g, 1.289 mmol) and 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.198 g, 1.32 mmol). Yield: 0.245 g (75%); M.p. 212-214 °C; IR(KBr) 3381, 2232, 2221, 1608, 1566, 1537, 1516, 1459, 1447, 1375, 1318, 1234, 1217, 822, 505 cm^{-1}; ^{1}H NMR(DMSO-d_6) δ 9.14(s, 1H), 7.43(d, J=8 Hz, 2H), 7.09(d, J=8 Hz, 2H), 3.58(s, 3H), 2.24(s, 3H); ^{13}C NMR(DMSO-d_6) δ 148.70, 136.89, 131.07, 129.13, 118.21, 118.16, 113.11, 109.64, 108.83, 31.83, 20.31; MS(EI/70eV) m/z 237(M^+, 100%), 222(14), 207(11), 195(4), 131(5), 116(7), 105(48), 91(17), 77(10), 65(15), 51(6), 43(9); Hrms. calcd for $C_{13}H_{11}N_5$: 237.1014; found 237.1016

4,5-Dicyano-1-methyl-2-N-phenylaminoimidazole(5c)

Reagents: aniline (0.34 mL, 3.74 mmol) and 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.555 g, 3.70 mmol). Yield: 0.698 g (82%); TLC(2:1 Hexane/EtOAc) R_f 0.17; M.p. 205-206 °C; IR(KBr) 3374, 2232, 2221, 1614, 1573, 1540, 1504, 1474, 1446, 1380, 1326, 1241, 1217, 1163, 1117, 1102, 1089, 757, 692, 484 cm^{-1}; ^{1}H NMR(DMSO-d_6) δ 9.25(s, 1H), 7.58(d, 2H), 7.30(d, 2H), 6.99(d, 1H), 3.60(s, 3H); ^{13}C NMR(DMSO-d_6) δ 148.44, 139.45, 128.70, 122.06, 118.11, 118.00, 113.03, 109.56, 108.96, 31.89; MS(EI/70eV) m/z 223(M^+, 100%), 207(16), 195(5), 181(7), 118(7), 103(8), 91(42), 77(18), 51(18); Hrms calcd for $C_6H_9N_5$: 223.0858; found 223.0852.

S$_N$Ar REACTIONS INVOLVING DIAMINES

1,4-Bis(4,5-dicyano-1-methyl-2-imidazolylamino)benzene(6a)

Reagents: 1,4-phenylenediamine (0.078 g, 0.722 mmol) and 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.214 g, 1.427 mmol). Yield: 0.168 g (62%, bright red powder) TLC(2:1 Hexane/EtOAc) R_f 0.01; M.p. >382 °C; IR(KBr) 3338, 2243, 2229, 1592, 1561, 1542, 1510 1465, 1419, 1379, 1324, 1298, 1221, 844 cm^{-1}; MS(EI/70eV) m/z 368(M$^+$, 100%), 353(5), 293(7), 236(44), 222(31), 207(21), 149(20), 105(24), 91(20), 57(25), 43(14); Hrms calcd for $C_{18}H_{12}N_{10}$: 368.1246; found 368.1261.

4,4'-Bis(4,5-dicyano-1-methyl-2-imidazolylamino)diphenylether(6b)

Reagents: 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.394 g, 2.627 mmol) and 4,4'-diaminodiphenylether(0.263 g, 1.315 mmol) Yield: 0.423 g (70%). M.p. 322-324 °C; TLC(2:1 Hexane/EtOAc) R_f0.01; IR(KBr) 3356, 2231, 2223, 1613, 1574, 1539, 1500, 1462, 1376, 1324, 1259, 1219, 831, 506 cm^{-1}; ^{1}H NMR(DMSO-d$_6$) δ 9.25(s, br, 1H), 7.50(d, *J*=8.5 Hz, 2H), 6.93(d, *J*=8.5 Hz, 2H), 3.59(s, 3H); ^{13}C NMR(DMSO-d$_6$) δ 152.13, 148.97, 135.02, 120.14, 118.81, 118.14, 113.03, 109.60, 108.99, 31.84; MS(EI/70eV) m/z 460(M$^+$, 100%), 356(43), 330(54), 238(25), 222(16), 207(12), 108(25), 65(20), 90(12), 65(13), 43(9). Hrms calcd for $C_{24}H_{16}N_{10}O$: 460.1509; found: 460.1502; Anal. calcd for $C_{24}H_{16}N_{10}O{\cdot}0.8\ H_2O$: C, 60.70, H, 3.74, N, 29.50; found: C, 60.83, H, 3.58, N, 29.03.

4,4'-Bis(4,5-dicyano-1-methyl-2-imidazolylamino)diphenylmethane(6c)

Reagents: 4,5-dicyano-2-fluoro-1-methylimidazole(**2**, 0.378 g, 2.520 mmol) and 4,4'-diaminodiphenylmethane(0.248 g, 1.253 mmol). Yield: 0.406 (71%). TLC (2:1 Hexane/EtOAc) R_f0.01; M.p. 235-237 °C; IR(KBr) 3359, 2232, 2222, 1611, 1568, 1539, 1512, 1379, 1322, 1240, 1219, 1112, 1104, 1096, 1050 cm^{-1}; ^{1}H NMR(DMSO-d$_6$) δ 9.52(s, 1H), 7.51(d, *J*=8.5 Hz, 2H), 7.13(d, *J*=8.5 Hz, 2H), 3.82(s, 1H), 3.66(s, 3H); ^{13}C NMR(DMSO-d$_6$) δ 148.83, 137.57, 135.26, 128.88, 118.45, 118.08, 113.17, 109.73, 109.02, 39.84, 32.18; MS(EI/70eV) m/z 458(M$^+$, 100%), 354(14), 328(29), 312(27), 236(56), 182(13), 165(16), 106(14), 57(7); Hrms calcd for $C_{25}H_{18}N_{10}$: 458.1716; found: 458.1724; Anal calcd for $C_{25}H_{18}N_{10}{\cdot}H_2O$: C, 63.02, H, 4.23, N, 29.39; found: C, 63.36, H, 4.65, N, 29.02.

1,2-Bis(4,5-dicyano-1-methyl-2-imidazolyl)hydrazine(6d)

Reagents: 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.300 g, 2.0 mmol) and hydrazine (0.03 mL, 0.956 mmol). The product was crystallized from water/acetone to give fluffy solid. Yield: 0.099 g (44%); M.p. >190 °C(dec.); IR(KBr) 3309, 2234, 1576, 1558, 1541, 1522, 1464, 1456, 1378, 1324, 1227, 1051, 921, 717, 508, 502, 490 cm^{-1}; ^{1}H NMR(DMSO-d$_6$) δ 9.63(s, 2H), 3.59(s, 6H); ^{13}C NMR(DMSO-d$_6$) δ 152.42, 118.30, 112.84, 110.02, 109.19, 31.75; MS(EI/70eV) m/z 292(M$^+$, 23), 277(10), 261(55), 236(10), 158(9), 147(100%), 132(40), 119(24), 105(18), 93(15), 77(25), 67(61), 53(30), 43(40); Hrms. calcd for $C_{12}H_8N_{10}$ 292.0933; found 292.0923.

4,5-Dicyano-1-methyl-2-N-(4-nitrophenyl)aminoimidazole(7)

Method A

Sodium hydride (0.304 g, 60% w/w, 7.60 mmol) was washed with hexanes under N_2 and was suspended in DMSO (8.0 mL). A solution of 2-amino-4,5-dicyano-1-methylimidazole (1.010 g, 0.687 mmol) in DMSO (6.0 mL) was added to the NaH suspension dropwise at rt. H_2(g) evolution was noticed along with the formation of a grey-white precipitate. Upon completion of the H_2(g) evolution, a solution of 4-nitrofluorobenzene (0.74 mL, 0.698 mmol) in DMSO (7.0 mL) was added dropwise upon which the reaction mixture turned bright-red. The reaction mixture was stirred at rt for 18 h. The reaction mixture was poured into excess water (30 mL) and the aqueous suspension was acidified to pH≈5-7 when a yellow solid precipitated which was filtered and crystallized from water/acetone (2:1 v/v). Yield: 1.303 g(71%); TLC(1:1 Hexanes/EtOAc) R_f 0.02; M.p. 246-248 °C; IR(KBr) 3320, 2242, 2228, 1621, 1595, 1581, 1542, 1508, 1477, 1400, 1378, 1344, 1328, 1309, 1281, 1251, 1183, 1114, 853, 836, 747 cm^{-1}; ^{1}H NMR(DMSO-d_6) δ 10.07(s, 1H), 8.22(s, 2H), 7.78(s, 2H), 3,72(s, 3H); ^{13}C NMR(DMSO-d_6) δ 146.79, 145.91, 140.98, 125.20, 117.88, 116.89, 112.74, 110.05, 109.26, 32.48; MS(EI/70eV) m/z 268(M^+, 100%), 238(28), 221(25), 207(35), 148(9), 136(29), 106(15), 67(12); Hrms calcd for $C_{12}H_8N_6O_2$: 268.0709; found 268.0706.

Method B

Sodium hydride(0.064 g, 20% w/w, 1.6 mmol) was washed with hexanes under N_2 to remove the mineral oil and was suspended in DMSO (2.0 mL). A solution of 4-nitroaniline (0.199 g, 1.44 mmol) in DMSO (2.0 mL) was added to the sodium hydride suspension dropwise. A dark-yellow precipitate was formed in the reaction flask along with the evolution of H_2(g). After the evolution of H_2(g), a solution of 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.214 g, 1.427 mmol) in DMSO (2.0 mL) was added to the reaction mixture dropwise upon which the reaction mixture turned bright red. The reaction mixture was stirred for 24 h at rt and was poured into water (10 mL) to give a red aqueous solution. The aqueous solution was acidified with aqueous 10% HCl solution to pH≈5-7 when a yellow solid was precipitated. The precipitate was filtered and crystallized from acetone/water (1:2). Yield: 0.115 g (30%); TLC(1:1 Hexanes/EtOAc) R_f 0.02; M.p. 245-248 °C; IR(KBr) 3320, 2242, 2228, 1621, 1595, 1581, 1542, 1508, 1477, 1400, 1378, 1344, 1328, 1309, 1281, 1251, 1183, 1114, 853, 836, 747 cm^{-1}.

2-N-carbazolyl-4,5-dicyano-1-methylimidazole(9)

The procedure used was similar to the the synthesis of **7**. Reagents: carbazole (0.165 g, 0.987 mmol), sodium hydride (0.058 g, 1.45 mmol, 60% w/w), 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.155 g, 1.033 mmol). Yield: 0.112 g (38%). TLC (2:1 Hexane/EtOAc) R_f 0.29; M.p. 190-193 °C; IR(KBr) 2240, 1685, 1600, 1531, 1509, 1484, 1472, 1454, 1449, 1400, 1336, 1312, 1226, 749, 723 cm^{-1}; ^{1}H NMR(DMSO-d_6) δ 8.24 (d, J=7.7 Hz, 2H), 7.49(d, J=3.8 Hz, 4H), 7.38 (m, 2H), 3.63 (s, 3H); ^{13}C NMR(DMSO-d_6) δ 142.09, 139.56, 126.99, 123.54, 122.12, 120.85, 119.23, 116.42, 114.60, 112.28, 110.55, 33.90; MS (EI/70eV) m/z 297(M^+, 100%), 282(6), 255(6), 207(4), 192(5), 179(22), 166(10), 149(16), 140(10), 75(5), 63(4), 32(67); Hrms calcd for $C_{18}H_{11}N_5$: 297.1014; found 297.1009.

SYNTHESIS OF 4,5-DICYANO-3-(4,5-DICYANO-1-METHYL-2-IMIDAZOLYL)-1-METHYL-2-IMIDAZOLONE(10a)

A. Reaction of 2 with Sodium Nitrite

Into a solution of 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.380 g, 2.533 mmol) in N,N-dimethylacetamide (1.0 mL) was added sodium nitrite (0.239 g, 3.464 mmol) and the reaction mixture was heated to 60 °C under nitrogen for 24 h. A white solid precipitated from the reaction mixture. The reaction mixture was cooled to rt and the solid precipitated was filtered and washed with water to remove the salts present. Finally the filtered solid was washed with ether and the crude product obtained was dried at rt for 24 h (0.192 g, 55%). Crystallization of the crude product from water/acetone mixture (2:1 v/v) gave colorless, crystalline solid. Yield: 0.124 g (35%). M.p. 257-258 °C; TLC(2/1 Hexanes/EtOAc) R_f 0.11; IR(KBr) 2241, 1763, 1741, 1538, 1491, 1452, 1407, 1393, 1370, 1316, 1261, 743, 734, 690, 472 cm^{-1}; ^1H NMR(acetone-d_6) δ 3.92(s, 3H), 3.47(s, 3H); ^{13}C NMR(acetone-d_6) δ 149.02, 138.66, 120.68, 116.08, 113.23, 112.02, 108.39, 108.24, 107.98, 105.39, 35.26, 30.91; MS(EI/70eV) m/z 278(M^+, 80), 263(15), 249(27), 159(41), 119(29), 84(37), 67(100%), 49(42), 43(77). Hrms. calcd for $C_{12}H_6N_8O$: 278.0665; found: 278.0671; Anal. calcd for $C_{12}H_6N_8O$: C, 51.80, H, 2.16, N, 40.29; found: C, 51.42, H, 1.97, N, 40.29.

B. Reaction of 2 with Potassium Carbonate

Into a solution of 4,5-dicyano-2-fluoro-1-methylimidazole (**2**, 0.380 g, 2.533 mmol) in DMSO (0.5 mL) was added anhydrous potassium carbonate (0.172 g, 1.244 mmol) and the reaction mixture was stirred at rt-50 °C for 12 h. Thin layer chromatography of the reaction mixture after 12 h showed formation of the imidazolone (M^+ 278) in addition to the starting material. The reaction mixture was heated at 60 °C for another 16 h. The reaction mixture turned red from yellow and the insoluble potassium carbonate suspension appeared to have consumed. The GC/MS of the reaction mixture showed mostly the M^+ 278 component along with traces of M^+ 162 component. The reaction mixture was cooled to rt, poured into excess water (30 mL) when a white solid precipitated which was filtered. The solid product was crystallized from CH_3CN/water (1:2 v/v). Yield: 0.187 g (53%); M.p. 255-258 °C; TLC(2/1 Hexanes/EtOAc) R_f 0.11; IR(KBr) 2241, 1763, 1741, 1538, 1491, 1452, 1407, 1393, 1370, 1316, 1261, 743, 734, 690, 472 cm^{-1}; MS(EI/70eV) m/z 278(M^+, 80), 263(15), 249(27), 159(41), 119(29), 84(37), 67(100%), 49(42), 43(77).

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