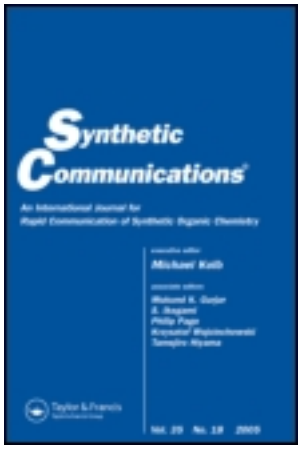

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Silica-Supported Ferric Chloride ($FeCl_3$-SiO_2): An Efficient and Recyclable Heterogeneous Catalyst for the Preparation of Arylaminotetrazoles

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SILICA-SUPPORTED FERRIC CHLORIDE ($FeCl_3$-SiO_2): AN EFFICIENT AND RECYCLABLE HETEROGENEOUS CATALYST FOR THE PREPARATION OF ARYLAMINOTETRAZOLES

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An efficient method for preparation of 5-arylamino-1H-tetrazole and 1-aryl-5-amino-1H-tetrazole derivatives is reported using $FeCl_3$-SiO_2 as an effective heterogeneous catalyst. Generally, when the substituent in arylcyanamide is a strongly electron-withdrawing group, the position of the equilibrium would shift toward 5-arylamino-1H-tetrazole, whereas with an electron-releasing substituent, the position of the equilibrium would shift toward 1-aryl-5-amino-1H-tetrazole.

Keywords: 1-Aryl-5-amino-1*H*-tetrazole; 5-arylamino-1*H*-tetrazole; arylcyanamide; $FeCl_3$-SiO_2; heterogeneous catalyst

INTRODUCTION

The growth of tetrazole chemistry over the past 25 years has been significant, mainly as a result of the roles played by tetrazoles in coordination chemistry as ligands, in medicinal chemistry as stable surrogates for carboxylic acids, and in material applications, including explosives, agriculture, and photography.[1–4] Another important application of tetrazoles is preparation of imidoylazides.[5] The earliest published methods for preparation of aminotetrazole derivatives included the following: (1) diazotation of aminoguanidine derivatives,[6] (2) azidation of carbodiimides,[7] cyanamides,[8] and aminoiminomethanesulfonic acid,[9] and (3) nucleophilic substitution by N_3^- of sulfur from thioureas in the presence of mercury[10] or lead salts.[6]

More recently, 5-monosubstituted amino-1*H*-tetrazoles were synthesized by thermal isomerization of 1-substituted-5-amino-1*H*-tetrazoles in boiling ethylene or melt state (180–200 °C)[6,8b] Herbst and Garbrecht have shown that cyanamides may be converted to aminotetrazoles using hydrazoic acid, which often results in a mixture of isomers (Scheme 1).[8a]

These methods suffer from one or more disadvantages such as poor yield, long reaction times, harsh reaction conditions, lack of easy availability or easy preparation of the starting materials, and use of expensive and toxic reagents (the in situ–generated hydrazoic acid is highly toxic and explosive). If hydrazoic acid is

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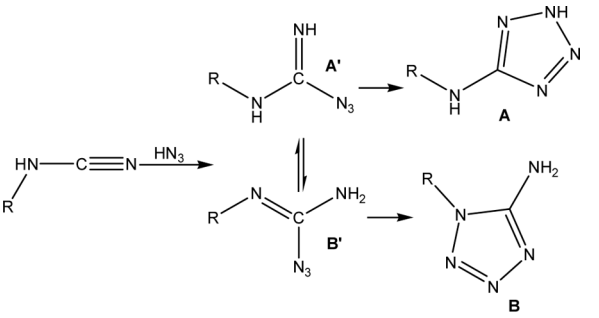
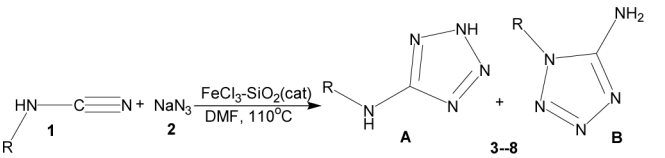


Scheme 1. Conversion of arylcyanamide to the corresponding aminotetrazole using hydrazoic acid.

used, care must be taken by monitoring the concentration of hydrazoic acid in the reaction mixture to avoid an explosion.[2a] Because of the safety considerations, we required a method that does not use hydrazoic acid or an azide source that produced hydrazoic acid in situ because of the associated hazards.

Great efforts in catalysis researches have been devoted in recent years to the introduction and application of effective and safe heterogeneous catalysts.[11] Organic synthesis on silica-supported reagents[12–14] have received considerable attention because of the ease of handling, enhanced reaction rates, greater selectivity, simple workup, and recoverability of the catalysts.[13,14]

In continuation of our recent work on the synthesis of heterocycles[15] and application of heterogeneous reagents for development of the useful synthetic methodologies,[16] we herein report a new protocol for preparation of arylaminotetrazole **3–8** derivatives from cyanamides **1** using $FeCl_3$-SiO_2 as a heterogeneous catalyst (Scheme 2, Table 1). This catalyst is safe, easy to handle, and environmentally benign



Scheme 2. Conversion of arylcyanamides to the corresponding arylaminotetrazoles using $FeCl_3$-SiO_2.

Table 1. Synthesis of various arylaminotetrazoles **3–8** in the presence of $FeCl_3$-SiO_2 by reaction of sodium azide **2** and cyanamides **1** at 110 °C

Entry	R	Product	Yield (%)[a]	Time [min]	Ratio of isomers (**A**/**B**)[b]
1	2,5-$(Cl)_2C_6H_3$	**3**	76	120	1.9
2	2-ClC_6H_4	**4**	75,73[c]	120	1.7
3	4-$NO_2C_6H_4$	**5**	75	125	1.8
4	4-$OCH_3C_6H_4$	**6**	74	75	0.5
5	2,4-$(CH_3)_2C_6H_3$	**7**	77	75	0.5
6	4-$CH_3C_6H_4$	**8**	73	75	0.4

[a]Yield refer to the pure isolated product.
[b]Determined by ^{1}H NMR analysis.
[c]Yield after the third cycle.

with fewer disposals problems. Silica-supported ferric chloride was prepared from the reaction of silica gel with anhydrous ferric chloride.[14e,15a]

EXPERIMENTAL

General

All reagents were purchased from Merck and Aldrich and used without further purification. ^{13}C NMR and ^{1}H NMR spectra were recorded on Brucker 300- and 500-MHz instruments using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in parts per million, and coupling constants are reported in hertz. Infrared (IR) spectra were recorded on a Shimadzu 470 spectrophotometer. Thin-layer chromatography (TLC) was performed on Merck precoated silica-gel 60-F254 plates.

General Procedure for Preparation of 3–8

$FeCl_3$-SiO_2 (0.1 g, mmol% loading of $FeCl_3$: ~0.04[15a]) was added to a mixture of cyanamide **1** (2 mmol), NaN_3 **2** (3 mmol), and distilled dimethylformamide (7 mL) and stirred at 110 °C for the appropriate time (Table 1). After completion of the reaction (as monitored by TLC), the mixture was cooled to room temperature. The catalyst was filtered, and the filtrate was treated with ethyl acetate (35 mL) and 5 N HCl (20 mL) and stirred vigorously. The resultant organic layer was separated, and the aqueous layer was again extracted with ethyl acetate (25 mL). The combined organic layers were washed with water, and the solvent was removed and crystallized with aqueous ethanol to give the crystalline arylaminotetrazoles **3–8**. The pure products were characterized by IR and NMR.

Spectroscopic Data

R = 2,5-$(Cl)_2$ in Scheme 2 and Table 1, Entry 1. IR (KBr): 3320, 3165, 1649, 1575, 1524, 1481, 1450, 1396, 1301, 1240, 880, 817, 665, 641, 581 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6) isomer **A**: δ 6.12 (1H, s, br), 6.98 (1H, dd, $J = 8.6$ Hz, $J = 2.5$ Hz), 7.37 (1H, d, $J = 8.6$ Hz), 7.88 (1H, s, br), 8.49 (1H, s, $J = 2.5$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6) isomer **A**: δ 119.4, 119.6, 121.8, 130.3, 131.8, 138.0, 155.3; ^{1}H NMR (500 MHz, acetone-d_6) isomer **B**: δ 6.46 (2H, s, br), 7.70 (1H, dd, $J = 8.7$ Hz, $J = 2.4$ Hz), 7.76 (1H, d, $J = 8.7$ Hz), 7.81 (1H, d, $J = 2.4$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6) isomer **B**: δ 130.0, 130.2, 131.6, 131.7, 132.2, 132.5, 155.7.

R = 2-Cl in Scheme 2 and Table 1, Entry 2. IR (KBr): 3420, 3315, 3190, 1651, 1590, 1528, 1497, 1438, 1355, 1313, 1122, 1091, 1078, 1033, 755, 731, 689, 651 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) isomer **A**: δ 5.98 (1H, s, br), 6.95 (1H, td, $J = 7.8$ Hz, $J = 1.6$ Hz), 7.23 (1H, td, $J = 8.6$ Hz, $J = 1.4$ Hz), 7.35 (1H, dd, $J = 8.0$ Hz, $J = 1.5$ Hz), 8.31 (1H, dd, $J = 8.4$ Hz, $J = 1.5$ Hz); ^{13}C NMR (125 MHz, acetone-d_6) isomer **A**: δ 121.8, 121.9, 123.4, 129.4, 131.6, 137.8, 156.3; ^{1}H NMR (300 MHz, acetone-d_6) isomer **B**: δ 6.30 (2H, s, br), 7.58–7.74 (4H, m); ^{13}C NMR (125 MHz, acetone-d_6) isomer **B**: δ 128.1, 129.7, 130.6, 131.9, 132.7, 133.1, 156.8.

R = 4-NO_2 in Scheme 1 and Table 1, Entry 3. IR (KBr, cm^{-1}) : 3390, 3300, 3125, 1637, 1588, 1517, 1490, 1341, 1291, 1258, 1125, 1090, 1069, 1048, 872, 863, 855, 840, 746, 689; ^{1}H NMR (500 MHz, acetone): isomer **A**: δ 5.94 (1H, d, br), 7.77 (2H, d, $J = 9.2$ Hz), 8.14 (2H, d, $J = 9.2$ Hz), 9.16 (1H, s, br); ^{13}C NMR (125 MHz, DMSO-d_6): isomer **A**: δ 116.8, 125.1, 140.3, 147.1, 155.0; ^{1}H NMR (500 MHz, acetone): isomer **B**: δ 6.58 (2H, s, br), 8.01 (2H, d, $J = 7.2$ Hz), 8.49 (2H, d, $J = 7.2$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6): isomer **B**: δ 124.6, 125.3, 138.6, 146.9, 155.4.

R = 4-(OMe) in Scheme 2 and Table 1, Entry 4. IR (KBr): 3425, 3300, 3130, 2985, 2975, 2830, 1645, 1575, 1545, 1505, 1339, 1290, 1249, 1167, 1080, 1015, 834, 817, 629, 610, 551 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) isomer **A**: δ 3.67 (3H, s), 5.70 (1H, s), 6.78 (2H, d, $J = 8.7$ Hz), 7.26 (2H, d, $J = 8.7$ Hz), 8.33 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6) isomer **A**: δ 55.1, 113.8, 119.4, 133.7, 153.9, 156.2; ^{1}H NMR (500 MHz, DMSO-d_6) isomer **B**: δ 3.81 (3H, s), 6.73 (2H, s), 7.11 (2H, d, $J = 8.7$ Hz), 7.45 (2H, d, $J = 8.7$ Hz); ^{13}C NMR (125 MHz, DMSO-d_6) isomer **B**: δ 55.6, 114.9, 126.0, 126.1, 155.1, 159.7.

R = 2,4-$(Me)_2$ in Scheme 2 and Table 1, Entry 5. IR (KBr): 3425, 3300, 3010, 2900, 1649, 1619, 1590, 1537, 1524, 1507, 1352, 1312, 1263, 1223, 1132, 1034, 825, 799, 758, 653, 614, 555 cm^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6) isomer **A**: δ 2.15 (3H, s), 2.21 (3H, s), 5.92 (1H, s), 6.89 (1H, d, $J = 8.0$ Hz), 6.93 (1H, s), 7.60 (1H, d, $J = 8.0$ Hz), 7.61 (1H, s, br); ^{13}C NMR (125 MHz, DMSO-d_6) isomer **A**: δ 17.8, 20.3, 121.4, 126.4, 127.4, 130.5, 130.9, 135.5, 156.3; ^{1}H NMR (500 MHz, DMSO-d_6) isomer **B**: δ 2.01 (3H, s), 2.38 (3H, s), 6.68 (2H, s), 7.21 (1H, d, $J = 8.0$ Hz), 7.24 (1H, d, $J = 8.0$ Hz), 7.29 (1H, s); ^{13}C NMR (125 MHz, DMSO-d_6) isomer **B**: δ 16.8, 20.7, 127.3, 127.7, 129.5, 131.8, 134.9, 140.1, 155.7.

R = 4-Me in Scheme 2 and Table 1, Entry 6. IR (KBr): 3415, 3304, 3145, 2980, 2915, 1648, 1589, 1568, 1542, 1514, 1118, 1092, 1087, 842, 811 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6) isomer **A**: δ 2.19 (3H, s), 5.74 (1H, s), 6.99 (2H, d, $J = 8.2$ Hz), 7.25 (2H, d, $J = 8.2$ Hz), 8.37 (1H, s); ^{13}C NMR (75 MHz, DMSO-d_6) isomer **A**: δ 20.3, 117.8, 123.9, 130.2, 138.1, 154.9; ^{1}H NMR (300 MHz, DMSO-d_6) isomer **B**: δ 2.38 (3H, s), 6.80 (2H, s), 7.39 (2H, d, $J = 8.1$ Hz), 7.43 (2H, d, $J = 8.1$ Hz); ^{13}C NMR (75 MHz, DMSO-d_6) isomer **B**: δ 20.7, 128.9, 129.6, 130.9, 138.9, 156.2.

RESULTS AND DISCUSSION

The general synthetic method is depicted in Scheme 2. Arylaminotetrazoles **3–8** were obtained from the reaction of cyanamides **1** with sodium azide **2** in the presence of $FeCl_3$-SiO_2 as a heterogeneous catalyst at 110 °C for appropriate time in excellent yields, as summarized in Table 1.

We have studied the cycloaddition reaction of cyanamides with sodium azide in the presence of PPh_3, LiCl, and $FeCl_3$-SiO_2 (Table 2). Results show that in all cases the products were obtained in good yields. However, PPh_3 and LiCl, being homogeneous reagents, could not be recycled from the reaction mixture. In contrast to the reaction conditions with PPh_3 and LiCl, $FeCl_3$-SiO_2 is a cheap and nonhazardous solid acid catalyst that can be handled easily and is important from

Table 2. Comparison of different amounts of $FeCl_3$-SiO_2 catalyst with PPh_3 and LiCl in synthesis of 5-(2,5-dichlorophenyl)amino-1*H*-tetrazole (**A**) and 1-(2,5-dichlorophenyl)-5-amino-1*H*-tetrazole (**B**) by the reaction of sodium azide and 2,5-dichlorophenylcyanamide at 110 °C

Entry	Reagent or catalyst (g)	Solvent	Time (min)	Yield (%)	Product
1	PPh_3 (0.1)	DMF	120[a]	67	**A** + **B**
2	LiCl (0.1)	DMF	120[a]	61	**A** + **B**
3	$FeCl_3$-SiO_2 (0.14)	DMF	120	77	**A** + **B**
4	$FeCl_3$-SiO_2 (0.1)	DMF	120	76	**A** + **B**
5	$FeCl_3$-SiO_2 (0.1)	DMSO	120	75	**A** + **B**
6	$FeCl_3$-SiO_2 (0.08)	DMF	120	72	**A** + **B**
7	$FeCl_3$-SiO_2 (0.07)	DMF	120	70	**A** + **B**
8	None	DMF	120	0[b]	–

[a]Reaction was carried out at 120 °C.
[b]In the absence of catalyst at 110 °C, no reaction occurred after 120 min.

the environmental point of view because it produces little waste. It also has excellent activity and selectivity even on an industrial scale and in most cases can be recovered from the reaction mixtures by simple filtration and reused. In addition, to improve yield and because of the biological importance of aminotetrazole derivatives, we started to study this reaction by examining the different amounts of $FeCl_3$-SiO_2 catalyst for the reaction involving 2,5-dichlorophenylcyanamide (2 mmol) and sodium azide (3 mmol) to afford the product under thermal conditions. The best result was obtained with a 0.1 g (mmol% loading of $FeCl_3$: $\sim$0.04[15a]) of $FeCl_3$-SiO_2 and gave a mixture of 1-(2,5-dichlorophenyl)-5-amino-1*H*-tetrazole (**B**) and 5-(2,5-dichlorophenyl)amino-1*H*-tetrazole (**A**) (**3**, Table 1, entry 1) in excellent yield.

The cyanamides **1** were prepared according to the literature.[17] To include a reasonable range of electrical and steric effects, the aryl-substituted cyanamides were studied including various groups in *ortho, meta*, and *para* positions. According to Table 1, among the various cyanamides tested, electron-rich aromatic cyanamides reach completion at 110 °C after 75 min, whereas electron-poor aromatic species require more times (compare entries 1–3 with 4–6 in Table 1).

In addition, there is an excellent correlation between the effect of substitution on the benzene ring and the position of equilibrium. In other words, isomer ratios in tetrazoles **3–8** are affected by different types of substituents in arylcyanamide **1**. Generally, when the substitution on the aryl ring is strongly electron-withdrawing, the position of equilibrium would shift toward the isomer of 5-arylamino-1*H*-tetrazole **A** via guanidine azide intermediate **A′**, which appears to be the major product (Table 1, entries 1–3) and as the electropositivity of substituent increases, the position of equilibrium is shifted toward the isomer of 1-aryl-5-amino-1*H*-tetrazoles **B** via guanidine azide intermediate **B′** (Table 1, entries 4–6). This is similar to the substituent effect on the aryl ring of the mechanism that was presented by Henry and coworkers for thermal isomerization of **A** and **B**.[6,8a,8b,18]

$FeCl_3$-SiO_2 as catalyst was isolated from the reaction mixture by simple filtration. The purified catalyst was achieved through washing the solid residue catalyst by water and ethanol followed by drying in an oven at 100 °C for 30 min. In every experiment, more than 98% of the $FeCl_3$-SiO_2 was easily recovered from the reaction mixture. Catalytic activity of the recovered catalyst was tested and showed to be the

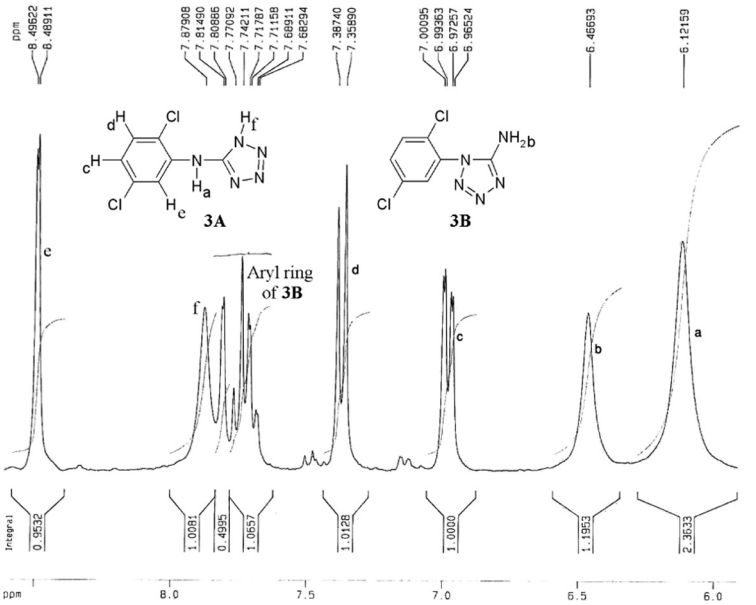


Figure 1. ^{1}H NMR spectrum (300 MHz) of 5-(2,5-dichlorophenyl)amino-1*H*-tetrazole **3A** and 5-amino-1-(2,5-dichlorophenyl)-1*H*-tetrazole **3B** in acetone-d_6.

same as $FeCl_3$-SiO_2 used for the first time. The recovered catalyst was reused three times without any loss of activity (Table 1, entry 2).

All products are known compounds and were identified by comparison of some of their spectral data [infrared (IR), ^{1}H NMR, and ^{13}C NMR] with those of authentic samples.[6,8,9,18,19] Elimination of one strong and sharp absorption band (CN stretching band) and appearance of two absorption bands in the range of 3140–3550 cm^{-1} (NH stretching bands) in the IR spectrum confirmed the formation of arylaminotetrazoles. The ^{13}C NMR spectra displayed signals for tetrazole ring carbons of arylaminotetrazoles in the range of 154–157 ppm (depending on the nature of the substituents in the amino functionality).[20]

A comparison of ^{1}H NMR spectra revealed that 5-arylamino-1*H*-tetrazole **A** generally shows a large separation in the chemical shifts of the aryl protons (Fig. 1). Isomers 1-aryl-5-amino-1*H*-tetrazoles **B** had a small separation of the aryl ring protons. Indeed, signals of the aryl ring protons of isomer 1-aryl-5-amino-1*H*-tetrazoles **B** contracted their multiplicities and shifted downfield (Fig. 1).

CONCLUSION

In conclusion, we have developed a novel and highly efficient method for the synthesis of various arylaminotetrazoles by treatment of cyanamides with sodium azide in the presence of $FeCl_3$-SiO_2 as an effective catalyst. The significant advantages of this methodology are good yields, elimination of dangerous and harmful hydrazoic acid, simple workup procedure, and easy preparation and handling of

the catalyst. The catalyst can be recovered by simple filtration and reused without loss of activity.

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