From Amides to Amidines: Preparations of Imidoylbenzotriazoles and Arylaminoheterocycles

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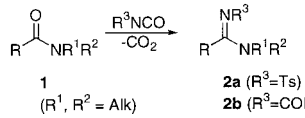
There are numerous classic and modern references to conversions of secondary amides into amidines $RCONHR^1 \rightarrow RC(NR^2R^3)=NR^1$ mediated by electrophilic activation at oxygen.[1] Most conventional conversions of tertiary amides into amidines $RCONR^1R^2 \rightarrow RC(NR^1R^2)=NR^3$ involve similar electrophilic activation at oxygen by (i) the condensation of the tertiary amides with primary amines in the presence of dehydrating reagents[2] or (ii) the addition of primary amines to the tertiary amides preactivated by triflic anhydride.[3a,b]

However, in a different approach, *p*-toluenesulfonyl isocyanate converts tertiary amides **1** at room temperature into tosylamidines **2a** (Scheme 1) in high yields.[4a,4b] Similar transformations of **1** to **2b** were reported for acyl isocyanates (Scheme 1).[5a,5b] Although phenyl isocyanate reacts with dimethylformamide to give 80% of *N*,*N*-dimethyl-*N*′-phenylformamidine,[6a] dimethylacetamide was reported to give complex reaction mixtures with none of the corresponding amidines found.[6b] It was reasoned[6b] that highly activated α-protons of the desired *N*,*N*-dimethyl-*N*′-phenylacetamidine become involved in further reaction with phenyl isocyanate; indeed, the products of some such reactions were recently elucidated.[7] Apparently, other than for dimethylformamide, no attempts were previously made to convert amides not possessing acidic α-protons into the corresponding amidines with aryl isocyanates. We now report such preparations of amidines from reactions of aryl isocyanates with *N*-acyl-1-benzotriazoles and with cyclic amides.

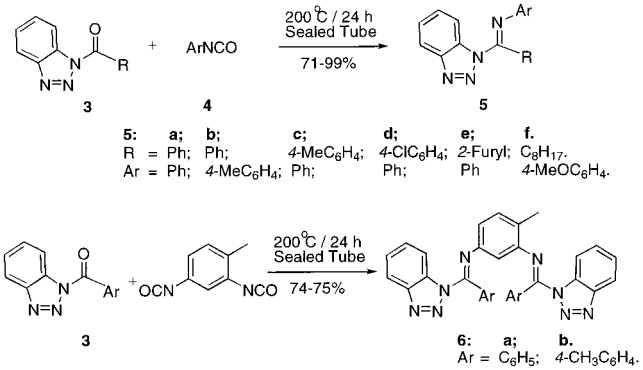
Results and Discussion

Imidoylbenzotriazoles. Imidoylbenzotriazoles **5** are synthetically useful as stable alternatives to the corresponding imidoyl chlorides.[8] Imidoylbenzotriazoles **5** were previously prepared by reactions of secondary amides with benzotriazole and $POCl_3$[9] or with 1,1′-sulfinylbenzotriazole.[8] We now apply Logemann and King's method[5a,5b] to provide advantageous preparations of **5a**−**f** and **6a**,**b** by the condensation of isocyanates with *N*-acyl-1-benzotriazoles (Scheme 2).

Scheme 1



Scheme 2



Aryl **5a**−**d**, heterocyclic **5e**, bulky aliphatic **5f**, and bisfunctionalized **6a**,**b**, 1-imidoylbenzotriazoles were obtained in 71−99% yields when the corresponding *N*-acyl-1-benzotriazole **3**[10] was heated neat with 3−5 equiv of the appropriate isocyanate **4** in a sealed tube at 200 °C for 24 h (Scheme 2). Compounds **5a**−**e** were isolated by crystallization from ethanol or ethyl acetate without using column chromatography. GC/MS indicated that compound **5e** was 100% pure; but the ^{13}C NMR spectrum showed twinned peaks in 1:6 intensity ratio which are believed to correspond to *E*/*Z* isomers.

However, the successful synthesis of imidoylbenzotriazoles **5** depended markedly on the nature of groups R (Scheme 2). The reactions proceeded well with R as unsubstituted phenyl (**5a**,**b** and **6a**), as mild electron donor such as tolyl and 2-furyl (**5c**, **6b**, and **5e**), and as acceptor such as 4-chlorophenyl (**5d**) moieties. Attempts to extend the method to R as phenyl containing strong electron-donating or -withdrawing groups (4-methoxyphenyl, 3,4,5-trimethoxyphenyl, 4-fluorophenyl, and 4-nitrophenyl) and bis-functional groups (phthaloyl, isophthaloyl, terephthaloyl, and 2,6-naphthalenedioyl) failed. These reactions produced isocyanate oligomers **17**[11] (30−91%), **18**[12] (20%), **19**[13] (20−45%), and **20**[14] (35−56%)

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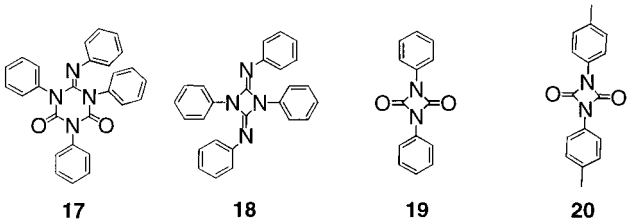


Figure 1. Structures of isocyanate oligomers.

(Figure 1) isolated by column chromatography. Although *N*-acyl-*1*-benzotriazoles **3** with bulky aliphatic acyl (e.g., 3,5,5-trimethylhexanoyl) react successfully, acetyl and *n*-butanoyl analogues led to the formation of aminoquinolines.[7]

Arylaminoheterocycles. Previous direct conversions of oxoheterocycles into arylaminoheterocycles are relatively uncommon: for example, conversion of 2,4-dihydroxyquinolinone into 4-arylamino-2-hydroxyquinoline involves heating to 190 °C for 12 h in the presence of an acid catalyst.[15] Now we report an alternative procedure via condensation of **7**, **9**, **11**, and **13** with the corresponding aryl isocyanates (Scheme 3).

Thus, 4-(substituted-anilino)quinolines **8a**−**c** were prepared from 4-quinolone and various isocyanates in 71−96% yields. Other heterocyclic compounds **10**, **12**, and **14** are also available by this procedure from the corresponding oxo compounds in 69−98% yields. The reaction with 2-pyrrolidinone (**15**) gave only addition product **16** (Scheme 3).

In conclusion, condensation of 1-(*N*-acyl)benzotriazoles **3** with isocyanates affords the corresponding amidines **5** or **6** in 71−99% yields. This method also allows for direct conversion of oxoheterocycles (**7**, **9**, **11**, and **13**) into the corresponding arylaminoheterocycles (**8** and **14**), or ureas (**10** and **12**) resulting from further reactions in 69−96% yields. This one-pot protocol utilizes readily available starting materials.

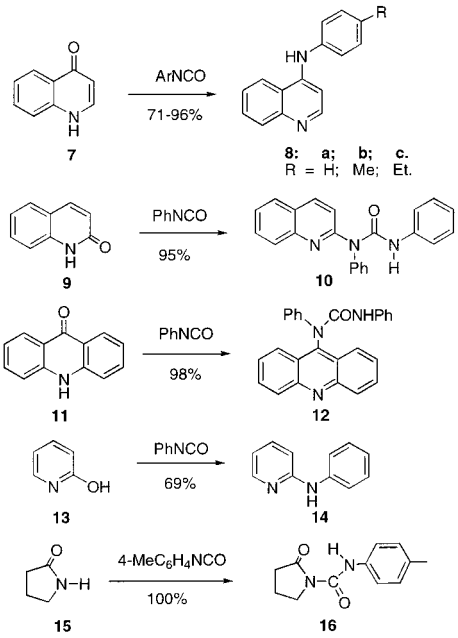
Experimental Section

General Methods. Melting points were determined on a MEL-TEMP capillary melting point apparatus equipped with a Fluke 51 digital thermometer. NMR spectra were taken in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H (300 MHz) or a solvent as the internal standard for ^{13}C (75 MHz). THF was distilled from sodium/benzophenone under nitrogen immediately prior to use. All reactions with moisture-sensitive compounds were carried out under dry argon atmosphere. Column chromatography was conducted with silica gel 230−400 mesh.

General Procedure for the Preparation of Compounds 3a−**e.** To a solution of 0.10 mol of acyl chloride and 11.90 g (0.10 mol) of benzotriazole in 300 mL of methylene chloride was added a solution of 11.10 g (0.10 mol) of triethylamine in 50 mL of methylene chloride at 0−20 °C dropwise during 30 min. The mixture was refluxed for 4 h, cooled to room temperature, and washed consecutively with 100 mL of water, 50 mL of saturated NH_4Cl, 50 mL of 10% $NaHCO_3$, and 100 mL of water. The organic layer was dried over anhydrous $MgSO_4$, hexane (about 60 mL) was added to the filtrate to make the solution milky, and the resultant mixture was kept at 0 °C overnight. The colorless crystals were isolated. The pure *N*-acyl-1-benzotriazole for analysis was obtained by recrystallization from 2-propanol.

***p*-Toluoyl-1*H*-1,2,3-benzotriazole (R = 4-MeC$_6$H$_4$, 3c):** 85%, white prisms, mp 122−123 °C; ^1H NMR δ 2.47 (s, 3H), 7.45 (d, 2H, J = 7.8 Hz), 7.64 (t, 1H, J = 7.5 Hz), 7.81 (t, 1H, J = 7.2 Hz), 8.05 (d, 2H, J = 8.1 Hz), 8.27 (d, 1H, J = 8.4 Hz), 8.28 (d, 1H, J = 8.1 Hz); ^{13}C NMR δ 21.3, 114.4, 119.9, 126.5, 128.5, 129.0, 130.5, 131.6, 131.8, 144.4, 145.1, 166.1. Anal. Calcd for $C_{14}H_{11}N_3O$: C 70.87, H 4.67, N 17.71; Found: C 70.64, H 4.63, N 17.79.

Scheme 3



2-Furoyl-1*H*-1,2,3-benzotriazole (R = 2-furyl, 3e): 87%, white needles, mp 166−167 °C (lit. mp,[16] 166 °C); ^1H NMR δ 6.37 (dd, 1H, J = 3.9, 3.3 Hz), 7.52 (t, 1H, J = 7.5 Hz), 7.67 (t, 1H, J = 7.5 Hz), 7.87 (s), 8.12−8.15 (m, 2H), 8.38 (d, 1H, J = 8.4 Hz); ^{13}C NMR δ 113.0, 114.7, 120.1, 124.8, 126.3, 130.5, 132.0, 144.5, 145.5, 148.9, 154.9. Anal. Calcd for $C_{11}H_7N_3O_2$: C 70.87, H 4.67, N 17.71; Found: C 70.64, H 4.63, N 17.79.

3,5,5-Trimethylhexanoyl-1*H*-1,2,3-benzotriazole (R = 2,4,4-trimethylpentyl, 3f): 91%, white needles, mp 157−158 °C; ^1H NMR δ 1.13 (s, 9H), 1.30 (d, 3H, J = 6.6 Hz), 1.42−1.65 (m, 2H), 2.58 (m, 1H), 3.46−3.57 (m, 2H), 7.65 (t, 1H, J = 6.3 Hz), 7.78 (t, 1H, J = 6.3 Hz), 8.26 (d, 1H, J = 8.2 Hz), 8.46 (d, 1H, J = 8.2 Hz); ^{13}C NMR δ 22.6, 26.7, 29.8, 30.9, 44.5, 50.5, 114.3, 119.9, 125.8, 130.0, 130.9, 145.9, 171.7. Anal. Calcd for $C_{15}H_{21}N_3O_2$: C 69.46, H 8.18, N 16.21; Found: C 69.20, H 8.54, N 16.52.

General Procedure for the Preparation of Compounds 5a−**f and 6a,b.** In a 50 mL sealed tube, the mixture of 2 mmol of an *N*-acyl-1-benzotriazole and 5−10 mmol of an aryl isocyanate was heated at 200 °C for 12−24 h and then was allowed to cool to room temperature. The reaction mixture was subjected to a column chromatography with hexane/ethyl acetate (10/1∼1/1) solvent mixture as an eluent to give the corresponding product. The pure product could be obtained by recrystallization from methylene chloride/ethanol. In the case of compound **5e** where a mixture of *E* and *Z* isomers was obtained, the ^{13}C NMR chemical shifts data for the minor diastereomer are in parentheses.

1-(*p*-Tolylbenzenecarboximidoyl)benzotriazole (5b): 71%, yellow needles, mp 127−128 °C; ^1H NMR δ 2.27 (s, 3H), 6.74 (d, 2H, J = 8.4 Hz), 7.02 (d, 2H, J = 8.1 Hz), 7.36−7.37 (m, 4H), 7.39−7.43 (m, 1H), 7.50 (t, 1H, J = 7.2 Hz), 7.61 (dt, 1H, J = 8.4, 0.6 Hz), 8.15 (d, 1H, J = 8.1 Hz), 8.46 (d, 1H, J = 8.1 Hz); ^{13}C NMR δ 20.8, 115.3, 119.9, 121.5, 125.5, 128.2, 129.2, 129.4, 130.1, 130.3, 130.5, 132.0, 133.9, 144.2, 146.4, 153.4. Anal. Calcd for $C_{20}H_{16}N_4$: C 76.90, H 5.16, N 17.94; Found: C 77.16, H 5.26, N 18.14.

1-(Phenyl-2-furancarboximidoyl)benzotriazole (5e): 87%, yellow prisms, mp 103−104 °C; ^1H NMR δ 6.61−6.63 (m, 1H), 6.89 (d, 1H, J = 3.6 Hz), 7.01 (d, 2H, J = 7.8 Hz), 7.17 (t, 1H, J

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= 7.2 Hz), 7.38 (t, 2H, *J* = 7.8 Hz), 7.58 (t, 1H, *J* = 7.8 Hz), 7.68−7.73 (m, 2H), 8.18 (d, 1H, *J* = 8.4 Hz), 8.29 (d, 1H, *J* = 8.4 Hz); ^{13}C NMR *δ* (data for the minor diastereomer are in parentheses) 112.5 (111.5), 115.2 (113.7), 120.4 (119.5), 120.5, 120.8 (121.4), 125.1 (125.4), 126.4 (126.0), 129.8 (129.4), 130.1 (129.6), 133.1, 143.4 (143.6), 146.6, 146.9, 148.7, 148.9. Anal. Calcd for $C_{17}H_{12}N_4O$: C 70.82, H 4.20, N 19.43; Found: C 70.68, H 4.09, N 19.54.

***N*-[(*Z*)-1-(1*H*-1,2,3-Benzotriazol-1-yl)-3,5,5-trimethylhexylidene]-4-methoxyaniline (5f):** 78%, glassy solid, mp 127−128 °C; ^{1}H NMR *δ* 1.09 (s, 9H), 1.26 (d, 3H, *J* = 6.6 Hz), 1.40−1.61 (m, 2H), 2.51−2.57 (m, 1H), 3.36−3.62 (m, 2H), 3.89 (s, 3H), 6.92 (d, 2H, *J* = 8.9 Hz), 7.09 (d, 2H, *J* = 8.9 Hz), 7.61 (t, 1H, *J* = 8.2 Hz), 7.75 (t, 1H, *J* = 8.2 Hz), 8.22 (d, 1H, *J* = 8.9 Hz), 8.41 (d, 1H, *J* = 8.9 Hz); ^{13}C NMR *δ* 22.6, 26.6, 29.7, 30.9, 44.4, 50.4, 55.1, 114.2, 114.4, 119.8, 121.7, 125.3, 125.7, 129.9, 130.8, 145.8, 157.0, 171.6. Anal. Calcd for $C_{22}H_{28}N_4O$: N 16.08; Found: N 16.28.

1-[Tolyl-2,4-bis(toluenecarboxyimidoyl-1-benzotriazole)] (6b): 74%, yellow needles, mp 186−187 °C; ^{1}H NMR *δ* 2.17 (s, 3H), 2.41 (s, 3H), 2.42 (s, 3H), 6.27 (dd, 1H, *J* = 1.8, 7.8 Hz), 6.36 (d, 1H, *J* = 2.1 Hz), 6.95 (d, 1H, *J* = 8.1 Hz), 7.03 (d, 2H, *J* = 8.1 Hz), 7.14 (d, 2H, *J* = 8.4 Hz), 7.20 (d, 4H, *J* = 3.6 Hz), 7.44−7.66 (m, 4H), 8.14 (dd, 2H, *J* = 8.4, 7.4 Hz), 8.34 (d, 1H, *J* = 8.1 Hz), 8.48 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR *δ* 17.8, 21.7, 114.0, 115.1, 116.3, 119.9, 120.0, 124.4, 125.4, 125.5, 127.2, 127.6, 128.8, 129.1, 129.2, 129.8, 130.2, 130.7, 132.0, 132.1, 140.6, 140.7, 145.4, 146.4, 146.6, 153.6. Anal. Calcd for $C_{35}H_{28}N_8$: C 74.98, H 5.03, N 19.99; Found: C 74.80, H 5.42, N 19.81.

General Procedure for the Preparation of Compounds 8a−c, 10, 12, and 14. In a 50 mL sealed tube, a mixture of 2 mmol of an oxoheterocycle and 5−10 mmol of an aryl isocyanate was heated at 200 °C for 12−24 h, and then it was cooled to room temperature. The reaction mixture was subjected to a column chromatography with hexane/ethyl acetate (0/1∼6/1) as an eluent to give the corresponding product. The pure product could be obtained by recrystallization from methylene chloride/ethanol.

4-(4-Methylanilino)quinoline (8b): 91%, colorless needles, mp 176−177 °C; ^{1}H NMR *δ* 2.35 (s, 3H), 6.85 (d, 1H, *J* = 5.4 Hz), 7.18 (m, 5H), 7.39−7.45 (m, 1H), 7.59−7.65 (m, 1H), 7.99 (t, 2H, *J* = 8.1 Hz), 8.49 (d, 1H, *J* = 5.4 Hz); ^{13}C NMR *δ* 21.1, 101.8, 119.7, 120.1, 123.5, 125.3, 129.5, 129.9, 130.3, 134.8, 137.2, 148.5, 149.3, 150.9. Anal. Calcd for $C_{16}H_{14}N_2$: C 82.02, H 6.02, N 11.96; Found: C 81.62, H 6.18, N 11.90.

***N*,*N*′-Diphenyl-*N*-(2-quinolinyl)urea (10):** 95%, colorless needles, mp 148−149 °C; ^{1}H NMR *δ* 6.53 (d, 1H, *J* = 9.0 Hz), 7.09 (t, 1H, *J* = 7.5 Hz), 7.33−7.39 (m, 4H), 7.45−7.58 (m, 4H), 7.71−7.77 (m, 4H), 7.89 (d, 1H, *J* = 9.0 Hz), 7.97 (d, 1H, *J* = 8.4 Hz), 13.8 (br s, 1H); ^{13}C NMR *δ* 114.5, 120.2, 123.6, 124.5, 125.7, 126.9, 127.9, 128.8, 129.3, 130.4, 130.5, 131.0, 138.6, 139.5, 140.2, 144.8, 153.8, 155.1. Anal. Calcd for $C_{22}H_{17}N_3O$: C 77.86, H 5.05, N 12.38; Found: C 78.10, H 5.06, N 12.46.

***N*,*N*′-Diphenyl-*N*-(9-acridinyl)urea (12):** 88%, yellow solid, mp 205−206 °C; ^{1}H NMR *δ* 6.59 (br s, 1H), 7.02 (t, 1H, *J* = 7.2 Hz), 7.13 (t, 1H, *J* = 6.6 Hz), 7.19−7.35 (m, 8H), 7.58 (t, 2H, *J* = 6.9 Hz), 7.76 (t, 2H, *J* = 7.8 Hz), 8.20 (dd, 4H, *J* = 8.7, 4.2 Hz); ^{13}C NMR *δ* 120.3, 123.4, 124.1, 124.9, 125.9, 128.1, 129.1, 129.5, 130.4, 130.9, 138.2, 142.4, 142.5, 150.5, 153.8. Anal. Calcd for $C_{26}H_{19}N_3O$: C 80.18, H 4.92, N 10.79; Found: C 80.18, H 4.92, N 10.79.

2-Anilino-pyridine (14): 69%, yellow cubes, mp 107−108 °C (106−108 °C);[17] ^{1}H NMR *δ* 6.71 (t, 1H, *J* = 6.9 Hz), 6.87 (d, 1H, *J* = 7.8 Hz), 7.02−7.07 (m, 2H), 7.31 (m, 2H), 7.33 (m, 2H), 7.44−7.50 (m, 1H), 8.19 (d, 1H, *J* = 8.1 Hz); ^{13}C NMR *δ* 108.4, 115.1, 120.6, 123.0, 129.5, 137.9, 140.8, 148.6, 156.4.

***N*-(4-Methylphenyl)-2-oxo-1-pyrrolidinecarboxamide (16):** 100%, colorless plates, mp 145−146 °C; ^{1}H NMR *δ* 2.04−2.09 (m, 2H), 2.30 (s, 3H), 2.65 (t, 2H, *J* = 8.1 Hz), 3.91 (t, 2H, *J* = 7.2 Hz), 7.10 (d, 2H, *J* = 8.1 Hz), 7.40 (d, 2H, *J* = 8.4 Hz), 10.5 (br s, 1H); ^{13}C NMR *δ* 16.9, 20.9, 33.6, 45.8, 120.1, 129.6, 133.7, 135.0, 150.3, 177.3. Anal. Calcd for $C_{12}H_{14}N_8O_2$: C 66.04, H 6.47, N 12.83; Found: C 66.08, H 6.69, N 12.82.

1,3,5-Triphenyl-6-(phenylimino)-1,3,5-triazin-2,4-dione (17): 30−91%, colorless needles, mp 277−278 °C (lit. mp,[11] 294−295 °C); ^{1}H NMR *δ* 6.27 (d, 2H, *J* = 7.2 Hz), 6.61 (t, 1H, *J* = 7.2 Hz), 6.80 (t, 2H, *J* = 7.8 Hz), 7.19−7.27 (m, 9H), 7.39−7.49 (m, 6H); ^{13}C NMR *δ* 120.5, 121.7, 127.9, 128.5, 128.6, 128.9, 129.0, 129.1, 129.2, 134.1, 135.8, 135.9, 145.0, 149.5. Anal. Calcd for $C_{27}H_{20}N_4O_2$: C 74.98, H 4.66, N 12.95; Found: C 74.64, H 5.01, N 12.75.

1,3-Diphenyl-2,4-diphenylimino-1,3-diazetine (18): 20%, colorless needles, mp 165−166 °C (lit. mp,[12] 162−164 °C); ^{1}H NMR *δ* 6.44 (d, 4H, *J* = 7.8 Hz), 6.75 (t, 2H, *J* = 7.5 Hz), 6.92 (t, 4H, *J* = 8.1 Hz), 7.10 (s, 10H); ^{13}C NMR *δ* 121.6, 122.3, 127.3, 128.1, 128.4, 128.7, 139.5, 143.0, 146.6. Anal. Calcd for $C_{26}H_{20}N_4$: C 80.39, H 5.19, N 14.42; Found: C 79.90, H 5.14, N 14.40.

Supporting Information Available: Characterization data for **3a**, **3d**, **5a**, **5c**, **5d**, **6a**, **8a**, **8c**, **19**, and **20**. This material is available free of charge via the Internet at http://pubs.acs.org.

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