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Simple, Novel Synthesis for 1-Carbamoyl-1*H*-benzotriazole and Some of Its Analogs

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Abstract: 1-Carbamoyl-1*H*-benzotriazole (benzotriazole-1-carboxamide, **2a**), an effective carbamoyl chloride substitute, and a range of its analogs can be synthesized in good yields in two very simple steps from 1,2-diaminobenzene. The facile preparation of the intermediate *o*-aminophenylurea is key to this process. A preliminary study of the reactivity of **2a** has shown that once in solution in tetrahydrofuran (THF), the 1-carbamoyl isomer equilibrates to give a mixture of both 1- and 2-isomers. If the solvent is ethanol or water, equilibration occurs rapidly compared to the ultimate formation of solvolysis products.

Keywords: Aminophenylthioureas, aminophenylureas, benzotriazole-1-carboxamide, thioureas, ureas

INTRODUCTION

The synthesis of substituted urea has recently become an area of considerable activity because of the significance of the urea functionality in several important groups of compounds (including enzyme inhibitors, peptidomimetics, intermediates for carbamate synthesis, dyestuffs, and antioxidants).[1,2] Katritzky et al. have highlighted the significance of a new reagent, 1-carbamoyl-1*H*-benzotriazole (**2a**), in the synthesis of mono- and di-substituted ureas and shown how it may be prepared from benzotriazole, via 1-cyano-1*H*-benzotriazole.[2,3]

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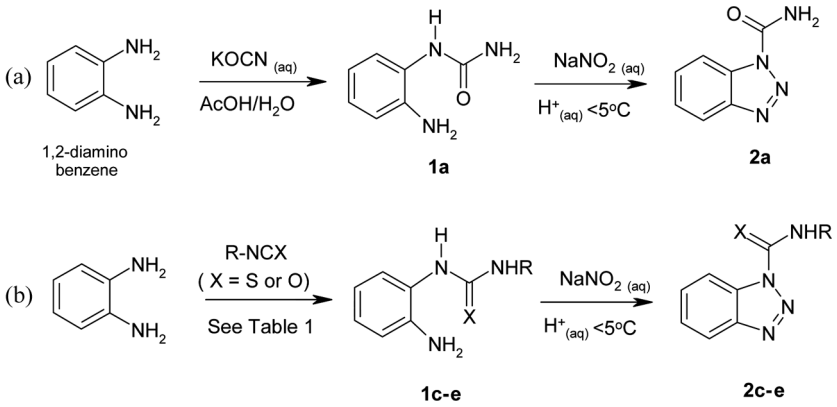
We report an inexpensive procedure that gives **2a** very readily compared to the previously published method, avoiding the use of cyanogen bromide[2] (or phosgene[4]) and lending itself, through appropriate adaptation, to the preparation of relatively large-scale batches of **2a** and its analogs in good yields (Schemes 1 and 2).

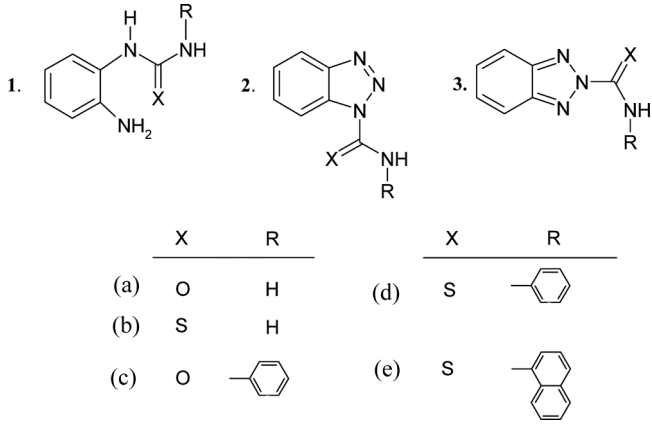
RESULTS AND DISCUSSION

The diazotization of *N*-substituted 1,2-diaminobenzenes in acidic aqueous solution to provide *N*-substituted benzotriazoles has been long established and was described by Fieser for the preparation of *N*-acetylbenzotriazole as far back as 1935.[5] More recently, it has been demonstrated[6] that *N*-(2-aminophenyl)-*N*′-alkylureas of the type **1a** with R = alkyl (prepared by reduction of *N*-(2-nitrophenyl)ureas to the corresponding amino compound) form benzotriazoles, chemoselectively, upon diazotization. This observation contrasts with the formation of a seven-membered benzotetrazepinone formed when using *N,N*′-dialkyl examples.[6] We have extended this observation to the unsubstituted parent urea itself (**1a**) and found that the -CO-NH_2 group survives the diazotization reaction to give the corresponding benzotriazole **2a**.

Key to the reported preparation is the ease with which 1,2-diaminobenzene reacts with cyanate ions in aqueous solution to furnish urea **1a** in good yield. This extension of a standard preparation for phenylurea[7]



Scheme 1. Simple routes from 1,2-diaminobenzene to some substituted *ortho*-aminophenylureas and substituted benzotriazoles. Cyanate ions give the N-substituted urea **1a** and subsequent benzotriazole **2a** (a). Isocyanates and isothiocyanates produce the N,N′-substituted ureas **1c–e** and their corresponding benzotriazoles **2c–e** on diazotization (b). See Scheme 2 for details of substituents.



Scheme 2. A key to the substituted areas and benzotriazoles prepared or attempted.

proceeds smoothly with none of the problems that might be expected from side reactions at the second amino function. We have also demonstrated that analagous substituted arylureas and arylthioureas (**1c–e**) are easily obtained directly from the corresponding isocyanates or isothiocyanates by reaction with 1,2-diaminobenzene. In contrast, our attempt to produce the analogous compound **1b** with thiocyanate ions has not been successful. All of the subsituted ureas **1a** and **1c–e** may be readily cyclized to their corresponding benzotriazoles by diazotization in aqueous hydrochloric acid, with acetic acid added to assist solvation where necessary (Schemes 1 and 2). Our survey of the literature has highlighted only one other similar, direct methodology that uses 4-nitro-1,2-diaminobenzene to facilitate regioselectivity in the *N*-acylation step prior to benzotriazole ring formation.[8,9] In the examples of *N*-carbamoylation and thiocarbamoylation reported here, such induced regioselectivity has proven unnecessary.

If **2a** is prepared as described here, the 1-carbamoyl isomer is isolated (which is also true for **2c–e**, based on IR and NMR evidence) but in keeping with some other examples of N-substituted benzotriazoles,[10–12] there is equilibration with the 2-carbamoyl isomer (**3a**) upon solvation. The rate of equilibration is clearly solvent dependent and is relatively fast in ethanol ($k_{eqm} \approx 1 \times 10^{-3} s^{-1}$ at 333 K) but slower in THF. When **2a** is refluxed in either solvent for periods in the range 1–20 h, there is a shift over time in $\nu_{C=O}$ from $\sim 1740\,cm^{-1}$ to $\sim 1652\,cm^{-1}$ in the solid material recovered (Fig. 1).

During equilibration in ethanol, the rate of ethanolysis of **2a** is sufficiently slow to allow equilibration to occur before the significant buildup

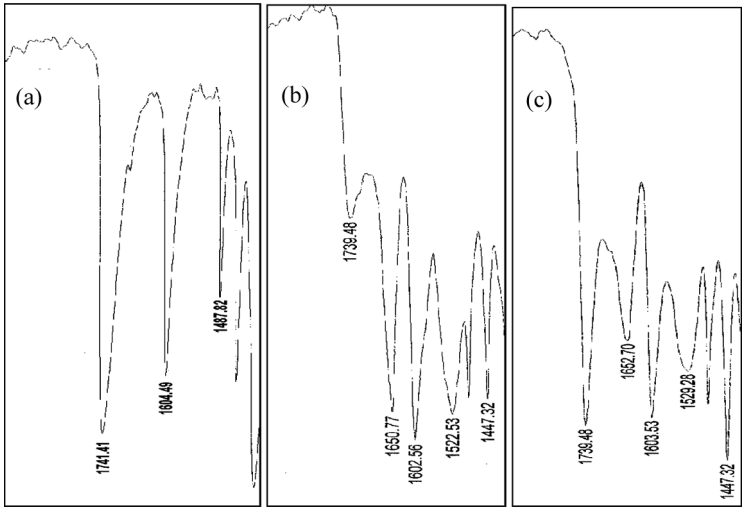


Figure 1. Details of reflectance FTIR spectra in the 1400 cm^{-1} to 2000 cm^{-1} region: (a) pure **2a**, (b) a mixture of **2a** and **3a** (prepared by boiling **2a** in absolute ethanol for 50 min and cooling the solution), and (c) a mixture of **2a** and **3a** (prepared by boiling **2a** in THF for 18 h and removing the solvent).

of solvolysis products. This is supported by both IR evidence (Fig. 1) and NMR evidence (Fig. 2). The residual isomeric mixtures obtained from solvent evaporation become increasingly contaminated with benzotriazole and ethylurethane over time. This is entirely consistent with the use of **2a** as a carbamoylating agent as described earlier.[2] These observations are interesting, because *N*-acylbenzotriazoles are reported as existing exclusively as the 1-isomers.[13] Furthermore, a cross-over intermolecular mechanism has been confirmed for the observed isomerization of *N*-(aminoalkyl)benzotriazoles in aprotic solvents.[10,11]

Monitoring the equlibration of dilute solutions of **2a** by change in ultraviolet (UV) absorbance in ethanol and water gives observed first-order kinetics, suggestive of a mechanism where ionization and recombination is occuring rapidly compared to the reaction with protic solvent. It can be postulated that resonance effects facilitate separation into $H_2{}^+N{=}C{=}O$ and benzotriazole anion, with or without solvent assistance, allowing isomerization to occur much more readily in **2a** than in N-acyl examples (Scheme 3). It is therefore conceivable that the mechanism of isomerization could be either intramolecular or intermolecular depending on the degree of solvent separation of $H_2{}^+N{=}C{=}O$ and benzotriazole anion. The relatively slow rates observed for solvolysis in protic solvents (ethanol and water) would indicate that the rate constants for

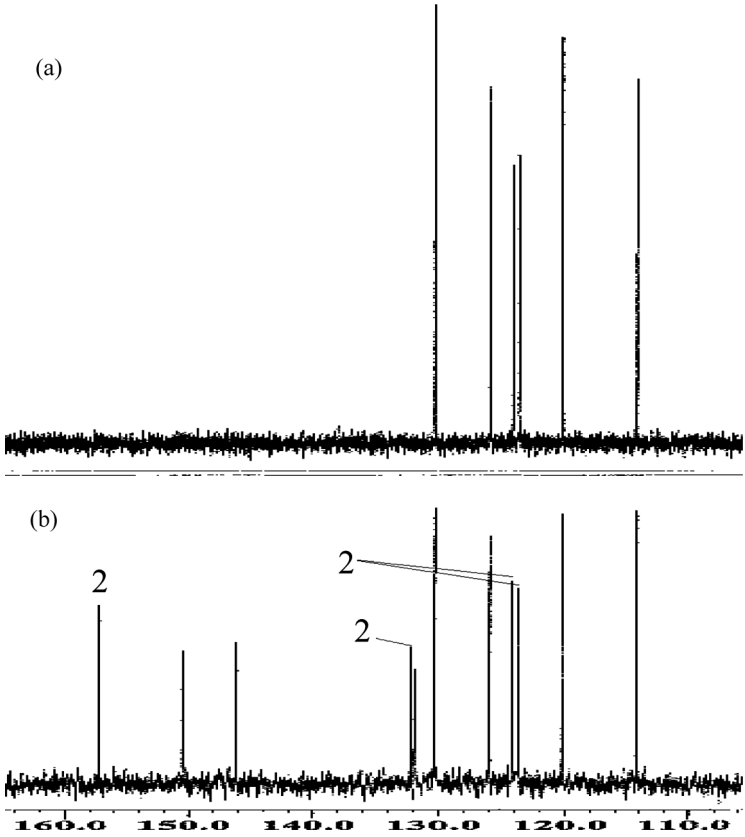
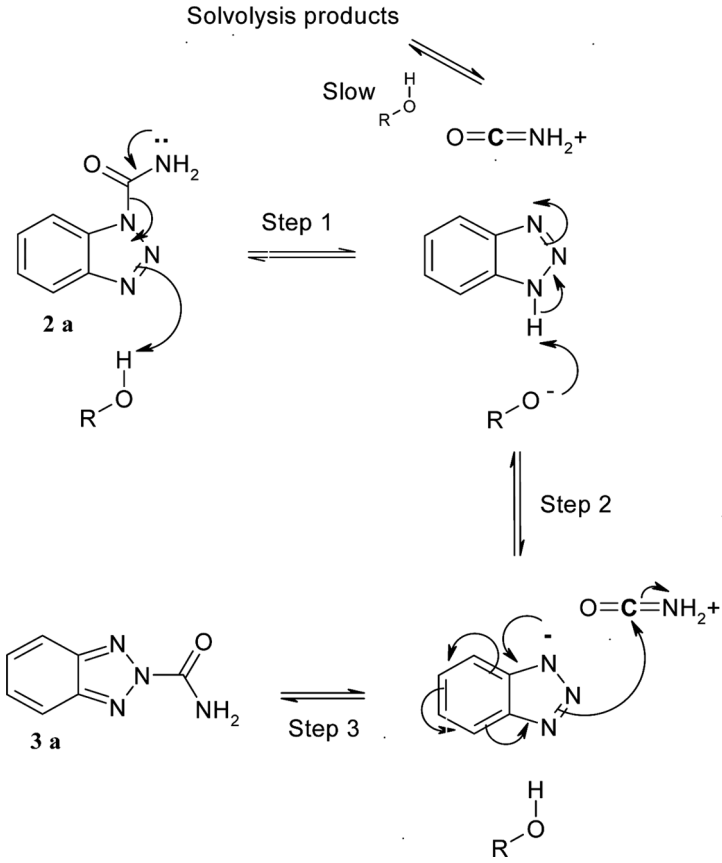


Figure 2. Details of ^{13}C NMR spectra for the mixture of **2a** and **3a** (prepared by boiling **2a** in absolute ethanol for 50 min and cooling the solution): (a) the DEPT-135 spectrum, confirming the 6 CH environments in the mixture, (b) all 11 of the carbon environments expected, with signals from the 2-isomer (3a) labeled 2.

equilibration in steps 1, 2, and 3 of Scheme 3 are large compared to those for the reaction of $H_2{}^+N{=}C{=}O$ with water or ethanol under neutral conditions. Preliminary experiments indicate that the observed *pseudo*-first-order rate constant for isomeric equilibration in water is very similar to that in ethanol. This would suggest no solvent involvement in the rate-determining step for isomerization, and this is therefore evidence of rapid pre-equilibration, with step 3 of Scheme 3 being the rate-determining step. Alternatively in an aprotic solvent such as THF, our data suggest a mechanism without solvent assistance, where the rate-determining step is likely to be the slow formation of the $H_2{}^+N{=}C{=}O$/benzotriazole anion pair. We have yet to study this system in further detail, but we have



Scheme 3. Suggested scheme for the equilibration of **2a** and **3a** via a solvent-assisted mechanism.

already established that while being very easy to synthesise, 1-carbamoyl-1*H*-benzotriazole has a more complex chemistry than hitherto reported and warrants further investigation, by itself and through the behavior of analogs such as **2c**–**e**.

EXPERIMENTAL

NMR spectra were recorded in D_6-DMSO at 270 MHz or 400 MHz (^{1}H NMR) and at 67.5 MHz or 100 MHz (^{13}C NMR) using tetramethylsilane (TMS) as the internal standard. Mass spectra were obtained using an HPP7 direct insertion probe attached to an HP 5973/5975 MSD instrument. Infrared spectra were recorded as Nujol mulls on a Nicolet

Impact 404 FT-IR, or neat on a Mattson Genesis II Reflectance FT-IR instrument. Melting-points were recorded using a capillary melting-point apparatus with mercury thermometer and are uncorrected. All CHN analysis was undertaken by Warwick Analytical Service, University of Warwick Science Park, UK.

N(2-Aminophenyl)urea (1a)

1,2-Diaminobenzene (0.1 mol, 10.8 g) was dissolved in glacial acetic acid (10 mL) and diluted to 100 mL with distilled water. Separately, potassium cyanate (0.1 mol, 8.1 g) was dissolved in 100 mL of distilled water and then added to the first solution, with stirring, at room temperature. After 1 h, the mixture was cooled in an ice bath for 30 min or left overnight in a refrigerator. The product was isolated by vacuum filtration, washed with ice-cold distilled water, dried at 100 °C, and recrystallized from methanol or ethanol if required. Off-white needles (78%); mp 166–168 °C[14]; ^{1}H NMR: δ 7.76 (s, 1H), 7.25 (m, 1H), 6.78 (m, 1H), 6.68 (m, 1H), 6.52 (m, 1H), 5.88 (s, 2H), 4.75 (br s, 2H); ^{13}C NMR δ 156.59, 140.64, 125.46, 123.89, 123.49, 116.64, 115.72: DEPT-135 confirms the three 4^{ry} C environments expected. MS *m*/*z* 151 (M^+), 134, 108 (100%). Anal. calcd. for $C_7H_9N_3O$: C, 55.62; H, 6.00; N, 27.88%. Found: C, 54.76; H, 5.90; N, 27.77%. IR (neat) 3417, 3333, 3288, 1646, 1620, 1525, 1355, 747 cm^{-1}.

N-(2-Aminophenyl)-*N*′-phenylurea (1c)

1,2-Diaminobenzene (0.1 mol, 10.8 g) was dissolved in sodium-dried Et_2O (300 mL) with stirring. Phenylisocyanate (0.1 mol, 11.9 g) was added dropwise, and the solution was stirred for a further 1 h, then cooled in an ice bath, whereupon **1c** precipitated. It was recrystallized from ethanol if required. White solid (90%); mp 189–191 °C, ^{1}H NMR: δ 8.77 (s, 1H), 7.73 (s, 1H), 7.45 (m, 2H), 7.35 (m, 1H), 7.25 (m, 2H), 6.94 (m, 1H), 6.84 (m, 1H), 6.74 (m, 1H), 6.58 (m, 1H), 4.80 (br s, 2H); ^{13}C NMR δ 153.1, 140.9, 140.1, 128.8, 124.7, 124.4, 123.8, 121.5, 117.9, 116.8, 115.9: DEPT-135 confirms the four 4^{ry} C environments expected. MS *m*/*z* 227 (M^+), 134 (100%), 119, 108, 93. Anal. calcd. for $C_{13}H_{13}N_3O$: C, 68.71; H, 5.77; N, 18.49%. Found: C, 68.54; H, 5.71; N, 18.34%. IR (neat) 3424, 3278, 1646 (shoulder), 1610, 1593, 1549, 743 cm^{-1}.

N-(2-Aminophenyl)-*N*′-phenylthiourea (1d)

1,2-Diaminobenzene (0.1 mol, 10.8 g) was dissolved in boiling $CHCl_3$ (200 mL) with stirring. Phenyl isothiocyanate (0.1 mol, 13.5 g) was added

dropwise. About 100 mL of $CHCl_3$ was removed by distillation, and the solution was cooled to room temperature, whereupon **1d** precipitated. recrystallized from ethanol. Off-white solid (75%); mp 147–148 °C, ^{1}H NMR: δ 9.59 (s, 1H), 9.07 (s, 1H), 7.52 (m, 2H), 7.31 (m, 2H), 7.10 (m, 2H), 6.97 (m, 1H), 6.75 (m, 1H), 6.56 (m, 1H), 4.90 (br s, 2H); ^{13}C NMR δ 180.1, 144.0, 139.6, 128.3, 128.1, 127.1, 124.2, 124.0, 123.6, 116.3, 115.9: DEPT-135 confirms the four 4^{ry} C environments expected. MS *m/z* 243 (M^+), 210, 150 (100%), 135, 108, 93. Anal. calcd. for $C_{13}H_{13}N_3S$: C, 64.17; H, 5.38; N, 17.27%. Found: C, 64.12; H, 5.37; N, 17.01%. IR (nujol mull) 3329, 3210, 1612, 1457, 1336, 761 cm^{-1}.

N-(2-Aminophenyl)-*N'*-(1-naphthyl)thiourea (1e)

Compound **1e** was forme as for **1d**, but using 1,2-diaminobenzene (0.05 mol, 5.4 g, dissolved in 100 mL $CHCl_3$) and 1-naphthyl isothiocyante (0.05 mol, 9.25 g, dissolved in the minimum volume of $CHCl_3$) in place of phenyl isothiocyanate. White solid (80%); mp 165–167 °C; ^{1}H NMR: δ 9.62 (br s, 1H), 9.08 (br s, 1H), 8.00 (m, 2H), 7.83 (m, 1H), 7.63–7.45 (m, 4H), 7.12 (m, 1H), 6.98 (m, 1H), 6.76 (m, 1H), 6.58 (m, 1H), 4.93 (br s, 2H); ^{13}C NMR δ 181.7, 144.2, 135.3, 133.9, 130.1, 128.4, 128.1, 127.2, 126.6, 126.0 (2 C), 125.6, 125.5, 124.2, 123.2, 116.4, 115.9: DEPT-135 confirms the six 4^{ry} C environments expected. MS *m/z* 293 (M^+), 258, 243, 185, 143 (100%), 108. Anal. calcd. for $C_{17}H_{15}N_3S$: C, 69.60; H, 5.15; N, 14.32%. Found: C, 69.35; H, 5.08; N, 14.12%. IR (nujol mull) 3313, 3132, 1612, 1456, 1371, 778 cm^{-1}.

Preparation of Benzotriazoles

The ureas and thioureas **1a** and **1c–e** were converted to the corresponding benzotriazoles by diazotization using either method 1 or method 2. Method 1 is applicable when the urea is readily soluble in aqueous HCl, and method 2 is employed when low solubility is observed.

Method 1

The substituted urea (0.05 mol) was mixed with 75 mL of water and 18 mL of conc. HCl. The mixture was cooled to 0–5 °C, stirring constantly. A separate solution of $NaNO_2$ (0.05 mol) in 18 mL of distilled water was then prepared and cooled to 0–5 °C. This solution was then added dropwise to the solution of urea, maintaining the temperature colder than 10 °C throughout. Efficient stirring was essential because

the mixture thickened considerably toward the end of the addition. The product was vacuum filtered immediately, washed with cold distilled water, and dried to constant weight in an oven at 60–70 °C.

Method 2

The substituted urea or thiourea (0.05 mol) was dissolved in 250 mL of glacial acetic acid with gentle heating, and then 18 mL of conc. HCl and 150 mL of distilled water were added. The mixture was cooled to 0–5 °C, stirring constantly. A separate solution of $NaNO_2$ (0.05 mol, 3.45 g) in 40 mL of distilled water was then prepared and cooled to 0–5 °C. With efficient stirring, this solution was then added in small aliquots to the solution of urea or thiourea, maintaining the temperature at less than 10 °C throughout. After 5 min of further stirring at or less than 5 °C, the product was vacuum filtered, washed with cold distilled water, and dried to constant weight in an oven at 60–70 °C or at room temperature in air, then over potassium hydrochloride (KOH) pellets in a dessicator in the case of **2e**. Where less than 0.05 mol of urea or thiourea was available (in particular for **2e**), the method was followed at a reduced scale throughout.

1-Carbamoyl-1*H*-benzotriazole (2a)

This was prepared from **1a** using method 1. White solid (77%); mp 164–166 °C (decomposes), (lit.[2] 160–161 °C, but also reported as having no definite mp,[16] which we also observed, depending on heating rate). ^{1}H NMR: δ 8.62 (br s, 1H), 8.29 (br s, 1H), 8.22 (m, 1H), 8.18 (m, 1H), 7.72 (m, 1H), 7.55 (m, 1H); ^{13}C NMR δ 149.96, 145.62, 131.38, 129.84, 125.44, 119.75, 113.76: MS *m/z* 162 (M^+), 134, 119, 91 (100%), 64. Anal. calcd. for $C_7H_6N_4O$: C, 51.85; H, 3.73; N, 34.55%. Found: C, 51.63; H, 3.72; N, 34.25%. IR (neat) 3331, 3242, 3163, 1741, 1605, 1403, 1299, 1053, 729 cm^{-1}. This material can be recrystallized from methanol if required but prolonged boiling causes significant isomeric equilibration and solvolysis.

1-(N-Phenyl)carbamoyl-1*H*-benzotriazole (2c)

This was prepared from **1c** using method 2. White solid (68%); mp 138–140 °C; ^{1}H NMR: δ 11.15 (s, 1H), 8.25 (m, 2H), 7.90–7.70 (m, 3H), 7.60 (m, 1H), 7.44 (m, 2H), 7.22 (m, 1H); ^{13}C NMR δ 147.0, 145.5, 137.2, 131.5, 130.1, 128.8, 125.8, 124.7, 121.2, 119.9, 113.7: DEPT confirms the four 4^{ry} C environments expected. MS *m/z* 238(M^+), 146,

119 (100%), 91, 64. Anal. calcd. for $C_{13}H_{10}N_4O$: C, 65.54; H, 4.23; N, 23.52%. Found: C, 65.46; H, 4.23; N, 23.47%. IR (neat) 3234, 1731, 1598, 1057, 743 cm^{-1}.

1-(N-Phenyl)thiocarbamoyl-1*H*-benzotriazole (2d)

This was prepared from **1d** using method 2. White solid (66%); mp 96–97 °C (lit.[15] 98–99 °C); ^1H NMR: δ 10.71 (br s, 1H), 8.92 (m, 1H), 8.12 (m, 1H), 7.76–7.55 (m, 3H), 7.54–7.36 (m, 3H), 7.33 (m, 1H); ^{13}C NMR δ 172.4, 147.2, 136.6, 132.3, 130.4, 129.1, 127.3, 125.8, 124.3, 120.3, 116.2: DEPT-135 confirms the four 4^{ry} C environments expected. MS *m/z* (254, M^+ not seen), 135 (100%), 119 (summing to 254), 91, 77, 64; IR (nujol mull) 3218, 1603, 1534, 1285, 752 cm^{-1}.

1-(N-(1-Naphthyl))thiocarbamoyl-1*H*-benzotriazole (2e)

This was prepared from **1e** (0.025 mol) using method 2. Yellow solid (75%); mp 76–79 °C (decomposes); ^1H NMR: δ 10.88 (br s, 1H), 8.95 (m, 1H), 8.18 (m, 1H), 8.06–7.87 (m, 4H), 7.76–7.48 (m, 5H); ^{13}C NMR δ 174.4, 147.3, 134.3, 132.5, 132.4, 130.6, 129.1, 128.8, 128.7, 127.1, 126.6, 126.0, 125.3, 125.1, 121.7, 120.5, 116.3: DEPT confirms the six 4^{ry} C environments expected. MS *m/z* (304, M^+ not seen), 185 (100%), 119 (summing to 304), 91, 64. Anal. calcd. for $C_{17}H_{12}N_4S$: C, 67.09; H, 3.97; N, 18.41%. Found: C, 66.94; H, 3.95; N, 18.24%. IR (nujol mull) 3175, 1594, 1156, 727 cm^{-1}.

Mixtures of 1-Carbamoyl-1*H*-benzotriazole (2a) and 2-Carbamoyl-1*H*-benzotriazole (3a)

Compound **2a** (2.0 g) was refluxed in absolute ethanol (50.0 mL) for 50 min and cooled in a freezer (−20 °C) for 2 h. A white solid (1.2 g, 60%) crystallized. This was identified as a roughly equimolar mixture of **2a** and **3a** only. IR C=O stretches are observed at 1740 cm^{-1} and 1651 cm^{-1} in the neat sample (Fig. 1B). ^{13}C NMR (signals due to **3a** are shown in bold type): **156.73**, 149.96, 145.62, **131.68**, 131.38, 129.84, 125.44, **123.70**, **123.24**, 119.75, 113.76: DEPT-135 confirms the five 4^{ry} C environments expected in the mixture (Fig. 2). A sample of **2a** (2.0 g) was also refluxed in analytical-grade THF (50.0 mL) for 18 h, and the solvent was removed by rotary evaporation. A white solid (2.0 g) was recovered. The IR spectrum of the neat sample suggests a mixture of **2a** and **2b**, with **2a** as the major component (Fig. 1C).

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