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PHENYLCARBAMOYLATION OF *N*-ACETYL-1,2,4-TRIAZOLIUM-4-AMINIDES REVISITED

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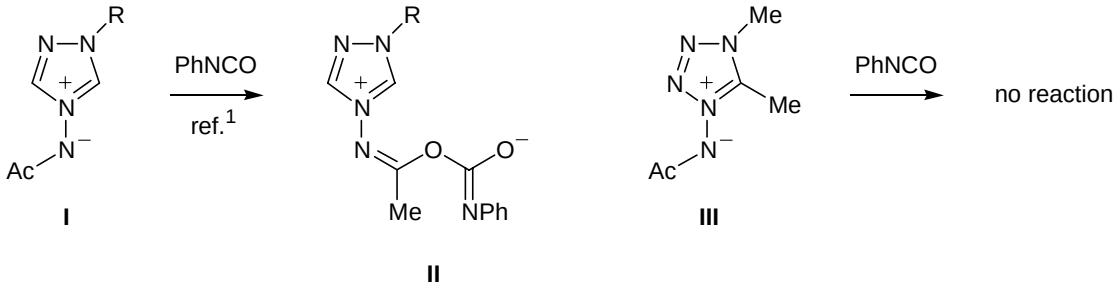
Abstract – The reaction of *N*-acetyl-1,2,4-triazolium-4-aminides (**I**, *i.e.* **1Aa-d**) with phenyl isocyanate affords ring functionalized products (**4a-d**) rather than linear adducts (**II**). Analogous compounds are obtained from the triazolium-1-aminide (**1Ae**) and the imidazolium congener (**1Af**). Twofold carbamoylation to give products of type (**8**) occurs on reaction of aminotriazolium salts (**7A**) in the presence of base. Azoliums having methyl at C(5) / (2) are inert throughout (**B** series).

INTRODUCTION

Many years ago during their studies on 1,2,4-triazolium-4-aminides, Becker and co-workers [1] reacted the derivatives (**I**; R = CH_2Ph, *n*-Bu) with phenyl isocyanate to illustrate the nucleophilic character of these compounds. As products the authors isolated materials that they believed to have structure (**II**).[1] In conjunction with recent work on tetrazolium aminides [2] we tried to obtain an analogous product from **III**. However, since we could not detect any reactivity toward the isocyanate,[3] we decided to duplicate Becker's findings.



I **II** **III**

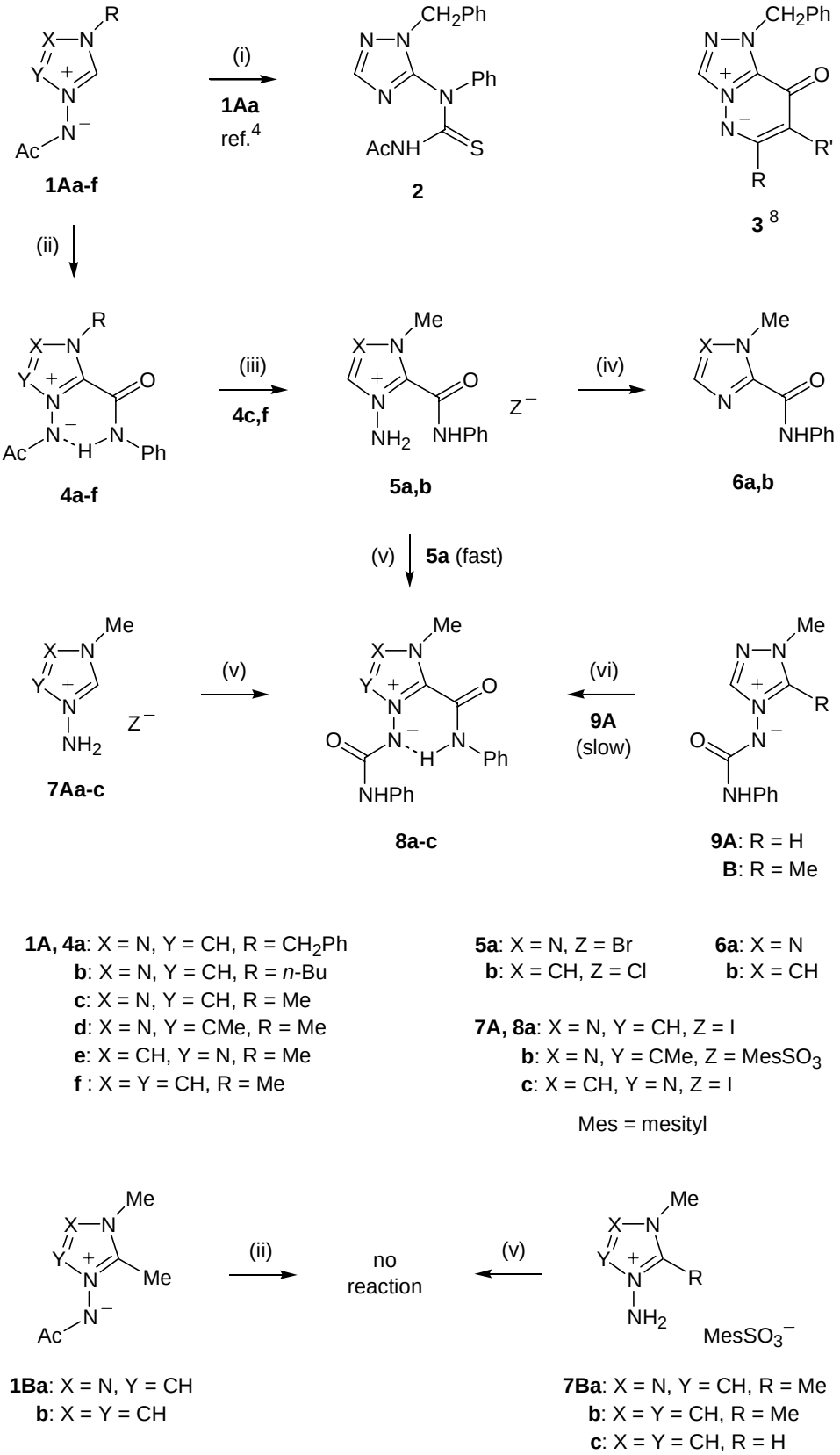
Scheme 1

RESULTS AND DISCUSSION

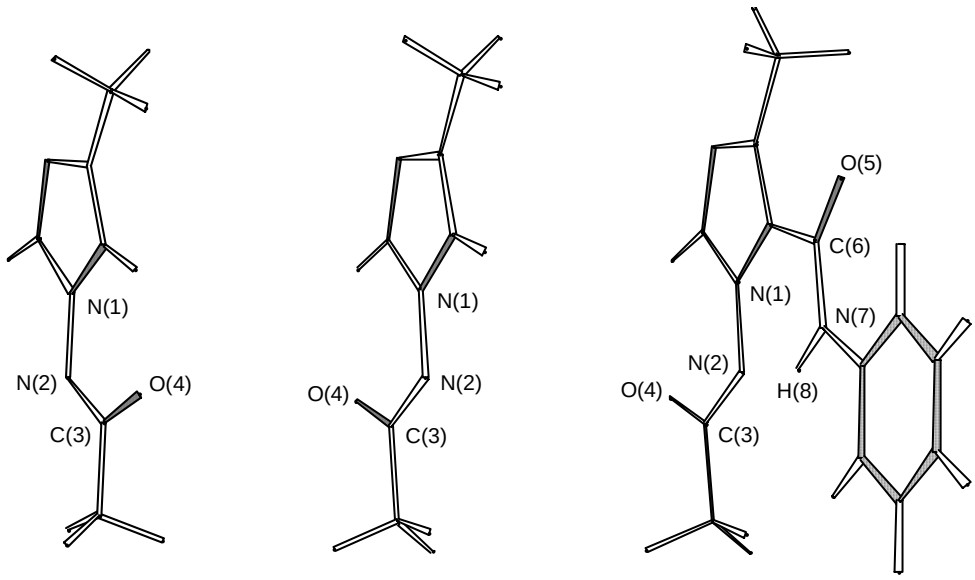
Treatment of the aminide (**I**; R = CH_2Ph) [*i.e.* (**1Aa**)] with phenyl isocyanate gave a crystalline substance (**X**) having mp and elemental composition as previously described for **II** (R = CH_2Ph).[1] Its spectra showed, in addition to the details reported,[1] broad IR absorptions at high wavenumbers and a broad ^{1}H NMR singlet at very low field. Analyzing the ^{13}C NMR spectrum, we found 7 doublets and 5 singlets [instead of 8 doublets and 4 singlets, which would be required for the claimed structure (**II**; R = CH_2Ph)]. This pointed to a functionalized triazole position. Hence, two constitutions were envisaged: the oxygen analogue of **2** in view of the 1,3-dipolar behaviour of **1Aa** towards phenyl isothiocyanate[4] and, secondly, the ring carbamoylation product (**4a**) because of the acidic hydrogen at C(5).[1, 5] Since the IR spectrum of **X** lacked a carbonyl band beyond 1700 cm^{-1} (*cf.* ref.[4]) and, moreover, only two of the ^{13}C NMR singlets appeared at $\delta \geq 150$,[7] the first structure (the acetylurea) does not fit so as to render **4a** the revised constitution of structure (**II**; R = CH_2Ph). This is evidenced below: (i) The benzylic protons of both **X** and the bicycle (**3**)[8] are remarkably deshielded with respect to those of the starting compounds (δ 5.4 $\rightarrow$ 6.1); (ii) the ring junction carbon of **3** (*e.g.* R = Et, R′ = Me) and the quaternary carbon of **X** that couples with the benzylic protons and also with 3-H of the triazolium ring both give low intensity signals and resonate at relatively high field (δ 138.8 [8b] / 133.9); (iii) action of phenyl isocyanate on **1Ab** [1] and **1Ac** afforded products having characteristics comparable to those of **X**; the material obtained from **1Ac**, on submission to acid hydrolysis followed by deamination, gave the known[9] carbanilide (**6a**).

The preferred geometry of **4c**, determined by B3LYP Density Functional Theory calculation using the 6-31G** basis set, represents a fully planar molecule (Fig. 1) which has a lengthened N(7)–H(8) bond compared to that of **6a** and in which the *Z* configurated aminide function is *ap* arranged towards the ring (contrary to the lowest energy conformation of **1Ac**). The pronounced ^{1}H NMR shifts of triazolium-3-H and the α protons of the R substituent are comprehensible in the light of this structure (*cf.* **1Aa** $\rightarrow$ **4a**: δ 8.38 $\rightarrow$ 9.86 and 5.43 $\rightarrow$ 6.04; **1Ab** $\rightarrow$ **4b**: δ 8.40 $\rightarrow$ 9.83 and 4.31 $\rightarrow$ 4.85; **1Ac** $\rightarrow$ **4c**: δ 8.35 [10] $\rightarrow$ 9.83 and 4.06 $\rightarrow$ 4.41).

Extending the preceding experiments to the triazolium aminides (**1Ad,e**) and (**1Ba**), we expectedly found that the derivatives of the **A** series by virtue of their acidic hydrogen at C(5) afford products of type (**4**) also very readily,[11] whereas **1Ba** which lacks this structural unit fails to react. This inertness corresponds to the aforementioned behaviour of the tetrazolium aminide (**III**) (Scheme 1). The 5-unsubstituted congener of **III**, however, should be reactive too, but this aminide is synthetically unavailable.[2] In addition to the triazolium aminides (**1Aa-e**), we checked the imidazolium derivative (**1Af**). This substrate, owing to the less active ring hydrogen (2-H), reacted more reluctantly (despite its good solubility) and gave the respective product (**4f**) in reduced yield.[12] As anticipated, the compound could be easily converted into the known [14] anilide (**6b**). Regarding the 2-methyl analogue (**1Bb**), this derivative, like **1Ba**, did not exhibit any reactivity toward the isocyanate.



Scheme 2. *Reagents and conditions*: (i), PhNCS, benzene, 80 °C, 8 h; (ii), PhNCO, $CHCl_3$, 20 °C, 1 h; or 65 °C, 18 h (**1Ac**), 4 h (**1Ae**), 24 h (**1Af**); (iii), 9 N HBr or 12 N HCl (**4f**), 20 °C, 12 h; (iv), 3 N HCl / $NaNO_2$, 0 °C, 30 min; (v), PhNCO / Et_3N, CH_2Cl_2, 20 °C, 1 h or 30 min (**5a**); (vi), PhNCO, CH_2Cl_2, 20 °C (see text)



1Ac (*sp)*

-489.53116
0.00

N(1)-N(2): 137.8
N(2)-C(3): 135.5
C(3)-O(4): 124.9

1Ac (*ap*)

-489.52585
3.33

N(1)-N(2): 137.9
N(2)-C(3): 135.8
C(3)-O(4): 124.4

4c (in parentheses: **6a**)

-889.30661 (-681.34692)

O(5)-C(6): 123.3 (123.0)
C(6)-N(7): 135.4 (136.4)
N(7)-H(8): 103.6 (101.5)
N(2)-H(8): 180.8
N(1)-N(2): 137.9
N(2)-C(3): 136.3
C(3)-O(4): 123.8

Figure 1. Structures of **1Ac** (*sp* and *ap* conformers) and **4c** according to B3LYP/6-31G** (gas phase); energies (a.u., kcal/mol) and selected bond lengths (pm) shown

Complementary experiments disclosed that 5-unsubstituted aminotriazolium salts such as **7Aa-c** are also prone to ring carbamoylation. In contrast to the reaction **1A** → **4**, the process requires a base (*cf.* the formation of **3** [8]) and is accompanied by side chain functionalization to give **8a-c**, even when using only one equivalent of the reagent. The conversion apparently starts with ring carbamoylation. This is inferred from the fact that the 5-methyl substituted salt (**7Ba**), different from the 3-methyl isomer (**7Ab**), was found fully unreactive. If, *vice versa*, carbamoylation of the amino group of **7A** should precede ring functionalization, under the above conditions the aminide (**9B**) would have arisen from **7Ba**. Regarding the second step in the process **7A** → **8**, model runs performed with the salt (**5a**) and the aminide (**9A**) showed that **5a** reacts distinctly faster. To understand the inertness of **7Ba-c**, two comments are added: (i) Triethylamine-mediated functionalization of the amino group as realized in the reaction **5a** → **8a** proceeds only if the group to be transformed is sufficiently acidic; this applies to **5a** because of the electron-withdrawing anilide moiety, and it is likewise true of the tetrazolium analogue of **7Ba** (Y = N in place of CH) [2] because of the more electronegative heterocycle. (ii) Concerning **7Bc**, the failure to undergo ring carbamoylation reflects the considerable decrease in kinetic acidity on passing from 1,2,4-triazoliums (5-H) to imidazoliums (2-H) [15] and parallels the modest reactivity of the imidazolium aminide (**1Af**).

EXPERIMENTAL

Mp: Linström apparatus; elemental analysis: Thermo Quest Flash EA 1112; IR: Philips PU-9800 FTIR, Thermo Nicolet FT-IR 200; NMR: Bruker DRX-400 (400.1 and 100.6 MHz for ^{1}H and ^{13}C, respectively). Theoretical calculations: Program package Gaussian 98, revision A.9.[16]

4-Acetamido-1-methyl-1*H*-1,2,4-triazolium Iodide (1Ac · HI). A mixture of **7Aa** [17] (0.45 g, 2 mmol), Ac_2O (2.20 g, 22 mmol), and AcOH (10 mL) was heated at reflux for 6 h. On addition of Et_2O crystals precipitated that were collected by filtration. – For data, see Tables 1 and 2.

***N*-Acetyl-1-methyl-1*H*-1,2,4-triazolium-4-aminide (1Ac)**. A solution of **1Ac** · HI (0.54 g, 2 mmol) was neutralized with 2 N KOH and concentrated *in vacuo*. From the residue the product (0.21 g, 75%) was extracted with warm acetone (3 x 10 mL); mp 184–186 °C (acetone) (lit.,[10] mp 214–215 °C); ^{1}H NMR ($CDCl_3$): δ 2.04 (s, 3H), 4.06 (s, 3H), 8.35 (s, 1H), 10.58 (s, 1H) (data in accordance with ref.[10]); ^{13}C NMR (DMSO-d_6): 22.7 (q), 38.3 (q), 139.6 (d), 142.3 (d), 171.8 (s).

Substituted *N*-Acetyl-1*H*-1,2,4-triazolium-4-aminides (1Ad, 1Ba). General procedure: A suspension of **7Ab** or **7Ba** (0.31 g, 1 mmol; for preparation, see below) in Ac_2O (5 mL) was heated at 90 °C for 4 h. Then unconsumed reagent was removed *in vacuo* and the residue was treated with aqueous K_2CO_3 (0.50 g, 10 mL). Extraction with $CHCl_3$ afforded an oily product that was purified on silica gel (MeOH as eluent). – For data, see Tables 1 and 2.

1-Acetamido-4-methyl-4*H*-1,2,4-triazolium Iodide (1Ae · HI). To a solution of *N*-(1*H*-1,2,4-triazol-1-yl)-acetamide [18] (1.00 g, 8 mmol) in anhydrous DMF (5 mL), prepared by gentle warming, was added MeI (2.13 g, 15 mmol) and the mixture was kept at 20 °C for 3 d. Concentration *in vacuo* left an oily residue that was dissolved in EtOH (*ca.* 2 mL). On addition of Et_2O the product crystallized out. – For data, see Tables 1 and 2.

***N*-Acetyl-4-methyl-4*H*-1,2,4-triazolium-1-aminide (1Ae)**. To a solution of **1Ae** · HI (0.27 g, 1 mmol) in warm acetone (*ca.* 2 mL) was added Et_3N (0.10 g, 1 mmol). The precipitate formed was filtered off. – For data, see Tables 1 and 2.

***N*-Acetyl-1,2-dimethyl-1*H*-imidazolium-3-aminide (1Bb)**. Adopting the procedure described in ref.,[19] **7Bb** [20] (1.24 g, 4 mmol) and K_2CO_3 (2.21 g, 16 mmol) were suspended in CH_2Cl_2 (40 mL). After cautious addition of AcCl (0.40 g, *ca.* 5 mmol), the stirred mixture was heated at reflux for 6 h and worked up accordingly.[19] – For data, see Tables 1 and 2.

Table 1. Yields, Melting Points, and Elemental Analyses (Calcd / Found) of New Compounds

Compd	Yield (%)	From	mp (°C)	Recryst. from	Formula	C	H	N
1Ac·HI	80	**7Aa**	162–163	EtOH	$C_5H_9IN_4O$	22.40 / 22.39	3.38 / 3.27	20.90 / 20.67
1Ae·HI	79	[a]	160–161	EtOH–Et_2O	$C_5H_9IN_4O$	22.40 / 22.54	3.38 / 3.37	20.90 / 20.79
1Ad	84	**7Ab**	[b]		$C_{12}H_{13}N_7O_8$ [j]	37.61 / 37.98	3.48 / 3.44	25.58 / 25.14
1Ae	71	**1Ae**·HI	207–209 [c]	Me_2CO	$C_5H_8N_4O$	42.95 / 42.92	5.75 / 5.82	39.98 / 40.07
1Ba	75	**7Ba**	[b]		$C_{12}H_{13}N_7O_8$ [k]	37.61 / 37.72	3.48 / 3.49	25.58 / 25.24
1Bb	31	**7Bb**	79–81 [d]	AcOEt	$C_{13}H_{14}N_6O_8$ [l]	40.84 / 40.87	3.69 / 3.64	21.98 / 21.85
4a	87	**1Aa**	148 [e]	EtOH	$C_{18}H_{17}N_5O_2$	64.46 / 64.21	5.11 / 5.11	20.89 / 20.86
4b	70	**1Ab**	109–111 [e]	EtOH–H_2O	$C_{15}H_{19}N_5O_2$	59.78 / 60.19	6.36 / 6.42	23.24 / 23.29
4c	77	**1Ac**	137–139	EtOH	$C_{12}H_{13}N_5O_2$	55.59 / 55.27	5.05 / 5.06	27.01 / 26.73
4d	84	**1Ad**	157–159 [c]	AcOEt	$C_{13}H_{15}N_5O_2$	57.13 / 57.22	5.53 / 5.52	25.63 / 25.67
4e	73	**1Ae**	166–168 [c]	Me_2CO	$C_{12}H_{13}N_5O_2$	55.59 / 55.50	5.05 / 5.02	27.01 / 27.13
4f	43	**1Af**	165–167 [d]	EtOH	$C_{19}H_{17}N_7O_9$ [m]	46.82 / 46.97	3.52 / 3.45	20.12 / 19.97
5a	74	**4c**	155–158	EtOH–H_2O	$C_{10}H_{12}BrN_5O$	40.29 / 40.10	4.06 / 3.99	23.49 / 23.47
7Ab	40	[f]	192–193	*i*-PrOH	$C_{13}H_{20}N_4O_3S$	49.98 / 49.98	6.45 / 6.39	17.93 / 17.76
7Ac	75	[g]	136–137	*i*-PrOH	$C_3H_7IN_4$	15.94 / 16.26	3.12 / 3.14	24.79 / 24.77
7Ba	50	[h]	146–148	*i*-PrOH	$C_{13}H_{20}N_4O_3S$	49.98 / 49.59	6.45 / 6.69	17.93 / 17.59
8a	95	**7Aa**	182–184	EtOH	$C_{17}H_{16}N_6O_2$	60.71 / 60.84	4.79 / 4.88	24.99 / 25.14
8b	49	**7Ab**	193–194	EtOH	$C_{18}H_{18}N_6O_2$	61.70 / 61.68	5.18 / 5.18	23.99 / 24.02
8c	82	**7Ac**	142–144	EtOH	$C_{17}H_{16}N_6O_2 \cdot H_2O$	57.62 / 57.47	5.12 / 5.13	23.72 / 23.71
9A	71	[i]	184–185	EtOH	$C_{10}H_{11}N_5O$	55.29 / 54.93	5.10 / 5.12	32.24 / 32.12

[a] *N*-(1*H*-1,2,4-Triazol-1-yl)acetamide. [b] Extremely hygroscopic, liquefied in air. [c] Decomp. [d] Hygroscopic. [e] Lit.,[1] mp 148 and 111 °C, respectively (literature structures different). [f] 1,3-Dimethyl-1*H*-1,2,4-triazole. [g] 1*H*-1,2,4-Triazol-1-amine. [h] 1,5-Dimethyl-1*H*-1,2,4-triazole. [i] 1-Phenyl-3-(4*H*-1,2,4-triazol-4-yl)urea. [j] Picrate, mp 162 °C (EtOH). [k] Picrate, mp 172–173 °C (EtOH). [l] Picrate, mp 184–185 °C (EtOH – Et_2O). [m] Picrate, mp 135–137 °C (EtOH).

Substituted *N*-Acetyl-5-(phenylcarbamoyl)-1*H*-/4*H*-1,2,4-triazolium-4-/1-aminides (4a–e). General procedure: To a solution or suspension of **1Aa,b**,[1] **1Ac** or **1Ad,e** (1 mmol) in $CHCl_3$ (20 mL) was added phenyl isocyanate (0.12 g, 1 mmol). The mixture was kept at 20 °C for 1 h (**1Aa,b,d**) or was heated at reflux (**1Ac** for 18 h, **1Ae** for 4 h). Removal of the solvent *in vacuo* gave the product. – For data, see Tables 1 and 2.

Reaction of *N*-Acetyl-1-methyl-1*H*-imidazolium-3-aminide (1Af) with Phenyl Isocyanate. The reagent and **1Af** [20] (0.14 g, 1 mmol), dissolved as above, were heated at reflux for 24 h. Chromatography on silica gel (ethyl acetate, then MeOH) yielded, successively, 0.05 g of unidentifiable material, mp 139–140 °C,[13] and 0.11 g of *N*-acetyl-1-methyl-2-(phenylcarbamoyl)-1*H*-imidazolium-3-aminide (**4f**). – For data, see Tables 1 and 2.

Degradation of the *N*-Acetylaminides (4c,f). (i) 4-Amino-1-methyl-5-(phenylcarbamoyl)-1*H*-1,2,4-triazolium bromide (**5a**). In an air stream at 20 °C a solution of **4c** (0.26 g, 1 mmol) in *ca.* 9 N HBr (2 mL) was concentrated to dryness and the residue was recrystallized. – For data, see Tables 1 and 2.

Table 2. Spectral Data of New Compounds

Compd	IR (ν cm^{-1}; KBr) // ^{1}H / ^{13}C NMR (δ; $CDCl_3$ or * DMSO-d_6)
1Ac·HI	3053, 1711 // * 2.14 (s, 3H), 4.14 (s, 3H), 9.48 (s, 1H), 10.48 (s, 1H), 12.38 (br s, 1H) / 20.5 (q), 39.6 (q), 144.0 (d), 144.9 (d), 169.2 (s)
1Ae·HI	3099, 1729 // * 2.15 (s, 3H), 3.98 (s, 3H), 9.26 (s, 1H), 10.43 (s, 1H), 12.84 (br s, 1H) / 20.4 (q), 34.9 (q), 144.29 (d), 144.33 (d), 169.1 (s)
1Ad	1582 // * 1.77 (s, 3H), 2.32 (s, 3H), 3.93 (s, 3H), 10.31 (s, 1H) / 9.7 (q), 22.8 (q), 37.9 (q), 140.0 (d), 150.2 (s), 171.8 (s)
1Ae	3144, 1591 // * 1.77 (s, 3H), 3.80 (s, 3H), 8.71 (s, 1H), 10.37 (s, 1H) / 23.2 (q), 33.4 (q), 135.4 (d), 139.6 (d), 171.2 (s)
1Ba	1572 // * 1.74 (s, 3H), 2.43 (s, 3H), 3.91 (s, 3H), 8.98 (s, 1H) / 8.5 (q), 22.5 (q), 37.0 (q), 142.6 (d), 147.3 (s), 172.9 (s)
1Bb	1556 // 2.00 (s, 3H), 2.43 (s, 3H), 3.70 (s, 3H), 6.92 (d, J = 2 Hz, 1H), 7.18 (d, J = 2 Hz, 1H) / 8.8 (q), 22.2 (q), 34.5 (q), 117.8 (d), 121.8 (d), 140.4 (s), 175.5 (s)
4a	3400 (br), 2900 (br), 1670 // 2.14 (s, 3H), 6.04 (s, 2H), 7.18−7.23 (m, 1H), 7.37−7.43 (m, 2H), 7.64−7.68 (m, 2H), 9.86 (s, 1H), 13.59 (br s, 1H) / 23.3 (q), 56.4 (t), 120.6 (d, 2C), 125.8 (d), 128.9 (d, 2C), 129.0 (d, 2C), 129.1 (d), 129.3 (d, 2C), 133.5 (s), 133.9 (s; weak), 136.5 (s), 143.0 (d), 150.2 (s), 173.4 (s)
4b	2750 (br), 1684 // 0.98 (t, J = 7 Hz, 3H), 1.41 (m_c, 2H), 1.93 (m_c, 2H), 2.15 (s, 3H), 4.85 (t, J = 7 Hz, 2H), 7.18−7.23 (m, 1H), 7.37−7.43 (m, 2H), 7.64−7.68 (m, 2H), 9.83 (s, 1H), 13.58 (br s, 1H) / 13.6 (q), 19.7 (t), 23.5 (q), 31.9 (t), 53.8 (t), 120.7 (d, 2C), 126.0 (d), 129.5 (d, 2C), 134.5 (s; weak), 136.8 (s), 143.0 (d), 150.4 (s), 173.6 (s)
4c	3152, 2750 (br), 1698 // 2.13 (s, 3H), 4.41 (s, 3H), 7.14−7.24 (m, 1H), 7.32−7.43 (m, 2H), 7.59−7.67 (m, 2H), 9.83 (s, 1H), 13.44 (br s, 1H) / 23.2 (q), 41.1 (q), 120.2 (d, 2C), 125.7 (d), 129.2 (d, 2C), 134.4 (s; weak), 136.3 (s), 142.6 (d), 150.2 (s), 173.3 (s); * 1.98 (s, 3H), 4.28 (s, 3H), 7.17−7.27 (m, 1H), 7.39−7.50 (m, 2H), 7.64−7.71 (m, 2H), 9.81 (s, 1H), 13.33 (br s, 1H) / 23.1 (q), 40.6 (q), 119.8 (d, 2C), 125.3 (d), 129.4 (d, 2C), 135.3 (s; weak), 136.8 (s), 142.4 (d), 150.6 (s), 171.7 (s)
4d	3400 (br), 2700 (br), 1684 // 2.15 (s, 3H), 2.47 (s, 3H), 4.33 (s, 3H), 7.29−7.34 (m, 1H), 7.36−7.42 (m, 2H), 7.64−7.67 (m, 2H), 12.46 (br s, 1H) / 10.5 (q), 22.0 (q), 40.4 (q), 120.3 (d, 2C), 125.8 (d), 129.2 (d, 2C), 136.3, 138.1 (s; weak), 149.8 (s), 153.6 (s), 175.9 (s)
4e	3200−2800 (br), 1681 // * 2.18 (s, 3H), 4.19 (s, 3H), 7.19−7.24 (m, 1H), 7.37−7.42 (m, 2H), 7.62−7.65 (m, 2H), 8.46 (s, 1H), 12.48 (br s, 1H) / 23.0 (q), 36.2 (q), 120.3 (d, 2C), 126.0 (d), 129.3 (d, 2C), 134.8 (s; weak), 136.3 (s), 141.8 (d), 150.2 (s), 177.0 (s)
4f	3430 (br), 2900 (br), 1684, 1600 // 2.15 (s, 3H), 4.22 (s, 3H), 7.05 (d, J = 1.9 Hz, 1H), 7.14−7.24 (m, 1H), 7.34−7.44 (m, 2H), 7.62−7.71 (m, 2H), 8.47 (d, J = 1.9 Hz, 1H), 13.51 (br s, 1H) / 23.6 (q), 38.8 (q), 120.4 (d, 2C), 121.2 (d), 124.3 (d), 125.3 (d), 128.7 (s; weak), 129.2 (d, 2C), 137.1 (s), 152.7 (s), 174.0 (s)
5a	3109, 2998, 2960, 1703 // * 4.21 (s, 3H), 7.25−7.30 (m, 1H), 7.35 (s, 2H), 7.46−7.50 (m, 2H), 7.74−7.78 (m, 2H), 9.40 (s, 1H), 11.68 (s, 1H) / 39.5 (q), 120.3 (d, 2C), 125.9 (d), 129.2 (d, 2C), 136.5 (s), 143.6 (s), 145.0 (d), 148.7 (s)
7Ab	3218, 3049 // * 2.19 (s, 3H), 2.47 (s, 3H), 2.50 (s, 6H), 3.96 (s, 3H), 6.25−6.75 (br, 2H), 6.77 (s, 2H), 9.99 (s, 1H) / 8.8 (q), 20.2 (q), 22.6 (q, 2C), 38.4 (q), 129.9 (d, 2C), 135.8 (s, 2C), 136.5 (s), 142.3 (s), 143.4 (d), 153.9 (s)
7Ac	3213, 3054 // * 3.87 (s, 3H), 7.38 (br s, 2H), 9.03 (s, 1H), 10.01 (s, 1H) / 34.3 (q), 140.7 (d), 143.4 (d)
7Ba	3256, 3140 // * 2.17 (s, 3H), 2.47 (s, 6H), 2.62 (s, 3H), 3.92 (s, 3H), 5.8−7.4 (br, 2H), 6.74 (s, 2H), 9.04 (s, 1H) / 8.4 (q), 20.3 (q), 22.7 (q, 2C), 37.8 (q), 129.9 (d, 2C), 135.8 (s, 2C), 136.4 (s), 142.4 (s), 144.1 (d), 152.0 (s)
8a	3341, 2800 (br), 1685, 1634 // * 4.30 (s, 3H), 6.81−6.86 (m, 1H), 7.18−7.24 (m, 3H), 7.40−7.44 (m, 2H), 7.51−7.60 (m, 2H), 7.77−7.81 (m, 2H), 8.85 (s, 1H), 9.61 (s, 1H), 13.25 (br s, 1H) / 39.5 (q), 117.9 (d, 2C), 120.1 (d), 120.6 (d, 2C), 125.3 (d), 128.3 (d, 2C), 129.1 (d, 2C), 135.1 (s; weak), 136.8 (s), 141.9 (d), 143.3 (s), 150.9 (s), 160.6 (s)
8b	3450−2900 (br; several bands), 1690, 1645 // * 2.42 (s, 3H), 4.28 (s, 3H), 6.77−6.85 (m, 1H), 7.11−7.23 (m, 3H), 7.35−7.45 (m, 2H), 7.52−7.61 (m, 2H), 7.69−7.77 (m, 2H), 8.97 (s, 1H), 13.15 (br, 1H) / 10.2 (q), 40.2 (q), 117.6 (d, 2C), 119.9 (d, 2C), 120.0 (d), 125.3 (d), 128.3 (d, 2C), 129.3 (d, 2C), 136.8 (s), 138.0 (s), 142.0 (s), 150.4 (s), 153.3 (s), 161.8 (s)
8c	3394, 3050 (br), 1686, 1621 // * 3.44 (s, *ca.* 2H), 4.06 (s, 3H), 6.78−6.84 (m, 1H), 7.15−7.20 (m, 3H), 7.34−7.41 (m, 2H), 7.54−7.57 (m, 2H), 7.67−7.71 (m, 2H), 8.92 (s, 1H), 9.03 (s, 1H), 12.89 (br s, 1H) / 35.7 (q), 117.6 (d, 2C), 119.7 (d, 2C), 120.0 (d), 125.2 (d), 128.3 (d, 2C), 129.2 (d, 2C), 134.6 (s; weak), 136.8 (s), 142.0 (s), 142.3 (d), 150.9 (s), 161.7 (s)
9A	1624 // * 3.98 (s, 3H), 6.69−6.74 (m, 1H), 7.07−7.14 (m, 2H), 7.52−7.56 (m, 2H), 8.11 (s, 1H), 8.95 (s, 1H), 10.19 (s, 1H) / 38.2 (q), 117.0 (d, 2C), 118.8 (d), 128.1 (d, 2C), 139.5 (d), 142.7 (s), 142.9 (d), 162.0 (s)

(ii) 1-Methyl-1*H*-1,2,4-triazole-5-carbanilide (**6a**) and 1-methyl-1*H*-imidazole-2-carbanilide (**6b**). General procedure: A solution of **4c** or **4f** (1 mmol) in 12 N HCl (5 mL) was concentrated as above. To the residual crude salt (**5a**; Z = Cl in place of Br) or (**5b**), dissolved in 3 N HCl (2 mL), was slowly added with stirring and ice cooling aqueous $NaNO_2$ (0.08 g, 2 mL). After 30 min the mixture was neutralized with 2 N KOH and the solid was filtered off to give: 0.14 g (69%) of **6a**, mp 81–83 °C (EtOH; lit.,[9] 84.5–86 °C; IR and ^{1}H NMR data in ac-

cordance with ref.[9]), or 0.11 g (55%) of **6b**, mp 104–106 °C (EtOH – water; lit.,[14a] 104–106 °C; IR and ^{1}H NMR data in accordance with ref.[14b]).

1-Amino-4-methyl-4*H*-1,2,4-triazolium Iodide (7Ac). To a solution of 1*H*-1,2,4-triazol-1-amine [21] (0.08 g, 1 mmol) in anhydrous DMF (1 mL) was added MeI (0.14 g, 1 mmol) and the mixture was allowed to stand at ambient temperature for 5 d. Then the solvent was distilled off *in vacuo* whereupon the residue slowly crystallized. – For data, see Tables 1 and 2.

4-Amino-1,3-/1,5-dimethyl-1*H*-1,2,4-triazolium Mesitylenesulfonates (7Ab, 7Ba). General procedure: A solution of 1,3-dimethyl- [22] or 1,5-dimethyl-1*H*-1,2,4-triazole [26] (0.10 g, 1 mmol) and *O*-mesitylsulfonylhydroxylamine (MSH) [29] (0.22 g, 1 mmol) in CH_2Cl_2 (30 mL) was kept at 20 °C for 24 h. Extraction with water and concentration of the aqueous layer *in vacuo* gave the product. – For data, see Tables 1 and 2.

Substituted *N*,5-Bis(phenylcarbamoyl)-1*H*-/4*H*-1,2,4-triazolium-4-/1-aminides (8a–c). (i) **8a-c** from **7Aa-c**: General procedure: To a suspension of **7Aa** [17] or **7Ab,c** (1 mmol) in CH_2Cl_2 (20 mL) was added Et_3N (0.15 g, 1.5 mmol) to be followed, after a clear solution had formed, by slow addition of phenyl isocyanate (0.24 g, 2 mmol). The mixture was stirred at 20 °C for 1 h and, regardless of a precipitate, was concentrated to dryness *in vacuo*. The residue was treated with aqueous K_2CO_3 (0.14 g, 10 mL) to afford a solid that was collected by filtration. – For data, see Tables 1 and 2.

(ii) **8a** from **5a**: To a suspension of **5a** (0.30 g, 1 mmol) in CH_2Cl_2 (20 mL) was added successively Et_3N (0.10 g, 1 mmol) and phenyl isocyanate (0.12 g, 1 mmol). Work-up performed 30 min later as above gave 0.31 g (92%) of **8a**; product identical (IR spectrum) to the material obtained by procedure (i).

(iii) **8a** from **9A**: A solution of **9A** (0.21 g, 1 mmol) and phenyl isocyanate (0.12 g, 1 mmol) in CH_2Cl_2 (20 mL) was stirred at 20 °C for 30 min. Evaporation of the solvent gave 0.18 g (54%) of **8a**; product identical (IR spectrum) to the material obtained by procedure (i).

1-Methyl-*N*-(phenylcarbamoyl)-1*H*-1,2,4-triazolium-4-aminide (9A). A suspension of 1-phenyl-3-(4*H*-1,2,4-triazol-4-yl)urea [6] (0.40 g, 2 mmol) in Me_2SO_4 (2 mL, *ca.* 20 mmol) was kept with occasional shaking at 20 °C for 24 h. Then Et_2O (10 mL) and aqueous Na_2CO_3 (1.00 g, 20 mL) were added, the mixture was vigorously stirred for 30 min, and the solid formed was filtered off. – For data, see Tables 1 and 2.

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