Unusual annelation of 2-methylimidazoline with arylisocyanates

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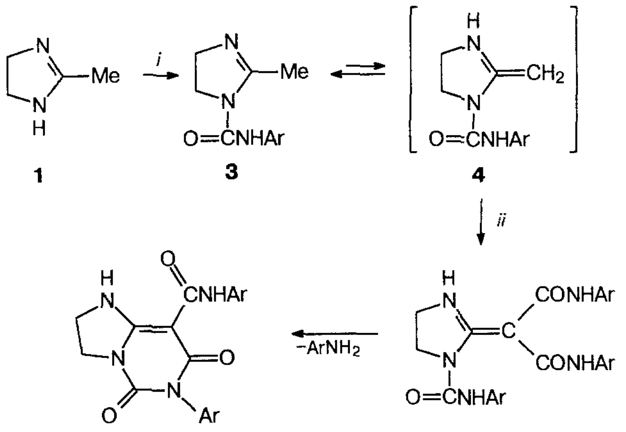
Reactions of acyclic amidines with isocyanates and isothiocyanates are widely used in the synthesis of 1,3diazetydinones, 1,3,5-triazine-2,4-diones, and their thioanalogs.[1] Analogously, the interaction between 1,2-dimethylimidazoline and MeNCS occurs by the same [2+2+2] cycloaddition stages.[2] In all these transformations the substituent at the *meso*-carbon of the amidine system is not affected. We have found a fundamentally different, unexpected direction of annelation of 2-methylimidazoline (**1**) with arylisocyanates (**2**), affecting the 2-methyl substituent and resulting in 6-aryl-8-arylcarbamoyl-1,2,3,5,6,7- hexahydroimidazo[1,2-*c*]pyrimidine-5,7-diones (**6**).



a: Ar = Ph, **b**: Ar = 4-MeC$_6$H$_4$, **c**: Ar = 1-C$_{10}$H$_7$
i. ArNCO (**2**); *ii*. 2ArNCO (**2**)

The formation of **6** seems to be caused by cyclization of intermediate **5**; the arylamine thus formed is trapped by **2** or **3** to give *symm*-diarylurea (**7**). 1-Carbamoylimidazoline **3c**, which was obtained from isocyanate **2c**, affords **6c** (78%) after additional treatment with 2 eq. of **2c**.

Previously described annelations of imidazolines or their 2-alkylideneimidazoline tautomers, involving the substituent at C(2) of the heterocycle require bifunctional electrophilic agents,[3—5] not monofunctional agents, which are used in the case under consideration.

2-Methyl-1-naphthylcarbamoylimidazoline (3c). A solution of 4.303 g of **2** in 15 mL abs. THF was added to a solution of 2.133 g of **1** in 10 mL abs. THF at 20 °C. The mixture was stirred at ~20 °C for 1.5 h, then 40 mL abs. ether was added and the mixture was kept at −10 °C for 24 h. The crystals obtained were filtered off and recrystalized from an abs.THF-ether mixture (1:3) to give **3c**. Yield 94%, m.p.166—168 °C. Found (%): C, 71.05; H, 6.13; N, 16.73. $C_{15}H_{15}N_3O$. Calculated (%): C, 71.15; H, 5.93; N, 16.60.

6-Aryl-8-arylcarbamoyl-1,2,3,5,6,7-hexahydroimidazo[1,2-c]-pyrimidine-5,7-diones (6). A mixture of **1** (12 mmol) and **2** (36 mmol) in 40 mL abs. THF was allowed to stand at ~20 °C for 5 days and **7** was filtered off. The filtrate was diluted with 60 mL of abs. ether, and the precipitated crystals of **6** were recrystalized from a CHCl-ether mixture. **6a**, yield 66 %, m.p. 295—297 °C. IR spectrum (v/cm^{-1}): 3337, 3140 (NH), 1715, 1680 (CO). MS, *m/z:* 348 [M$^+$] (65%), 347 [M$^+$−H] (100%). ^{1}H NMR spectrum (δ, ppm, *J*/Hz, DMSO-d$_6$): 3.83 (t, 2 H, CH$_2$, *J* = 9.4), 4.04 (t, 2 H, CH$_2$, *J* = 9.4), 7.01 (t, 2 H, H$_{Ar}$, *J* = 7.4), 7.25—7.31 (m, 6 H, H$_{Ar}$), 7.58 (d, 2 H, *J* = 7.8), 9.39 (s, 1 H, NH), 11.27 (s, 1 H, NH). ^{13}C NMR spectrum (δ, ppm, DMSO-d$_6$): 47.02, 47.10 (C-2, C-3), 84.34 (C-8), 123.11, 126.61, 132.06, 132.79, 133.23, 139.37, 142.73 (2 Ph), 151.60 (C-5), 161.28 (C-8'), 167.94, 168.15 (C-7 and CONH). Found (%): C, 65.80; H, 4.74; N, 15.92. $C_{19}H_{16}N_4O_3$. Calculated (%): C, 65.52; H, 4.60; N, 16.08.

6b, yield 57%, m.p. 273 °C. Found (%): C, 67.12; H, 5.32; N, 14.89. $C_{21}H_{20}N_4O_3$. Calculated (%): C, 67.56; H, 5.59; N, 14.75.

6c, yield 81%, m.p.>310 °C. Found (%): C, 72.54; H, 4.63; N, 13.17. $C_{27}H_{20}N_4O_3$. Calculated (%): C, 72.34; H, 4.46; N, 12.50.

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