# Pyridines; XVI.[1] Reactions of $N^1$-(Arylethenyl)benzamidines with Isocyanates and Phenyl Isothiocyanate. A Facile Synthesis of $N^1$-(1,2-Diarylethenyl)-$N^2$-(alkyl- or aryl-aminocarbonyl)benzamidines and Substituted 2-Oxo- or 2-Thioxo-1,2,3,4-tetrahydro-1,3,5-triazines

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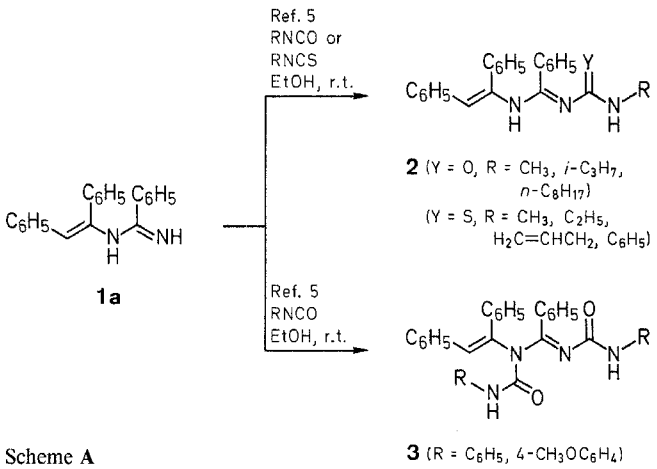
$N^1$-(1,2-Diarylethenyl)-$N^2$-(alkyl- or arylaminocarbonyl)benzamidines are easily prepared in good to high yields (61–90%) by reaction of various isocyanates with $N^1$-(1,2-diarylethenyl)benzamidines in tetrahydrofuran. When this addition reaction of the isocyanates (and also of phenyl isothiocyanate) with the amidines is performed in boiling toluene in the presence of catalytic amounts of quinuclidine the resultant $N^1$,$N^2$-disubstituted benzamidines are cyclized to give substituted 2-oxo- or 2-thioxo-1,2,3,4-tetrahydro-1,3,5-triazines in yields of 31–92%.

We have previously reported[2,3] the synthesis of pyridyl- and quinolyl-enamidines and their *N*-acylation with acyl chlorides. We now describe some new acylation reactions of enamidines with isocyanates and an isothiocyanate. The chemistry of enamidines has recently been studied.[4–6] From the reaction of enamidine **1a** with excess isocyanates or isothiocyanates in ethanol at room temperature there have been isolated[5] (Scheme **A**):

- mono(aminocarbonyl) or mono(aminothiocarbonyl) derivatives **2** in the case of alkyl isocyanates and alkyl or aryl isothiocyanates, respectively, the isothiocyanates reacting less readily;
- bis(aminocarbonyl) derivatives **3** in the case of aryl isocyanates.



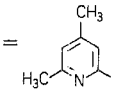
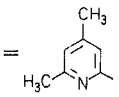

Scheme **A**

When boiling tetrahydrofuran is used instead of cold ethanol in the reaction of the same enamidine **1a** with some isocyanates and phenyl isothiocyanate (mol/mol), a further reaction occurs. In the case of cyclohexyl and phenyl isocyanates, we obtained the foreseeable mono(aminocarbonyl) derivatives **2a** and **2b** (Scheme **B** and Table 1), whereas from phenyl isothiocyanate, even in excess, neither the mono(aminothiocarbonyl) derivative **2** (Y = S, R = phenyl) (mp 195–196°C)[5] nor the bis(aminothiocarbonyl) derivative could be obtained. However, with phenyl isothiocyanate we obtained another product (not reported in Lit.[5]; mp 226°C) which was proven to be the 2-thioxo-1,2,3,4-tetrahydro-1,3,5-triazine **5a** (Scheme **B** and Table 1). The $^1$H-NMR spectrum showed:

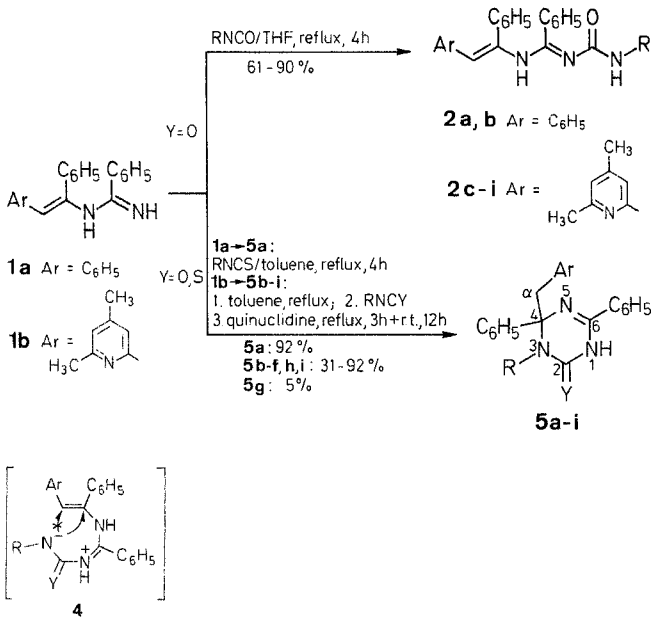
- the absence of the signal of an olefinic[2] proton at $\delta = 6.45$;
- the presence of two coupled doublets centered at $\delta = 3.48$ (1 H) and 3.98 (1 H) with a coupling constant $J = 14$ Hz, both due to a benzylic proton.

The IR spectrum of **5a** showed a strong absorption band at $\nu = 1670$ (C = N vibrations), a broad center at $\nu = 3150$ (N–H streching), and a strong peak at $\nu = 1230\ cm^{-1}$ (C = S vibrations). The structure of **5a** was further confirmed by its mass-spectral fragmentations (Table 2).

**Table 1.** $N^1$-(1,2-Diarylethenyl)-$N^2$-aminocarbonylbenzamidines **2** and 2-Oxo- or 2-Thioxo-1,2,3,4-tetrahydro-1,3,5-triazines **(5)** Prepared

| Product | Y | R | Yield (%) | mp (°C)[a] (solvent) | Molecular Formula[b] |
|---|---|---|---|---|---|
| Ar = $C_6H_5$ | | | | | |
| **2a** | O | *c*-$C_6H_{11}$ | 79 | 168 (toluene) | $C_{28}H_{29}N_3O$ (423.5) |
| **2b** | O | $C_6H_5$ | 79 | 195 (EtOAc/hexane) | $C_{28}H_{23}N_3O$ (417.5) |
| Ar =  | | | | | |
| **2c** | O | *n*-$C_3H_7$ | 90 | 139 (EtOAc) | $C_{26}H_{28}N_4O$ (412.5) |
| **2d** | O | *i*-$C_3H_7$ | 74 | 147 (EtOAc) | $C_{26}H_{28}N_4O$ (412.5) |
| **2e** | O | *n*-$C_4H_9$ | 83 | 157 (EtOAc) | $C_{27}H_{30}N_4O$ (426.6) |
| **2f** | O | *c*-$C_6H_{11}$ | 81 | 165 (*i*-$Pr_2O$) | $C_{29}H_{32}N_4O$ (452.6) |
| **2g** | O | *n*-$C_{18}H_{37}$ | 78 | 79 (cyclohexane) | $C_{41}H_{58}N_4O$ (622.8) |
| **2h** | O | $C_6H_5$ | 61 | 174 (EtOAc) | $C_{29}H_{26}N_4O$ (446.5) |
| **2i** | O | 3-Cl$C_6H_4$ | 64 | 156 (EtOAc) | $C_{29}H_{25}ClN_4O$ (480.9) |
| Ar = $C_6H_5$ | | | | | |
| **5a** | S | $C_6H_5$ | 92 | 226 (toluene) | $C_{28}H_{23}N_3S$ (433.5) |
| Ar =  | | | | | |
| **5b** | O | *n*-$C_3H_7$ | 85 | 255 (EtOAc) | $C_{26}H_{28}N_4O$ (412.5) |
| **5c** | O | *n*-$C_4H_9$ | 81 | 190 (EtOAc) | $C_{27}H_{30}N_4O$ (426.5) |
| **5d** | O | *n*-$C_{18}H_{37}$ | 39 | 108 (EtOAc) | $C_{41}H_{58}N_4O$ (622.8) |
| **5e** | O | $C_6H_5$ | 60 | 225 (EtOAc) | $C_{29}H_{26}N_4O$ (446.5) |
| **5f** | S | $C_6H_5$ | 92 | 219 (toluene) | $C_{29}H_{26}N_4S$[c] (462.6) |
| **5g** | O | 3-Cl$C_6H_4$ | 5 | 227 (*i*-$Pr_2O$) | $C_{29}H_{25}ClN_4O$ (480.9) |
| **5h** | O | 4-Cl$C_6H_4$ | 69 | 229 (*i*-$Pr_2O$) | $C_{29}H_{25}ClN_4O$ (480.9) |
| **5i** | O | 3-$CF_3C_6H_4$ | 31 | 248 (EtOH) | $C_{30}H_{25}F_3N_4O$ (514.5) |

[a] Melting points determined with a Kofler hot plate and uncorrected.
[b] Satisfactory microanalyses obtained: C ±0.36, H ±0.28, N ±0.23, O ±0.44, Cl ±0.19, F −0.04.
[c] Exact Mass (peak matching technique): calc. 462.1876, found 462.1894.




Scheme B

**Table 2.** Mass-Spectral Data of Some Compounds **2** and **5**

| Compound | MS (70 eV) *m/z* (relative intensity, %) |
|---|---|
| **2i** | 481 ($M^{\cdot+}$, 3); 438 ([M – HNCO]$^+$, 14); 354 ([M – $ClC_6H_5N$]$^+$, 16); 326 (354 – CO, 10); 221 (diphenylimidazolium cation, 100); 155, 153 ($ClC_6H_4NCO^+$, 13 and 35) |
| **5a** | 433 ($M^{\cdot+}$, 3); 342 ([M – $C_6H_5N$]$^+$, 65); 136 ($C_6H_5NCSH^+$, 7); 135 ($C_6H_5NCS^+$, 13); 104 ($C_6H_5CNH^+$, 100); 103 (23), 91 (18) |
| **5f** | 462 ($M^{\cdot+}$, 16); 429 ([M – SH]$^+$, 9); 342 (M – 120, 74); 327 (M – $C_6H_5NCS$, 38); 326 (54); 223 (80); 221 (diphenylimidazolium, 100); 136 (46); 135 ($C_6H_5NCS^+$, 100); 121 (2,4-dimethylazatropylium cation, 100); 104 ($C_6H_5CNH^+$, 95); 103 (94); 77 (100) |
| **5g** | 481 ($M^{\cdot+}$, 2); 360 (M – 120, 49); 354 (M – $ClC_6H_4N$, 23); 326 (354 – CO, 3); 155, 153 ($ClC_6H_4NCO^+$, 4 and 12); 122 (2,4,6-trimethylpyridinium cation, 100); 121 (100); 120 (35); 104 ($C_6H_5CNH^+$, 100) |
| **5i** | 514 ($M^{\cdot+}$, 22); 394 (M – 120, 100); 354 (M – $CF_3C_6H_5N$, 29); 326 (354 – CO, 5); 223 (326 – $C_6H_5CN$, 12); 186 ($CF_3C_6H_3NCO^+$, 29); 145 ($CF_3C_6H_4^+$, 36); 123, 122, 121, 120 (100 each); 104 ($C_6H_5CNH^+$, 100); 103 (52), 77 (47) |

**Table 3.** Spectral Data of Compounds **2**

| 2 | IR (KBr) $\nu$ ($cm^{-1}$) | $^1$H-NMR ($CDCl_3$/TMS; 27 °C) $\delta$, $J$ (Hz) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 4-$CH_3$ (s, 3H) | 6-$CH_3$ (s, 3H) | $\beta$-$H_{Pyr}$ | $H_{olefin}$ (s, 1H) | NH[a] (br s) | $H_{arom}$ | Miscellaneous |
| **a** | 3210 (m), 3060 (br m, NH); 2930 (s), 2860 (m, $H_{aliph}$); 1685 (s, C=O); 1630 (s, C=C) | | | | 6.15 | 9.85 (1H) | 6.75–7.60 (m, 16H, with 1NH) | 1.05–2.20 (m, centered at 1.40, 10H); 3.40–4.10 (m, centered at 3.80, 1H) |
| **b** | 3380 (w), 3220, 3130 (m, NH); 1695 (s, C=O); 1630 (s, C=C) | | | | 6.25 | 8.45 (1H); 12.20 (1H) | 6.90–7.80 (m, 20H) | |
| **c** | 3200 (m), 3090 (m, NH); 2975 (s), 2870 (m, $H_{aliph}$); 1675 (v s, C=O); 1640 (v s, C=C); 1605 (m) | 2.25 | 2.44 | 6.75 (s, 1H) | 6.28 | 8.40–9.40 (v br, 1H) | 6.85–7.70 (m, 12H, with 1$\beta$-pyridyl H and 1NH) | 0.95 (t, 3H, $J$ = 7, $CH_3CH_2CH_2$); 1.58 (sext, 2H, $J$ = 7, $CH_3CH_2CH_2$); 3.30 (t, 2H, $J$ = 7, $CH_3CH_2CH_2$) |
| **d** | 3200 (m), 3080 (w, NH); 2960 (s, $H_{aliph}$); 1680 (s, C=O); 1620 (s, C=C) | 2.25 | 2.44 | 6.72 (s, 1H) | 6.25 | 8.70–9.70 (v br, 1H) | 6.80–8.00 (m, 12H, with 1$\beta$-pyridyl H and 1NH) | 1.18 [d, 6H, $J$ = 6, $CH(CH_3)_2$]; 4.00 [h, 1H, $J$ = 6, $CH(CH_3)_2$] |
| **e** | 3210 (s), 3120 (s, NH); 2950 (s), 2920, 2850 (m, $H_{aliph}$); 1678 (s, C=O); 1628 (s, C=C); 1600 (s) | 2.25 | 2.44 | 6.75 (s, 1H) | 6.28 | 8.90–9.80 (v br, 1H) | 6.85–8.00 (m, 12H, with 1$\beta$-pyridyl H and 1NH) | 0.88 [m, 3H, $J$ = 6, $CH_3(CH_2)_3$]; 1.10–1.90 [m centered at 1.48, 4H, $CH_3(CH_2)_2CH_2$]; 3.30 [~t, 2H, $J$ = 6, $CH_3(CH_2)_2CH_2$] |
| **f** | 3205 (m), 3080 (br m, NH); 2925 (s), 2850 (m, $H_{aliph}$); 1680 (s, C=O); 1635 (s, C=C); 1605 (s) | 2.25 | 2.44 | 6.78 (s, 1H) | 6.35 | 8.18 (1H); 9.82 (0.6H) | 6.90–7.80 (m, 11H, with 1$\beta$-pyridyl H) | 0.90–2.20 [m, 10H, $(CH_2)_5$ in cyclohexyl]; 3.90–4.10 (m, 1H, CH in cyclohexyl); 5.25 (s, 0.4H, isourea OH) |
| **g** | 3210 (m), 3090 (br m, NH); 2920 (v s), 2850 (s, $H_{aliph}$); 1680 (s, C=O); 1640 (s, C=C); 1600 (m) | 2.25 | 2.44 | 6.72 (s, 1H) | 6.28 | 8.90–9.90 (v br, 1H) | 6.85–8.00 (m, 12H, with 1$\beta$-pyridyl H and 1NH) | 0.86 [m, 3H, $CH_3(CH_2)_{17}$]; 1.25 [s, 30H, $CH_3(CH_2)_{15}CH_2CH_2$]; 1.62–2.05 [m, 2H, $CH_3(CH_2)_{15}CH_2CH_2$]; 3.30 [m, 2H, $CH_3(CH_2)_{16}CH_2$] |
| **h** | 3218 (m), 3030 (br m, NH); 2960 (m); 1690 (s, C=O); 1645 (br s, C=C) | 2.20 | 2.40 | 6.74 (s, 1H) | 6.22 | | 6.80–8.30 (m, 18H, with 1$\beta$-pyridyl H and 2NH) | |
| **i** | 3400 (w), 3210 (m), 3100 (br m, NH); 1685 (s, C=O); 1640 (s, C=C) | 2.22 | 2.42 | 6.74 (s, 1H) | 6.18 | | 6.80–8.20 (m, 17H, with 1$\beta$-pyridyl H and 2NH) | |

[a] Exchangeable H with $D_2O$.

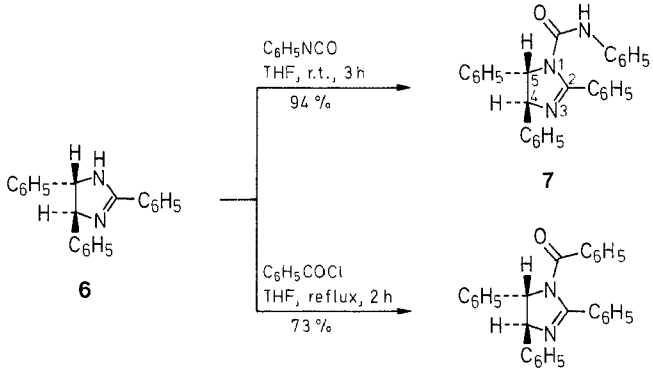
The triazinethione **5a** resulted from spontaneous cyclization of the intermediate **4** (Y = S, Ar = R = phenyl; Scheme **B**) which is formed by nucleophilic addition of phenyl isothiocyanate to the terminal N-atom of **1a**. The cyclization reaction **1a** → **5a** was extended to enamidine **1b**[2] which reacted with isocyanates and phenyl isothiocyanate in suitable solvents:

(a) When using refluxing tetrahydrofuran, *N'*-aminocarbonylamidines **2c–i** were obtained (Scheme **B**, Table 1);

(b) When using toluene with quinuclidine as catalyst (0.25 equiv for 1 equiv of isocyanates or phenyl isothiocyanate), only 2-oxo- or 2-thioxo-1,2,3,4-tetrahydro-1,3,5-triazines **5b–i** were obtained (Scheme **B**, Table 1).

We initially assumed that the heterocyclic compounds obtained were 1,3 or 5,6,7-tetrahydro-2*H*-1,3,5-triazepin-2-ones or -2-thiones, whose structures were at first sight compatible with all spectral data. Postulated syntheses of triazepine derivatives, in particular, of the claims of synthesis of triazepines, and various oxohydro-1,3,5-triazepines, in the early chemical literature, may be questioned and structural misassigments are prevalent according to Peet.[7] Triazepine ring systems are in general difficult to synthesize. It appears that when the opportunity of smaller-sized ring formation exists, the smaller-sized rings will often result.[7] In our case, other structural possibilities, specially $\Delta^2$-imidazolines like **7** were considered, but can be rejected on the basis of spectral data. (These data which are given in the Experimental Part should be compared with data in Tables 1–4).

The isomeric compound **7**[8] was obtained by reaction of (±)-isoamarine **(6)** with phenyl isocyanate[9] under mild conditions (Scheme **C**). The IR and $^1$H-NMR spectra of this colorless crystalline product (mp 140 °C) were totally different from those of compounds **5**; in particular, the absence[10] of coupling between the benzylic H-4 and H-5 protons (see Experimental Part) is remarkable.




Scheme **C**

(±)-Isoamarine **(6)** also reacts with benzoyl chloride[11] to give a crystalline white powder **8**[12] (mp 179 °C) whose IR fingerprint region and $^1$H-NMR spectra showed close similarity to those of **7** and the noteworthy absence of coupling between H-4 and H-5. Note that the published coupling constants $J_{AB}$ of (±)-*N*-benzoylamarine (*erythro* form) and (±)-*N*-benzoylisoamarine (*threo* form) are 8[12] or 8.4[13] and 3.4 Hz,[13] respectively, and that they are smaller than those of compounds **5** (12–15 Hz, see Table 4).

According to the suggestion of a referee, only a study by crystal X-ray diffraction could unequivocally prove the structures of products **5** and eliminate the possibility of a structural assignment as 1,3,5-triazepine derivatives. Such a study[14] shows unambiguously that compound **5h** is a 1,2,3,4-tetrahydro-1,3,5-triazin-2-one (Figure). Thus, the structures of compounds **5** given in Scheme **B** are corroborated.

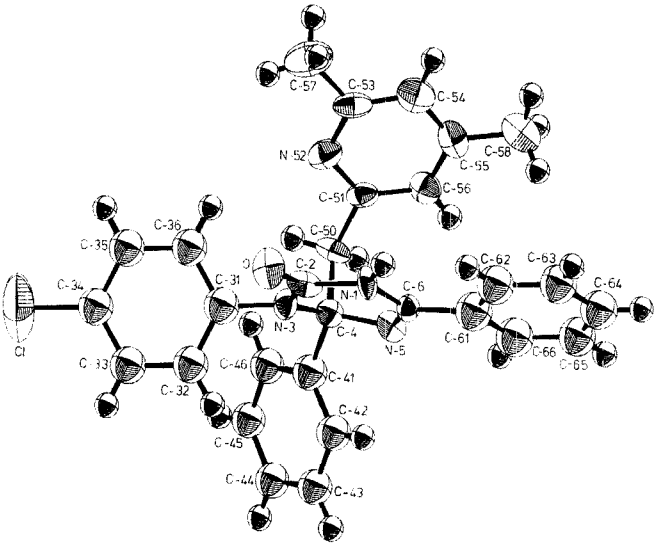



**Figure.** X-Ray Structure of Compound **5h**, ORTEP view.

Both coupled doublets centered at $\delta$ = 3.48 (1 H) and 3.98 (1 H) with a coupling constant $J$ = 14 Hz, result from two diastereotopic benzylic (or picolinic) protons and not from a $^3J$ coupling between two heterotopic protons. Tautomerism can exist among these triazines, namely with nitrogen at positions 1 and 5. From **5a**, no loss of the SH$^\cdot$ fragment from the molecular ion $M^{\cdot+}$ was observed. This fact seems to indicate the absence of a neighbouring proton and suggests the presence of a 5-H tautomer. However the $C_6H_5NCSH^+$ ion at $m/z$ = 136, which accompanies the peak at $m/z$ = 135, can involve the presence of a 1-H isomer. On the other hand, the mass spectrum of **5f** (see Table 2) showed loss of SH$^\cdot$ from $M^{\cdot+}$ and the peak at $m/z$ = 136; thus, in this case the 1-H tautomer appears more probable. In fact, the crystal X-ray diffraction shows that in **5h** (Figure), the hydrogen is located at N-1.

Chlorocarbonyl isocyanate reacts with **1b** to give the $N^1$-(1,2-diarylethenyl)-$N^3$-benzoylbiuret **9** in a chelated form.

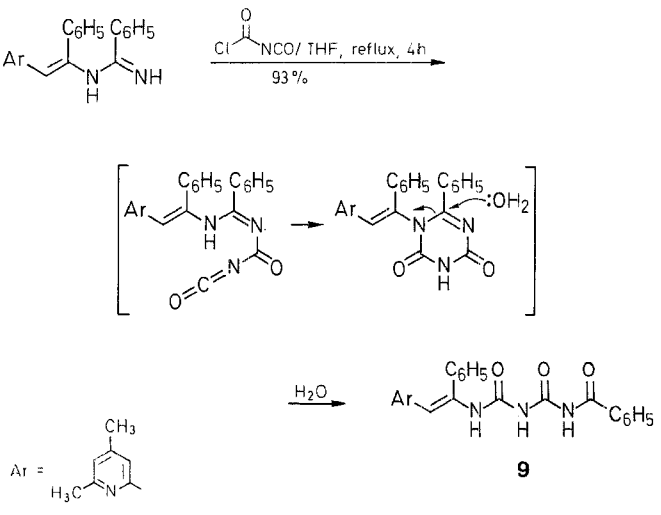


**Table 4.** Spectral Data of Compounds **5**

| 5 | IR (KBr) $\nu$ (cm$^{-1}$) | $^1$H-NMR ($CDCl_3$/TMS; 27 °C) $\delta$, $J$(Hz) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 4'-$CH_3$ (s, 3H) | 6'-$CH_3$ (s, 3H) | $H_{Pyr}$ | NH[a] (br s) | $H_{arom}$ | Miscellaneous |
| **a** | 3200, 3150 (br m, NH); 1670 (s, C=N); 1230 (s, C=S) | | | | 8.28 (1H) | 6.20–6.70 (m, centered at 6.45, 1H); 6.70–7.90 (m, 19H) | 3.48 (d, 1H, $J$ = 14, H-α); 3.98 (d, 1H, $J$ = 14, H-α) |
| **b** | 3230 (w), 3165 (w, NH); 2970 (m), 2940 (m), 2880 (w, $H_{aliph}$); 1655 (br s, C=O); 1605 (m) | 2.00 | 2.38 | 6.80 (~s, 2H) | 8.20 (1H) | 7.00–8.00 (m, 10H) | 0.55–0.85 (m, 3H, $CH_3CH_2CH_2$); 1.10–1.60 (m, 2H, $CH_3CH_2CH_2$); 2.80–3.20 (m, 2H, $CH_3CH_2CH_2$); 3.45 (d, 1H, $J$ = 12, H-α); 3.90 (d, 1H, $J$ = 12, H-α) |
| **c** | 3440 (w), 3230 (m), 3100 (m, NH); 2962 (m), 2940, 2870 (w, $H_{aliph}$); 1665 (br s, C=O); 1610 (m) | 1.92 | 2.30 | 6.70 (s, 1H); 6.78 (s, 1H) | 9.12 (1H) | 7.00–8.00 (m, 10H) | 0.30–1.70 (m, 7H, $C_3H_7CH_2$); 2.70–3.50 (m, 2H, $C_3H_7CH_2$); 3.42 (d, 1H, $J$ = 12, H-α); 3.88 (d, 1H, $J$ = 12, H-α) |
| **d** | 3220 (m), 3110 (w, NH); 2920 (s), 2858 (s, $H_{aliph}$); 1660 (s, C=O); 1610 (m) | 1.95 | 2.36 | 6.75 (~s, 1H); 6.82 (~s, 1H) | 8.20 (1H) | 7.05–8.00 (m, 10H) | 0.45–1.50 [m, 33H, $H(CH_2)_{16}CH_2CH_2$]; 1.55–1.70 [m, 2H, $H(CH_2)_{16}CH_2CH_2$]; 2.75–3.20 [m, 2H, $H(CH_2)_{17}CH_2$]; 3.45 (d, 1H, $J$ = 12, H-α); 3.92 (d, 1H, $J$ = 12, H-α) |
| **e** | 3460 (v w), 3240 (m), 3180 (m), 3070 (m, NH); 1660 (s, C=O), 1610 (m) | 1.90 | 2.40 | 6.70 (~s, 1H); 6.78 (~s, 1H) | 8.78 (1H) | 6.92–7.50 (m, 13H); 7.50–7.85 (m, 2H, 2 *o*-H of 6-$C_6H_5$) | 3.32 (d, 1H, $J$ = 13, H-α); 4.02 (d, 1H, $J$ = 13, H-α) |
| **f** | 3430 (w), 3200 (br m, NH); 3050 (m); 1665 (s, C=N); 1609 (s); (s, C=S) | 1.98 | 2.52 | 6.80 (~s, 2H) | 8.05 (1H) | 5.90–6.32 (m, 1H); 6.98–7.80 (m, 13H); 8.50–8.80 (m, 1H) | 3.25 (d, 1H, $J$ = 15, H-α); 4.14 (d, 1H, $J$ = 15, H-α) |
| **g** | 3420 (w), 3230 (m), 3190 (m, NH); 3060; 1660 (br s, C=O); 1610 (m) | 1.80 | 2.32 | 6.70 (~s, 2H) | 8.30 (1H) | 6.82–7.85 (m, 14H) | 3.20 (d, 1H, $J$ = 15, H-α); 3.90 (d, 1H, $J$ = 15, H-α) |
| **h** | 3420 (w), 3222 (m), 3180, 3120, 3060 (m, NH); 1673 (s), 1650 (s, C=O); 1605 (m) | 1.95 | 2.46 | 6.78 (s, 2H) | 8.50 (1H) | 7.00–7.50 (m, 12H); 7.50–7.90 (m, 2H, 2 *o*-H of 6-$C_6H_5$) | 3.30 (d, 1H, $J$ = 13, H-α); 4.00 (d, 1H, $J$ = 13, H-α) |
| **i**[b] | 3230 (m), 3180, 3120 (m), 3060 (NH); 3040; 1660 (s, C=O); 1610 (m) | 1.90 | 2.50 | 7.00 (s, 1H) | 11.00 (1H) | 7.10–7.75 (m, 11H, with 1$H_{Pyr}$); 7.75–8.94 (m, 3H); 8.68 (s, 1H) | 3.45 (d, 1H, $J$ = 13, H-α); 4.22 (d, 1H, $J$ = 13, H-α) |

[a] H-atom exchangeable with $D_2O$.
[b] $^1$H-NMR spectrum recorded in pyridine-$d_5$/$TMS_{int}$ for **5i**.

In conclusion, "this paper shows how small changes in the conditions of a previously known reaction may produce a different range of compounds" (a referee's remark) and it confirms the difficult access to various tetrahydro-1,3,5-triazepin-ones and -thiones (1,3,5-triazine derivatives were obtained instead) and the necessity of an incontestable structural assignment in these series, proving the correctness of Peet's assertions.[7]

Mass spectra were recorded on a AEI MS902 spectrometer (direct introduction, 70 eV). IR spectra were recorded on a Perkin-Elmer 577 spectrometer. $^1$H-NMR spectra were recorded on a Perkin-Elmer R24 spectrometer.

All reactions are carried out under an argon or nitrogen atmosphere.

**$N^1$-(1,2-Diarylethenyl)-$N^2$-(alkyl- or arylaminocarbonyl)benzamidines 2; General Procedure:**

To a stirred solution of the $N^1$-(1,2-diarylethenyl)benzamidine[2] **1a** (596.77 mg, 2 mmol) or **1b** (654.86 mg, 2 mmol) in anhydrous THF (30 mL) at room temperature is added the isocyanate (2.2 mmol). The mixture is heated at reflux temperature with stirring for 4 h. The THF is then removed under reduced pressure and diisopropyl ether is added to the residue. The crude product **2** precipitates from the solution. It is isolated by suction, washed with diisopropyl ether, and recrystallized from a suitable solvent (Tables 1, 2 and 3).

**$N^1$-[2-(4,6-Dimethyl-2-pyridinyl)-1-phenylethenyl]-$N^3$-benzoylbiuret (9):**

Obtained from amidine **1b** and chlorocarbonyl isocyanate using the above procedure; yield: 93%; mp 224 °C (EtOH).

$C_{24}H_{22}N_4O_3$ (414.45) calc. C 69.55 H 5.35 N 13.52
found 68.78 5.32 13.40

MS (70 eV): $m/z$ = 414 ($M^{+}$, 21%); 293 ([$M - C_6H_5CONH_2$]$^+$, 33); 223 [293 – $N(CO)_2$, 100]; 208 (223 – NH, 17); 147 (29); 121 (15); 120 (14); 105 ($C_6H_5CO^+$, 82); 77 (68).

IR (KBr): $\nu$ = 3210 (br m), 3100 (NH); 1730 (s), 1685, 1660 (v s, C=O); 1635 (s, C=C) cm$^{-1}$.

$^1$H-NMR ($CDCl_3$/TMS): $\delta$ = 2.25 (s, 3H, 4-$CH_3$); 2.53 (s, 3H, 6-$CH_3$); 6.00 (s, 1$H_{olefin}$); 6.80 (s, 1$H_{pyridine}$); 6.90 (s, 1$H_{pyridine}$); 7.05–7.65 (m, 8$H_{arom}$); 7.65–8.10 (m, 2 *o*-$H_{arom}$); 10.72 (br s, 1H, NH); 11.22 (br s, 1H, NH); 12.32 (br s, 1H, NH).

**2-Oxo- and 2-Thioxo-1,2,3,4-tetrahydro-1,3,5-triazines 5; General Procedure:**

To a stirred, boiling solution of the $N^1$-(1,2-diarylethenyl)benzamidine[2] **1a** (596.77 mg, 2 mmol) or **1b** (654.86 mg, 2 mmol) in anhydrous toluene (30 mL) is added the isocyanate or isothiocyanate (2.2 mmol) and quinuclidine (55.60 mg, 0.5 mmol). The mixture is refluxed for 3 h and stirring is continued for 1 night at room temperature. Toluene is then removed under reduced pressure and diisopropyl ether (~ 50 mL) is added to the residue. The crude product **5** which precipitates from this mixture is isolated by suction, washed with diisopropyl ether, and recrystallized from a suitable solvent (Tables 1, 2 and 4).

**(±)-2,4*r*,5*t*-1-Phenylaminocarbonyl-2,4,5-triphenyl-4,5-dihydroimidazole (7):**

(±)-Isoamarine (Aldrich) **(6)** (596.77 mg, 2 mmol) is treated according to the General Procedure, and stirring is maintained for 3 h at room temperature [Note that the $^1$H-NMR spectrum of (±)-isoamarine **(6)** shows a singlet (2 H) at $\delta = 4.85$ for the two benzylic H-4 and H-5 protons according to Lit.[12] in which a singlet ($\delta = 4.9$) for **6** and (±)-amarine is reported]; yield of **7**; 785 mg (94%); mp 140°C (diisopropyl ether).

| | | | | | |
|---|---|---|---|---|---|
| $C_{28}H_{23}N_3O$ | calc. | C 80.55 | H 5.55 | N 10.07 | O 3.83 |
| (417.5) | found | 80.32 | 5.60 | 10.13 | 4.09 |

MS (70 eV): $m/z = 299$ (6%); 298 (isoamarine$^+$, 25); 194 (17), 193 (298 – $C_6H_5CHNH$, 100); 90 (193 – $C_6H_5CN$, $C_7H_6^+$, 16), 89 (12); 119 ($C_6H_5NCO^+$, 100); 91 (119 – CO, 33).

IR (KBr): $\nu = 3420$ (m, NH); 1723 (s, $N_2C=O$); 1630 (m, C=N); 1600 (s) cm$^{-1}$.

$^1$H-NMR ($CDCl_3$/TMS): $\delta = 5.20$ (s, 2H, H-4, H-5); 6.45 (br s, 1 H, exchangeable with $D_2O$, NH), 7.02, 7.32, 7.44 (m, 18 $H_{arom}$); 7.80–8.10 (m, 2 *o*-$H_{arom}$ of 2-$C_6H_5$).

**(±)-2,4*r*,5*t*-1-Benzoyl-2,4,5-triphenyl-4,5-dihydroimidazole (8):**

(±)-Isoamarine (Aldrich) (**6**; 596.77 mg, 2 mmol) is treated according to the General Procedure, but using benzoyl chloride (309.3 mg, 2.2 mmol) in place of phenylisocyanate and stirring the mixture under reflux for only 2 h. Then, the mixture is neutralized with *s*-collidine, the solvent is removed under vacuum, and diisopropyl ether (50 mL) is added to the residue. The precipitate is isolated by suction, washed thoroughly with water, and recrystallized from diisopropyl ether; yield of **8**: 588 mg (73%); mp 179°C (diisopropyl ether) [Lit.[11] mp 178°C (petroleum ether).

IR (KBr): $\nu = 1675$ (s, NC=O); 1630 (m, C=N); 1600 (w) cm$^{-1}$.

$^1$H-NMR ($CDCl_3$/TMS): $\delta = 5.20$ (s, 2H, H-4, H-5); 7.0–7.5 (m centered at 7.30, 16 $H_{arom}$); 7.5–8.0 (m, 4H, 2 *o*-$H_{arom}$ of $COC_6H_5$, 2 *o*-$H_{arom}$ of 2-$C_6H_5$).

*The authors thank Perrey D. (Laboratoire de Synthèse et d'Electrosynthèse organométalliques, UA 33) for recording the mass spectra.*

Received: 21 July 1987; revised 14 January 1988

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