# Reactions of Some Active Carbonyl Compounds with 4-Aryl-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile Derivatives 

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#### Abstract

Synthesis of the corresponding 1-alkylidenaminopyridone, $[1,2,4]$ triazolo $[1,5-a]$ pyridine, and pyrido $[1,2-b][1,2,4]$ triazepine derivatives by condensation of some 4 -aryl-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile derivatives with ethyl acetoacetate, phenylacetic acid, $N^{\prime}$ ethoxymethylenebenzohydrazide, acetaldehyde, acetone, aromatic aldehydes, acetophenone, and pentane-1,4-dione in different reaction conditions is described.


Polyfunctional pyridines are highly reactive reagents that have been extensively used in heterocyclic synthesis $[1-3]$. Triazolopyridines are also interesting compounds due to their pronounced biological activity, as they can be used as antidepressants [4, 5]. In continuation of the previous work concerning the use of $\alpha, \beta$-unsaturated nitriles in heterocyclic synthesis $[6,7]$, we report here on the utility of ylidene malononitriles $I$ and cyanoacetohydrazide $I I$ as readily obtainable starting materials to prepare the corresponding 4-aryl-1,6-diamino-2-oxo-1,2-dihydropyridine-3,5dicarbonitrile III according to the earlier reported procedure by Soto et al. [8] to utilize them in the synthesis of some fused pyridones by reacting them with some carbonyl compounds in different reaction conditions.

Thus the starting $I I I a$ and $I I I b$ [8] were reacted with ethyl acetoacetate in a comparable way. In the presence of acid catalyst (perchloric acid) and ethanol as solvent, the keto function in the $\beta$-keto ester was condensed with the $N$-amino function in compounds IIIa and IIIb via water elimination leading to the corresponding ethyl 3 -[(6-amino-4-aryl-3,5-dicyano-2-oxo-1,2-dihydropyridin-1-yl)imino]butyrates $I V a$ and $I V b$ (Scheme 1).

Compounds $I I I a$ and $I I I b$ were reacted with ethyl acetoacetate in methanolic sodium methoxide solution to give the corresponding 9 -aryl-4-methyl-2,7-dioxo-2,3,6,7-tetrahydro- $1 H$-pyrido $[1,2$ - $b][1,2,4]$ triazepine- 8 , 10-dicarbonitriles $V a$ and $V b$ via EtOH and $\mathrm{H}_{2} \mathrm{O}$ elimination (Scheme 2). Structures $I V$ and $V$ were confirmed on the basis of elemental and spectral analyses (Tables $1-3$ ). The IR (KBr) and ${ }^{1} \mathrm{H}$ NMR spectra of the isolated products showed that compounds $V$ are present in one tautomer only. However, compounds $I V$ exist as three possible tautomers A, B, and C. This
may explain why the ester carbonyl stretching vibration occurs in the $\tilde{\nu}=1670 \mathrm{~cm}^{-1}$ region at a quite different frequency from that of the expected frequency in the $\tilde{\nu}=1730 \mathrm{~cm}^{-1}$ region, and this may be due to the intramolecular hydrogen bonding between the oxygen atom of the ester group and NH in tautomer A. On the other hand, the ${ }^{1} \mathrm{H}$ NMR spectra showed the appearance of a signal at $\delta=8.3$ due to $6-\mathrm{NH}_{2}$ and the disappearance of the signal at $\delta=5.5$ [8] due to $\mathrm{N}-\mathrm{NH}_{2}$ in products $I V a$ and $I V b$, i.e. the $\mathrm{N}-\mathrm{NH}_{2}$ is more reactive than $6-\mathrm{NH}_{2}$ in compounds $I I I$.

On the other hand, the 7 -aryl-2-benzyl-5-oxo-4,5-dihydro- 1 H - $[1,2,4]$ triazolo[1,5-a] pyridine-6,8-dicarbonitriles VIa and VIb were easily achieved in high yields by reaction of compounds IIIa and IIIb with phenylacetic acid in the presence of polyphosphoric acid. Structure VI was confirmed on the basis of the elemental analyses and spectral data. The IR spectrum of the isolated product VIa (for example) revealed absorption bands at $\tilde{\nu}=3285 \mathrm{~cm}^{-1}$ (NH), 2220, 2225 $\mathrm{cm}^{-1}$ two (CN), $1685 \mathrm{~cm}^{-1}(\mathrm{C}=\mathrm{O})$ and at $\tilde{\nu}=1635$ $\mathrm{cm}^{-1}(\mathrm{C}=\mathrm{N})$. The ${ }^{1} \mathrm{H}$ NMR spectroscopy revealed also the NH signal at $\delta=10.9$ besides the characteristic signal at $\delta=3.5$ due to $-\mathrm{CH}_{2}-\mathrm{Ph}$.

N -Acylethoxymethylene hydrazones were found to be efficient reagents for the ring closure as well as a source of carbon fragments in organic synthesis [9]. Thus, reaction of $N^{\prime}$-ethoxymethylenebenzohydrazide VII [10] with IIIa in refluxing propan-2-ol and the elemental and spectral features showed that the expected 7 -(4-nitrophenyl)-5-oxo-4,5-dihydro- 1 H [1,2,4] triazolo[1,5-a]pyridine-6,8-dicarbonitrile (VIIIa) was isolated as a major yield. However, a product having molecular formula $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{~N}_{10} \mathrm{O}_{5}(m / z=578)$, which may be formulated as the corresponding 7-(4-


Scheme 2


Scheme 3
nitrophenyl)-5-oxo-4,5-dihydro-1 H - [1,2,4]triazolo[1,5a] pyridine-6,8-bis( $N$-dibenzoylcarbohydrazonamide) (IXa) was isolated in low yield (Scheme 3). The proposed structure $I X$ was supported by the following spectral features. The IR spectrum of the isolated product revealed the absence of the two cyano function absorption bands in the $\tilde{\nu}=2215-2225 \mathrm{~cm}^{-1}$ region which appeared in the IR spectrum of compound VIIIa. Also, the ${ }^{1} \mathrm{H}$ NMR spectrum of $I X a$ showed the presence of a signal at $\delta=6.9$ due to four protons
(deuterium oxide-exchangeable, partially overlapped by aromatic protons) of two amino groups; in addition to signals at $\delta=11.1,11.0$, and 10.7 due to three protons (deuterium oxide-exchangeable) of two - CONH and triazolo NH groups. We assume that the N $\mathrm{NH}_{2}$ group in compound III reacted with compound VII via ethanol elimination to give the corresponding intermediate $X$, which then cyclized under the reaction conditions, by elimination of benzohydrazide $X I$ to give the corresponding VIII. In the mean-

Table 1. Physical and Analytical Data of the Newly Prepared Compounds

| Compound | Formula | $M_{\mathrm{r}}$ | $\begin{gathered} w_{i}(\text { calc. }) / \% \\ w_{i}(\text { found }) / \% \end{gathered}$ |  |  |  | $\frac{\text { Yield }}{\%}$ | $\frac{\text { M.p. }}{{ }^{\circ} \mathrm{C}}$ | Solvent |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | C | H | Cl | N |  |  |  |
| IVa | $\mathrm{C}_{19} \mathrm{H}_{16} \mathrm{~N}_{6} \mathrm{O}_{5}$ | 408.37 | 55.88 | 3.95 |  | 20.58 | 76 | 287 | Ethanol |
|  |  |  | 55.67 | 3.81 |  | 20.79 |  |  |  |
| IVb | $\mathrm{C}_{19} \mathrm{H}_{16} \mathrm{ClN}_{5} \mathrm{O}_{3}$ | 397.82 | 57.36 | 4.05 | 8.91 | 17.61 | 75 | 215 | Ethanol |
|  |  |  | 57.43 | 4.12 | 9.13 | 17.87 |  |  |  |
| Va | $\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{~N}_{6} \mathrm{O}_{4}$ | 362.30 | 56.35 | 2.75 |  | 23.20 | 64 | 245 | Ethanol |
|  |  |  | 56.14 | 2.89 |  | 23.47 |  |  |  |
| Vb | $\mathrm{C}_{17} \mathrm{H}_{10} \mathrm{ClN}_{5} \mathrm{O}_{2}$ | 351.75 | 58.04 | 2.87 | 10.08 | 19.91 | 65 | 187 | Ethanol |
|  |  |  | 57.78 | 2.59 | 9.76 | 19.71 |  |  |  |
| VIa | $\mathrm{C}_{21} \mathrm{H}_{12} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 396.36 | 63.63 | 3.05 |  | 21.21 | 54 | 242 | Hexane |
|  |  |  | 63.69 | 3.31 |  | 21.21 |  |  |  |
| VIb | $\mathrm{C}_{21} \mathrm{H}_{12} \mathrm{ClN}_{5} \mathrm{O}_{2}$ | 385.80 | 65.38 | 3.14 | 9.19 | 18.15 | 52 | 198 | Hexane |
|  |  |  | 65.52 | 3.33 | 8.85 | 17.87 |  |  |  |
| VIIIa | $\mathrm{C}_{14} \mathrm{H}_{6} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 306.24 | 54.90 | 1.98 |  | 27.45 | 70 | 287 | Ethyl acetate |
|  |  |  | 54.90 | 1.73 |  | 27.59 |  |  |  |
| VIIIb | $\mathrm{C}_{14} \mathrm{H}_{6} \mathrm{ClN}_{5} \mathrm{O}_{2}$ | 295.70 | 56.87 | 2.05 | 11.99 | 23.69 | 64 | 225 | Acetic acid |
|  |  |  | 56.70 | 1.78 | 12.21 | 23.74 |  |  |  |
| IXa | $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{~N}_{10} \mathrm{O}_{5}$ | 578.54 | 58.13 | 3.83 |  | 24.21 | 15 | 239 | Hexane |
|  |  |  | 58.09 | 3.69 |  | 23.87 |  |  |  |
| IXb | $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{ClN}_{9} \mathrm{O}_{3}$ | 567.99 | 59.21 | 3.90 | 6.24 | 22.19 | 17 | 174 | Hexane |
|  |  |  | 59.00 | 3.60 | 6.45 | 22.35 |  |  |  |
| XIIa | $\mathrm{C}_{28} \mathrm{H}_{22} \mathrm{~N}_{10} \mathrm{O}_{3}$ | 542.50 | 61.99 | 3.34 |  | 25.82 | 58 | 282 | Acetic acid |
|  |  |  | 62.23 | 3.48 |  | 26.09 |  |  |  |
| XIIb | $\mathrm{C}_{28} \mathrm{H}_{18} \mathrm{ClN}_{9} \mathrm{O}$ | 531.95 | 63.22 | 3.41 | 6.66 | 23.70 | 62 | 223 | Ethanol/ |
|  |  |  | 63.11 | 3.64 | 6.81 | 23.46 |  |  | Acetic acid |
| XIIIa | $\mathrm{C}_{15} \mathrm{H}_{10} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 322.28 | 55.90 | 3.13 |  | 26.08 | 54 | 197 | Ethanol |
|  |  |  | 56.18 | 3.41 |  | 26.23 |  |  |  |
| XIIIb | $\mathrm{C}_{15} \mathrm{H}_{10} \mathrm{ClN}_{5} \mathrm{O}$ | 311.73 | 57.79 | 3.23 | 11.37 | 22.47 | 50 | 129 | Ethanol |
|  |  |  | 57.61 | 3.45 | 11.70 | 22.40 |  |  |  |
| XIVa | $\mathrm{C}_{16} \mathrm{H}_{12} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 336.31 | 57.14 | 3.60 |  | 24.99 | 75 | 182 | Toluene |
|  |  |  | 57.49 | 3.45 |  | 25.32 |  |  |  |
| XIVb | $\mathrm{C}_{16} \mathrm{H}_{12} \mathrm{ClN}_{5} \mathrm{O}$ | 325.75 | 58.99 | 3.71 | 10.88 | 21.50 | 86 | 156 | Toluene |
|  |  |  | 58.46 | 4.08 | 11.25 | 21.95 |  |  |  |
| $X V a^{*}$ | $\mathrm{C}_{20} \mathrm{H}_{9} \mathrm{FN}_{6} \mathrm{O}_{3}$ | 400.32 | 60.00 | 2.27 |  | 21.00 | 74 | 250 | Dioxan |
|  |  |  | 59.79 | 2.46 |  | 21.23 |  |  |  |
| $X V b^{* *}$ | $\mathrm{C}_{20} \mathrm{H}_{9} \mathrm{ClFN}_{5} \mathrm{O}$ | 389.77 | 61.63 | 2.33 | 9.10 | 17.97 | 78 | 282 | Ethanol |
|  |  |  | 61.82 | 2.19 | 9.23 | 17.69 |  |  |  |
| XVIIIa | $\mathrm{C}_{21} \mathrm{H}_{14} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 398.37 | 63.31 | 3.54 |  | 21.10 | 61 | 205 | Ethanol/ |
|  |  |  | 63.22 | 3.75 |  | 21.43 |  |  | Acetic acid |
| XVIIIb | $\mathrm{C}_{21} \mathrm{H}_{14} \mathrm{ClN}_{5} \mathrm{O}$ | 387.82 | 65.03 | 3.64 | 9.14 | 18.06 | 58 | 165 | Dioxan |
|  |  |  | 64.87 | 3.43 | 9.38 | 18.27 |  |  |  |
| XIXa | $\mathrm{C}_{29} \mathrm{H}_{20} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 500.50 | 69.59 | 4.03 |  | 16.79 | 12 | 126 | Toluene |
|  |  |  | 69.81 | 4.26 |  | 16.90 |  |  |  |
| XIXb | $\mathrm{C}_{29} \mathrm{H}_{20} \mathrm{ClN}_{5} \mathrm{O}$ | 489.95 | 71.09 | 4.11 | 7.24 | 14.30 | 10 | 119 | Toluene |
|  |  |  | 71.28 | 4.33 | 7.51 | 14.49 |  |  |  |
| XXIIa | $\mathrm{C}_{18} \mathrm{H}_{12} \mathrm{~N}_{6} \mathrm{O}_{3}$ | 360.33 | 60.00 | 3.36 |  | 23.33 | 75 | 251 | Dioxan |
|  |  |  | 59.79 | 3.51 |  | 23.69 |  |  |  |
| XXIIb | $\mathrm{C}_{18} \mathrm{H}_{12} \mathrm{ClN}_{5} \mathrm{O}$ | 349.77 | 61.81 | 3.46 | 10.14 | 20.02 | 72 | 289 | Dioxan |
|  |  |  | 61.72 | 3.41 | 9.20 | 20.39 |  |  |  |

*Analysis for $\mathrm{F}: w_{\mathrm{i}}($ calc. $)=4.75 ; w_{\mathrm{i}}($ found $)=4.61$.
${ }^{* *}$ Analysis for $\mathrm{F}: w_{\mathrm{i}}($ calc. $)=4.87 ; w_{\mathrm{i}}($ found $)=4.66$.
time, the two cyano groups in VIII reacted with two molecules from the eliminated hydrazide $X I$ to give the corresponding $I X$. Similar results were detected when compound IIIb reacted with compound VII under similar reaction conditions. On the other hand, by the treatment of one mole of compounds VIIIa and $V I I I b$ with two moles of the hydrazide $X I$ in refluxing ethanolic sodium methoxide solution, the correspond-
ing $I X a$ and $I X b$ were not isolated. However, the corresponding 7 -aryl-6,8-bis(5-phenyl- $4 \mathrm{H}-1,2,4$-triazol-3-yl)-4,5-dihydro-1 $H$ - $[1,2,4]$ triazolo [1,5- $a]$ pyridine- $5-$ ones XIIa and XIIb were obtained. Formation of XII from VIII and XI in ethanolic sodium methoxide solution is assumed to proceed via addition of the two $-\mathrm{NHNH}_{2}$ groups in two molecules from compound $X I$ to the two cyano functions in compound $V I I I$ to

Table 2. IR Spectral Data of the Newly Prepared Compounds

| Compound | $\tilde{\nu} / \mathrm{cm}^{-1}$ |
| :---: | :---: |
| $I V a$ | 3335 and $3293\left(\mathrm{NH}_{2}\right) ; 2220$ and $2215(\mathrm{CN})$; 1665 (CO ester); 1655 (ring CO) and $1625(\mathrm{C}=\mathrm{N})$ |
| $I V b$ | 3340 and $3330\left(\mathrm{NH}_{2}\right) ; 2225$ and 2220 (CN); 1660 ( CO ester); 1650 (ring CO) and 1620 ( $\mathrm{C}=\mathrm{N}$ ) |
| $V a$ | 3270 (NH); 2220 and 2215 (CN); 1635 (CONH) and 1630 (C=N) |
| Vb | 3260 (NH); 2225 and 2220 (CN); 1635 (CONH) and 1630 (C=N) |
| VIa | 3285 (NH); 2225 and 2220 (CN); 1685 (CO) and 1635 (C=N) |
| VIb | 3310 (NH); 2220 and 2215 (CN); 1690 (CO) and 1630 (C=N) |
| VIIIa | 3285 (NH); 2220 and 2215 (CN); 1680 (CO) and 1630 (C=N) |
| VIIIb | 3290 (NH); 2225 and 2215 (CN); 1675 (CO) and 1630 (C=N) |
| IXa | $3360-3400\left(\mathrm{NH}_{2}\right.$ and NH$)$; $3090\left(\mathrm{CH}_{\text {arom }}\right) ; 1650-1670$ (ring CO and CONH$)$ and $1630(\mathrm{C}=\mathrm{N})$ |
| $I X b$ | $3360-3395\left(\mathrm{NH}_{2}\right.$ and NH$) ; 3100\left(\mathrm{CH}_{\text {arom }}\right) ; 1645-1670$ (ring CO and CONH) and $1630(\mathrm{C}=\mathrm{N})$ |
| XIIa | $3310-3330(\mathrm{NH}) ; 3090\left(\mathrm{CH}_{\text {arom }}\right) ; 1680(\mathrm{CO})$ and $1630(\mathrm{C}=\mathrm{N})$ |
| XIIb | $3310-3330$ (NH); $3100\left(\mathrm{CH}_{\text {arom }}\right) ; 1675(\mathrm{CO})$ and $1635(\mathrm{C}=\mathrm{N})$ |
| XIIIa | $3390-3410\left(\mathrm{NH}_{2}\right) ; 2220$ and $2210(\mathrm{CN}) ; 1675(\mathrm{CO})$ and $1630(\mathrm{C}=\mathrm{N})$ |
| XIIIb | $3395-3405\left(\mathrm{NH}_{2}\right) ; 2220$ and $2215(\mathrm{CN}) ; 1670(\mathrm{CO})$ and $1640(\mathrm{C}=\mathrm{N})$ |
| XIVa | $3400-3410\left(\mathrm{NH}_{2}\right) ; 2225$ and $2220(\mathrm{CN}) ; 1680(\mathrm{CO})$ and $1635(\mathrm{C}=\mathrm{N})$ |
| XIVb | $3400-3410\left(\mathrm{NH}_{2}\right) ; 2225$ and $2215(\mathrm{CN}) ; 1685(\mathrm{CO})$ and $1640(\mathrm{C}=\mathrm{N})$ |
| $X V a$ | $3375-3390\left(\mathrm{NH}_{2}\right) ; 2225$ and $2220(\mathrm{CN}) ; 1690(\mathrm{CO})$ and $1635(\mathrm{C}=\mathrm{N})$ |
| $X V b$ | $3370-3385\left(\mathrm{NH}_{2}\right) ; 2223$ and 2220 (CN); 1690 (CO) and $1635(\mathrm{C}=\mathrm{N})$ |
| XVIIIa | $3370-3385\left(\mathrm{NH}_{2}\right) ; 2223$ and $2220(\mathrm{CN}) ; 1695(\mathrm{CO})$ and $1630(\mathrm{C}=\mathrm{N})$ |
| XVIIIb | $3380-3390\left(\mathrm{NH}_{2}\right) ; 2225$ and $2220(\mathrm{CN}) ; 1690(\mathrm{CO})$ and $1630(\mathrm{C}=\mathrm{N})$ |
| XIXa | $3270-3380$ (NH); 2220 and 2215 (CN); 1680 (CO) and 1580-1620 (C=N) |
| XIXb | $3275-3385(\mathrm{NH}) ; 2225$ and $2222(\mathrm{CN}) ; 1680$ (CO) and 1580-1620 (C=N) |
| XXIIa | 3010 (NH); $2935\left(\mathrm{CH}_{3}\right) ; 2225$ and $2225(\mathrm{CN}) ; 1680(\mathrm{CO})$ and $1630(\mathrm{C}=\mathrm{N})$ |
| XXIIb | 3010 (NH); $2950\left(\mathrm{CH}_{3}\right) ; 2220$ and $2217(\mathrm{CN}) ; 1682(\mathrm{CO})$ and $1627(\mathrm{C}=\mathrm{N})$ |

Table 3. ${ }^{1}$ H NMR Spectral Data of the Newly Prepared Compounds

| Compound | Chemical shift, $\delta$ |
| :---: | :---: |
| $I V a$ | $\begin{aligned} & 1.1\left(\mathrm{t}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right)^{\mathrm{A}} ; 1.7\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{A}} ; 4.1\left(\mathrm{q}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Me}\right)^{\mathrm{A}} ; 4.5(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})^{\mathrm{A}} ; 8.5\left(\mathrm{br}, 4 \mathrm{H}, \mathrm{NH}_{2}\right)^{\mathrm{A}, \mathrm{~B}} ; 9.7 \\ & (\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})^{\mathrm{A}} \text { and } 1.2\left(\mathrm{t}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right)^{\mathrm{B}} ; 1.8\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{B}} ; 3.7\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)^{\mathrm{B}} ; 4.4\left(\mathrm{q}, 2 \mathrm{H}, \text { ester } \mathrm{CH}_{2}\right)^{\mathrm{B}} ; 1.0 \\ & \left(\mathrm{t}, 3 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)^{\mathrm{C}} ; 1.9\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{C}} ; 4.3\left(\mathrm{q}, 2 \mathrm{H}, \text { ester } \mathrm{CH}_{2}\right)^{\mathrm{C}} ; 4.7(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})^{\mathrm{C}} ; 8.7\left(\mathrm{br} \mathrm{~s}, 2 \mathrm{H}, \mathrm{NH}_{2}\right)^{\mathrm{C}} ; 12.5 \\ & (\mathrm{~s}, 1 \mathrm{H}, \mathrm{OH})^{\mathrm{C}} \text { and } 7.4-7.8\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)^{\mathrm{A}, \mathrm{~B}, \text { and C }} \end{aligned}$ |
| $I V b$ | $\begin{aligned} & 1.0\left(\mathrm{t}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right)^{\mathrm{A}} ; 1.7\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{A}} ; 4.1\left(\mathrm{q}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Me}\right)^{\mathrm{A}} ; 4.2(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})^{\mathrm{A}} ; 8.3\left(\mathrm{br} \mathrm{~s}, 2 \mathrm{H}, \mathrm{NH}_{2}\right)^{\mathrm{A}} ; 9.8 \\ & (\mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})^{\mathrm{A}} ; 1.1\left(\mathrm{t}, 3 \mathrm{H}, \mathrm{CH}_{3} \mathrm{CH}_{2}\right)^{\mathrm{B}} ; 1.8\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{B}} ; 3.8\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)^{\mathrm{B}} ; 4.4\left(\mathrm{q}, 2 \mathrm{H}, \text { ester } \mathrm{CH}_{2}\right)^{\mathrm{B}} ; 8.6(\mathrm{br}, \\ & \left.2 \mathrm{H}, \mathrm{NH}_{2}\right)^{\mathrm{B}} ; 1.2\left(\mathrm{t}, 3 \mathrm{H}, \mathrm{CH}_{2} \mathrm{CH}_{3}\right)^{\mathrm{C}} ; 1.9\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{C}} ; 4.3\left(\mathrm{q}, 2 \mathrm{H}, \text { ester } \mathrm{CH}_{2}\right)^{\mathrm{C}} ; 4.8(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})^{\mathrm{C}} ; 8.7(\mathrm{br}, 2 \mathrm{H}, \\ & \left.\mathrm{NH}_{2}\right)^{\mathrm{C}} ; 10.3(\mathrm{~s}, 1 \mathrm{H}, \mathrm{OH})^{\mathrm{C}} \text { and } 7.1-7.5\left(\mathrm{~m}, 12 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)^{\mathrm{A}, \mathrm{~B}, \text { and C }} \end{aligned}$ |
| $V a$ | $2.4\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 3.6\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) ; 7.1-8.2\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and 11.7 (br s, $\left.1 \mathrm{H}, \mathrm{NH}\right)$ |
| Vb | $2.4\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 3.7\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right) ; 7.1-7.5\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and $11.8(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, \mathrm{NH})$ |
| VIa | $3.5\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}\right) ; 7.1-8.2\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and 10.9 (br s, $\left.1 \mathrm{H}, \mathrm{NH}\right)$ |
| VIb | 3.5 ( $\left.\mathrm{s}, 2 \mathrm{H}, \mathrm{CH}_{2} \mathrm{Ph}\right) ; 7.0-7.4\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and 11.0 (br s, $\left.1 \mathrm{H}, \mathrm{NH}\right)$ |
| VIIIa | $7.5-8.2\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{H}_{\text {arom }}\right.$ and triazolo H) and 10.9 (br s, $1 \mathrm{H}, \mathrm{NH}$ ) |
| VIIIb | $7.1-7.4\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{H}_{\text {arom }}\right.$ and triazolo H$)$ and 10.9 (br s, $\left.1 \mathrm{H}, \mathrm{NH}\right)$ |
| IXa | $6.9-8.2\left(\mathrm{~m}, 19 \mathrm{H}, 2 \mathrm{NH}_{2}, \mathrm{H}_{\text {arom }}\right.$ and triazolo H$) ; 10.7(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, \mathrm{NH})$ and $11.0-11.1(\mathrm{br} \mathrm{m}, 2 \mathrm{H}, 2 \mathrm{NH})$ |
| $I X b$ | $6.9-7.8\left(\mathrm{~m}, 19 \mathrm{H}, 2 \mathrm{NH}_{2}, \mathrm{H}_{\text {arom }}\right.$ and triazolo H$) ; 10.8(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, \mathrm{NH})$ and $11.0-11.1(\mathrm{br} \mathrm{m}, 2 \mathrm{H}, 2 \mathrm{NH})$ |
| XIIa | $7.1-8.2$ ( $\mathrm{br} \mathrm{m}, 15 \mathrm{H}, \mathrm{H}_{\text {arom }}$ and triazolo H ) and 10.9-11.2 (br m, $3 \mathrm{H}, 3 \mathrm{NH}$ ) |
| XIIb | $7.1-7.5$ (br m, 15H, $\mathrm{H}_{\text {arom }}$ and triazolo H$)$ and $11.0-11.3$ (br m, $3 \mathrm{H}, 3 \mathrm{NH}$ ) |
| XIIIa | $2.1\left(\mathrm{~d}, J=7 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 7.1-8.1\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right) ; 8.2(\mathrm{q}, J=7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH})$ and $8.4\left(\mathrm{br} \mathrm{s}, 2 \mathrm{H}, \mathrm{NH}_{2}\right)$ |
| XIIIb | $2.2\left(\mathrm{~d}, J=7 \mathrm{~Hz}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 7.1-8.2\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right) 8.1(\mathrm{q}, J=7 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{CH})$ and 8.3 (br s, $2 \mathrm{H}, \mathrm{NH}_{2}$ ) |
| XIVa | $2.1\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 2.3\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 7.1-8.2\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and 8.4 (br s, $2 \mathrm{H}, \mathrm{NH}_{2}$ ) |
| XIVb | $2.0\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 2.1\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 7.1-7.5\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and 8.3 (br s, $\left.2 \mathrm{H}, \mathrm{NH}_{2}\right)$ |
| $X V a$ | $7.0-7.4\left(\mathrm{~m}, 8 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ and 10.7 (s, 1H, NH) |
| $X V b$ | $7.2-7.6$ (m, 8H, Harom) and 10.8 (s, 1H, NH) |
| XVIIIa | $2.1\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 5.6\left(\mathrm{br} \mathrm{s}, 2 \mathrm{H}, \mathrm{NH}_{2}\right)$ and $7.1-8.2\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ |
| XVIIIb | $2.1\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 5.6\left(\mathrm{br} \mathrm{s}, 2 \mathrm{H}, \mathrm{NH}_{2}\right)$ and $7.0-8.2\left(\mathrm{~m}, 9 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ |
| XIXa | $1.7\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 2.9-3.1\left(2 \mathrm{H}, \mathrm{AB} J=12 \mathrm{~Hz}, \mathrm{CH}_{2}\right) ; 3.6(\mathrm{~s}, 2 \mathrm{H}, \mathrm{NH})$ and $7.1-8.2\left(\mathrm{~m}, 14 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ |
| XIXb | $1.6\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right) ; 2.8-3.0\left(2 \mathrm{H}, \mathrm{AB} J=12 \mathrm{~Hz}, \mathrm{CH}_{2}\right) ; 3.4(\mathrm{~s}, 2 \mathrm{H}, \mathrm{NH})$ and $7.0-7.6\left(\mathrm{~m}, 14 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)$ |
| XXIIa | $\begin{aligned} & 2.3\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{A}} ; 2.4\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{A}} ; 3.5\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)^{\mathrm{A}} ; \text { and } 7.5-8.2\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)^{\mathrm{A} \text { and } \mathrm{B}} ; 1.7(\mathrm{~s}, 6 \mathrm{H}, \\ & \left.2 \mathrm{CH}_{3}\right)^{\mathrm{B}} ; 4.2(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})^{\mathrm{B}} \text { and } 9.9(\mathrm{br} \mathrm{~s}, 1 \mathrm{H}, \mathrm{NH})^{\mathrm{B}} \end{aligned}$ |
| XXIIb | $2.3\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{A}} ; 2.4\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{CH}_{3}\right)^{\mathrm{A}} ; 3.5\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{CH}_{2}\right)^{\mathrm{A}}$ and $7.1-7.5\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{H}_{\text {arom }}\right)^{\mathrm{A} \text { and } \mathrm{B}} ; 1.7\left(\mathrm{~s}, 6 \mathrm{H}, 2 \mathrm{CH}_{3}\right)^{\mathrm{B}}$; $4.1(\mathrm{~s}, 1 \mathrm{H}, \mathrm{CH})^{\mathrm{B}}$ and $9.9(\mathrm{br} \mathrm{s}, 1 \mathrm{H}, \mathrm{NH})^{\mathrm{B}}$ |



XIV


$\boldsymbol{X} \mathbf{I I}$

$X I I I-X V I$ a $\mathrm{Ar}=\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{NO}_{2}-(p)$
$b \mathrm{Ar}=\mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Cl}-(p)$
Scheme 4
give the undetected intermediate $I X$, which immediately cyclizes under the reaction conditions to give the final product XII. Structure XII was supported by the IR spectra which revealed in each case the absence of the characteristic bands due to the $\mathrm{NH}_{2}$ and CN at $\tilde{\nu}$ $=3360-3400 \mathrm{~cm}^{-1}$ and $\tilde{\nu}=2220-2225 \mathrm{~cm}^{-1}$. Also, the ${ }^{1} \mathrm{H}$ NMR revealed the appearance of the characteristic signals at $\delta=11.0-11.3$ due to deuterium oxide-exchangeable three triazolo NH's.

Compounds $I I I a$ and $I I I b$ were stirred with acetaldehyde and acetone in methanol at room temperature in the presence of catalytic amount of sulfuric acid. The $1: 1$ condensation adducts followed by water elimination were isolated. The corresponding 6 -amino- 4 -aryl-1-ethylidenamino- 2 -oxo- 1,2 -dihydropyridine-3,5-dicarbonitrile derivatives having structures XIII and the corresponding 6-amino-4-aryl-1-isopropylidenamino-2-oxo-1,2-dihydropyridine-3,5dicarbonitrile derivatives having structures XIV (Scheme 4) seem possible for the isolated products based on their elemental and spectral analyses. The IR spectra of either compounds XIII or XIV revealed the presence of the strong absorption band at $\tilde{\nu}=$ $3390-3410 \mathrm{~cm}^{-1}$ due to the pyridine 6 -amino group. Also, ${ }^{1} \mathrm{H}$ NMR spectroscopy revealed the disappearance of the $1-\mathrm{NH}_{2}$ group signal at $\delta=5.6$. However, the $6-\mathrm{NH}_{2}$ group signal at $\delta=8.3-8.4$ appeared in addition to the appearance of either one methyl group signal at $\delta=2.1-2.2$ in the case of compounds XIIIa and XIIIb or two methyl group signals at $\delta=2.0$ 2.3 in the case of compounds $X I V a$ and $X I V b$, also the appearance of the 1-alkylidenamino proton at $\delta=$ 8.1-8.2 in the case of XIIIa and XIIIb was observed.

At the same time, 4-fluorobenzaldehyde was reacted with compounds $I I I a$ and $I I I b$ in refluxing ethanol in the presence of catalytic amount of sulfuric acid. The corresponding 7 -aryl-2-(4-fluorophenyl)-5-oxo-1,5-dihydro- 1 H - $[1,2,4]$ triazolo $[1,5$ - $a$ ]pyridine- 6,8 dicarbonitrile derivatives having structures $X V a$ and $X V b$ were considered for the isolated products on the basis of their elemental and spectral analyses. Char-
acteristic IR absorption for $X V a$ (as an example) can be observed in the regions $\tilde{\nu}=3340 \mathrm{~cm}^{-1}, 2220$ $2222 \mathrm{~cm}^{-1}$, and $1680 \mathrm{~cm}^{-1}$ indicating the presence of stretching vibrations due to NH , two CN and amidic $\mathrm{C}=\mathrm{O}$ groups, respectively. ${ }^{1} \mathrm{H}$ NMR spectrum of $X V a$ revealed also the presence of a single signal at $\delta=$ 10.8 due to 1 H (deuterium oxide-exchangeable NH ) besides 8 H (aromatic protons) at $\delta=7.2-7.6$. Also, the appearance of the molecular ion peak $\left(m / z=M_{\mathrm{r}}\right)$ as the base peak for each one in the mass spectrometry indicates that the isolated product is $X V a$ and not its dihydro derivative $X V I$.

On the other hand, an attempt to prepare the 2 -methyl-7-(4-nitrophenyl)-5-oxo-2-phenyl-2,3,4,5-tetra-hydro- 1 H - $[1,2,4]$ triazolo $[1,5-a]$ pyridine- 6,8 -dicarbonitrile ( $X V I I a$ ) by reaction of compound IIIa with acetophenone in methanol in the presence of catalytic amount of sulfuric acid was unsuccessful. However, the elemental and spectral measurements revealed that the 6 -amino-4-(4-nitrophenyl)-2-oxo-1-[(1-phenylethyliden)amino]-1,2-dihydropyridine-3,5-dicarbonitrile (XVIIIa) was isolated as the major yield product of the reaction. In addition to compound XVIIIa, the corresponding 4-methyl-2,4-diphenyl-9-(4-nitrophenyl)-7-oxo-3,4,6,7-tetrahydro- 5 H -pyrido-[1,2-b][1,2,4] triazepine-8,10-dicarbonitrile (XIXa) was isolated as reaction by-product (Scheme 5).

Structure $X I X$ was confirmed on the basis of the elemental analyses and spectral data of the isolated product which revealed the characteristic IR absorption in the regions $\tilde{\nu}=3270-3380$ and 1580-1620 $\mathrm{cm}^{-1}$, due to $\mathrm{N}-\mathrm{H}$ stretching vibrations and coupled stretching vibrations of the $\mathrm{C}=\mathrm{N}$ and $\mathrm{C}=\mathrm{C}$ bonds in bicyclic ring skeleton. Also, the ${ }^{1} \mathrm{H}$ NMR data show methylene group signals at $\delta=2.9 / 3.1$ due to AB spin patterns with $J=12 \mathrm{~Hz}$, one methyl group signal at $\delta=1.7$ in addition to 14 H (aromatic protons) at $\delta=7.1-8.2$ and $\mathrm{N}-\mathrm{H}$ signals at $\delta=3.6$. Higher yield of product $X I X a$ was obtained by reaction of 1 mol of $I I I a$ with 2 mol of acetophenone in similar reaction conditions. Formation of compound XIX


Scheme 5


Scheme 6
may be rationalized in terms of the initial condensation reaction between the 1 -amino function in compound III and acetophenone carbonyl group to give the corresponding intermediate $X X$, which then condenses with another molecule from acetophenone via $\mathrm{H}_{2} \mathrm{O}$ elimination under the reaction conditions to give $X X I$. Then, the formed intermediate $X X I$ eliminates $\mathrm{H}_{2} \mathrm{O}$ to give $X I X$. Similar results were obtained when acetophenone reacted with $I I I b$ under similar reaction conditions to give the corresponding XVIIIb as well as the corresponding $X I X b$.

On treatment of compound $I I I a$ with pentane-2,4dione in ethanol in the presence of catalytic amount of perchloric acid, a product of molecular formula compatible with $\mathrm{C}_{18} \mathrm{H}_{12} \mathrm{~N}_{6} \mathrm{O}_{3}(m / z=360)$ was isolated. In contrast to the starting diaminopyridone IIIa, the IR spectrum of the isolated product revealed the absence of any $-\mathrm{NH}_{2}$ group absorption vibrations in the $\tilde{\nu}$ $=3320-3450 \mathrm{~cm}^{-1}$ region. However, it displayed instead an - $\mathrm{C}=\mathrm{N}$ - absorption at $\tilde{\nu}=1630 \mathrm{~cm}^{-1}$. Furthermore, the ${ }^{1} \mathrm{H}$ NMR spectrum revealed the presence of two methyl group signals at $\delta=2.3$ and $\delta=$ 2.4 , in addition to methylene group signal at $\delta=3.5$.

Also, the ${ }^{1} \mathrm{H}$ NMR showed the presence of six protons (two methyls) and one-proton - $\mathrm{CH}-$ signals at $\delta=$ 1.7 and $\delta=4.2$, respectively; as well as the presence of - NH - signals at $\delta=9.9$. Thus, the corresponding 2,4-dimethyl-9-(4-nitrophenyl)-7-oxo-6,7-dihydro$3 H$-pyrido $[1,2-b][1,2,4]$ triazepine- 8,10 -dicarbonitrile having the structure XXIIa which may be in two tautomers $(\mathrm{A}$ and B$)$ is the suitable structure for the isolated product (Scheme 6). Also, compound IIIb reacted with pentane-2,4-dione under the same experimental conditions to give the corresponding XXIIb.

## EXPERIMENTAL

Compounds IIIa and IIIb [8] as well as VII [10] were prepared by known procedures. All melting points were uncorrected. The microanalytical unit at the Cairo University measured microanalytical data (Table 1). IR (KBr) spectra were recorded on Shimadzu 408 spectrophotometer (Table 2). Mass spectra were taken on GCMS-QP1000 Ex mass spectrometer with ionization potential of $70 \mathrm{eV} .{ }^{1} \mathrm{H}$ NMR spectra were measured on a 90 MHz Varian EM- 390 spectrom-
eter with hexadeuterodimethyl sulfoxide as solvent, using $\mathrm{Me}_{4} \mathrm{Si}$ as an internal standard (Table 3).

## Ethyl 3-[(6-Amino-4-aryl-3,5-dicyano-2-oxo-1,2-dihydropyridin-1-yl)imino]butyrates IVa and IVb

A catalytic amount of perchloric acid (1 drop) was added to a suspension of each IIIa or IIIb $(0.01 \mathrm{~mol})$ and ethyl acetoacetate ( 0.01 mol ) in ethanol. The reaction mixture was allowed to stand at room temperature, after 5 d the reaction was complete as evidenced by TLC. Partial removal of the solvent on rotary evaporator gave white crystals, which were filtered off and washed with diethyl ether and recrystallized from the proper solvent.

## 9-Aryl-4-methyl-2,7-dioxo-2,3,6,7-tetrahydro$1 H$-pyrido $[1,2-b][1,2,4]$ triazepine-8,10dicarbonitriles $V a$ and $V b$

To a solution of each IIIa or IIIb ( 0.01 mol ) in $20 \mathrm{~cm}^{3}$ of dry methanol containing sodium methoxide ( 0.015 mol ), ethyl acetoacetate ( 0.01 mol ) was added. The reaction mixture was refluxed under nitrogen gas for 1 h , concentrated, allowed to stand at room temperature. The solid product that formed was collected by filtration and crystallized from the proper solvent to give greenish yellow crystals.

## 7-Aryl-2-benzyl-5-oxo-4,5-dihydro-1 H-[1,2,4]-triazolo[1,5-a] pyridine-6,8-dicarbonitriles VIa and VIb

A mixture of equimolar amounts of each $I I I a$ or $I I I b$, phenylacetic acid ( 0.05 mol ), and polyphosphoric acid ( $20 \mathrm{~g}, 85 \%$ ) was heated with stirring at $180^{\circ} \mathrm{C}$ for 4 h and then poured into excess dilute ammonium hydroxide. The solid which formed was collected, washed well with water, and recrystallized from the proper solvent.

## Reaction of IIIa and IIIb with $N^{\prime}$ Ethoxymethylenebenzohydrazide (VII)

Equimolar amounts of each IIIa or IIIb ( 0.01 mol ) and VII ( $1.92 \mathrm{~g} ; 0.01 \mathrm{~mol}$ ) in isopropyl alcohol (50 $\mathrm{cm}^{3}$ ) were heated under reflux for 10 h . The reaction mixture was concentrated. After few hours of standing at room temperature, the formed crystalline precipitate was filtered off and recrystallized from the proper solvent to give the corresponding 7 -aryl-5-oxo- $4,5-$ dihydro- $1 H$ - $[1,2,4]$ triazolo $[1,5-a]$ pyridine- 6,8 -bis $\left(N^{\prime}\right.$ dibenzoylcarbohydrazonamide) $I X a$ and $I X b$. The filtrated reaction mixture was evaporated to dryness and water ( $20 \mathrm{~cm}^{3}$ ) was added, the corresponding 7 -aryl-5-oxo- 4,5 -dihydro- 1 H - $[1,2,4]$ triazolo $[1,5-a]$ pyridine- 6,8 dicarbonitriles VIIIa and VIIIb were separated, col-
lected by filtration and crystallized from the proper solvent. The remaining aqueous filtrate was evaporated to dryness, treated with absolute ethanol (5 $\mathrm{cm}^{3}$ ) and kept at $-15^{\circ} \mathrm{C}$ for 2 h . The insoluble hydrazide $X I$ separated and it was collected by filtration.

## 7-Aryl-6,8-bis(5-phenyl-4H-1,2,4-triazol-3-yl)-4,5-dihydro-1 $H$ - $[1,2,4]$ triazolo $[1,5-a]$ pyridine-5ones XIII and XIIb

To a solution of each VIIIa or VIIIb ( 0.01 mol ) in dry ethanol $\left(50 \mathrm{~cm}^{3}\right)$ containing sodium methoxide $(0.03 \mathrm{~mol})$, benzohydrazide $X I(0.02 \mathrm{~mol})$ was added. The reaction mixture was refluxed for 1 h , concentrated, allowed to stand at room temperature to cool and then poured into ice-cooled dilute HCl . The solid product that formed was collected by filtration and crystallized from the proper solvent to give yellow crystals.

## 6-Amino-4-aryl-1-ethylidenamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitriles XIIIa and XIIIb

Solution of IIIa or IIIb ( 0.01 mol ) and acetaldehyde ( 0.01 mol ) in methanol ( $50 \mathrm{~cm}^{3}$ ) and concentrated sulfuric acid ( $0.5 \mathrm{~cm}^{3}$ ) was stirred at room temperature for 10 h . The yellow precipitate that formed was filtered off, washed well with ethanol and recrystallized from the proper solvent.

## 6-Amino-4-aryl-1-isopropylidenamino-2-oxo-1,2-dihydropyridine-3,5-dicarbonitriles XIVa and $X I V b$

To a solution of $I I I a$ or $I I I b(0.01 \mathrm{~mol})$ and acetone ( 0.01 mol ) in methanol $\left(50 \mathrm{~cm}^{3}\right)$ concentrated sulfuric acid $\left(0.5 \mathrm{~cm}^{3}\right)$ was added. The reaction mixture was stirred at room temperature for 10 h . The solvent was then evaporated and the solid that formed was collected by filtration and recrystallization from the proper solvent.

## 7-Aryl-2-(4-fluorophenyl)-5-oxo-1,5-dihydro$1 H$ - $[1,2,4]$ triazolo $[1,5-a]$ pyridine-6,8dicarbonitriles $X V a$ and $X V b$

To a solution of $I I I a$ or $I I I b(0.01 \mathrm{~mol})$ and 4fluorobenzaldehyde ( $1.24 \mathrm{~g}, 0.01 \mathrm{~cm}^{3}$ ) in methanol ( 50 $\mathrm{cm}^{3}$ ) concentrated sulfuric acid ( $0.25 \mathrm{~cm}^{3}$ ) was added. The reaction mixture was refluxed for 10 h . The yellow precipitate formed by cooling was filtered off and recrystallized from the proper solvent.

## Reaction of IIIa and IIIb with Acetophenone

To a solution of IIIa or IIIb ( 0.01 mol ) and acetophenone ( $0.01-0.02 \mathrm{~mol}$ ) in methanol (30-50
$\mathrm{cm}^{3}$ ) concentrated sulfuric acid $\left(0.25-0.50 \mathrm{~cm}^{3}\right)$ was added. The reaction mixture was refluxed for 10 h . The yellow precipitate which formed by cooling was filtered off and recrystallized from the proper solvent to give the corresponding 9 -aryl-4-methyl-2,4-diphenyl-7-oxo-3,4,6,7-tetrahydro- 5 H -pyrido $[1,2-b][1,2,4]$ triaze-pine-8,10-dicarbonitrile derivatives $X I X a$ or $X I X b$. Concentration of the filtrated reaction mixture to dryness and recrystallization of the resulting solid from the proper solvent gave the corresponding 6 -amino-4-aryl-2-oxo-1-[(1-phenylethyliden)amino]-1,2-dihydro-pyridine-3,5-dicarbonitrile XVIIIa or XVIIIb.

9-Aryl-2,4-dimethyl-7-oxo-6,7-dihydro-3Hpyrido $[1,2-b][1,2,4]$ triazepine-8,10-dicarbonitriles $X X I I a$ and $X X I I b$

Catalytic amounts of perchloric acid (1 drop) were added to suspensions of $I I I a$ or $I I I b(0.01 \mathrm{~mol})$ and pentane-2,3-dione ( $1 \mathrm{~g} ; 0.01 \mathrm{~mol}$ ) in methanol ( 50 $\mathrm{cm}^{3}$ ). The reaction mixtures were stirred at room temperature for 10 h . When TLC showed that all starting materials had been consumed, the yellow crystals that formed were filtered off and washed with light petroleum ether $\left(40-60^{\circ} \mathrm{C}\right)$.

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