A Novel Synthesis of 5-Hydrazono-4a,7-dihydrodipyrazolo[3,4-*b*;4,3-*e*]pyridin-3(2*H*)-ones and their Cyclization to Fused Triazines

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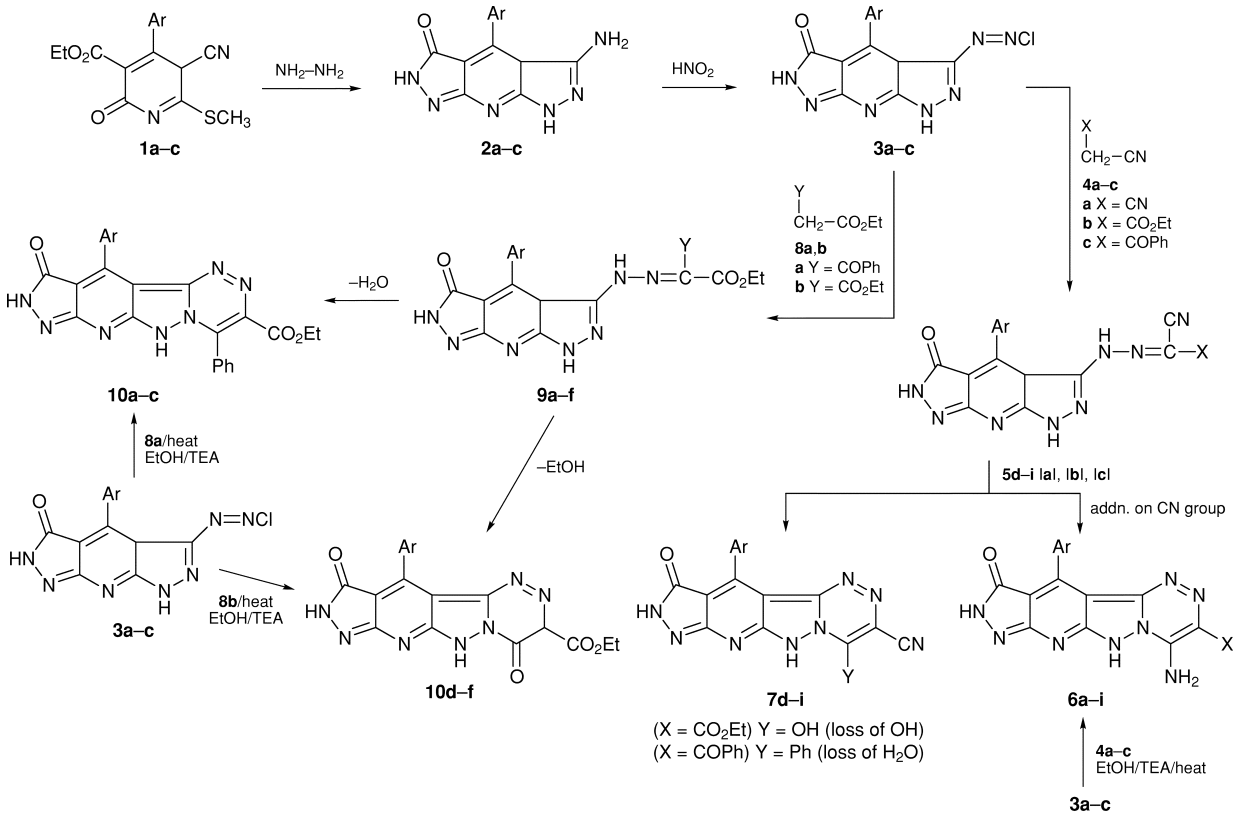
Several 5-hydrazono-4a,7-dihydrodipyrazolo[3,4-*b*;4,3-*e*]pyridin-3(2*H*)-ones and triazines derived thereform were synthesized *via* the reaction of diazotized dipyrazolopyridines with active-methylene-containing reagents.

In conjunction with our previous work[1–5] and the reported biological activities of pyrazolopyridines[8] as well as pyrazolotriazines[9] we were interested to synthesize new compounds for our medicinal chemistry programme and to investigate novel chemical transformations.

It has been found that 5-diazotized-4a,7-dihydrodipyrazolo[3,4-*b*;4,3-*e*]pyridin-3-(2*H*)ones (**3a–c**) couple with malononitrile (**4a**) to give the 4-amino-6,9-dihydro-10*H*-pyrazolo[4″,3″:5′,6′]pyrido[2′,3′:3,4]pyrazolo[5,1-*c*][1,2,4]-triazin-10-one derivatives **6a–c**, respectively. In contrast to the behaviour of **4a** towards coupling with **3a–c**, it was found that both ethyl cyanoacetate (**4b**) and ω-cyanoacetophenone (**4c**) coupled with each of **3a–c** to give the corresponding 5-hydrazono derivatives **5d–i**, respectively, which cyclized to give the 4-amino-6,9-dihydro-10*H*-pyrazolo-[4″,3″:5′,6′]pyrido[2′,3′:3,4]pyrazolo[5,1-*c*][1,2,4]triazin-10-one derivatives **6d–i** respectively (Scheme 1).

The synthetic potential of **3a–c** was further investigated through their reaction with other active-containing reagents. Thus **3a** coupled with each of ethyl benzoylacetate (**8a**) and diethyl malonate (**8b**) to give the corresponding 5-hydrazono derivatives **9a–f** respectively. Compounds **9a–f** were cyclized

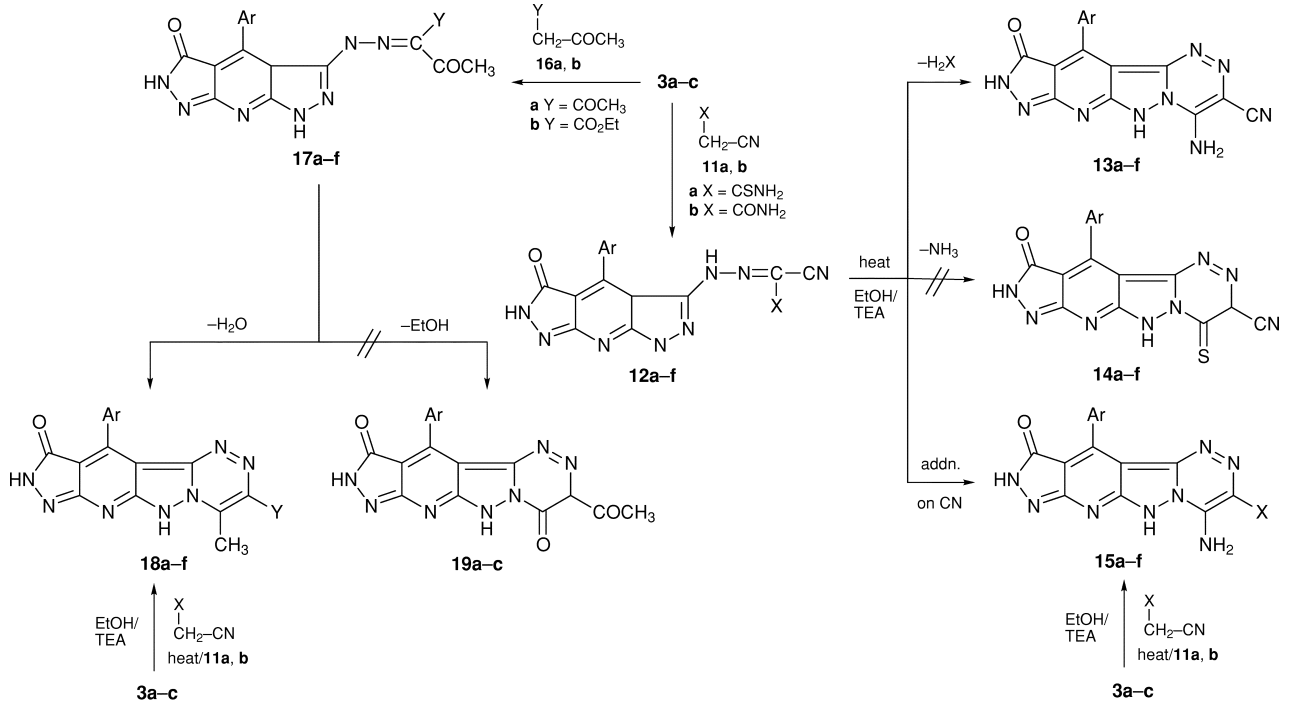


5,6	X	Ar
a	CN	Ph
b	CN	C_6H_4-*p*-Cl
c	CN	C_4H_3-O-α
d	CO_2Et	Ph
e	CO_2Et	C_6H_4-*p*-Cl
f	CO_2Et	C_4H_3-O-α
g	COPh	Ph
h	COPh	C_6H_4-*p*-Cl
i	COPh	C_4H_3-O-α

9	Y	Ar
a	COPh	Ph
b	COPh	C_6H_4-*p*-Cl
c	COPh	C_4H_3-O-α
d	CO_2Et	Ph
e	CO_2Et	C_6H_4-*p*-Cl
f	CO_2Et	C_4H_3-O-α

Scheme 1

*To receive any correspondence.



12,15	X	Ar
a	$CSNH_2$	Ph
b	$CSNH_2$	C_6H_4-*p*-Cl
c	$CSNH_2$	C_4H_3-*p*-O-α
d	$CONH_2$	Ph
e	$CONH_2$	C_6H_4-*p*-Cl
f	$CONH_2$	C_4H_3-*p*-O-α

17,18	Y	Ar
a	$COCH_3$	Ph
b	$COCH_3$	C_6H_4-*p*-Cl
c	$COCH_3$	C_4H_3-O-α
d	CO_2Et	Ph
e	CO_2Et	C_6H_4-*p*-Cl
f	CO_2Et	C_4H_3-O-α

Scheme 2

in boiling ethanol that contained triethylamine to afford **10a**–**f**, respectively. The synthetic potential of **3a**–**c** was also further investigated through their reactions with cyanothioacetamide (**11a**) and cyanoacetamide (**11b**) to afford the corresponding 5-hydrazono derivatives **12a**–**f**, respectively. Compounds **12a**–**f** readily underwent addition to the CN group to give the pyrazolo[4″,3″:5′,6′]pyrido[2′,3′:3,4]-pyrazolo[5,1-*c*][1,2,4]triazin-10-ones **15a**–**f**, respectively (Scheme 2). The synthons **3a**–**c** also reacted with each of acetylacetone (**16a**) and ethyl acetoacetate (**16b**) to afford the corresponding 5-hydrazono derivatives **17a**–**f**, respectively. Compounds **17a**–**f** were cyclized to afford **18a**–**f**, respectively, *via* loss of water.

Techniques used: ^{1}H NMR, FT-IR, UV and mass spectrometry

Schemes: 2

References: 13

Table 1: Physical and analytical data of the compounds prepared

Table 2: IR and ^{1}H NMR spectral data of the newly synthesized compounds

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