11

A Facile Synthesis of Some Pyrazolo Analogues of Tricyclic Purine Derivatives *via* Hydrazonoyl Halides

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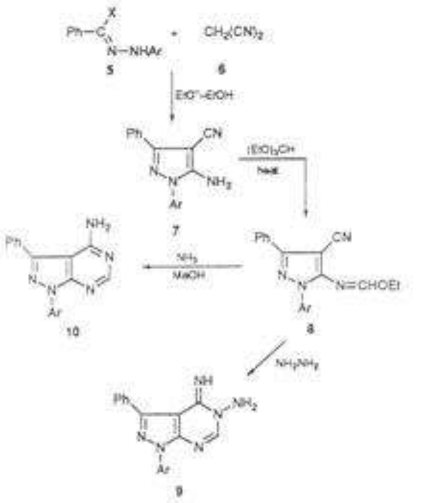
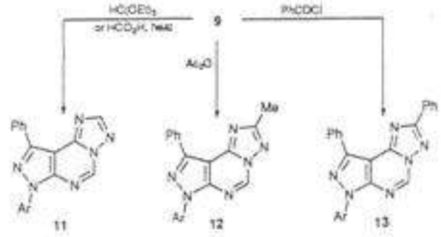
We describe a facile synthesis of the title compounds using hydrazonoyl halides as starting materials. Treatment of the 5-amino-4-cyanopyrazoles **7a**,**b**, prepared from the hydrazonoyl halides **5a**,**b** and malononitrile as previously described,[illegible] with triethyl orthoformate in acetic anhydride at reflux afforded the corresponding ethoxymethyleneamino derivatives **8a**,**b** in >90% yield (Scheme 1). Hydrazinolysis of the latter in ethanol at room temperature yielded the 5-amino-4-iminopyrazolo[3,4-*d*]pyrimidines **9**. Ammonolysis of **8a** in methanol yielded 4-amino-1,3-diphenyl-1*H*-pyrazolo[3,4-*d*]pyrimidine **10a**, in 70% yield, identical in all respects (mp, mixed mp and spectra) with an authentic sample[7] obtained by refluxing **7a** with formamide (Scheme 1). The structures of products **8** and **9** were determined on the basis of elemental analyses, spectral data (mass and ^{1}H NMR) and the chemical transformations outlined below.



a X = Cl, Ar = Ph
b X = Br, Ar = 4-NO$_2$C$_6$H$_4$

Scheme 1

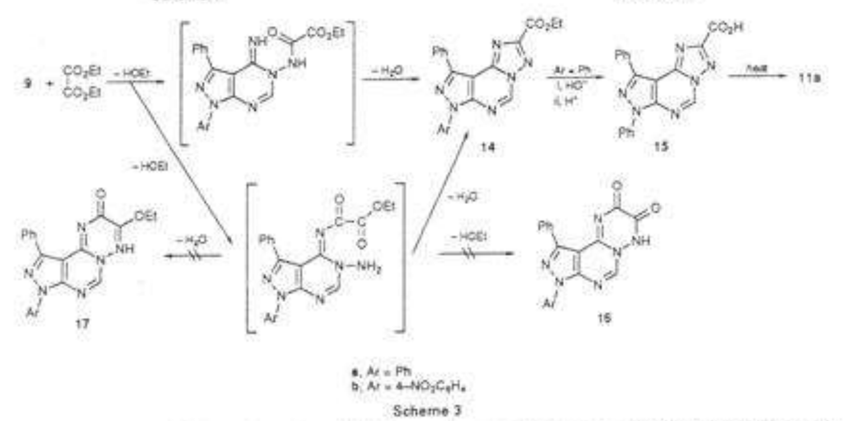
When **9** was refluxed with triethyl orthoformate or formic acid it afforded the corresponding 7,9-diaryl-7*H*-pyrazolo[4,3-*e*][1,2,4]triazolo[1,5-*c*]pyrimidine **11** (Scheme 2), while with acetic anhydride and benzoyl chloride the respective 2-methyl (**12**) and 2-phenyl (**13**) derivatives were obtained.



a Ar = Ph
b Ar = 4-NO$_2$C$_6$H$_4$

Scheme 2

Reaction of **9** with diethyl oxalate at reflux yielded **14**, which upon saponification was converted into the acid **15**. Decarboxylation of the latter afforded **11** (Scheme 3).

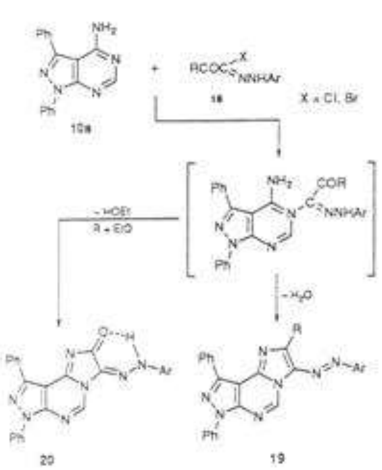


a, Ar = Ph
b, Ar = 4-NO$_2$C$_6$H$_4$

Scheme 3

Reactions of **10a** with the hydrazonoyl halides **18a–c** in benzene in the presence of triethylamine furnished the corresponding derivatives **19a**, **19b** and **20** respectively (Scheme 4).

In summary the present investigation offers rapid and



a R = Me, Ar = 4-MeC$_6$H$_4$
b R = 2-thienyl, Ar = Ph
c R = EtO, Ar = Ph

Scheme 4

Techniques used: IR, ^{1}H NMR, mass spectrometry

References: 16

Schemes: 4

Table 1: Mps, % yields and elemental analytical data for the reaction products **7**–**20**

Table 2: IR and ^{1}H NMR data for the reaction products **7**–**20**

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