Synthesis of 2-Hetaryl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazoles

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A novel efficient synthesis of 2-hetaryl-4-methyl-6-phenyl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazoles was achieved by the reaction of 5-amino-3-methyl-4-nitroso-1-phenyl-1*H*-pyrazole with heterocyclic amines followed by air oxidation in the presence of cupric acetate.

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Compounds with fused 1,2,3-triazole ring attract special attention on account of their strong fluorescence [1]. Some fused and pendant 1,2,3-triazolyl compounds have been reported by us previously [2,3]. The synthesis of model compounds of fused hetaryltriazoles requires a primary amino group capable of coupling with an aryldiazonium salt in the adjacent vacant position to result in an *ortho*-aminoarylazo derivative. The *ortho*-aminoarylazo heterocycle on subsequent air oxidation in the presence of a cupric salt [4] yields 2-arylhetaryl-1,2,3-triazoles.

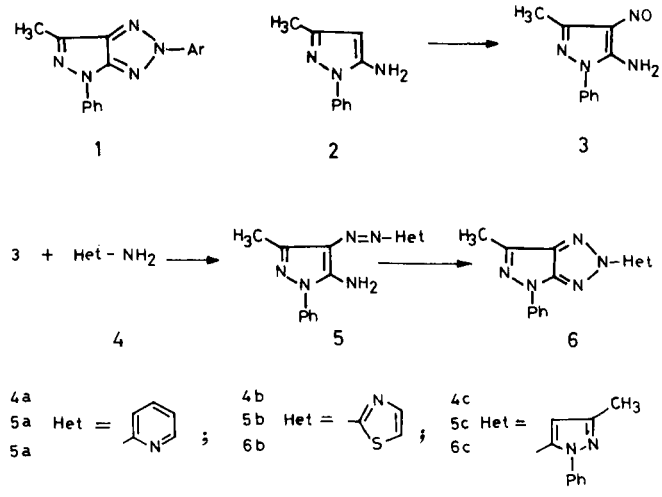
5-Amino-4-methyl-1-phenyl-1*H*-pyrazole (**2**) can successfully be coupled with aryldiazonium salts to yield 5-amino-4-arylazo-3-methyl-1-phenyl-1*H*-pyrazoles which on air oxidation in the presence of cupric acetate give 2-aryl-4-methyl-6-phenyl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazoles **1**. The striking fluorescent properties of **1** have found applications to whiten synthetic fibers.

We wish to report in this communication the synthesis of 2-hetaryl-4-methyl-6-phenyl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazoles **6** by a novel method. Although several fused heterocycles involving 2-aryl-fused hetero-1,2,3-triazoles are known, 2-hetaryl-fused hetero-1,2,3-triazoles are uncommon. This is probably because of the inaccessibility of hetaryl diazonium salts from heterocyclic amines such as 2-aminopyridine (**4a**) which are required for coupling with suitable heterocyclic amines such as **2**, capable of coupling at its vacant 4-position to result 5-amino-4-hetarylazo-3-methyl-1-phenyl-1*H*-pyrazole **5**, precursors of **6**.

In connection with our interest to study fluorescent properties of **6**, we have devised the following route for efficient synthesis of **5**, precursors of **6**.

The aminopyrazole **2** was converted to 5-amino-4-nitroso-3-methyl-1-phenyl-1*H*-pyrazole (**3**) following procedure described in literature [5]. Hetaryl amines, such as 2-aminopyridine (**4a**), 2-aminothiazole (**4b**) and 5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**4c**) (same as 2) are condensed with **3** to give excellent yields 77-81% of *ortho*-aminohetaryl azo compounds **5a-5c**. The condensation of an arylamine with an arylnitroso compound has been reported to take place in acetic acid [6]. Better yields of **5** are resulted using refluxing 50% sodium hydroxide solution. The compounds **5a-5c** were converted to **6a-6c** using cupric acetate in refluxing pyridine or *N*,*N*-dimethylformamide in the current of bubbling air.

Scheme 1



The scope of the synthesis can be widen by the availability of *ortho*-nitrosoamino compounds which can be condensed with several hetaryl amines to result *ortho*-aminohetarylazo derivatives precursors in the end-products.

The fluorescent properties of the compounds have been studied and the wavelength of absorption maxima, fluorescence emission maxima and values of logarithm of extinction coefficient are recorded. The application to synthetic fibers (polyester and polyamide) resulted in moderate whitening of the fibers.

EXPERIMENTAL

4-(Pyrid-2-yl)azo-5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**5a**).

To mixture of 4.04 g (0.02 mole) of 5-amino-3-methyl-4-nitroso-1-phenyl-1*H*-pyrazole (**3**) and 1.88 g (0.02 mole) of 2-aminopyridine (**4a**) 20 ml of 50% sodium hydroxide solution was added. The temperature was brought to reflux. The reflux temperature was maintained for 5 hours. After cooling to room temperature, the reaction mass was poured into 60 g of crushed ice with vigorous stirring. The solid was filtered, washed with water until free of alkali and dried. Recrystallization from ethanol:DMF (1:1) yielded 4.45 g (80%) of **5a** as an orange crystalline solid, mp 267°.

Anal. Calcd. for $C_{15}H_{14}N_6$: C, 64.75; H, 5.04; N, 30.22. Found: C, 64.53; H, 5.08; N, 30.07.

2-(Pyrid-2-yl)-4-methyl-6-phenyl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazole (**6a**).

To a solution of 2.89 g (0.01 mole) of **5a** in 20 ml pyridine was added 1 g (5.5 mmoles) of cupric acetate. The reaction mixture was brought to reflux temperature. Air was continuously bubbled through the reaction mixture and the reflux was continued for 5 hours. The reaction mixture was kept overnight to cool at room temperature. The white product which separated was filtered, washed with ethanol, dried and recrystallized from DMF to yield 2.26 g (82%) of **6a** as a white crystalline solid, mp >360°. ^{1}H nmr (trifluoroacetic acid): δ 2.8 (s, 3H, CH_3), 7-7.6 (m, 9H, H-2, H-3, H-4 and H-5 of 2-pyridyl and H-2, H-3, H-4, H-5 and H-6 of 6-phenyl); λ max absorption 375 nm, λ max emission 442 nm, log ε 3.97.

Anal. Calcd. for $C_{15}H_{12}N_6$: C, 65.22; H, 4.35; N, 30.43. Found: C, 65.38; H, 4.26; N, 30.20.

4-(Thiazol-2-yl)azo-5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**5b**) and 4-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)azo-5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**5c**).

The same procedure as described for the condensation of **3** and **4a** to **5a** was applied in the condensation of **3** and **4b** and **3** and **4c** yielding 4-(thiazol-2-yl)azo-5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**5b**, 81%, recrystallized from acetic acid, mp 278-280°) and 4-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)azo-5-amino-3-methyl-1-phenyl-1*H*-pyrazole (**5c**, 77%, recrystallized from acetic acid, mp 249-250°), respectively.

Anal. Calcd. for $C_{13}H_{12}N_6S$: C, 54.93; H, 4.23; N, 29.58; S, 11.27. Found **5b**: C, 54.82; H, 4.12; N, 29.70; S, 11.45.

Anal. Calcd. for $C_{20}H_{19}N_7$: C, 67.23; H, 5.32; N, 27.45. Found **5c**: C, 67.48; H, 5.50; N, 27.22.

2-(Thiazol-2-yl)-4-methyl-6-phenyl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazole (**6b**) and 2-(3-Methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methyl-6-phenyl-6*H*-pyrazolo-[3,4-*d*]-1,2,3-triazole (**6c**).

The same procedure as described for the oxidation of **5a** to **6a** was applied to the oxidation of **5b** and **5c**, except that instead of pyridine, DMF was used as solvent, yielding 2-(thiazol-2-yl)-4-methyl-6-phenyl-6*H*-pyrazolo[3,4-*d*]-1,2,3-triazole **6b**, 77%, recrystallized from acetic acid, mp >360°; ^{1}H nmr (trifluoroacetic acid): δ 2.8 (s, 3H, CH_3), 7.2-9.6 (m, 7H, H-4 and H-5 of 2-thiazolyl and H-2, H-3, H-4, H-5 and H-6 of 6-phenyl); λ max absorption 426 nm, λ max emission 530 nm, log ε 4.07 and 2-(3-methyl-1-phenyl-1*H*-pyrazol-5-yl)-4-methyl-6-phenyl-6*H*-pyrazolo-[3,4-*d*]-1,2,3-triazole **6c**, 72%, recrystallized from ethanol, mp 202-204°; ^{1}H nmr (trifluoroacetic acid): δ 2.6 (s, 3H, CH_3), 2.8 (s, 3H, CH_3), 7.0 (s, 1H, H-4 of pyrazolyl), 7.1-9.4 (m, 10H, H-2, H-3, H-4, H-5 and H-6 of 1-phenyl of pyrazolyl and H-2, H-3, H-4, H-5 and H-6 of 6-phenyl of pyrazolotriazole), respectively.

Anal. Calcd. for $C_{13}H_{10}N_6S$: C, 55.32; H, 3.55; N, 29.79; S, 11.35. Found **6b**: C, 55.58; H, 3.65; N, 29.52; S, 11.20.

Anal. Calcd. for $C_{20}H_{17}N_7$: C, 67.61; H, 4.79; N, 27.61. Found **6c**: C, 67.78; H, 4.70; N, 27.40.

REFERENCES AND NOTES

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