New Routes to the Synthesis of Pyridazinone, Ethoxypyridine, Pyrazole and Pyrazolo[1,5-*a*]pyrimidine Derivatives Incorporating a Benzotriazole Moiety

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Received March 8, 2000

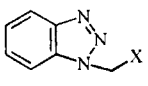
A new approach to the synthesis of pyridazinone, ethoxypyridine, pyrazole and 7-aminopyrazolo-[1,5-*a*]pyrimidine derivatives. The structure of the newly synthesized compounds was elucidated by elemental analyses, ir, ^{1}H nmr spectra and in some cases by ^{13}C nmr investigations.

J. Heterocyclic Chem., **37**, 1617 (2000).

Benzotriazole derivatives have attracted a great deal of interest due to their biological activities such as antimicrobial [1-3], anticancer [4], analgesic [5], herbicidal [6] and anti-inframmatory activity [7]. In continuation of our interest in the synthesis of heterocycles containing a benzotriazole moiety [8-9], we report here on the facile route to several new ethoxypyridine, pyridazinone, pyrazole and pyrazolo[1,5-*a*]pyrimidine derivatives in which a benzotriazole ring is incorporated.

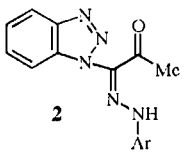
Thus compound **1a** coupled readily with benzene diazonium chloride and *p*-methoxybenzene diazonium chloride to yield the arylhydrazone **2a,b** in excellent yields. However, under a variety of conditions **1b** failed to couple with aromatic diazonium salt. The reactivity of the arylhydrazone **2** towards some carbon nucleophiles was investigated. Thus upon fusion of **2a,b** with malononitrile, ethyl cyanoacetate, cyanoacetophenone and diethyl malonate in the presence of ammonium acetate and acetic acid afforded the pyridazinones **4a-d** (Scheme 1). The structure of the latter product was established on the basis of its elemental analysis and spectral data. The IR spectrum of the reaction product **4a** showed bands at 2160 cm^{-1} corresponding to a nitrile function in addition to a strong carbonyl band at 1667 cm^{-1}. Its mass spectrum revealed molecular ion peak at *m/z* 328 (M$^+$), and the, ^{13}C nmr of the product revealed carbonyl carbon at δ157.67 ppm. Treatment of phenylhydrazone (**2a**) with ethyl cyanoacetate afford a product identical in all respects (mp and spectra) with that obtained previously from the reaction **2a** with malononitrile.

Condensation of 1-(benzotriazol-1-yl)acetonitrile (**1b**) with arylidenemalononitrile (**5a-c**) in ethanolic sodium



1

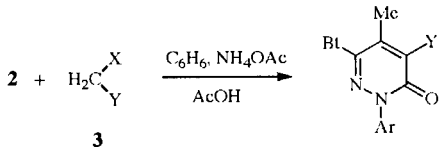
a, X = COMe
b, X = CN



2

a, Ar = Ph
b, Ar = *p*-MeOC$_6$H$_4$

Scheme 1



3

a, X = Y = CN
b, X = CN, Y = COOEt
c, X = CN, Y = COPh
d, X = Y = COOEt

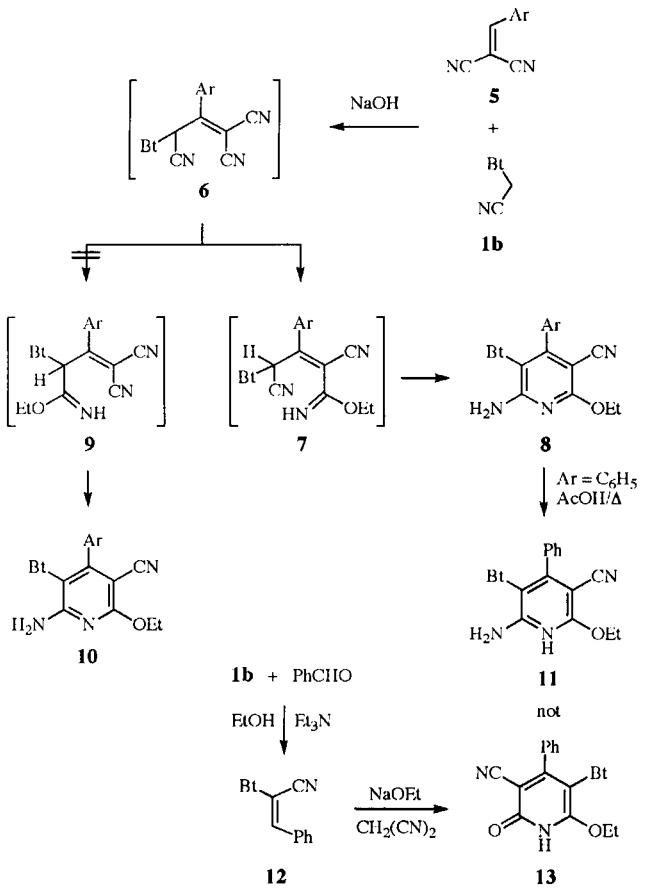
4

a, Y = CN, Ar = Ph
b, Y = CN, Ar = p-MeOC$_6$H$_4$
c, Y = COPh, Ar = Ph
d, Y = COOEt, Ar = Ph
Bt = 1*H*-Benzotriazol-1-yl

ethoxide at reflux temperature to afford 6-amino-4-aryl-5-(benzotriazol-1-yl)-2-ethoxypyridine-3-carbonitrile (**8a-c**) (Scheme 2). The structure of the isolated product was confirmed on the bases of its elemental analysis and spectral data. Thus, the IR spectrum of the reaction product **8a**, showed amino and nitrile absorptions at 3384, 3331 and 2220 cm^{-1} respectively, which are compatible with the assigned structure. The structure may be formed *via* initial addition of carbanion **1b** across the activated double bond system in the arylidenemalonotrile to form intermediate **6**, followed by addition of the ethoxide ion to one of the cyano groups to afford the iminoether **7**, which is cyclised *via* a nucleophilic attack of an NH group on a cyano carbon, followed by aromatization to 6-aminoethoxypyridine **8**. This sequence of events has been recently suggested to account for the formation of alkoxypyridine [10,11]. Heating compound **8a** in acetic acid for fifteen minutes afforded, in excellent yield, product that was identified as 5-(benzotriazol-1-yl)-2-ethoxy-6-oxo-4-phenyl-1,6-dihydropyridine-3-carbonitrile (**11**). The IR spectrum of compound **11** showed two characteristic absorption bands at 2211 and 1628 cm^{-1} corresponding to nitrile and carbonyl functions, respectively and a band for the amino group was not observed (Scheme 2). The ^{13}C nmr spectrum of the product revealed a carbonyl carbon at resonating 166 ppm. A further evidence for the proposed structure **11** was obtained by independent synthesis of compound **11** *via*

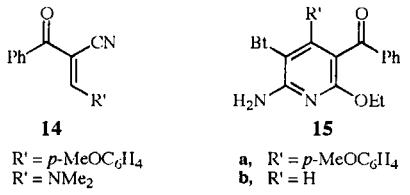
treatment of **1b** with benzaldehyde in refluxing ethanol in the presence of a catalytic amount of triethylamine to afford product **12**.

Scheme 2



5-10 **a**, Ar = C_6H_5; **b**, Ar = *p*-$MeOC_6H_4$; **c**, Ar = *p*-ClC_6H_4; Bt = 1*H*-benzotriazol-1-yl

The latter compound was treated with malononitrile in refluxing ethanolic sodium ethoxide to afford a product **13**. The spectral data for compound **13** is nearly identical with its isomer obtained from hydrolysis of compound **8a** in acetic acid. However both compounds have different melting points.



14

a, R' = *p*-$MeOC_6H_4$
b, R' = NMe_2

15

a, R' = *p*-$MeOC_6H_4$
b, R' = H

In a similar manner, compounds **14a,b** reacts with 1-(benzotriazolyl)acetonitrile (**1b**) under the same experimental conditions as with arylidenemalonitrile to afford **15a,b**. The spectral data for compounds **15a** and **15b** were in complete agreement with their proposed structures.

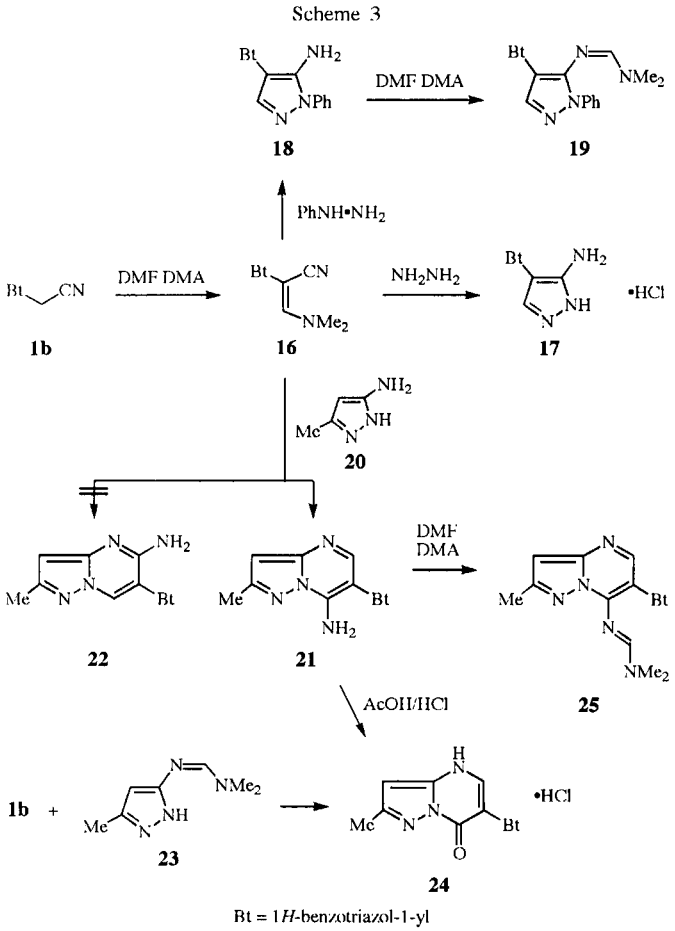
Treatment of 2-(benzotriazol-1-yl)acetonitrile (**1b**) with dimethylformamide dimethylacetal (DMF-DMA) in refulxing xylene afforded the corresponding enaminonitrile **16** in excellent yield. The ^1H nmr spectrum of isolated product exhibited two singlets at δ 3.26 and 8.31 ppm due to the *N,N*-dimethylamino and methine protons respectively in addition to an aromatic multiplet in the region at δ 7.33-8.20 ppm. The reactivity of compound **16** towards some nitrogen nucleophiles was investigated. When **16** was treated with hydrazine hydrate and with phenylhydrazine in refluxing ethanol the novel aminopyrazoles **17** and **18**, respectively were produced (Scheme 3). Thus, IR spectra of compounds **17** and **18** were free of nitrile functional and showed absorption bands for NH_2 in the region 3431-3327 cm^{-1}; compound **17** also showed an absorption due to an NH group at 3219 cm^{-1}. Treatment of 1-(5'-amino-1'-phenylpyrazol-4'-yl)benzotriazole (**18**) with dimethylformamide dimethylacetal (DMF-DMA) in refluxing xylene afforded the corresponding 1-(5'-dimethylaminomethylenimino-1'-phenylpyrazol-4'-yl)benzotriazole (**19**) in excellent yield.

The results described above prompted us to investigate the behaviour of **16** towards some heterocyclic amines as potential precursors for fused heterocyclic systems [9]. Thus, treatment of compound **16** with 5-amino-3-methyl-1*H*-pyrazole (**20**) in refluxing ethanol in the presence of a catalytic amount of hydrochloric acid afford a single product identified as pyrazolo[1,5-*a*]pyrimidine derivative **21** (Scheme 3) which is in contrast to a recent report [9]. The IR spectrum of compound **21** showed two characteristic absorption bands at 3324 and 3287 cm^{-1} due to the amino group and did not show a band due to the nitrile functional group. Compound **21** in acetic acid and in the presence of catalytic amount of hydrochloric acid at reflux temperature can readily be converted into a single product identified as 6-(benzotriazol-1-yl)-2-methyl-7-oxo-4,7-dihydropyrazolo[1,5-*a*]pyrimidinium hydrochloride (**24**). The structure of the isolated product was confirmed on the basis of its elemental analysis and spectral data.

Further evidence for proposed structure **24** was attempted by an independent synthesis of compound **24** *via* treatment of 5-(dimethyl-aminomethylenimino)-(1*H*)-3-methylpyrazole (**23**) with 2-(benzotriazol-1-yl)-acetonitrile (**1b**) in acetic acid to afford a product identical in all respects (mp, TLC and spectra) with that obtained previously from the hydroysis of **21** as described before.

Note that compound **21** reacts smoothly with dimethylformamide dimethylacetal (DMF-DMA) in refluxing xylene to afford only one isoluble product, identified as 6-(benzotriazol-1-yl)-7-(dimethylaminomethylenimino)-2-methylpyrazolo[1,5-*a*]pyrimidine (**25**) in excellent yield. The structure of the latter product was established on the basis of its elemental analysis and spectral data. The IR spectrum of the isolated product did not show absorptions due to an amino group.

Scheme 3



Acknowledgement.

This work was financed by the University of Kuwait research grant SC 100. We are grateful to the Faculty of Higher Studies at Kuwait University for their financial support of Mr. Osama Yousef Abd El-Hay. We are also grateful to the Faculty of Science, Chemistry Department, SAF facility for the spectral and analytical data. Also we are grateful to Prof. A. R. Katritzky for his valuable advice.

EXPERIMENTAL

Melting points are uncorrected. IR spectra were recorded on a Shimadzu 2000 FTIR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 80 and 400 MHz with dimethyl-d_6 sulfoxide or deuteriochloroform as solvent and tetramethylsilane as an internal standard; chemical shifts are reported as δ units (ppm). Mass spectra were measured on GS/MS INCOL XL Finningan MAT. Microanalysis were performed on a LECO-CHNS 932 analyzer. Compounds **1a,b, 2a,b** and **23** were prepared by the following published procedure [12-13], [8] and [9], respectively.

General Procedure for the Synthesis of **4a-d**.

A suspension of each of **2a,b** (10 mmol) in benzene (30 mL), ammonium acetate (1.0 g) and acetic acid (2 mL) was treated with each of (10 mmol) **3a-d**. The reaction mixture was fused at 180 °C for 5 minutes, left to cool to room temperature overnight and then triturated with ethanol. The solid product, so formed, was collected by filtration and recrystallized from ethanol.

6-(Benzotriazol-1-yl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyridazine-4-carbonitrile (**4a**).

This compound was obtained as dark red crystals in 74% yield, mp, 120-121 °C, ir: ν 2160 (CN), 1667 cm^{-1} (ring amide CO); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 2.56 (s, 3H, Me) and 7.10-8.25 (m, 9H, Ar-H); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ_c 157.67 (C-3), 145.67, 143.29, 134.72, 130.27, 130.19, 129.29, 128.28, 127.55, 125.18, 123.42, 120.33, 119.55, 117.08, 115.95 (arom. carbons & CN) and 25.78 ppm (Me), ms: (EI), *m/z* = 328 (M$^+$).

Anal. Calcd. For $C_{18}H_{12}N_6O$: C, 65.84; H, 3.68; N, 25.06. Found: C, 66.10; H, 3.77; N, 25.47.

6-(Benzotriazol-1-yl)-2-(*p*-methoxyphenyl)-5-methyl-3-oxo-2,3-dihydropyridazine-4-carbonitrile (**4b**).

This compound was obtained as dark brown crystals in 76% yield, mp, 122-123 °C, ir: ν 2175 (CN), 1660 cm^{-1} (ring amide CO); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 2.56 (s, 3H, Me), 3.81 (s, 3H, OMe) and 7.47-8.40 (m, 8H, Ar-H).

Anal. Calcd. For $C_{19}H_{14}N_6O_2$: C, 63.68; H, 3.94; N, 23.45. Found: C, 63.57; H, 4.07; N, 23.16.

6-(Benzotriazol-1-yl)-4-benzoyl-5-methyl-2-phenyl-2,3-dihydropyridazine-3-one (**4c**).

This compound was obtained as dark brown crystals in 71% yield, mp, 111-112 °C, ir: ν 1676 (CO) and 1625 cm^{-1} (ring amide CO); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 2.66 (s, 3H, Me) and 7.27-8.40 (m, 14H, Ar-H).

Anal. Calcd. For $C_{24}H_{17}N_5O_2$: C, 70.75; H, 4.21; N, 17.19. Found: C, 70.94; H, 4.53; N, 17.29.

Ethyl-6-(benzotriazol-1-yl)-5-methyl-3-oxo-2-phenyl-2,3-dihydropyridazine-4-carboxylate (**4d**).

This compound was obtained as dark brown crystals in 75% yield, mp, 123-124 °C, ir: ν 1720 (ester CO) and 1671 cm^{-1} (ring amide CO); ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.26 (t, 3H, J = 7 Hz, Me), 2.67 (s, 3H, Me), 4.05 (q, 2H, J = 7Hz, OCH_2) and 7.24-8.35 ppm (m, 9H, Ar-H); ms: (EI), *m/z* = 379 (M$^+$).

Anal. Calcd. For $C_{20}H_{17}N_5O_3$: C, 63.99; H, 4.56; N, 18.66. Found: C, 64.14; H, 4.82; N, 18.83.

General Procedure for the Synthesis of **8a-c.**

A mixture of **1b** (10 mmol) and arylidenemalononitrile **5a-c** in absolute ethanol (50 mL) was treated with sodium ethoxide (prepared from 0.6 g sodium metal and 60 mL of ethanol). The reaction was refluxed for 3 hours, then poured into cold water and neutralized with hydrochloric acid (10%). The solid product was collected and recrystallized from ethanol.

6-Amino-5-(benzotriazol-1-yl)-2-ethoxy-4-phenylpyridine-3-carbonitrile (**8a**).

This compound was obtained as yellow crystal in 82% yield, mp 250-252 °C; ir: ν 3484 and 3331 (NH_2) and 2220 cm^{-1} (CN). ^{1}H nmr (dimethyl-d_6 sulfoxide): δ 1.41 (t, 3H, J = 7 Hz, Me),

4.50 (q, 2H, J = 7 Hz, OCH_2) and 7.06-7.60 ppm (m, 10H, Ar-H & NH_2) and 7.99-8.05 ppm (m, 1H, Ar-H); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ_c 150.36, 145.06, 139.22, 131.63, 130.31, 129.83, 129.79, 129.88, 129.45, 129.34, 129.01, 128.29, 125.41, 123.73, 119.01 and 111.44 (arom. carbons & CN) and 63.55 (OCH_2) and 14.38 ppm (Me).

Anal. Calcd. for $C_{20}H_{16}N_6O$: C, 67.40; H, 4.53; N, 23.58. Found: C, 67.37; H, 4.64; N, 23.28.

6-Amino-5-(benzotriazol-1-yl)-2-ethoxy-4-(*p*-methoxyphenyl)-pyridine-3-carbonitrile (**8b**).

This compound was obtained as yellow crystal in 79% yield, mp 220-222 °C; ir: ν 3347 and 3213 (NH_2) and 2188 cm^{-1} (CN). ^1H nmr (dimethyl-d_6 sulfoxide): δ 1.34 (t, 3H, J = 7 Hz, Me), 3.75 (s, 3H, OMe), 4.43 (q, 2H, J = 7 Hz, OCH_2) and 6.96-8.20 ppm (m, 10H, Ar-H & NH_2).

Anal. Calcd. for $C_{21}H_{18}N_6O_2$: C, 65.27; H, 4.70; N, 21.75. Found: C, 65.56; H, 4.70; N, 21.98.

6-Amino-5-(benzotriazol-1-yl)-4-(*p*-chlorophenyl)-2-ethoxy-pyridine-3-carbonitrile (**8c**).

This compound was obtained as brown crystal in 79% yield, mp 240-242 °C; ir: ν 3351 and 3215 (NH_2) and 2191 cm^{-1} (CN). ^1H nmr (dimethyl-d_6 sulfoxide): δ 1.34 (t, 3H, J = 7 Hz, Me), 4.50 (q, 2H, J = 7 Hz, OCH_2) and 7.42-8.20 ppm (m, 10H, Ar-H & NH_2).

Anal. Caldc. for $C_{20}H_{15}N_6OCl$: C, 61.45; H, 3.86; N, 21.50. Found: C, 61.20; H, 3.79; N, 21.12.

5-(Benzotriazol-1-yl)-2-ethoxy-6-oxo-4-phenyl-1,6-dihydropyridine-3-carbonitrile (**11**).

A solution of **8** (3.56 g, 10 mmol) in acetic acid (10 mL) was heated for 15 minutes. The solvent was then evaporated under reduced pressure. The solid product was collected by filtration and recrystallization from ethanol as pale yellow crystal in 72% yield, mp. 231-232 °C; ir: ν 3350 (NH), 2211 (CN) and 1628 cm^1 (ring amide CO). ^1H nmr (dimethyl-d_6 sulfoxide): δ 1.39 (t, 3H, J = 7 Hz, Me), 4.36 (q, 2H, J = 7 Hz, OCH_2), 7.05-8.04 ppm (m, 9H, Ar-H) and 8.19 ppm (br, 1H, NH); ^{13}C nmr (dimethyl-d_6 sulfoxide); δ 166.12 (C-6), 150.27, 142.20, 138.61, 136.20, 134.38, 132.25, 131.36, 130.49, 129.84, 129.22, 127.55, 125.25, 123.59, 119.51 and 110.25 (arom. carbons & CN), 62.61 (OCH_2) and 14.32 (Me).

Anal. Calcd. For $C_{20}H_{15}N_5O_2$: C, 67.22; H, 4.23; N, 19.60. Found: C, 67.21; H, 4.20; N, 19.52.

2-(Benzotriazol-1-yl)-3-phenyl-2-propenenitrile (**12**).

A solution of **1b** (1.58 g, 10 mmol) in ethanol (20 mL) was treated with benzaldehyde and few drops of triethylamine. The reaction mixture was refluxed for 5 hours. The solvent was then evaporated under reduced pressure. The solid product was collected by filtration and recrystallization from ethanol as brown crystals, in 80% yield, mp. 75-77 °C, ir: ν 2229 cm^{-1} (CN). ^1H nmr (dimethyl-d_6 sulfoxide): δ 7.49-7.87 (m, 8H, Ar-H), 7.94-8.25 (m, 1H, Ar-H) and 8.49 ppm (s, 1H, H-3), ms (EI), *m/z* 246 (M^+).

Anal. Calcd. for $C_{15}H_{10}N_4$: C, 73.15; H, 4.09; N, 22.75. Found: C, 73.29; H, 4.35; N, 22.67.

5-(Benzotriazol-1-yl)-6-ethoxy-4-phenyl-2-oxo-1,2-dihydro-pyridine-3-carbonitrile (**13**).

A suspension of **12** (2.46 g, 10 mmol) and malononitrile (0.66g, 10 mmol) in absolute ethanol (30 mL) was treated with a sodium ethoxide solution (prepared from 0.60 g of sodium metal and 60 mL of ethanol). The reaction mixture was refluxed for 3 hours, then poured into ice cold water and neutralized with hydrochloric acid (10%). The solid product, so formed, was collected by filtration and recrystallized from ethanol as pale yellow crystal in 73% yield, mp. 190-192 °C; ir: ν 3351 (NH); 2211 (CN) and 1619 cm^{-1} (ring amide CO); ^1H nmr (deuteriochloroform): δ 1.40 (t, 3H, J = 7 Hz, Me), 4.38 (q, 2H, J = 7 Hz, OCH_2), 7.05-8.00 (m, 9H, Ar-H) and 8.20 ppm (br, 1H, NH); ^{13}C nmr (acetone-d_6): 166.40 (C-2), 156.30, 145.80, 137.90, 129.60, 128.95, 128.81, 128.66, 128.55, 128.33, 128.26, 128.23, 124.24, 120.02, 119.80 and 110.38 (arom. carbons & CN), 62.97 (OCH_2) and 14.31 ppm (Me).

Anal. Calcd. for $C_{20}H_{15}N_5O_2$: C, 67.22; H, 4.23; N, 19.60. Found: C, 67.23; H, 4.35; N, 19.73.

2-Benzoyl-3-(*p*-Methoxyphenyl)-acrylonitrile (**14a**).

A suspension of α-cyanoacetophenone (1.38 g, 10 mmol) and *p*-methoxybenzaldeyde in absolute ethanol (30 mL) and a few drops of triethylamine were added. The reaction mixture was refluxed for 3 hours, then poured into ice cold water and neutralized with hydrochloric acid (10%). The solid product, so formed, was collected by filtration and recrystallized from ethanol as yellow crystal in 93% yield, mp 95-97 °C; ir: ν 2222 (CN) and 1646 cm^{-1} (CO). ^1H nmr (deuteriochloroform): δ 3.86 (s, 3H, OMe), 6.98 (d, 2H, J = 7 Hz, Ar-H); 7.50 (d, 2H, J = 7 Hz, Ar-H), 7.78-8.06 (m, 5H, Ar-H) and 8.15 ppm (s, 1H, H-3).

Anal. Calcd. for $C_{17}H_{13}NO_2$: C, 77.56; H, 4.94; N, 5.32. Found: C, 77.44; H, 5.09; N, 5.08.

2-Benzoyl-3-dimethylaminoacrylonitrile (**14b**).

A suspension of α-cyanoacetophenone (1.38 g,10 mmol) in xylene (20 mL) was treated with dimethylformamide dimethyl-acetal (DMF-DMA) (1.33 g, 10 mmol). The reaction mixture was refluxed for 30 minutes. Then allowed to cool at 0 °C. The solid product, so formed, was collected by filtration and recrystallized from ethanol as yellow crystals in 90% yield, mp 98-100 °C; ir: ν 2221 (CN) and 1640 cm^{-1} (CO). ^1H nmr (deuteriochloroform): δ 3.16 (s, 3H, NMe), 3.18 (s, 3H, NMe), 7.36-7.83 (m, 5H, Ar-H) and 8.25 ppm (s, 1H, H-3).

Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.02; H, 6.03; N, 13.83.

General Procedure for the Synthesis of **15a,b**.

A mixture of compound **1b** (1.58 g, 10 mmol) and each of **14a** or **14b** (10 mmol) was refluxed in 30 mL sodium ethoxide solution (prepared from 0.6 g in 30 mL absolute ethanol) for 4 hours. The reaction mixture was allowed to cool to room temperature and neutralized with hydrochloric acid (10%). The solid product, so formed, was collected by filtration and recrystallized from ethanol.

2-Amino-3-(benzotriazol-1-yl)-5-benzoyl-6-ethoxy-4-(*p*-methoxy-phenyl)pyridine (**15a**).

This compound was obtained as yellow crystals in 70% yield, mp 140- 142 °C; ir: ν 3350 and 3183 (br, NH_2) and 1646 cm^{-1} (CO); ^1H nmr (dimethyl-d_6 sulfoxide); 1.26 (t, 3H, J = 7 Hz, Me), 3.74 (q, 2H, J = 7 Hz, OCH_2); 3.88 (s, 3H, OMe) and 6.40-8.2 ppm (m, 15H, Ar-H & NH_2); ms: (EI), *m/z* = 465 (M^+).

Anal. Calcd. for $C_{27}H_{23}N_5O_3$: C, 69.66; H, 4.98; N, 15.05. Found: C, 69.49; H, 5.15; N, 14.98.

2-Amino-3-(benzotriazol-1-yl)-5-benzoyl-6-ethoxypyridine (**15b**).

This compound was obtained as brown crystals in 75% yield, mp 120-122 °C; ir: ν 3333 and 3183 (NH_2) and 1615 cm^{-1} (CO); ^1H nmr (dimethyl-d_6 sulfoxide): δ 1.31 (t, 3H, J = 7 Hz, Me), 4.04 (q, 2H, J = 7 Hz, OCH_2), 7.49-8.07 (m, 11H, Ar-H & NH_2), and 8.43 ppm (s, 1H, H-4), ms: (EI), *m/z* = 360 (M^+).

Anal. Calcd. for $C_{20}H_{17}N_5O_2$: C, 66.78; H, 4.73; N, 19.47. Found: C, 66.55; H, 4.50; N, 19.48.

2-(Benzotriazol-1-yl)-3-dimethylamino-2-propenenitrile (**16**).

A suspension of **1b** (1.58 g, 10 mmol) in xylene (30 mL) was treated with dimethylformamide dimethylacetal (DMF-DMA) (1.33 g, 10 mmol). The reaction mixture was refluxed for 5 hours, then allowed to cool at 0 °C. The solid product, so formed, was collected by filtration and recrystallized from ethanol as orange crystal in 75% yield, mp 110-111 °C; ir: ν 2203 cm^{-1} (CN). ^1H nmr (dimethyl-d_6 sulfoxide): δ 3.26 (s, 6H, NMe_2), 7.33-8.20 (m, 4H, Ar-H) and 8.31 (s, 1H, H-3); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ 152.70 (C-3), 144.06 (C-3a'), 133.01 (C-7a'), 126.87 (C-6'), 124.87 (C-2), 123.04 (C-5'), 118.7 (C-4'), 116.45 (CN), 108.95 (C-7') and 41.10 ppm (NMe_2); ms (EI), *m/z* = 213.10 (M^+).

Anal. Calcd. for $C_{11}H_{11}N_5$: C, 61.95; H, 5.20; N, 32.85. Found: C, 61.92; H, 5.20; N, 32.93.

General Procedure for the Synthesis of **17** and **18**.

To a solution of **16** (10 mmol) in ethanol (20 mL) and hydrochloric acid (1 mL) was treated with hydrazine hydrated or phenyl hydrazine (10 mmol). The reaction mixture was refluxed for 4 hours, then allowed to cool at room temperature. The solid product, so formed, was collected by filtration and recrystallized from ethanol.

1-(5-Amino-1*H*-pyrazol-4-yl)benzotriazole hydrochloride (**17**).

This compound was obtained as yellow crystals in 80% yield, mp 171-172 °C; ir: ν 3389 and 3327 cm^{-1} (NH_2) and 3219 (NH). ^1H nmr (dimethyl-d_6 sulfoxide) δ 5.83 (br, 2H, NH_2), 7.47-8.16 (m, 5H, Ar-H, H-3') and 12.26 (br, 1H, NH).

Anal. Calcd. for $C_9H_8N_6$•HCl: C, 45.67; H, 3.83; N, 35.51. Found: C, 45.96; H, 4.09; N, 35.57.

1-(5-Amino-1-phenylpyrazol-4-yl)benzotriazole (**18**).

This compound was obtained as yellow crystal in 86% yield, mp 288-290 °C; ir: ν 3431 and 3334 cm^{-1} (NH_2). ^1H nmr (dimethyl-d_6 sulfoxide) δ 5.69 (br, 2H, NH_2), 7.40-7.75 (m, 8H, Ar-H), 7.84 (s, 1H, H-3'), 8.10 ppm (m, 1H, Ar-H); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ_C 145.74 (C-5'), 143.43, 139.56 (C-3a, C-4'), 137.37 (C-3'), 135.08; 130.24, 128.80, 128.11, 124.96, 124.36, 120.19, 111.57 and 102.04 ppm (arom. carbons); ms (EI); *m/z* = 276.1 (M^+).

Anal. Calcd. for $C_{15}H_{12}N_6$: C, 65.20; H, 4.38; N, 30.42. Found: C, 65.22; H, 4.52; N, 30.12.

1-(5-Dimethylaminomethylenimino-1-phenylpyrazol-4-yl)benzotriazole (**19**).

A suspension of **18b** (2.76 g, 10 mmol) in xylene (30 mL) was treated with dimethylformamide dimethylacetal (DMF DMA) (1.33 g, 10 mmol). The reaction mixture was refluxed for 3 hours, then allowed to cool at 0 °C. The solid product, so formed, was collected by filtration and recrystallized from ethanol as brown crystals in 80% yield, mp 142-143 °C; ^1H nmr (dimethyl-d_6 sulfoxide): δ 2.66 (s, 3H, NMe), 2.77 (s, 3H, NMe), 7.20-7.84 (m, 9H, Ar-H & methylenic CH), 8.00 (s, 1H, H-3') and 8.15-8.25 (m, 1H, Ar-H); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ_C 156.14, 145.32, 140.03, 137.18, 134.44, 129.49, 128.83, 127.00, 124.93, 124.12, 123.54, 119.95, 111.28, 106.49 (arom. carbons & methylenic CH), 41.11 (NMe) and 34.0 ppm (NMe).

Anal. Calcd. For $C_{18}H_{17}N_7$: C, 65.24; H, 5.17; N, 29.59. C, 65.35, H, 5.22, N, 29.29.

7-Amino-6-(benzotriazol-1-yl)-2-methylpyrazolo[1,5-*a*]pyrimidine (**21**).

A solution of **16** (2.13 g, 10 mmol) in ethanol (30 mL) was treated with 3-amino-5-methylpyrazole (0.97 g, 10 mmol) and 2 mL of hydrochloric acid. The mixture was refluxed for 3 hours. The solvent was evaporated under reduced pressure. The solid product, so formed, was collected by filtration and recrystallized from ethanol as a pale yellow crystal in 79% yield, mp 211-212 °C; ir: ν 3324 and 3287 cm^{-1} (NH_2). ^1H nmr (dimethyl-d_6 sulfoxide): δ 2.47 (s, 3H, Me), 6.42 (s, 1H, H-3), 7.46-7.58 (m, 2H, Ar-H), 7.95-8.06 (m, 2H, Ar-H), 8.49 (br, 2H, NH_2) and 8.89 (s, 1H, H-5); ^{13}C nmr (dimethyl-d_6 sulfoxide/deuteriochloroform): δ 155.42 (C-7), 150.39, 148.84, 146.19, 145.84, 135.95, 129.03, 127.09, 124.96, 120.38, 111.16, 99.99, (arom. carbons) and 14.78 ppm (Me).

Anal. Calcd. for $C_{13}H_{11}N_7$: C, 58.86; H, 4.18; N, 36.96. Found: C, 58.82; H, 4.13; N, 36.58.

6-(Benzotriazol-1-yl)-2-methyl-7-oxo-4,7-dihydropyrazolo[1,5-*a*]-pyrimidinium hydrochloride (**24**).

A suspension of **1b** (1.58 g, 10 mmol) in acetic acid (30 mL) and hydrochloric acid (3 mL) was treated with **23** (1.52 g, 10 mmol)l. The mixture was refluxed for 6 hours, then left to cool at room temperature. The solvent was evaporated under reduced pressure. The solid product, so formed, was collected by filtration and recrystallized from ethanol as yellow crystals in 78% yield, mp 243-244 °C; ir: ν 3355 (NH) and 1647 cm^{-1} (ring amide CO). ^1H nmr (dimethyl-d_6 sulfoxide): δ 2.19 (s, 3H, Me), 6.22 (s, 1H, H-3); 7.03-7.13 (m, 3H, Ar-H & H-5), 7.69-7.81 (m, 2H, Ar-H) and 10.35 (br, 1H, NH); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ 169.91 (C-7), 153.56, 148.75, 146.15, 145.95, 136.24, 129.31, 125.24, 124.48, 120.46, 119.88 and 111.72 (arom. carbons) and 15.20 ppm (Me).

Anal. Calcd. for $C_{13}H_{10}N_6O$.HCl: C, 51.40; H, 3.64; N, 27.66. Found: C, 51.11; H, 3.81; N, 28.05.

6-(benzotriazol-1'-yl)-7-dimethylaminomethylenimino-2-methylpyrazolo-[1,5-*a*]pyrimidine (**25**).

A suspension of **21** (2.65 g, 10 mmol) in xylene (30 mL) was treated with dimethylformamide dimethylacetal (DMF DMA) (1.33 g, 10 mmol). The reaction mixture was refluxed for 3 hours, then allowed to cool at 0 °C. The solid product, so formed, was collected by filtration and recrystallized from ethanol as yellow crystals in 75% yield, mp 140-141 °C; ^1H nmr (dimethyl-d_6 sulfoxide): δ 2.46 (s, 3H, Me), 3.07 (s, 3H, NMe), 3.30 (s, 3H, NMe), 6.50 (s, 1H, H-3), 7.46-7.55 (m, 3H, Ar-H), 8.05-8.20 (m, 1H, Ar-H), 8.45 (s, 1H, methylenic CH) and 9.35 ppm (s, 1H, H-5); ^{13}C nmr (dimethyl-d_6 sulfoxide): δ 159.52 (C-7), 155.67, 152.17, 148.74, 145.75, 145.67, 135.26, 128.50, 124.88, 120.10, 112.77, 109.88, 96.32 (arom. carbons & methylenic carbon); 41.60 (NMe), 34.36 (NMe), and 15.46 ppm (Me), ms (EI): *m/z* = 320.3 (M^+).

Anal. Calcd. for $C_{16}H_{16}N_8$: C, 59.98; H, 5.03; N, 34.98. Found: C, 59.94; H, 4.95; N, 34.79.

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