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Further studies on the reaction of ethyl benzoylacetate with malononitrile: synthesis of some novel pyridine and pyridazine derivatives☆

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Abstract—2-Cyano-5-phenyl-3,5-dioxopentanonitrile undergoes alcoholysis followed by Knoevenagel condensation to afford ethyl 4,4-dicyano-3-phenyl-3-butenoate, a thermo dynamically controlled product, which undergoes cyclization in acid medium to afford 2,6-dihydroxy-4-phenylnicotinonitrile. Some azo derivatives of nicotinonitriles and of 2-aminopyran are described. 5-Arylazo-2-aminopyrans are transformed by acid treatment into pyridazine derivatives, whereas without the arylazo substituent pyridines are obtained.

In the last decade we have been involved in an agrochemical programme aiming to develop new simple routes to functionally substituted heterocycles with anticipated biological activity.[1–3] We have recently reported that ethyl benzoylacetate reacts with malononitrile to afford the pentanonitrile derivative **1** (Scheme 1) as a Claisen condensation product.[4] Now we report the results of further investigations on this reaction and the synthesis of some new pyridazine derivatives.

When the pentanonitrile **1** (prepared as previously reported[4]) was left in an ethanolic solution at room temperature for about 15 days, a solid crystalline product appeared in the flask. After separation and purification, this solid had a melting point 190°C. Mass spectral measurements showed a molecular ion peak at *m/z* 240. The IR spectrum showed absorption bands at 2207 and 1712 cm^{-1} corresponding to cyano and ester carbonyl functions, respectively. The ^1H NMR spectrum revealed a triplet (3H) at δ 1.2 (J=7 Hz), a quartet (2H) at δ 3.8 (J=7 Hz) and a singlet (2H) at δ 4.3 besides an aromatic multiplet (5H) at δ 7.3–7.85. On the basis of these data the Knoevenagel condensation structure **4** was assigned to this product (Scheme 1).

The structure of compound **4** was consistent with its reaction with elemental sulfur to afford the thiophene derivative **5**.[5–7] The structure of the thiophene **5** was assigned on the basis of analytical and spectral data.

Compound **4** also undergoes the coupling reaction with the diazonium salts **6a–d** to afford the coloured hydrazo derivatives **7a–d**, respectively. Elemental analysis and spectral data are in agreement with the proposed structures. Compounds **7a–d** could be cyclized on fusion with ammonium acetate in an oil bath at 200°C to afford the pyridazine derivatives **8a–d**, which were identical with the same compounds obtained previously by another route.[4]

It now became clear that the reaction of ethyl benzoylacetate with malononitrile proceeds via initial Claisen condensation to afford product **1** as a kinetically controlled product which, on long standing in ethanol, undergoes alcoholysis to give back the reacting constituents which then undergo a Knoevenagel condensation to afford **4** as the thermodynamically controlled product, presumably via the intermediate steps **2** and **3** according to the sequence shown in Scheme 1.

It should be mentioned that the reaction of ethyl benzoylacetate with malononitrile has been previously reported to afford an oily product which was thought to be the Knoevenagel condensation **4**.[8,9] This oily product afforded the pyridine derivative **10a** (mp 288–290°C)[8] on heating with 70% sulfuric acid on a boiling water bath.

In our hands, boiling of the oily product **1** (in an ethanolic solution) directly after the reaction time with conc. HCl led to precipitation of a pale yellow crystalline solid product (mp 293°C) in 70% yield. The IR and ^1H NMR spectra of this product revealed that it is the same pyridine derivative described above.[8] Structure **10a** or its tautomeric **10b** or **10c** was assigned to this product.[10]

As compound **10** could not be obtained from **1** but through

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Keywords: nicotinonitriles; azo derivatives; pyridazines.

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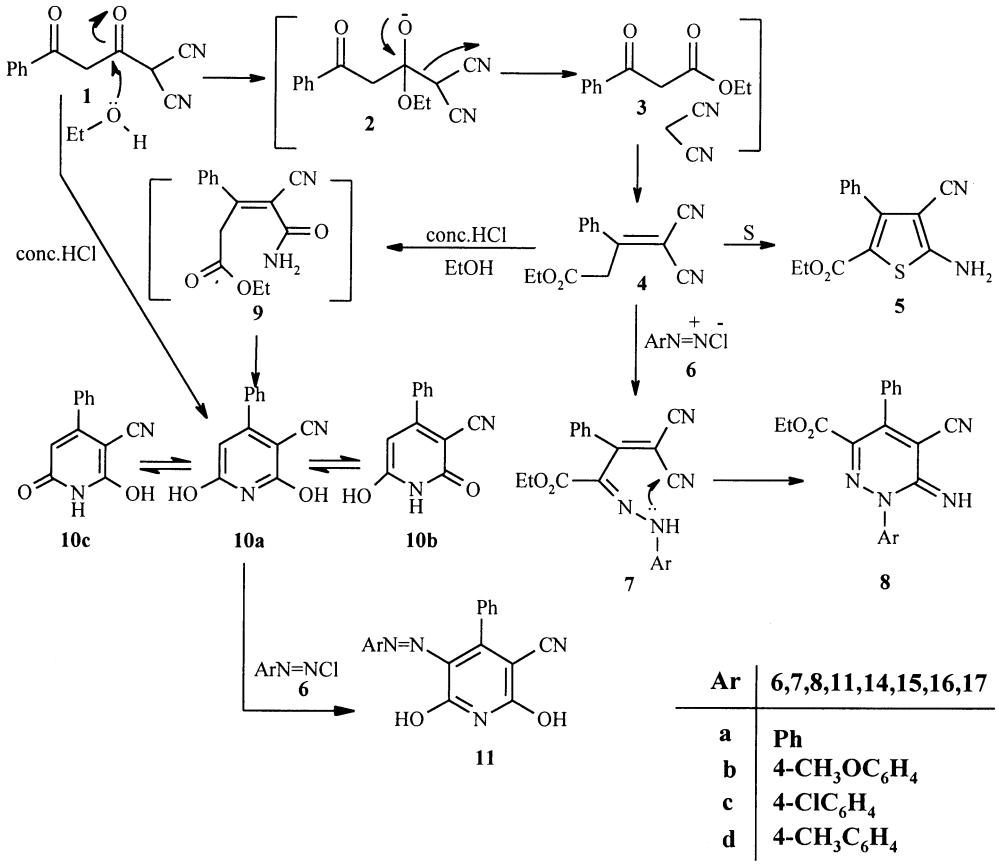
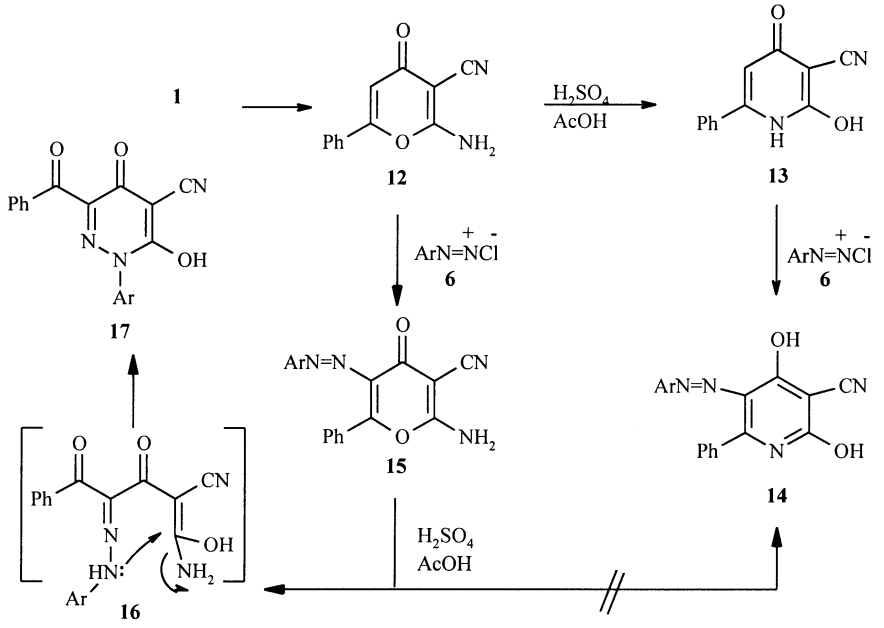


Scheme 1.

4, it is assumed that the presence of conc. HCl or H_2SO_4 has enhanced the process of alcoholysis of **1** by protonation of the carbonyl group creating a positive charge on the carbonyl carbon atom, thus facilitating attack by ethanol to afford **4**. Compound **4** (as intermediate in this process) then undergoes hydration of one of the cyano functions to afford the amide intermediate **9** which eliminates ethanol to afford the nicotinonitrile derivative **10**.

In support of this assumption, compound **4** could be transformed into **10** upon reflux in ethanolic conc. HCl presumably via the intermediacy of **9**.



Scheme 2.

The 5-azo derivatives of 2,6-disubstituted-4-methylnicotinonitriles have found wide applications in the dyeing of polyester, acrylic, cellulosic and polyamide fibers and PVC.[10] This prompted us to prepare the azo derivatives of the pyridine-3-carbonitrile derivatives described in this work that may find a similar application.

Thus, compound **10** couples with the diazonium salts **6a–d** in the free 5-position to afford the azo/hydrazo derivatives **11a–d**, respectively, as inferred from the analytical and spectral data.

On the other hand the pentanonitrile **1** was cyclized into the 4-oxopyran **12** which was in turn transformed into the 4-oxodihydropyidine **13** upon reflux in $AcOH/H_2SO_4$.[4] Azo coupling of **13** with **6a–d** gave new azo derivatives for which structures **14a–d** were assigned, respectively, on the basis of their analytical and spectral data, Scheme 2.

In order to prove the structure of compounds **14a–d** chemically, it was thought to obtain them from the corresponding 5-arylazo derivatives of 4-oxopyran: **15a–d** by reflux in $AcOH/H_2SO_4$. Thus compounds **15a–d** were prepared by azo coupling of **12** with **6a–d** and coloured azo compounds have been obtained and their structures were established on the basis of their analytical and spectral data. Refluxing these azo derivatives **15a–d** in acetic/sulfuric acid mixture did not, however, afford the azo derivatives **14a–d** but afforded other new compounds. Analytical and spectral data of these new compounds suggested the pyridazine structures **17a–d** (Scheme 2).

The formation of the pyridazines **17** apparently proceeded via hydrolysis of the azo pyrans **15** to afford the acyclic intermediates **16** which then undergo cyclization via the attack of the hydrazone NH on the enamine carbon atom with loss of ammonia. Similar transformations of azopyrans into pyridazines are known in the literature.[11]

1. Experimental

1.1. General

Melting points were determined on an electrothermal (9100) apparatus and are uncorrected. The IR spectra were recorded as KBr pellets on a Perkin–Elmer 1430 spectrophotometer. The ^{1}H-NMR spectra were taken on a Varian Gemini 200 MHz spectrometer in DMSO-d_6 using TMS as internal standard. Mass spectra were taken on a Shimadzu GCMS-GB 1000 PX (70 eV). Elemental analyses were carried out by the Microanalytical Center at Cairo University.

1.1.1. Ethyl 4,4-dicyano-3-phenyl-3-butenoate 4. The oily product **1** (21.2 g, 100 mmol; prepared as previously described[4]) was left in ethanol for 15 days at room temperature. The solid crystalline precipitate was collected by filtration and recrystallized from ethanol to give **4** as colourless needle crystals. (12.0 g, 50%); mp 190°C [Found: C, 70.10; H, 5.10; N, 11.60. $C_{14}H_{12}N_2O_2$ requires C, 69.99; H, 5.03; N, 11.66]; ν_{max} 2207 (CN), 1712 (C=O); δ_H (200 MHz, DMSO-d_6) 1.25 (t, J=7 Hz, 3H, CH_3), 3.8 (q, J=7 Hz, 2H, CH_2), 4.3 (s, 2H, CH_2), 7.25–7.80 (m, 5H, arom); *m/z* 240 (M^+, 27.5%), 195 (17.5%), 168 (100%), 77 (21.5%).

1.1.2. Ethyl 2-amino-3-cyano-4-phenylthiophene-5-carboxylate 5. To a solution of **4** (2.4 g, 10 mmol) in 25 mL ethanol and elemental sulfur (10 mmol), a catalytic amount of triethylamine was added and refluxed for 3 h, then filtered hot and left to cool to room temperature. The solid product formed was filtered off and recrystallized from ethanol/DMF to afford **5** as dark brown powder. (1.6 g, 60%); mp 310°C [Found: C, 61.80; H, 4.50; N, 10.20; S, 11.70. $C_{14}H_{12}N_2O_2S$ requires C, 61.74; H, 4.44; N, 10.28; S, 11.77]; ν_{max} 3400–3200 (NH_2) 2222 (CN), 1710 (C=O); δ_H (200 MHz, DMSO-d_6) 1.2 (t, J=7 Hz, 3H, CH_3), 3.9 (q, J=7 Hz, 2H, CH_2), 7.29–7.55 (m, 5H, arom), 7.57 (bs, 2H, NH_2).

1.1.3. 2,6-Dihydroxy-4-phenyl-3-pyridinecarbonitrile 10. *Method A*: To the oily product **1**[4] (21.2 g, 100 mmol) directly after the reaction time is up was added 2 mL of concentrated hydrochloric acid and then boiled with scratching for 30 min, the precipitated solid was filtered off and recrystallized from ethanol/DMF to afford **10** as yellowish brown crystals. (14.8 g, 70%); mp 293°C (EtOH/DMF), [Found: C, 67.70; H, 3.90; N, 13.10. $C_{12}H_8N_2O_2$ requires C, 67.92; H, 3.80; N, 13.20]; ν_{max} 3440 (br, OH), 2221 (CN); δ_H (200 MHz, DMSO-d_6) 5.70 (s, 1H, pyridine H-5), 7.45 (s, 1H, OH), 7.48–7.52 (m, 5H, arom), 7.55 (s, 1H, OH; *m/z* 212 (M^+, 100%).

Method B: To a solution of **4** (2.4 g, 10 mmol) in 25 mL ethanol was added 2 mL of concentrated hydrochloric acid and the reaction mixture was refluxed for 3 h, then left to cool to room temperature. The solid product formed was filtered off and recrystallized from ethanol/DMF to afford 1.6 g (75%) of a product, which is identical to that obtained from method A.

1.2. Ethyl 2-arylazo-4,4-dicyano-3-phenyl-3-butenoates 7a–d, 5-Arylazo-2,6-dihydroxy-4-phenyl-3-pyridinecarbonitriles 11a–d, 5-arylazo-2,4-dihydroxy-6-phenyl-3-pyridine-carbonitriles 14a–d and 5-arylazo-2-amino-6-phenyl-4-oxo-4*H*-pyran-3-carbonitriles 15a–d (general procedure)

To a cold solution of **4**, **10**, **13** or **12** (10 mmol) and sodium acetate 1.5 g in 35 mL of ethanol was added dropwise a cold solution of diazotized amines **6a–d** (aniline, *p*-anisidine, *p*-chloroaniline, *p*-toluidine, 10 mmol) while stirring. The addition took about 30 min, after which stirring was continued for further 1 h. The coloured solid precipitates were collected by filtration, washed with cold water, and recrystallized from ethanol to afford the title compounds, respectively.

1.2.1. Compound 7a. Brown crystals (2.93 g, 85%), mp 263°C (EtOH); [Found: C, 69.80; H, 4.80; N, 16.40. $C_{20}H_{16}N_4O_2$ requires C, 69.76; H, 4.68; N, 16.27]; ν_{max} (KBr) 3320 (NH), 2210 (CN), 1690 (C=O); δ_H (200 MHz, DMSO-d_6) 1.15 (t, J=7 Hz, 3H, CH_3), 4.1 (q, J=7 Hz, 2H, CH_2), 7.20–7.45 (m, 10H, arom), 7.55 (s, 1H, NH).

1.2.2. Compound 7b. Red powder (2.99 g, 80%), mp 278°C (EtOH); [Found: C, 67.20; H, 4.90; N, 15.10. $C_{21}H_{18}N_4O_3$ requires C, 67.37; H, 4.85; N, 14.96]; ν_{max} (KBr) 3320 (NH), 2215 (CN), 1690 (C═O); δ_H (200 MHz, DMSO-d_6) 1.15 (t, J=7 Hz, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.1 (q, J=7 Hz, 2H, CH_2), 7.02 (d, 2H, arom), 7.25 (d, 2H, arom), 7.40–7.45 (m, 5H, arom), 7.55 (s, 1H, NH); m/z 373 (M^+, 85%), 345 (10.5%), 301 (16.7%), 77 (22.7%).

1.2.3. Compound 7c. Brown powder (2.94 g, 78%), mp 162°C (EtOH); [Found: C, 63.50; H, 3.90; N, 14.90; Cl, 9.40. $C_{20}H_{16}N_4O_2Cl$ requires C, 63.41; H, 3.99; N, 14.79, Cl, 9.36]; ν_{max} (KBr) 3320 (NH), 2210 (CN), 1695 (C═O); δ_H (200 MHz, DMSO-d_6) 1.2 (t, J=7 Hz, 3H, CH_3), 4.0 (q, J=7 Hz, 2H, CH_2), 7.12 (d, 2H, arom), 7.25 (d, 2H, arom), 7.35–7.45 (m, 5H, arom), 7.62 (s, 1H, NH).

1.2.4. Compound 7d. Light brown powder (2.68 g, 75%), mp 170°C (EtOH); [Found: C, 70.50; H, 5.10; N, 15.70. $C_{21}H_{18}N_4O_2$ requires C, 70.38; H, 5.06; N, 15.63]; ν_{max} (KBr) 3330 (NH), 2220 (CN), 1685 (C═O); δ_H (200 MHz, DMSO-d_6) 1.14 (t, J=7 Hz, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.9 (q, J=7 Hz, 2H, CH_2), 7.08 (d, 2H, arom), 7.22 (d, 2H, arom), 7.28–7.48 (m, 5H, arom), 7.60 (s, 1H, NH).

1.2.5. Compound 11a. Dark yellow crystals (2.20 g, 70%), mp 252°C (EtOH); [Found: C, 68.30; H, 3.70; N, 17.80. $C_{18}H_{12}N_4O_2$ requires C, 68.35; H, 3.82; N, 17.71]; ν_{max} (KBr) 3417–3330 (b, OH), 2214 (CN); δ_H (200 MHz, DMSO-d_6) 5.56 (s, 1H), 7.20–7.52 (m, 10H, arom), 7.65 (s, 1H).

1.2.6. Compound 11b. Dark red crystals (2.56 g, 74%), mp 278°C (EtOH); [Found: C, 65.80; H, 4.10; N, 16.10. $C_{19}H_{14}N_4O_3$ requires C, 65.89; H, 4.07; N, 16.18]; ν_{max} (KBr) 3450–3380 (OH), 2210 (CN), 1690 (C═O); δ_H (200 MHz, DMSO-d_6) 3.84 (s, 3H, CH_3), 5.52 (s, 1H), 6.98 (d, 2H, J=8 Hz, arom), 7.25 (d, 2H, J=8 Hz arom), 7.52–7.55 (m, 5H, arom), 7.66 (s, 1H).

1.2.7. Compound 11c. Yellow crystals (2.52 g, 72%), mp>330°C (EtOH/DMF); [Found: C, 61.60; H, 3.20; N, 16.10; Cl, 10.10. $C_{18}H_{11}$ Cl N_4O_2 requires C, 61.64; H, 3.16; N, 15.97; Cl, 10.11]; ν_{max} (KBr) 3400–3350 (OH), 2212 (CN), 1695 (C═O); δ_H (200 MHz, DMSO-d_6) 5.65 (s, 1H), 6.95 (d, 2H, J=8 Hz, arom), 7.22 (d, 2H, J=8 Hz, arom), 7.40–7.50 (m, 5H, arom), 7.64 (s, 1H).

1.2.8. Compound 11d. Orange crystals (2.47 g, 75%), mp 263°C (EtOH); [Found: C, 69.0; H, 4.20; N, 17.10. $C_{19}H_{14}N_4O_2$ requires C, 69.08; H, 4.27; N, 19.96]; ν_{max} (KBr) 3440–3370 (b, OH), 2215 (CN); δ_H (200 MHz, DMSO-d_6) 2.35 (s, 3H, CH_3), 5.45 (s, 1H), 6.93 (d, 2H, arom), 7.16 (d, 2H, arom), 7.30–7.45 (m, 5H, arom), 7.60 (s, 1H).

1.2.9. Compound 14a. Dark brown powder (2.1 g, 66%), mp>330°C (EtOH/DMF); [Found: C, 68.30; H, 3.90; N, 17.80. $C_{18}H_{12}N_4O_2$ requires C, 68.35; H, 3.82; N, 17.71]; ν_{max} (KBr) 3417–3330 (b, OH), 2210, (CN), 1550 (N═N); δ_H (200 MHz, DMSO-d_6) 7.20–7.42 (m, 10H, arom), 8.4 (bs, 2H, 2OH).

1.2.10. Compound 14b. Redish brown powder (2.35 g, 68%), mp 213°C (EtOH); [Found: C, 66.0; H, 4.10; N, 16.20. $C_{19}H_{14}N_4O_3$ requires C, 65.89; H, 4.07; N, 16.18]; ν_{max} (KBr) 3350–3300 (b, OH), 2210 (CN), 1570 (N═N); δ_H (200 MHz, DMSO-d_6) 3.78 (s, 3H, CH_3), 6.88 (d, 2H, J=8 Hz, arom), 7.10 (d, 2H, J=8 Hz arom), 7.20–7.30 (m, 5H, arom), 8.30 (s, 2H, 2OH).

1.2.11. Compound 14c. Brown powder (2.52 g, 72%), mp 293°C (EtOH/DMF); [Found: C, 61.70; H, 3.20; N, 16.10; Cl, 10.20. $C_{18}H_{11}ClN_4O_2$ requires C, 61.64; H, 3.16; N, 15.97; Cl, 10.11]; ν_{max} (KBr) 3400–3350 (OH), 2214(CN), 1575 (N═N); δ_H (200 MHz, DMSO-d_6) 6.98 (d, 2H, J=8 Hz, arom), 7.23 (d, 2H, J=8 Hz, arom), 7.30–7.38 (m, 5H, arom), 8.35 (s, 2H, OH).

1.2.12. Compound 14d. Dark brown powder (2.34 g, 71%), mp>330°C (EtOH/DMF); [Found: C, 69.20; H, 4.30; N, 17.00. $C_{19}H_{14}N_4O_2$ requires C, 69.08; H, 4.27; N, 19.96]; ν_{max} (KBr) 3340–3300 (b, OH), 2210 (CN), 1585 (N═N); δ_H (200 MHz, DMSO-d_6) 2.35 (s, 3H, CH_3), 6.93 (d, 2H, arom), 7.12 (d, 2H, arom), 7.25–7.35 (m, 5H, arom), 8.39 (s, 2H, OH).

1.2.13. Compound 15a. Yellowish green crystals (2.21 g, 70%), mp 310°C (EtOH/DMF); [Found: C, 68.40; H, 3.70; N, 17.70. $C_{18}H_{12}N_4O_2$ requires C, 68.35; H, 3.82; N, 17.71]; ν_{max} (KBr) 3400–3230 (b, OH, NH_2), 2204, (CN), 1560 (N═N); δ_H (200 MHz, DMSO-d_6) 7.25–7.55 (m, 10H, arom), 7.65 (bs, 2H, NH_2).

1.2.14. Compound 15b. Crimson red powder (2.69 g, 78%), mp 248°C (EtOH); [Found: C, 65.80; H, 4.10; N, 16.10. $C_{19}H_{14}N_4O_3$ requires C, 65.89; H, 4.07; N, 16.18]; ν_{max} (KBr) 3410–3290 (b, OH, NH_2), 2210 (CN), 1580 (N═N); δ_H (200 MHz, DMSO-d_6) 3.75 (s, 3H, CH_3), 6.96 (d, 2H, J=7.7 Hz, arom), 7.26 (d, 2H, J=7.7Hz, arom), 7.45–7.55 (m, 5H, arom), 7.62 (s, 2H, NH_2).

1.2.15. Compound 15c. Dark yellow crystals (2.66 g, 76%), mp 262°C (EtOH/DMF); [Found: C, 61.60; H, 3.10; N, 16.10; Cl, 10.10. $C_{18}H_{11}ClN_4O_2$ requires C, 61.64; H, 3.16; N, 15.97; Cl, 10.11]; ν_{max} (KBr) 3400–3350 (OH, NH_2), 2205 (CN), 1595 (N═N); δ_H (200 MHz, DMSO-d_6) 6.94 (d, 2H, J=8 Hz, arom), 7.15 (d, 2H, J=8 Hz, arom), 7.30–7.36 (m, 5H, arom), 8.28 (bs, 2H, NH_2).

1.2.16. Compound 15d. Lemon green crystals (2.34 g, 71%), mp 300°C (EtOH/DMF); [Found: C, 69.10; H, 4.40; N, 16.90. $C_{19}H_{14}N_4O_2$ requires C, 69.08; H, 4.27; N, 16.96]; ν_{max} (KBr) 3330–3200 (b, OH, NH_2), 2214 (CN), 1566 (N═N); δ_H (200 MHz, DMSO-d_6) 2.34 (s, 3H, CH_3), 6.90 (d, 2H, arom), 7.10 (d, 2H, arom), 7.25–7.38 (m, 5H, arom), 8.32 (s, 2H, NH_2).

1.3. Ethyl 1-aryl-5-cyano-6-imino-4-phenyl-1,6-dihydropyridazine-3-carboxylates 8a–d

A mixture of (10 mmol) of each of the azo derivatives **7a–d** and 1 g of ammonium acetate (15 mmol) was fused on an oil bath at 200°C for 2 h. The melt was left to cool to room temperature and triturated with ethanol. The solid precipitates were filtered off and recystallized from acetic acid to

afford the title compounds, which were identical to those previously reported.[4] The identity of the compounds was inferred from comparison of mp, mixed mp, TLC and spectral data.

1.4. 1-Aryl-3-benzoyl-6-hydroxy-4-oxo-1,4-dihydropyridazine-5-carbonitriles 17a–d

To a solution of each of the azopyrans **15a–d** (10 mmol) in 30 mL of glacial acetic acid was added 1 mL of concentrated sulfuric acid and the mixture was refluxed for 1 h, then left to cool to room temperature. The precipitated solid was filtered off and recrystallized to afford **17a–d**.

1.4.1. Compound 17a. Brown crystals (2.0 g, 65%), mp 300°C (EtOH/DMF); [Found: C, 68.30; H, 3.60; N, 13.30. $C_{18}H_{11}N_3O_3$ requires C, 68.14; H, 3.49; N, 13.24]; ν_{max} (KBr) 3380 (br, OH), 2215 (CN), 1720 and 1655 (2 C=O); δ_H (200 MHz, DMSO-d_6), 7.05–7.30 (m, 10H, arom), 11.8 (s, 1H, OH).

1.4.2. Compound 17b. Crimson red powder (2.39 g, 69%), mp 280°C (EtOH/DMF); [Found: C, 65.60; H, 3.90; N, 12.20. $C_{19}H_{13}N_3O_3$ requires C, 65.70; H, 3.77; N, 12.10]; ν_{max} (KBr) 3350 (br, OH), 2210 (CN), 1715 and 1665 (2 C=O); δ_H (200 MHz, DMSO-d_6), 3.80 (s, 3H, CH_3), 6.90 (d, 2H, J=8 Hz, arom), 7.18 (d, 2H, J=8 Hz, arom), 7.25–7.35 (m, 5H, arom), 11.75 (s, 1H, OH).

1.4.3. Compound 17c. Brick red powder (2.0 g, 58%), mp 288°C (EtOH/DMF); [Found: C, 61.40; H, 3.00; N, 12.10; Cl, 10.00. $C_{18}H_{10}$ Cl N_3O_3 requires C, 61.46; H, 2.87; N, 11.95; Cl, 10.08]; ν_{max} (KBr) 3330 (br, OH), 2204 (CN), 1710 and 1668 (2 C=O); δ_H (200 MHz, DMSO-d_6) 6.84 (d, 2H, J=8 Hz, arom), 7.10 (d, 2H, J=8 Hz, arom), 7.24–7.32 (m, 5H, arom), 11.65 (s, 1H, OH).

1.4.4. Compound 17d. Brown powder (2.0 g, 62%), mp 320°C (EtOH/DMF); [Found: C, 69.00; H, 4.10; N, 12.70. $C_{19}H_{13}N_3O_3$ requires C, 68.88; H, 3.95; N, 12.68]; ν_{max} (KBr) 3350 (br, OH), 2210 (CN), 1700 and 1655 (2 C=O); δ_H (200 MHz, DMSO-d_6) 2.36 (s, 3H, CH_3), 6.94 (d, 2H, arom), 7.10 (d, 2H, arom), 7.20–7.34 (m, 5H, arom), 11.69 (s, 1H, OH).

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