Studies with 3-substituted 2-arylhydrazono-3-oxoaldehydes: new routes for synthesis of 2-arylhydrazono-3-oxonitriles, 4-unsubstituted 3,5-diacylpyrazoles and 4-arylazophenols

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Compounds **1a–c** reacts with hydroxylamine-*O*-sulfonic acid or with hydroxylamine hydrochloride in aqueous acetic acid in the presence of sodium acetate to yield the 3-oxoalkanonitriles **3**, which were converted into arylazoisoxazole and 1,2,4-triazine derivatives **10**. The hydrazones **1a–c** reacted with chloroacetone or with phenacyl bromide in refluxing ethanol and in presence of K_2CO_3 to yield the pyrazoles **12a–e**, formed most likely *via* intermediately formed **11a–e**. The reaction of **1a,b** with acetone afforded the arylazophenols.

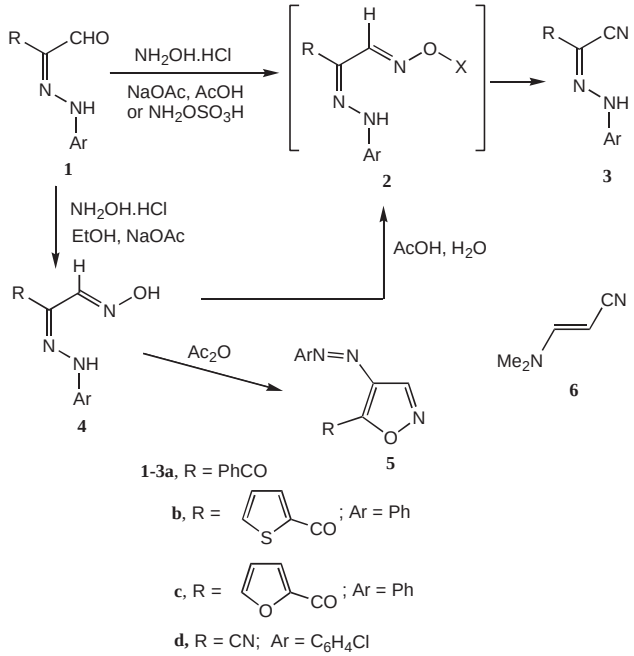
Keywords: oxoalkanonitriles, isoxazoles, pyrazoles, arylazophenols, azo compounds, hydrazones

The utility of 2-arylhydrazonoaldehydes in heterocyclic synthesis has in the past decade received considerable attention.[1-8] In previous work[1,3,4] it has been shown that **1a–c** react with active methylene reagents to yield either 4-arylazopyranones[3] or 6-oxopyridazinones,[1,4,8] depending on the reaction conditions. On the other hand, Jolivet[9] has reported that **1d** reacts with β-keto esters to yield either furopyrrolidines or pyridazinones. The reactivity of 2-arylhydrazonoaldehydes towards substituted acetone,[10] hydrazines,[2] hippuric acid,[3] substituted acetonitriles[3] and dimethyl acetylenedicarboxylate[5] has also been investigated. In conjunction to our interest in exploring the chemistry of arylhydrazonoaldehydes, we report here some results of our investigation into the reactivity of the arylhydrazonoaldehydes **1a–d** toward a variety of nucleophiles. The work offers new simple and efficient routes to 2-arylhydrazono-3-oxonitriles, 3,5-diacylpyrazoles and arylazophenols.

Results and discussion

Compounds **1a–c** reacted with hydroxylamine hydrochloride in refluxing aqueous acetic acid and in the presence of sodium acetate to yield the 3-oxoalkanonitriles **3a–c**, formed *via* intermediacy of the oxime acetates **2a–c**; X = $COCH_3$) (Scheme 1)

Compounds **3a,b** have also been formed on treatment of oximes **4a,b**, prepared from **1a** and hydroxylamine hydrochloride as described earlier,[3] with aqueous acetic acid, whereas reflux in acetic anhydride afforded, as reported earlier,[2] arylazoisoxazoles **5**. It is believed that **4** are acylated in acetic acid solution and that these acylated (**2;** X = $COCH_3$) derivatives either undergo thermal elimination of acetic acid to yield **3** or cyclise *via* attack of the oxime lone pair on carbonyl carbon depending on applied reaction conditions. Compounds **1a–c** were also converted into **3** on short reflux with hydroxylamine *O*-sulfonic acid.; attempts to isolate intermediate oximesulfonates (**2**; X = SO_3H) failed. This is understandable in the light of the facile sulfuric acid elimination that would lead to compounds **3a–c**. Compound **3a** has been obtained via coupling 3-amino-3-phenylacrylonitrile[12] or benzoylacetonitrile[13] with benzene diazonium chloride. Compounds **3b,c** were also prepared earlier from reaction of cyanide ions with aroylhydrazonyl halides.[14] More recently, Abdul Khalik *et al.* reported formation of **3a–c** via treatment of arylhydrazonopropanals in pyridine.[2] Reported syntheses of **3a–c** are limited in scope either by the difficulty in obtaining the starting materials in good yields or by the necessity of involvement of cyanide ion in the synthesis. Abdul Khalik's synthesis[2] when repeated by us afforded **3a–c** in a maximum of 30% yield.



Scheme 1

We were interested to see if this conversion of arylhydrazonals into nitriles is a general one. Consequently, the enaminonitrile **6**, prepared as described in the literature[15] was coupled with *p*-chlorobenzenediazonium chloride and then the arylhydrazone **1d** was treated with hydroxylaminesulfonic acid in refluxing ethanol, whereby 2-[(4-chlorophenyl)hydrazono]malononitrile **3d** was formed in excellent yield. However, we failed to convert **1d** into **3d** with hydroxylamine hydrochloride and sodium acetate.

Compounds **3a–c**, so formed, proved valuable precursors to arylazoazoles. For example, reacting **3a,b** with hydroxylamine hydrochloride in ethanol in the presence of sodium acetate afforded the amidoximes **7a,b**. Compound **7a** was cyclised to the isoxazole **8** on reflux in ethanolic sodium ethoxide. Amidoxime **7a** and isoxazole **8** have been obtained earlier by one of us.[16]

Reacting **7b** with dimethylformamide dimethylacetal afforded a product that may be formulated as **9** or the isomeric **10.** Structure **10** was preferred for this reaction product, based on the fact that irradiation of the dimethylamino proton signal at δ 3.6 ppm enhances the aryl proton absorptions. Such enhancement in **9** is not possible (*cf.* Scheme 2).

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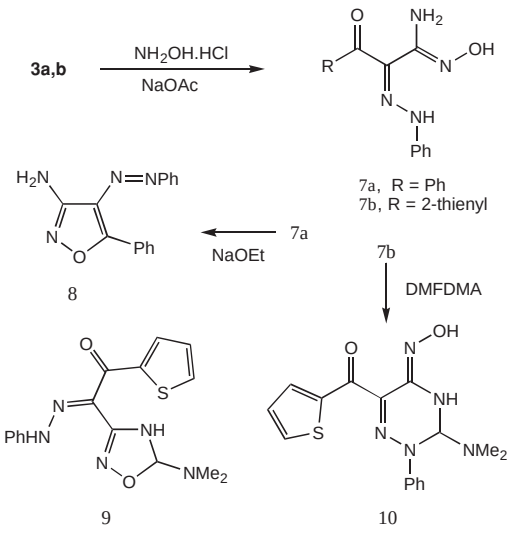
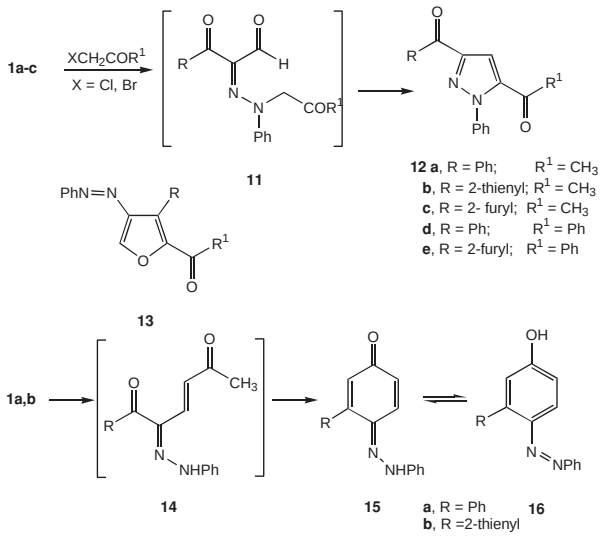


Scheme 2



Scheme 3

Compounds **1a–c** reacted with chloroacetone to give products that may be formulated as pyrazoles **12a–e** or isomeric arylazofurans **13a–e**. Similarly reaction of **1a–c** with phenacyl bromide afforded **12d,e** or **13d,e**. The furan structure **13** was readily ruled out based on the observed coupling between the carbon and pyrazole H-4 is HMBC experiments. Thus, structure **12** could be established. It is believed that **12a–e** are formed *via* intermediates **11a–e** which, however, could not be isolated.

Since this reaction represents a new simple and efficient route to hitherto unreported 3,5-aroylacyl and diaroyl pyrazoles, we tried to expand its scope to enable also synthesis of 4-substituted 3,5-diacylpyrazoles. However, under a variety of conditions, we failed to react 2-arylhydrazono-1,3-diketones, 2-arylhydrazono-3-oxo esters and 2-aryl-hydrazono-3-oxonitriles with chloroacetone. In all cases, unreacted arylhydrazones were isolated. Although in theory, formation of intermediate alkylated hydrazone can occur in a way parallel to the reaction with **1a–c**, cyclisation of this alkylated product to a pyrazole is difficult on account of steric crowding in the resulting pyrazole. It seems that the alkylated pyrazole readily reverts to starting if it does not further cyclise.

Compounds **1a,b** reacted with acetone in the presence of catalytic amounts of triethylamine to yield the arylazophenols **16**, formed most likely *via* intermediacy of **14** and **15**. This finds a parallel in the recently reported formation of arylazophenols on reacting benzotriazolylacetone with **2a–c**[10] (Scheme 3). The same azo derivative has been claimed as an oil, resulting from the coupling of 3-biphenylol with benzenediazonium chloride.[11] This is in contrast to the finding that our product is a solid of melting point 160 °C, as could be expected for phenylazophenols. It is quite possible that the previously reported product is an isomer of our compound in which coupling occurred at an *ortho* position to the phenolic group.

Experimental

IR spectra were recorded in KBr with a Pye Unicam SP 1100 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian EM-390, 400 MHz spectrometer, in DMSO as solvent unless otherwise stated, and using TMS as internal standard; chemical shifts are reported in δ units (ppm). Mass spectra were measured on MS 30 and MS 9 (AEI) spectrometers, with EI 70 eV. Microanalyses were performed on a LECO CHNS-932 instrument. Compounds **1a–c** were prepared following published procedure.[1] Similarly, compounds **4a,b** were prepared according to the literature.[2]

2-p-Chlorophenylhydrazono-3-oxopropionitrile (**1d**): A solution of *p*-chlorobenzenediazonium chloride, prepared from 0.01 mol of *p*-chloroaniline and appropriate amount of hydrochloric acid and sodium nitrite as earlier described[17], was added to a solution of **6** (10 mmol) in ethanol (10 ml) containing anhydrous sodium acetate (1g) with stirring, over 15 minutes. The reaction mixture was left to stand at room temperature for two hours and the solid product which formed was was collected by filtration and crystallised from ethanol.

Compound **1d** formed red crystals, yield 1.35 g (65%), m.p. 156 °C; IR (cm^{-1}) 3400–3300 (CN) and 1705 (CO); MS (EI) *m/z* (%) = 207 [M$^+$]; ^{1}H NMR: δ 13.2 (s,1H, NH), 10.0 (s, 1H, formyl H) and 8.4–8.0 (dd, 4H, aryl H); ^{13}C NMR: δ 196.7 (formyl C); 113.5 (CN); 133.9 (C=N), 130.6; 129.8, 127.4, 122.6 (aryl C). Anal. Calcd. for $C_9H_6ClN_3O$ (207.65): C, 52.05; H, 2.91; N, 20.23. Found: C, 52.30; H, 2.92; N, 20.56 %.

General procedures for the preparation of compounds **3a–d**

Method A: To a stirred suspension of the hydrazono-aldehyde (**1a–d**) (10 mmol) in acetic acid (10 ml) containing sodium acetate (3g), hydroxylamine hydrochloride (10 mmol) was added. The reaction mixture was heated under reflux for 4 h, and then poured onto water. The solid product which separated was collected by filtration and crystallised from ethanol.

3-Oxo-3-phenyl-2-(phenylhydrazono)-propionitrile (**3a**) formed yellow crystals; yield: 2.16 g (87%); m.p. 141 °C, (lit.[12,13] m.p. 131–136 °C), IR (cm^{-1}): 3500–3300 (chelated H), 2214 (CN); 1653 (CO); MS (EI) *m/z* (%) 249 [M$^+$]; ^{1}H NMR: δ 9.5 (s,1H, NH), 8.04–7.23 (m, 10H, arom H). ^{13}C NMR: δ 188.5 (CO), 117.4 (CN), 143.6 (C=N), 112.5, 114.2, 126.1, 129.1, 130.5, 130.8, 133.3, 137.4 (arom. C). Anal. Calcd. for $C_{15}H_{11}N_3O$ (249.27): C, 72.27; H, 4.44; N, 16.85. Found: C, 72.27; H, 4.49; N, 16.88 %.

3-Oxo-2-(phenylhydrazono)-3-(thien-2-yl)-propionitrile (**3b**) formed yellow crystals; yield: 2.24 g (88%) , m.p. 214 °C (lit.[14] m.p. 193–195 °C): IR (cm^{-1}) 3448–3300 (NH); 2216 (CN); 1686 (CO), MS (EI) *m/z* (%) 255 [M$^+$]. ^{1}H NMR: δ 12.38 (s,1H, NH), 8.10 (1H; thienyl H-5), 8.00 (1H; thienyl H-3), 7.60 (d, 2H arom H-2 and H-6), 7.44 (m, 2H phenyl H-2 and H-5), 7.21 (m, 1H thienyl H-4), ^{13}C NMR: δ 178.3 (CO), 117.9 (CN), 143.0 (C=N), 138.8, 137.2, 136.0, 130.6, 128.9, 126.3, 114.3, 112.1 (arom. C). Anal. Calcd. for $C_{13}H_9N_3OS$ (255.30): C, 61.16; H, 3.55; N, 16.45; S, 12.56. Found: C, 61.20; H, 3.81; N, 15.75; S, 12.36 %.

3-(Furan-2-yl)-3-oxo-2-(phenylhydrazono)-propionitrile (**3c**) formed yellow crystals, yield 2.0 g (84%), m.p. 164 °C (lit.[13] m.p. 164 °C); IR (cm^{-1}) 3448–3226 (NH), 2214 (CN); 1685 (CO); MS: *m/z* (%) 239 [M$^+$]; ^{1}H NMR: δ 12.35 (s,1H, NH), 8.12-6.80 (m, 8H, Ph and furyl H-3, H-4, H-5), ^{13}C NMR: δ 174.0 (CO), 117.7 (CN), 149.9 (C=N), 149.3, 143.1, 130.6, 126.2, 122.5, 113.8, 113.7, 112.1 (arom. C). Anal. Calcd. for $C_{13}H_9N_3O_2$ (239.23): C, 65.26; H, 3.79; N, 17.56. Found: C, 66.32; H, 3.79; N, 17.22 %.

2-[(4-chlorophenyl)hydrazono]-malononitrile (**3d**) formed yellow crystals; m.p. 189 °C (lit.[18] m.p. 191 °C). IR (cm^{-1}) 3350 (NH); 2210 (CN), MS (EI, 70 EV) *m/z* (%) = 204 [M$^+$].

Method B: A solution of **1a–d** (10 mmol) in acetic acid (10 ml) containing sodium acetate (3g) was treated with hydroxylamine-*O*-sulfonic acid (10 mmol). The reaction mixture was refluxed for 4h, then left to stand at room temperature. The solid product so formed

was collected by filtration and crystallised from ethanol. Compounds **3a–d** were formed in 90, 89, 85 and 60% yields, respectively.

General procedure for the preparation of compounds **7a,b**

Compound **3a,b** (10 mmol), hydroxylamine hydrochloride (0.69 g, 10 mmol) and sodium acetate (3 g) in ethanol (20 ml) were heated under reflux for 2h. The solvent was reduced under vacuum and the residue was poured onto water. The solid product was collected by filtration and crystallised from ethanol.

N-hydroxy-3-oxo-3-phenyl-2-(phenylhydrazono)-propionamidine (**7a**) formed yellow crystals, yield 2.49 g (88%), m.p. 148 °C, IR (cm^{-1}) 3482 (OH), 3371–3080 (NH, NH_2) and 1612 (CO); MS (EI) *m/z* (%) 282 [M^+]; ^{1}H NMR: δ 13.68 (s,1H, NH), 10.29 (s,1H, OH), 7.79–7.00 (m, 10H arom H), 5.62 (2H, NH_2) Anal. Calcd. for $C_{15}H_{14}N_4O_2$ (282.30): C, 63.82; H, 4.99; N, 19.84. Found: C, 63.99; H, 5.00; N, 19.47 %.

N-hydroxy-3-oxo-2-(phenylhydrazono)-3-thiophen-2-yl-propionamidine (**7b**) formed yellow crystals, yield 1.96 g (68%), m.p. 154 °C, IR (cm^{-1}) 3450 (OH), 3338–3200 (NH,NH_2) and 1646 (CO), MS (EI) *m/z* (%) 288 [M^+]; ^{1}H NMR: δ 13.82 (1H, hydrazone NH); 10.34 (1H, oxime OH); 8.05–7.11 (8H, arom and thienyl H); 6.50 (2H, NH_2). ^{13}C NMR: δ 195.8 (CO); 186.9 (amidoximyl C), 143.2 (CNO-); 139.0, 138.7, 137.5, 134.3, 133.9, 130.9, 130.1, 128.0 (arom, thienyl C). Anal. Calcd. for $C_{13}H_{12}N_4O_2S$ (288.32): C, 54.15; H, 4.19; N, 19.43; S, 11.12. Found: C, 54.72; H, 4.21; N, 19.09; S, 11.10 %.

5-Phenyl-4-(phenylazo)isoxazol-3-ylamine (**8**): The amidoxime **7a** (2.82 g, 10 mmol) in ethanolic sodium ethoxide was refluxed for 2h. The solvent was reduced under vacuum, and the remaining material was poured into water and neutralised with dilute hydrochloric acid. The solid product was collected by filtration and crystallised from ethanol.

Compound **8** formed yellow crystals, yield 2.25 g (85%), m.p. 173 °C, lit.[16] m.p. 186 °C. IR (cm^{-1}) 3443, 3268 (NH_2); 1623 (N=N), MS (EI) *m/z* (%) 264 [M^+]; ^{1}H NMR: δ 8.21–7.52 (m, 10H, 2Ph); 6.65 (s, 2H, NH_2), ^{13}C NMR: δ 167.8, 157.3, 153.2, 132.5, 132.1, 130.7, 130.3, 128.7, 127.7, 125.3, 123.3, (isoxazole and arom. C), Anal. Calcd. for $C_{15}H_{12}N_4O$ (264.28): C, 68.17; H, 4.57; N, 21.19. Found: C, 68.31; H, 4.61; N, 21.12 %.

3-Dimethylamino-2-phenyl-6-(thiophene-2-carbonyl)-3,4-dihydro-2H-1,2,4-triazin-5-one oxime (**10):** The amidoxime **7b** (0.5 g) was stirred at room temperature overnight with dimethylformamide dimethylacetal (1.0 ml). The solid product formed was triturated with water, collected by filtration, and crystallised from ethanol.

Compound **10** formed yellow crystals, m.p. 168 °C; yield 65%. IR (cm^{-1}) 3422 (NH), 1684, 1654 (CO and C=N). ^{1}H NMR: δ 8.56 (s, H, NH), 8.52–6.80 (m, 8H, arom and thienyl H), 6.51 (s, 1H, triazine H-6) and 3.36 [6H, $N(CH_3)_2$], Anal. Calcd. For $C_{16}H_{17}N_5O_2S$ (343.11): C, 55.96; H, 4.99; N, 20.39; S, 9.34. Found: C, 56.59; H, 4.37; N, 20.75; S, 9.74 %.

General procedure for the preparation of compounds **12a–e**

Each of compounds **1a–c** (10 mmol) were added to the appropriate α-haloketone (10 mmol) in ethanol (20 ml) in the presence of potassium carbonate (1.38 g). The reaction mixture was refluxed for 3h, then poured onto water. The solid product so formed was collected by filtration and crystallised from dioxane.

1-(5-Benzoyl-2-phenyl-2H-pyrazol-3-yl)ethanone (**12a**): orange crystals, yield 2.40 g (83%), m.p. 160 °C. IR (cm^{-1}) 1701, 1685 (CO), MS (EI) *m/z* (%) 290 [M^+]; ^{1}H NMR ($CDCl_3$): δ 8.43-7.23 (m, 11H, Arom and pyrazole H-4), 2.6 (s, 3H, CH_3), ^{13}C NMR: δ 189.4 (CO); 187.6 (CO), 150.7, 141.9, 141.1, 137.3, 134.3, 131.2, 129.9, 129.8, 129.6, 126.9, 116.5, (arom and pyrazolyl carbons), 29.9 (CH_3), Anal. Calcd. for $C_{18}H_{14}N_2O_2$ (290.32): C, 74.46; H, 4.85; N, 9.64. Found: C, 74.39; H, 4.92; N, 9.64 %.

1-[2-Phenyl-5-(thiophene-2-carbonyl)-2H-pyrazol-3-yl]-ethanone (**12b**): brown crystals, yield 2.58 g (87%); m.p. 172 °C, IR (cm^{-1}) 1650, 1654 (CO), MS (EI) *m/z* (%) 296 [M^+]; ^{1}H NMR ($CDCl_3$): δ 8.55–7.00 (m, 9H, thienyl and pyrazole H), 2.6 (s, 3H, CH_3); ^{13}C NMR (DMSO): δ 189.4 (CO), 178.6 (CO), 150.4 (pyrazole C-3), 142.0 (pyrazolyl C-5), 142.4 (thienyl C-2), 141.1 (thienyl C-5), 125.8 (thienyl C-4), 115.8 (pyrazolyl C-4), 137.4, 137.20, 130.0, 129.9, 129.8 (phenyl and thienyl C-3), 29.9 (CH_3), Anal. Calcd. for $C_{16}H_{12}N_2O_2S$ (296.34): C, 64.84; H, 4.08; N, 9.45; S, 10.82. Found: C, 64.02; H, 4.01; N, 9.78; S, 10.78 %.

1-[5-(Furan-2-carbonyl)-2-phenyl-2H-pyrazol-3-yl)-ethanone (**12c**): yield: 2.20 g (78%); m.p. 162 °C; IR (cm^{-1}) 1687, 1646 (CO); MS (EI) *m/z* (%) 280 [M^+]. ^{1}H NMR ($CDCl_3$): δ 8.00–7.28 (m, 8H, furyl and phenyl H), 6.60 (s, 1H, pyrazolyl H-4) and 2.59 (s, 3H, CH_3). ^{13}C NMR (DMSO): δ 189.3 (CO); 173.5 (CO); 151.2, 150.1, 149.9, 141.9, 141.1, 129.9, 129,8, 126.8, 124.0, 115.8, 113.9 (arom; pyrazolyl and thienyl carbons), 29.95 (CH_3). Anal. Calcd. for $C_{16}H_{12}N_2O_3$ (280.28): C, 68.56; H, 4.31; N, 9.99. Found: C, 68.46; H, 4.40; N, 9.96 %.

(5-Benzoyl-1-phenyl-1H-pyrazol-3-yl)-phenyl-methanone (**12d**) formed brown crystals, yield 2.01 g (57%); m.p. 147 °C, IR (cm^{-1}) 1663, 1652 (CO). MS (EI) *m/z* (%) 352 [M^+]. ^{1}H NMR: δ 8.26 (d, *J* = 11 Hz ,C-3 benzoyl H-4), 7.97 (d, *J* = 11 Hz ,C-5 benzoyl H-4), 7.77–7.45 (m, 13H, other Aryl H), 7.40 (s, 1H, pyrazolyl H-4), ^{13}C NMR: δ 187.8 (CO); 186.0 (CO), 150.7, 141.3, 140.3, 137.3, 137.0, 135.4, 134.4, 131.2, 130.7, 130.3, 130.0, 130.0, 129.6, 126.0, 116.2 (arom and pyrazolyl carbons), Anal. Calcd. for $C_{23}H_{16}N_2O_2$ (352.39): C, 78.39; H, 4.57; N, 7.94. Found: C, 78.41; H, 4.62; N, 8.10 %.

(5-Benzoyl-1-phenyl-1H-pyrazol-3-yl)-furan-2-yl-methanone (**12e**) formed dark brown crystals, yield 1.80 g (53%); m.p. 162 °C, IR (cm^{-1}) 1717,1646 (CO); MS (EI) *m/z* (%) 342 [M^+]. ^{1}H NMR: δ 7.74 (s, H, pyrazolyl H-4), 8.16–7.46 (m, 13H, arom and furyl H). ^{13}C NMR: δ 185.9 (CO); 173.7 (CO), 151.2, 149.9, 150.1 (pyrazole C-3 and C-5 and furyl C-2 not necessarily respectively), 114.0 (pyrazole C-4), 115.5 (furyl C-4), 141.3, 140.3, 136.9, 135.4, 130.7, 130.3, 130.0, 130.0, 125.9, 124.3 (arom and furyl carbons C-3 and C-5), Anal. Calcd. for $C_{21}H_{14}N_2O_3$ (342.35): C, 73.67; H, 4.12; N, 8.18. Found: C, 73.16; H, 4.24; N, 8.32 %.

General Procedure for the preparation of compounds **16a,b:** Compound **1a,b** (10 mmol) was refluxed in acetone (0.58 g, 10 mmol) in the presence of triethylamine (2 ml) for 4 h. The solvent was reduced under vacuum. The remaining product was poured onto water and neutralised with dilute hydrochloric acid. The solid product was collected by filtration and crystallised from dioxane.

6-(Phenylazo)biphenyl-3-ol (**16a**) formed brown crystals, yield: 2.00 g (73%), m.p. 160 °C; IR (cm^{-1}) 3448 (OH); MS (EI) *m/z* (%) 274 [M^+]. Anal. Calcd. for $C_{18}H_{14}N_2O$ (274.32): C, 78.81; H, 5.14; N, 10.21. Found: C, 78.62; H, 5.28; N, 10.46 %.

4-(Phenylazo)-3-thiophen-2-yl-phenol (**16b**) formed brown crystals, yield 1.80 g (64%), m.p. 158 °C; IR (cm^{-1}): 3450 (OH); MS (EI) *m/z* (%): 280 [M^+]. Anal. Calcd. for $C_{16}H_{12}N_2OS$ (280.34): C, 68.54; H, 4.31; N, 9.99; S, 11.43. Found: C, 68.79; H, 4.33; N, 10.03; S, 11.16 %.

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