

Enaminones as building blocks in organic syntheses: on the reaction of 3-dimethylamino-2-propenones with malononitrile

Saleh M. Al-Mousawi,*^a Moustafa Sherief Moustafa,^a Mervat Mohammed Abdelkhalik,^b and Mohamed Hilmy Elnagdi^a

^a*Department of Chemistry, Faculty of Science; University of Kuwait: Safat; 13060: P.O. Box 12613, Kuwait*

^b*Applied Science Department, College of Technological Studies, Public Authority for Applied Education and Training, P.O. Box 5969 Safat, 13060, Kuwait*
E-mail: saleh.almousawi@hotmail.com

Abstract

An X-ray crystal structure for the product of reacting enaminones and malononitrile in ethanol with piperidine conclusively established its structure as dienamides **4a,b** that cyclize to 1,2-dihydropyridine-3-carbonitriles **5** on treatment with acetic anhydride in the presence of hydrochloric acid. Reaction of **4a** with a second mol equivalent of malononitrile afforded 2-[3-(dimethylamino)-3-phenyl-2-propenylidene]malononitrile **7** that was also converted into **5**, and to 5-phenyl-1*H*-pyrazole **9** via treatment with hydrazine hydrate. Reaction of enaminone **1a** with ethyl cyanoacetate in the presence of piperidine afforded the pyranone derivative **12**.

Keywords: Enaminones, malononitrile, dienonitrile, pyridones, dienodinitrile, and pyranone

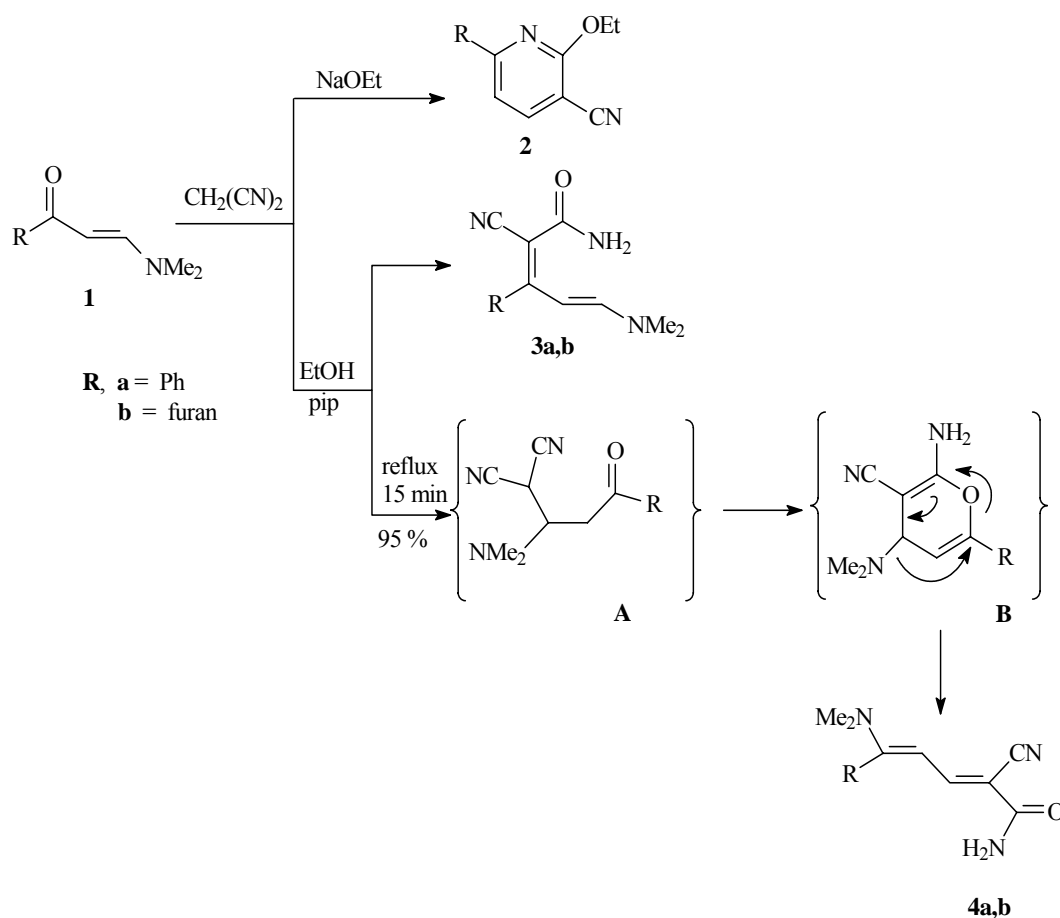
Introduction

Enaminones are versatile building blocks in organic synthesis and their chemistry has received considerable interest.¹ In the last decade we have reported efficient syntheses of polyfunctional molecules utilizing enaminones as starting materials.²⁻¹⁰ Our synthetic approaches have attracted attention.¹¹⁻¹⁵ Sometime ago we reported that enaminones **1** react with malononitrile in refluxing ethanolic sodium ethoxide solution to yield alkoxyppyridines **2**.¹⁶ However, it was subsequently noted that in ethanolic piperidine solution compound **3** was produced.¹⁷ Recently Kappe *et al.*¹⁸ reported a 1,4-addition of malononitrile to enaminones using microwave heating. This led us to reconsider the structure assigned for **3**, as if it were correct it would be the only example of 1,2-addition of an active methylene to an enaminone. Recently we¹⁹ concluded that **3** actually has structure **4** based on spectral data (*cf.* Scheme 1). It seemed to us of value to further confirm this

conclusion and to explore the chemistry of this newly formed diene. In addition, examining the behavior of other active methylenes towards **1b** under similar conditions seemed of value.

Results and Discussion

Both **1a,b** were reacted with malononitrile in ethanolic piperidine to yield products whose analytical and spectral data agree well with both the old structures **3a,b** and revised ones **4a,b**. Firstly we obtained an X-ray crystal structure for the product of reacting **1a** with malononitrile in ethanolic piperidine. We assume that malononitrile initially undergoes 1,4 addition to the double bond in **1a,b** yielding the adduct **A** that cyclizes into aminopyran **B** before undergoing a rearrangement to **4a,b** via a 1,3-nitrogen shift. The X-ray data²⁰ established the structure of 2-cyano-5-(dimethylamino)-5-(furan-2-yl)-penta-2,4-dienamide **4b**, clearly confirming previous recent conclusion.¹⁹ It also shows that the molecule adapts the (*E,E*) form indicated (*cf.* Figure 1 and Table 1).



Scheme 1. Syntheses of dienonitriles **4a,b**.

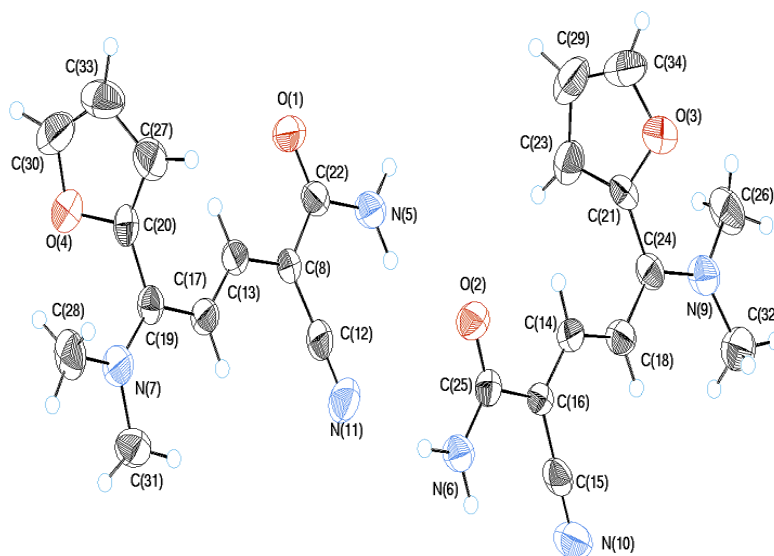


Figure 1. X-ray crystal structure of compound **4b** 2-cyano-5-(dimethylamino)-5-(furan-2-yl)penta-2,4-dienamide. Typical bond lengths and bond angles are reported in Table 1.

Table 1. Selected bond lengths and bond angles for compound **4b**

Bond lengths		Bond angles	
Atoms numbers	Geometric parameters (Å, °)	Atoms numbers	Geometric parameters (Å, °)
N7—C19	1.350 (5)	C19—N7—C28	122.6 (3)
N7—C28	1.469 (5)	C19—N7—C31	121.4 (3)
N7—C31	1.451 (5)	C28—N7—C31	115.5 (3)
C8—C13	1.372 (5)	C12—C8—C13	119.8 (3)
C8—C22	1.467 (5)	C12—C8—C22	119.8 (3)
C13—C17	1.406 (5)	C18—C8—C22	120.3 (3)
C17—C19	1.377 (5)	C8—C13—C17	126.3 (3)
		C13—C17—C19	124.2 (3)
		N7—C19—C17	122.2 (3)
		N7—C19—C20	117.0 (3)
		C17—C19—C20	120.8 (3)

Compound **4a** could be converted into pyridone **5** upon treatment with acetic anhydride in the presence of hydrochloric acid whereas in AcOH/HCl compound **6** was produced. It is logical to assume the hydrolysis of the initially formed **5** under this condition. Unexpectedly, reacting **4a** with malononitrile in ethanolic piperidine resulted in the formation of the dienodinitrile **7** in an excellent yield (95 %). We assume that malononitrile initially added to **4a** forming the Michael adduct **8** that then loses cyanoacetamide to yield 2-(3-(dimethylamino)-3-

phenylallylidene)malononitrile **7**. Structure **7** was confirmed by an X-ray crystal structure¹⁶ determination (*cf.* Figure 2).

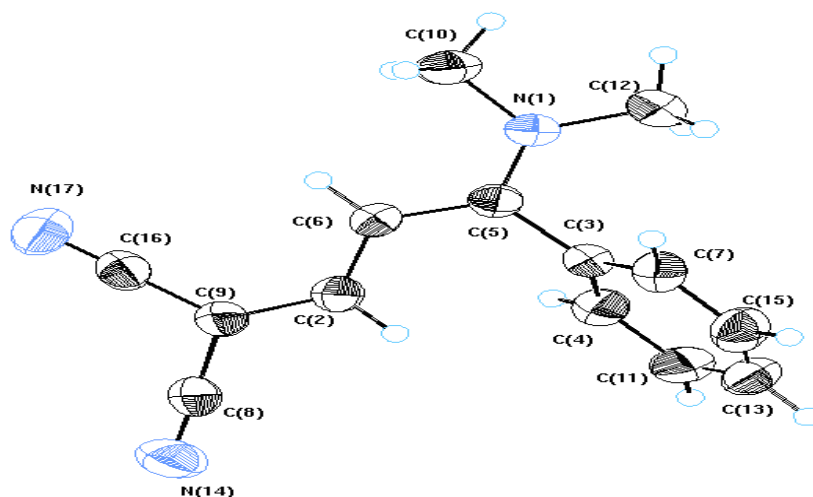


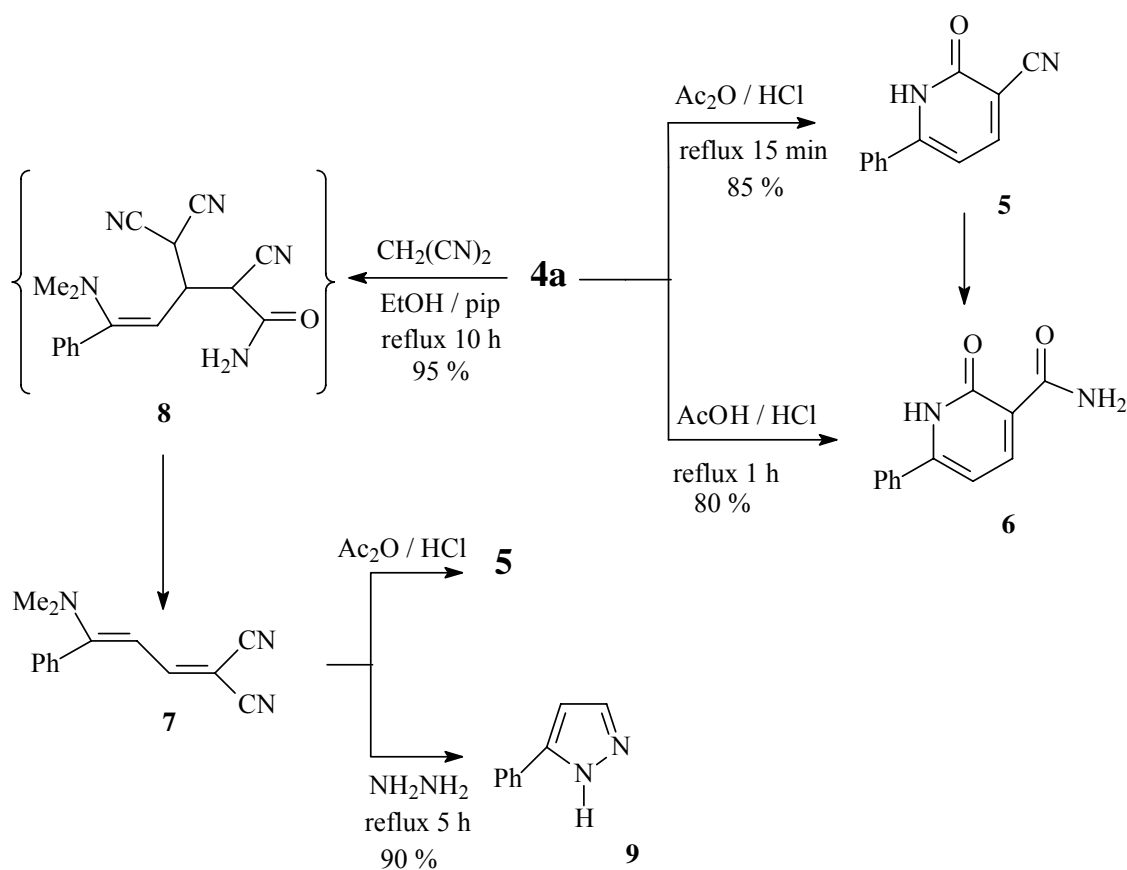
Figure 2. X-ray crystal structure of 2-(3-(dimethylamino)-3-phenylallylidene)-malononitrile **7**.

The data clearly indicate that, the molecule adapts an E configuration. In Table 2 selected bond lengths and bond angles are reported.

Table 2. Selected bond lengths and bond angles for compound **7**

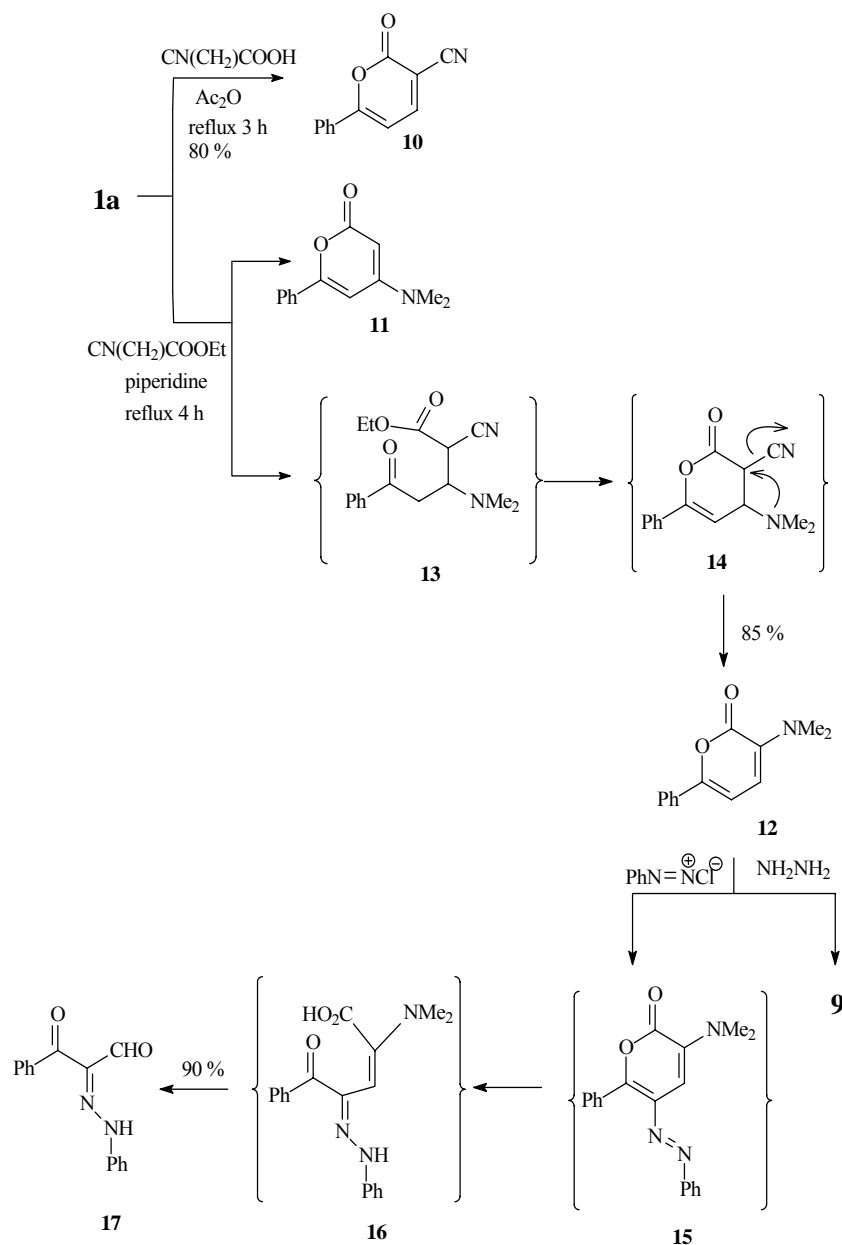
Bond lengths		Bond angles	
Atoms numbers	Geometric parameters (Å, °)	Atoms numbers	Geometric parameters (Å, °)
N1—C5	1.336 (2)	C5—N1—C10	121.6 (2)
N1—C10	1.466 (2)	C5—N1—C12	123.35 (15)
N1—C12	1.467 (2)	C10—N1—C12	114.89 (14)
C2—C6	1.399 (2)	C6—C2—C9	126.7 (2)
C2—C9	1.379 (2)	N1—C5—C3	117.7 (2)
C3—C5	1.494 (2)	N1—C5—C6	122.4 (2)
C5—C6	1.391 (2)	C3—C5—C6	119.91 (15)
		C2—C6—C5	122.3 (2)
		C2—C9—C8	121.1 (2)
		C2—C9—C16	123.0 (2)
		C8—C9—C16	115.8 (2)

Compound **7** was readily converted into **5** on refluxing with $\text{Ac}_2\text{O}/\text{HCl}$. Reacting **7** with hydrazine hydrate afforded 5-phenylpyrazole **9**¹⁶ (cf. Scheme 2).



Scheme 2. Syntheses of pyridone **5** and dienodinitrile **7**.

In the light of the established behavior of **1** toward malononitrile we inspected its behavior toward other active methylene reagents. Reaction of **1a** with cyanoacetic acid in Ac_2O afforded the pyranone **10** while reaction with ethyl cyanoacetate in ethanolic piperidine gave a product that could be assigned structure **11** or its isomer **12**, based on the analytical and the spectral data. ^1H NMR data indicated the presence of two doublet protons at $\delta = 5.81$ and $\delta = 7.71$ ppm with $J = 12$ Hz, typical for adjacent *cis* protons. Thus structure **12** is preferred over **11**. It is assumed that the initially formed Michael adduct **13** cyclized to **14** and that the latter then undergoes a 1,2-dimethylamino group shift accompanying the elimination of the cyano group to yield the final isolable **12**. The latter was readily converted into compound **9** when reacted with hydrazine hydrate. Coupling 3-(dimethylamino)-6-phenyl-2*H*-pyran-2-one **12** with benzenediazonium chloride afforded the known phenylhydrazone **17**. It is believed that initially **15** is formed then undergoes ring opening to **16** and then is hydrolyzed under coupling reaction conditions to yield phenylhydrazone **17** (cf. Scheme 3). At the moment we are looking into the behavior of **1b** with a variety of other enaminones.



Scheme 3. Syntheses of pyranone **10** and phenylhydrazone **17**.

Conclusions

We could thus revise, with certainty, the reported structures for products of reacting enaminones **1a** with malononitrile and proved that the product is the diene 2-cyano-5-(dimethylamino)-5-phenylpenta-2,4-dienamide **4a**.

Experimental Section

General Procedures. All melting points are uncorrected and were determined on a Sanyo (Gallaenkamp) instrument. Infrared spectra were recorded in KBr on a Perkin-Elmer 2000 FT-IR system. ^1H -NMR and ^{13}C -NMR spectra were determined on a Bruker DPX spectrometer operating at 400 MHz for ^1H -NMR and 100 MHz for ^{13}C -NMR using in CDCl_3 or $\text{DMSO}-d_6$ as solvents and TMS as internal standard; chemical shifts are reported in δ (ppm). Mass spectra were measured on VG Autospec Q MS 30 and MS 9 (AEI) spectrometers, with EI 70 EV. Elemental analyses were measured by means of LEOCHNS-932 Elemental Analyzer. General purpose silica gel on polyester 20 x 20 cm TLC plates with UV indicator were used in TLC experiments.

Synthesis of 2-cyano-5-(dimethylamino)-5-phenylpenta-2,4-dienamide (4a). A mixture of **1a** (1.75 g, 0.01 mol) and malononitrile (0.66 g, 0.01 mol) in ethanol (15 mL) as a solvent was treated with piperidine (5 drops). The reaction mixture was refluxed for 15 min, and then was poured into ice-water. The solid, so formed, was collected by filtration and recrystallized from *N,N*-dimethylformamide (DMF) to give yellow crystals; yield 95%; mp 259-60 °C. *Anal.* Calcd for $\text{C}_{14}\text{H}_{15}\text{N}_3\text{O}$ (241.29): C, 69.69; H, 6.27; N, 17.41% Found: C, 69.78; H, 5.93; N, 17.48% IR (KBr): $\nu_{\text{max}} = 333, 3293 (\text{NH}_2), 2193 (\text{CN}), 1647 (\text{CO})$; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ , ppm = 2.50 (s, 3H, CH_3), 2.78 (s, 3H, CH_3), 5.63 (d, $J = 12$ Hz, 1H, CH), 6.82 (s, 2H, NH_2 , D_2O exchangeable), 7.11 (d, $J = 12$ Hz, 1H, CH), 7.25-7.55 (m, 5H, Ar-H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ , ppm = 165.55, 164.71, 153.38, 133.92, 129.65, 128.83 (2C), 128.78 (2C), 119.01, 99.03, 87.53, 66.38, 42.01. MS: m/z (%) 241 (M^+ , 100), 223 (15), 197 (75), 182 (15), 158 (40), 127 (15), 118 (35), 91 (10), 77 (20).

Synthesis of 2-oxo-6-phenyl-1,2-dihydropyridine-3-carbonitrile (5). A mixture of compound **4a** (2.41 g, 0.01 mol) and acetic anhydride (Ac_2O) (15 mL) as a solvent was treated with hydrochloric acid (5 mL), then the mixture was refluxed for 15 min. The reaction mixture was cooled and poured into ice-water. The solid, so formed, was collected by filtration and recrystallized from ethanol to give faint yellow product; yield 85%; mp 295-97 °C. *Anal.* Calcd for $\text{C}_{12}\text{H}_8\text{N}_2\text{O}$ (196.21): C, 73.46; H, 4.11; N, 14.28% Found: C, 73.09; H, 3.97; N, 14.25% IR (KBr): $\nu_{\text{max}} = 3151 (\text{NH}), 2222 (\text{CN}), 1648 (\text{CO})$; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ , ppm = 6.77 (d, $J = 8$ Hz, 1H, CH), 7.53-7.82 (m, 5H, Ar-H), 8.21 (d, $J = 8$ Hz, 1H, CH), 12.79 (br, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ , ppm = 161.27, 152.82, 148.59, 132.21, 131.18, 128.99 (2C), 127.59 (2C), 116.69, 104.83, 100.7 4. MS: m/z (%) 196 (M^+ , 100), 168 (40), 140 (15), 115 (10), 77 (10).

Synthesis of 2-oxo-6-phenyl-1,2-dihydropyridine-3-carboxamide (6). A mixture of compound **4a** (2.41 g, 0.01 mol) in acetic acid (15 mL) as a solvent was treated with hydrochloric acid (10 mL), was refluxed for 1 h. The reaction mixture was cooled to room temperature and then poured onto ice-water. The solid, so formed, was collected by filtration and recrystallized from petroleum ether (60-80) to give faint yellow product; yield 80%; mp 270-72 °C. *Anal.* Calcd for

C₁₂H₁₀N₂O₂ (214.22): C, 67.28; H, 4.71; N, 13.08% Found: C, 67.19; H, 4.82; N, 13.14% IR (KBr): ν_{\max} = 3481, 3375 (NH₂), 3274 (NH), 1745 (CO), 1658 (CO); ¹H NMR (400 MHz, DMSO-*d*₆): δ , ppm = 6.76 (br, 2H, NH₂, D₂O exchangeable), 6.80 (d, *J* = 8 Hz, 1H, CH), 7.51-7.85 (m, 5H, Ar-H), 8.20 (d, *J* = 8 Hz, 1H, CH), 12.78 (br, 1H, NH, D₂O exchangeable); ¹³C NMR (100 MHz, DMSO-*d*₆): δ , ppm = 165.55, 163.14, 161.27, 148.59, 145.93, 144.20, 131.37, 129.00 (2C), 127.60 (2C), 116.68. MS: *m/z* (%) 214 (M⁺, 65), 196 (100), 168 (40), 140 (20), 115 (25), 77 (15), 64 (10).

Synthesis of 2-(3-(dimethylamino)-3-phenylallylidene)-malononitrile (7). A mixture of compound **4a** (2.41 g, 0.01 mol) and malononitrile (0.66 g, 0.01 mol) in ethanol (30 mL) as a solvent was treated with piperidine (3 drops). The reaction mixture was refluxed for 10 h. The mixture was cooled and then was poured onto ice-water. The solid, so formed, was collected by filtration and recrystallized from benzene to give yellow crystals; yield 95%; mp 184-86 °C. *Anal.* Calcd for C₁₄H₁₃N₃ (223.28): C, 75.31; H, 5.87; N, 18.82% Found: C, 74.85; H, 5.50; N, 18.99% IR (KBr): ν_{\max} = 2202 (2CN); ¹H NMR (400 MHz, DMSO-*d*₆): δ , ppm = 2.88 (s, 3H, CH₃), 3.27 (s, 3H, CH₃), 5.81 (d, *J* = 12 Hz, 1H, CH), 6.52 (d, *J* = 12 Hz, 1H, CH), 7.29-7.59 (m, 5H, Ar-H); ¹³C NMR (100 MHz, DMSO-*d*₆): δ , ppm = 167.56, 157.78, 132.64, 130.22, 129.02 (2C), 128.50 (2C), 126.88, 118.29, 116.16, 98.63, 56.52, 42.89. MS: *m/z* (%) 223 (M⁺, 100), 197 (10), 158 (30), 131 (20), 118 (15), 91 (20), 77 (20).

Synthesis of 5-phenyl-1H-pyrazole (9). A mixture of compound **7** (2.23 g, 0.01 mol) and hydrazine monohydrate (0.50 g, 0.01 mol) in ethanol (10 mL) as a solvent was refluxed for 5 h (followed by TIC testing using ethyl acetate: petroleum ether 1:1 until completion). The mixture was cooled and then poured onto ice-water. The solid, so formed, was collected by filtration and recrystallized from petroleum ether (60-80) to give white crystals; yield 90%; mp 78-80 °C. *Anal.* Calcd for C₉H₈N₂ (144.128): C, 74.98; H, 5.59; N, 19.43% Found: C, 74.63; H, 5.19; N, 19.25% IR (KBr): ν_{\max} = 3165 (NH); ¹H NMR (400 MHz, CDCl₃): δ , ppm = 6.64 (d, *J* = 4 Hz, 1H, CH), 7.33-7.45 (m, 3H, Ar-H), 7.64 (d, *J* = 4 Hz, 1H, CH), 7.77-7.80 (m, 2H, Ar-H), 8.53 (br, 1H, NH, D₂O exchangeable); ¹³C NMR (100 MHz, CDCl₃): δ , ppm = 149.36, 133.44, 132.32, 129.00 (2C), 128.27, 126.03 (2C), 102.88. MS: *m/z* (%) 144 (M⁺, 100), 115 (25), 89 (15), 77 (20), 63 (15).

Synthesis of 2-oxo-6-phenyl-2H-pyran-3-carbonitrile (10). A mixture of compound **1a** (1.75 g, 0.01 mol) and cyanoacetic acid (0.85 g, 0.01 mol) in acetic anhydride (15 mL) as a solvent, was refluxed for 3 h (followed by TIC testing using ethyl acetate: petroleum ether 1:1 until completion). The mixture was cooled and then poured onto ice-water. The solid, so formed, was collected by filtration and recrystallized from ethanol to give dark yellow product; yield 80%; mp 178-80 °C. *Anal.* Calcd for C₁₂H₇NO₂ (197.19): C, 73.09; H, 3.58; N, 7.10% Found: C, 72.64; H, 3.15; N, 7.44% IR (KBr): ν_{\max} = 2225 (CN), 1727 (CO); ¹H NMR (400 MHz, DMSO-*d*₆): δ , ppm = 7.35 (d, *J* = 8 Hz, 1H, CH), 7.56-7.99 (m, 5H, Ar-H), 8.50 (d, *J* = 8 Hz, 1H, CH); ¹³C NMR (100 MHz, DMSO-*d*₆): δ , ppm = 164.31, 158.18, 154.08, 132.64, 129.86, 129.43 (2C), 126.51 (2C), 115.03, 102.24, 98.49. MS: *m/z* (%) 196 (M⁺, 90), 168 (100), 139 (20), 104 (50), 76 (50).

Synthesis of 3-(dimethylamino)-6-phenyl-2H-pyran-2-one (12). A mixture of compound **1a** (1.75 g, 0.01 mol) and ethylcyanoacetate (1.13 g, 0.01 mol) in ethanol (20 mL) as a solvent, was refluxed for 4 h (followed by TIC testing using ethyl acetate : petroleum ether 1 : 1 until completion). The mixture was cooled to room temperature and then poured onto ice-water. The solid, so formed, was collected by filtration and recrystallized from ethanol to give faint yellow product; yield 85%; mp 93-95 °C. *Anal.* Calcd for $C_{13}H_{13}NO_2$ (215.25): C, 72.54; H, 6.09; N, 7.51% Found: C, 72.48; H, 6.15; N, 7.59% IR (KBr): ν_{\max} = 1657 (CO); 1H NMR (400 MHz, DMSO- d_6): δ , ppm = 2.91 (s, 3H, CH_3), 3.14 (s, 3H, CH_3), 5.81 (d, J = 12 Hz, 1H, CH), 7.43-7.48 (m, 3H, Ar-H), 7.71 (d, J = 12 Hz, 1H, CH), 7.87-7.89 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, DMSO- d_6): δ , ppm = 185.70, 154.19, 152.83, 140.23, 130.78, 128.15 (2C), 127.17 (2C), 90.89, 83.21, 44.51, 37.12. MS: m/z (%) 214 (M^+ , 80), 185 (50), 157 (25), 134 (15), 108 (100), 93 (15), 80 (80), 67 (10), 53 (20).

Synthesis of 3-oxo-3-phenyl-2-(2-phenylhydrazono)-propanal (17). A solution of compound **12** (2.15 g, 0.01 mol) in ethanol (50 mL) was treated with sodium acetate (5 g). Aniline diazonium chloride (prepared according to the standard literature procedures from aniline (0.93 g, 0.01 mol), which was added gradually with stirring to a cooled mixture of concentrated hydrochloric acid, and sodium nitrite). After complete addition of the diazonium salt, the reaction mixture was kept at room temperature for one hour. The solid, so formed, was collected by filtration and crystallized from benzene to give orange dark crystals; yield 90%; mp 96-97 °C (literature mp 96 °C). *Anal.* Calcd for $C_{15}H_{12}N_2O_2$ (252.27): C, 71.42; H, 4.79; N, 11.10% Found: C, 71.63; H, 4.47; N, 11.37% IR (KBr): ν_{\max} = 3431 (NH), 1645 (CO), 1631 (CO); 1H NMR (400 MHz, $CDCl_3$): δ , ppm = 7.21-7.99 (m, 10H, Ar-H), 10.20 (s, 1H, CHO), 10.76 (br, 1H, NH, D_2O exchangeable); ^{13}C NMR (100 MHz, $CDCl_3$): δ , ppm = 191.98, 189.75, 141.31, 137.23, 132.50, 132.39, 130.58 (2C), 129.97 (2C), 127.97 (2C), 126.68, 116.77 (2C); MS: m/z (%) 252 (M^+ , 60), 223(20), 132 (70), 105 (90), 93(60), 77 (100), 65 (30).

Acknowledgements

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