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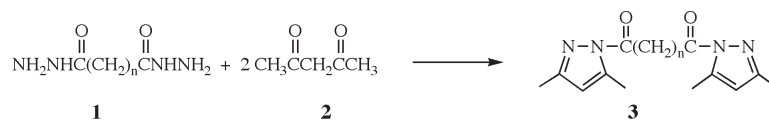
Phenylmalonic acid dihydrazide reacted with 2,4-pentanedione to give, unexpectedly, 5,7-dimethyl-1,3-dioxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazole-4-ylum **5**. The structure of the product is confirmed by X-ray crystallography.

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Pyrazoles have attracted much attention in recent years due to their biological and pharmaceutical activities [1-4]. During the course of our work directed at synthesizing substituted bis-pyrazoles, we observed an unusual behavior in the reaction of malonic acid dihydrazide with 1,3-diketones. Accordingly, we undertook an investigation to identify the products of this reaction.

The reaction of acid dihydrazide **1** (*n* = 0, 2,3,4) with 2,4-pentanedione **2**, gave smoothly the desired bis-pyrazoles **3** (Scheme 1) [5].

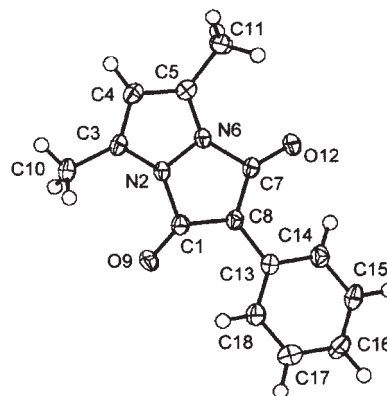
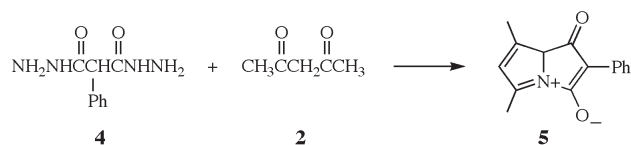
Scheme 1



In contrast the reaction of malonic acid dihydrazide **1** (*n*=1) with 2,4-pentanedione **2**, took a different route. Thus at room temperature, a red solution was obtained. Work-up of the reaction mixture gave a red gummy product which was difficult to solidify. To overcome this, 2-phenylmalonic acid dihydrazide **4** was used. Thus, reaction of **4** with 2,4-pentandione **2** in absolute ethanol at room temperature afforded after the usual work-up orange crystals of pyrazolo[1,2-*a*]pyrazol-4-ylum-3-olate **5** (Scheme 2). In the NMR spectrum of **5** the peaks at δ 8.05 and 7.25 are assigned for the aromatic protons, whereas the singlet at δ 6.12 is assigned to H-6 proton. The methyl protons resonate at δ 2.50. Furthermore the structure of **5** was unambiguously assigned by X-ray crystallography (Figure 1). It is worth noting that compound **5** was previously prepared *via* different route [6,7].

Some characteristic structural features of **5** are given below. The compound shows equal C-O bond lengths. The positive charge of the cation is mainly delocalized over the pyrazolium ring N2-C3-C4-N6; this is obvious by the equal bond lengths (N2-C3, N6-C5) and (C3-C4, C4-C5). The negative charge is delocalized mainly over the CO-C-CO part of the other ring.

Scheme 2

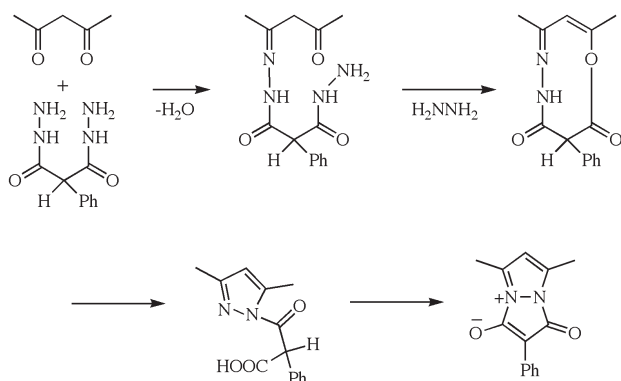
Figure 1. ORTEP diagram of molecule **5**.

It is clear that the reaction proceeds *via* a different mechanism from that reported previously [5] which involves the condensation of dihydrazide with one equivalent of the diketone accompanied by the elimination of a hydrazine molecule.

A plausible mechanism for the formation of **5** is given in Scheme 3.

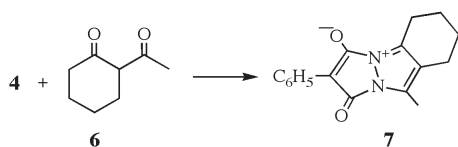
In order to check the generality of the reaction, acid dihydrazide **4** was treated with 2-acetylcyclohexanone **6** in

Scheme 3



the same way to give the hexahydropyrazolo[1,2-*a*]indazole-4-ium-3-olate **7** (Scheme 4). The structure of **7** was confirmed by NMR spectroscopy by comparison with **5**. Thus, the aromatic protons resonate at δ 8.05, 7.31 and 7.08. The methyl protons resonate as a singlet at δ 2.52. The methylene protons appeared at δ 3.01, 2.38 and 1.98.

Scheme 4



EXPERIMENTAL

Melting points were determined on an electro thermal-digital melting point apparatus and are uncorrected. The ^1H -nmr spectra were recorded on Bruker AC-250 spectrometer and reported in δ values in deuterated chloroform (CDCl_3) with tetramethylsilane (TMS) as the internal standard. The ^{13}C -NMR spectra were recorded on Bruker AC-250 spectrometer. Infrared spectra were recorded on Perkin Elmer FT-IR SP-2000 spectrometer as potassium bromide (KBr) pellets. Elemental analyses were determined at M.H.W. Laboratories., Phoenix, Az. USA. Chemicals were purchased from Aldrich and Fluka and were used without further purification.

X-ray data were collected at 293 K on a syntax P3-diffractometer with a graphite monochromator, λ (Mo- $\text{K}\alpha$) = 0.71073 Å. The structure was solved by direct methods. The refinement converged at R_1 = 0.0354 and R_2 = 0.0459.

5,7-Dimethyl-1,3-dioxo-2-phenyl-2,3-dihydro-1*H*-pyrazolo[1,2-*a*]pyrazole-4-ium (5).

To a stirred solution of 2-phenyl malonic acid dihydrazide **4**, (3.12 g, 15 mmol) in absolute ethanol (35 ml), 1,3-diketones **2**

or **6** (15 mmol) were added. The reaction mixture was stirred at room temperature for 2 hrs. The reaction mixture was left standing at room temperature for about 12 hrs. The formed red crystalline product was collected by filtration, washed with hexane and dried to give **5**: 3.42 g (90%) mp 212–213°; ir (KBr): 1675, 1590 cm^{-1} . ^1H -nmr (CDCl_3): δ 8.05(d, J = 5Hz, 2H, aromatic); 7.25(m, 3H, aromatic); 6.12(s, 1H, H-6); 2.50(s, 6H, 2CH₃). ^{13}C -nmr (CDCl_3) δ : 159.3, 143.1, 132.2, 128.1, 124.2, 111.7, and 11.1.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$: C 69.80; H 5.03; N 11.66. Found: C, 69.69; H, 5.07; N, 11.77.

Crystal Data of 5.

Crystallographic data is deposited with the Cambridge Crystallographic Data Center, CCDC 232795; $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$, MW = 240.26. Crystal system: monoclinic, space group P 2₁/c with cell parameters: a = 70421(1) Å, b = 11.564 (2) Å, c = 13.992 (4) Å, v = 1196.3 Å³, d = 1.333 mg m^{-3} , α = 90 deg, β = 94.63 (3) deg, γ = 90 deg.

9-Methyl-1,3-dioxo-2-phenyl-2,3,5,6,7,8-hexahydro-1*H*-pyrazolo[1,2-*a*]indazole-10-ylum (7).

Compound **4** (3.12 g, 15 mmol) reacted with compound **6** (2.10 g, 15 mmol) as described above to give **7** 3.86 g (87%); mp 193–194°; ir (KBr): 1690, 1580 cm^{-1} . ^1H -nmr (CDCl_3) δ : 8.05(d, J = 4Hz, 2H, aromatic); 7.31(t, J = 3Hz, 2H, aromatic); 7.08(t, J = 4Hz, 1H, aromatic); 3.01(t, J = 3Hz, 2H, CH₂); 2.52(s, 3H, CH₃); 2.38(t, J = 4Hz, 2H, CH₂), 1.98(m, 4H, 2CH₂). ^{13}C -nmr(CDCl_3) δ : 159.9, 159.3, 143.0, 140.4, 132.6, 128.0, 124.0, 123.9, 121.2, 21.6, 21.5, 20.9, 19.1, 9.5.

Anal. Calcd. for $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$: C, 72.84; H, 5.75; N, 9.99. Found: C, 72.64; H, 5.70; N, 10.13.

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