

SYNTHESIS OF 2-PYRAZOLIN-5-ONES, 3-PYRAZOLIN-5-ONES AND 3, 5-PYRAZOLIDINEDIONE DERIVATIVES

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Treatment of α -arylhazono derivatives of ethyl acetoacetate (Ia-d) with each of N, N-diphenylsulphonylhydrazine, *p*-acetamidobenzenesulphonylhydrazide and acetylhydrazine afforded 4-arylhazono-3-methyl-2-pyrazolin-5-ones (IIIa-d). On the other hand when (Ia, c) were treated with N-phenyl-N-phenylsulphonylhydrazine it gave the corresponding 1-phenyl derivatives (VIa, c). Interaction of α -N-methyl derivatives (VIIa-d) with phenylhydrazine afforded (IIIa-d) and 1-phenyl-4-methyl-3, 5-pyrazolidinedione (IX.).

INTRODUCTION

Literature survey indicates numerous examples of 2-pyrazolin-5-ones synthesized by the interaction of hydrazines with ethyl acetoacetate [1,2]. However, there seems to be few satisfactory instances of the pyrazolone synthesis from the interaction of α -arylhazono ethyl acetoacetate (I) with acid hydrazides [3].

This work deals with the synthesis of 4-arylhazono-3-methyl-2-pyrazolin-5-ones (IIIa-d) and the corresponding 1-phenyl derivatives (VI a,c).

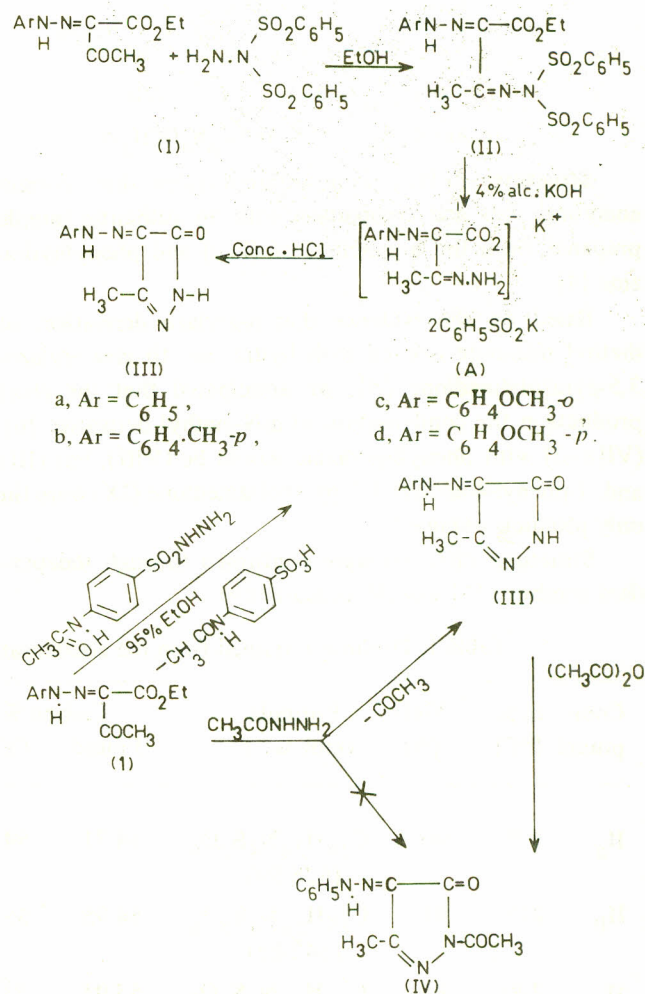
Thus treatment of α -arylhazono ethyl acetoacetate (Ia-d) with N, N-diphenylsulphonylhydrazine in ethanolic solution gave (IIa-d) which on further treatment with 4% alcoholic potassium hydroxide and acidification with concentrated hydrochloric acid afforded 4-arylhazono-3-methyl-2-pyrazolin-5-ones (IIIa-d).

Structures (IIa-d) were inferred from their correct analytical data and IR spectra, which showed well defined absorption bands at 1590, 1700 and 3230 cm^{-1} attributable to (C = N), (C = O ester) and (NH) stretching frequency.

Structures (IIIa-d) were confirmed from the fact that the products give the same analytical data and the same melting point as the 5-pyrazolone. The mixed melting point with the authentic specimen prepared from α -arylhazono derivatives of ethyl acetoacetate and hydrazine hydrate was also the same [4].

The intermediate hydrazone (A) derivatives have been isolated in some cases and they can be cyclised to the corresponding azo pyrazolones by boiling in acetic acid [5], but in our case, it was difficult to isolate.

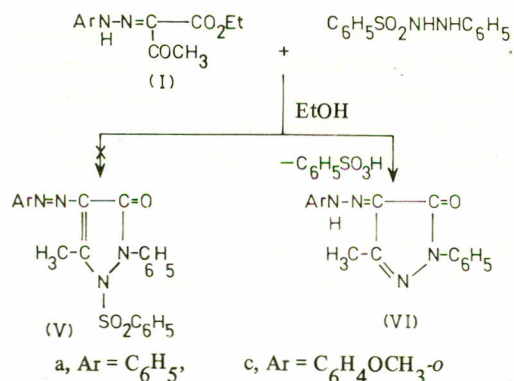
In view of the reported formation of 1-phenylsul-



phonyl-4-arylhazono-3-methyl-2-pyrazolin-5-ones [6], by the interaction of (I) with benzenesulphonylhydrazide, treatment of (Ia-d) with *p*-acetamidobenzenesulphonylhydrazide in 95% ethanolic solution afforded (IIIa-d).

An attempt was made to obtain (IV) by the action of acetylhydrazine on (Ia). This leads however to the formation of (IIIa). Structures (IIIa-d) were confirmed from independent synthesis [4].

Elguero *et al.* [7] have prepared 1,2,3-trimethyl-4-phenylazo-3-pyrazolin-5-one, by the reaction of *N,N*-dimethylhydrazine with α -phenylazoacetic ester. In the light of their investigations, we anticipated to obtain (Va,c), from the interaction of (Ia,c) and *N*-phenyl-*N*-phenylsulphonylhydrazine, but this attempt was unsuccessful and (VIa,c) were the only products obtained.

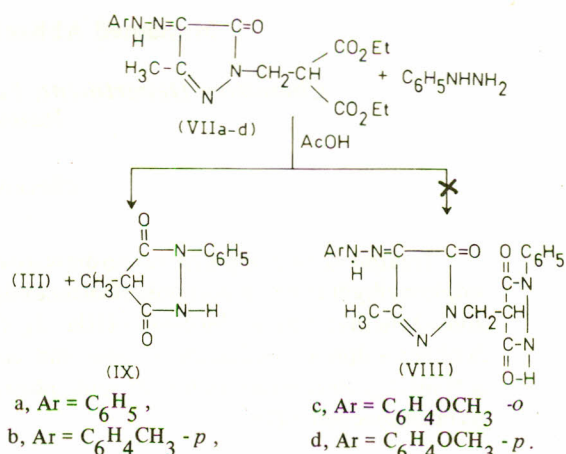


Structures (VIa,c) were inferred from their correct analytical data and comparison with an authentic sample prepared from the interaction of (Ia,c) and phenylhydrazine [4].

Based on the evidence that α -aryldazo derivatives of diethyl malonate reacted with hydrazines to give arylazo-3,5-pyrazolidinedione [8], we anticipated that the chief products in the condensation of α -*N*-methyl derivative [6] (VIIa-d) with phenylhydrazine would be (VIII), but (III) and 1-phenyl-4-methyl-3,5-pyrazolidinedione (IX) were the only products obtained.

Structures (IIIa-d) were confirmed through independent synthesis [4] and IR measurement.

Structure (IX) was established from the correct analytical data and IR spectrum, which showed absorption bands at 1665, 1655 cm⁻¹ (CO) and 3250 cm⁻¹ (NH) stretching frequency.



EXPERIMENTAL

Melting points (uncorrected) were determined on Gallenkamp electric melting point apparatus. IR spectra were recorded on KBr discs using a Unicam SP 2000 IR spectrophotometer.

: α -Aryldiazono Ethyl Acetoacetate (Ia-d). These compounds were prepared adopting the general procedure of treating ethyl acetoacetate with the appropriate diazonium salt [4].

Condensation of (Ia-d) with *N,N*-diphenylsulphonylhydrazine. Formation of (IIa-d). A mixture of the α -aryldiazono derivatives of ethyl acetoacetate (Ia-d) (0.01 mole) and *N,N*-diphenylsulphonylhydrazine (0.012 mole) in ethanol was refluxed for 3 hrs, set aside at room temperature over-night. The precipitated solid was filtered and crystallized from ethanol. The results are given in Table 1.

Table 1. Products obtained from the condensation of (Ia-d) with *N,N*-diphenylsulphonylhydrazine.

Com- pound	m.p. [°C]	Yield [%]	Formula (mol. wt.)	Carbon %		Hydrogen %		Nitrogen %		Sulphur %	
				Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
II _a	175	90	C ₂₄ H ₂₄ N ₄ S ₂ O ₆ (528.59)	54.71	54.52	4.59	4.57	10.61	10.59	12.41	12.13
II _b	215	95	C ₂₅ H ₂₆ N ₄ S ₂ O ₆ (542.62)	54.95	55.33	4.89	4.83	10.51	10.32	11.89	11.81
II _c	220	85	C ₂₅ H ₂₆ N ₄ S ₂ O ₇ (558.62)	53.91	53.74	4.71	4.69	10.21	10.03	11.50	11.48
II _d	195	90	C ₂₅ H ₂₆ N ₄ S ₂ O ₇ (558.62)	53.90	53.74	4.72	4.69	10.20	10.03	11.53	11.48

4-Arylhydrazono-3-methyl-2-pyrazolin-5-ones (IIIa-d). A suspension of (IIa-d) (0.5 g) in 4 % alcoholic potassium hydroxide solution (40 ml.) was refluxed for 1 hr, acidified with HCl (40 ml.), and heated for further 1 hr. The reaction mixture was left to stand over-night. The solid product that separated was filtered, recrystallised from ethanol and proved to be identical with those reported in literature.

Interaction of (Ia-d) with p-acetamidobenzenesulphonhydrazide and acetylhydrazine: Formation of (III). A mixture of (Ia-d) (0.01 mole) and p-acetamidobenzenesulphonhydrazide or acetylhydrazine (0.012 mole) in 95 % ethanol (30 ml.) was refluxed for 4 hr, left to stand over-night. The solid products, that separated were filtered, recrystallised from ethanol to yield (IIIa-d), (m.p. and mixed m.p.).

Condensation of (Ia,c) with N-phenyl-N-phenylsulphonylhydrazine: Formation of (VIa,c). To (0.01 mole) of (Ia,c) in (30 ml.) 95 % ethanol, (0.012 mole) N-phenyl-N-phenylsulphonylhydrazine was added. The reaction mixture was refluxed for five hours, left to cool, the solid product that separated was filtered and recrystallised from ethanol to yield (VIa,c).

4-Arylhydrazono-3-methyl-1-(1,1-dicarboethoxyethane)-2-pyrazolin-5-ones (VIIa-d). These compounds were prepared according to the method of Amer *et al.* [6].

Condensation of (VIIa-d) with phenylhydrazine: Formation of (III) and 1-phenyl-4-methyl-3, 5-pyrazolidi-

nedione ((IX). To (0.01 mole) of (VIIa-d) in 50 ml glacial acetic acid, (0.012 mole) phenylhydrazine was added. The reaction mixture was refluxed for 3 hr, left to stand for 6 hr. The solid products that separated were filtered and crystallised from ethanol to yield (IIIa-d), while the pale-yellow insoluble material was crystallised from benzene (yield 40 %) and characterised as (IX), m.p. 115° (IX).

(Found: C 62.80 H 5.51 N 14.92; C₁₀H₁₀N₂O₂, requires: C 63.14 H 5.29 N 14.73).

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