

NEW ROUTE FOR THE SYNTHESIS OF 3-ANILINO-4-ARYLHYDRAZONO-1-PHENYL-2-PYRAZOLIN-5-ONES

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SUMMARY : A convenient route was reported for the synthesis of 3-anilino-4- arylazo-1-phenyl -2-pyrazolin-5-ones to improve their yields. The structures of the obtained products were supported by spectral data.

Key Words: Phenylpyrazolin.

INTRODUCTION

An enormous number of 2-pyrazolin-5-ones have found use in medicine as analgesics and antipyretics and in color photography as magenta dye formers (1). An important addition to this class of compounds has been the 3-anilino-4-arylazo-1-phenyl-2-pyrazolin-5-ones. Our previous work (2-19) showed the validity of 2-pyrazolin-5-ones as key intermediate for the synthesis of several dyes, analgesics, and anticancer agents. Weiss berg (20) reported the formation of 3-anilino-1-phenyl-2-pyrazolin-5-one (2a-h) from fusion of 3-amino-1-phenyl-2-pyrazolin-5-one (1) with aromatic amines at 150-200°C. Worrel (21) synthesized the same compound by treatment of ethyl α -phenylthiocarbamylglyoxalate (3) with phenyl hydrazine. The purpose of the present study was to synthesize 3-anilino-4-arylazo-1-phenyl-2-pyrazolin-5-ones by alternate methods to improve the yield percentage.

The first method includes the synthesis of the known 3-amino-4-arylhydrazono-1-phenyl-2-pyrazolin-5-ones (6)⁽²²⁾ from fusion of (5) with phenyl hydrazine at 160-180°C, which underwent transamination to 3-anilino - 4 - arylhydrazono -1-phenyl-2-pyrazolin-5-ones (4) in 95% yield.

While the second method consists of coupling the aromatic diazonium salts with 3-anilino-1-phenyl-2-pyrazolin-5-ones (2) to give (4) in 92% yield. Their m.ps. and spectra (IR and ¹H-NMR) were found to be

identical with those of authentic materials synthesized according to the first method (Table 1).

In connection with the above methods the yield percentage ranged between 92 and 95% while the reported yields ranged between 65 and 78% (1,23).

EXPERIMENTAL

Melting points are uncorrected. Microanalysis of C and H were determined at Micro analytical Laboratory, Faculty of Science, University of Mansoura, IR spectra in KBr were recorded on a Pye Unicam SP 2000 Infrared Spectrophotometer, ¹H-NMR spectra in CDCl₃ were determined on a Bruker 400 MHz and Varian 200 MHz apparatus.

3-Amino-4-arylhydrazono-1-phenyl-2-pyrazolin-5 ones (6a-d) (4)

These compounds were prepared adopting the general procedure of fusion compounds 5 with phenyl hydrazine at 160-180°C (4). The solid products proved to be identical with those reported (m.p. and mixed m.p) IR and ¹H-NMR spectra (22).

3-Anilino-1-phenyl-2-pyrazolin-5-ones(2a-h)

These compounds were prepared according to the above method. Compounds 2a-c, g-h were reported Previously (23). The new derivatives are seen in Table 1.

3-Anilino-4-arylazo-1-phenyl-2-pyrazolin-5-ones (4a-i)

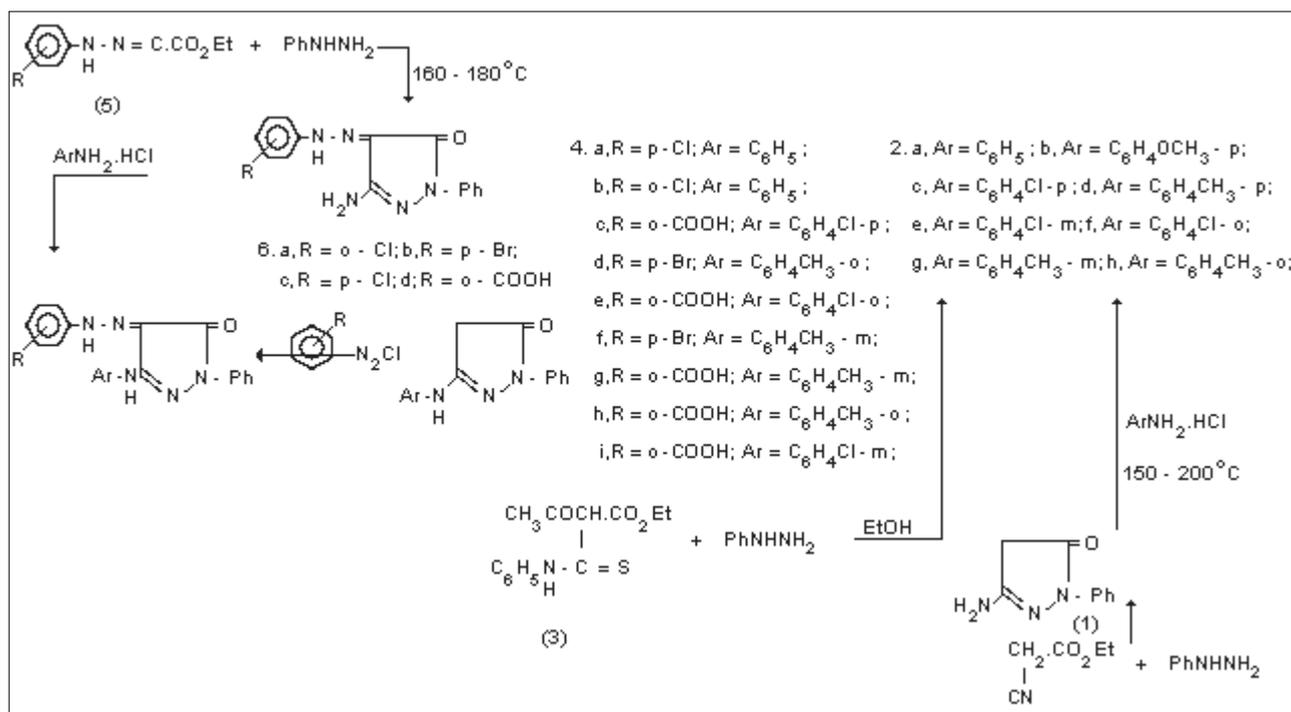
A mixture of 6 (0.01 mol) and the appropriate aromatic amine hydrochloride (0.015 mol) was fused at 180-200°C for 1-1.5 hrs, left to stand overnight and crystallized from ethanol to give compounds 4a-i, (Table 1).

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Table 1: Characterization data of compounds 2d-f and 4a-i.

¹ H-NMR Compd.	Color	Yield (%)	M.P. (°C)	Mol. formula (W.Wt)	Found (%), Calcd. (%)				IR (ppm)
					C	H	N	cm ⁻¹	
2d	Pale-yellow	91	165	C ₁₆ H ₁₅ N ₃ O (265.30)	72.51 (72.43)	5.59 5.59	15.91 15.83)	1690, 3190	2.0 (s,2H,CH ₂), 2.3 (s,3H,CH ₃) 7.8 (m,9H,ArH), 13.15 (s,1H,NH)
2e*	Page	92	175	C ₁₅ H ₁₂ N ₃ OCl (285.727)	63.13 (63.04)	4.29 4.23	14.61 14.70)	1685, 3205	1.9 (s,2H,CH ₂), 8.9-7.59 (m,9H,ArH), 13.2 (s,1H,NH)
2f*	Page	93	132	C ₁₅ H ₁₂ N ₃ OCl (285.727)	63.11 (63.04)	4.29 4.23	14.68 14.70)	see 2d	-
4a*	Brown	94	140	C ₂₁ H ₁₆ N ₅ OCl (389.837)	64.81 (64.69)	4.09 4.13	17.91 17.96)	1595, 1605 1705, 3195, 3210	7.2-7.9 (m,14H,Ar),13.15 (m,2H 2NH
4b*	Brown	92	105	C ₂₁ H ₁₆ N ₅ OCl (389.837)	64.71 (64.69)	4.21 4.13	17.89 17.96)	see 4a	-
4c*	Reddish-brown	91	>250	C ₂₂ H ₁₆ N ₅ O ₃ Cl (433.847)	61.01 (60.90)	3.69 3.71	16.19 16.14)	1590, 1600, 1710, 1750, 3180, 3230, 3420	6.95-7.69 (m,13H,ArH),13.25 (m,2H,2NH), 14.1(s,1H,OH)
4d*	Brown	94	217	C ₂₂ H ₁₈ N ₅ OBr (448.316)	59.04 (59.93)	4.11 4.04	15.53 15.62)	1600, 1610, 1720, 3105, 3215	2.35 (s,3H,CH ₃),7.15-7.9 (m, 13H,ArH), 13.12 (m,2H,2NH)
4e*	Brownish-red	92	230	C ₂₂ H ₁₆ N ₅ O ₃ Cl (433.847)	60.98 (60.90)	3.81 3.71	16.23 16.14)	see 4c	-
4f*	Reddish-brown	93	232	C ₂₂ H ₁₈ N ₅ OBr (448.316)	58.83 (58.93)	4.11 4.04	15.71 15.62)	see 4ds	2.31 (s,3H,CH ₃), 7.1-7.96 (m, 13H,ArH), 13.6 (m,2H,2NH)
4g	Brown	94	205	C ₂₃ H ₁₉ N ₅ O ₃ (413.42)	66.91 (66.81)	4.72 4.63	16.89 16.94)	see 4e	-
4h	Brown	91	225	C ₂₃ H ₁₉ N ₅ O ₃ (413.42)	66.93 (66.81)	4.71 4.63	17.09 16.94)	see 4e	-
4i*	Reddish-Brown	94	173	C ₂₂ H ₁₆ N ₅ O ₃ Cl (433.847)	60.89 (60.90)	3.59 3.71	16.19 16.14)	see 4e	-

* 2e, Cl%=(14.4), 14.59; 2f, Cl%=(14.4), 14.29; 4a; Cl% (9.09), 9.14; 4b, Cl% (9.09), 8.91; 4c, Cl%=(8.17), 8.31; 4d, Br%=(17.82), 17.96; 4e, Cl%=(8.17), 8.10. *4f, Br%=(17.82), 18.01; 4i, Cl%=(8.17), 8.41.



REFERENCES

1. Wiley RH, Wiley P : *Pyrazolones, Pyrazolidones and Derivatives*, Ed by A Weissberger, John Wiley and Sons, Inc, New York, NY, Part 2, Chapter 1 and 2, 1964.
2. Harhash AH, Amer FA, Metwally MA : *Mansoura Science Bulletin*, 4:223-236, 1977.
3. Amer FA, Harhash AH, Metwally MA : *Z Naturforsch*, 32b:943-947, 1977.
4. Metwally MA, Amer FA : *Die Pharmazie*, 38:172-173, 1983.
5. Metwally MA, Afsad ES : *Pakistan J Sci Ind Res*, 24:188-190, 1983.
6. Metwally MA, Amer FA : *Indian J Chem*, 22B:316-318, 1983.
7. Metwally MA, Afsad E : *Die Pharmazie*, 39:95, 1984.
8. Fadda AA, Metwally MA, Khalil AM : *Indian J Tex*, 8:82-84, 1983.
9. Metwally MA, Yousif MY, Ismaiel AM, Amer FA : *Indian J Chem Soc*, 62:54-56, 1985.
10. Metwally MA, Fadda AA, Hassan HM, Afsah E : *Org Prep Proc Int*, 17:198, 1985, CA, 103, 37411f, 1985.
11. Metwally MA, Younes MI, Metwally SA : *Indian J Chem*, 24B:970, 1985.
12. Metwally SA, Younes MI, Metwally MA : *Croatica Chem Acta*, 59:483-489, 1986.
13. Ismail AM, Yousif MY, Metwally MA, El-Kerdawy MM : *Indian J Chem*, 25B:1238-1242, 1986.
14. Metwally MA, Darwish YM, Amer FA : *Indian J Chem*, 28B:1069, 1989.
15. Metwally MA, Yousif MM, El-Ahl AS, Amer FA : *Mansoura Bull Sci*, 15:43-52, 1988.
16. Metwally MA, Yousif MM, El-Ahl AS, Amer FA : *Mansoura Bull Sci*, 15:53-65, 1988.
17. Metwally MA, Darwish YM, El-Hussini MM, Amer FA : *J Indian Chem Soc*, LXV:54, 1988.
18. Etman HA, Sadek EG, Metwally MA : *J Indian Chem Soc*, in press.
19. Sofan MA, Etman HA, Metwally MA : *Pakistan J Sci Ind Res*, 32:148, 1989.
20. Weissberger A, Porter D : *J Amer Chem Soc*, 64:2133, 1962.
21. Worrall DE : *J Amer Chem Soc*, 44:1551, 1922.
22. Elnagdi MH, Allah SDA : *J Prakt Chem*, 315:1009, 1973; *Chem Abstr*, 80:82349j, 1974.
23. Dolbin VN, Erokhim VK, Soloveva IA : *Khim Geterotsikl Soedin Sb I: Azotsoderzhashchie Geterotsikl 1967*, 92-7 (Russ) *Chem Abstr*, 70, 115056k, 1969.

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