

Table I. Physical and Spectral Data of 5a-l^a

compd	R ²	yield, %	mp, °C	recryst solvent	IR (KBr), cm ⁻¹					NMR data (CDCl ₃), δ
					ν _{Ar-H}	ν _{C=C}	ν _{C=N}	ν _{C=S}	φ _{C-H}	
R ¹ = 2-C ₄ H ₃ S; R ³ = C ₆ H ₅										
5a	4-CH ₃ OC ₆ H ₄	65	93-95	CHCl ₃ / <i>n</i> -hexane	3040	1595	1510	1175	990	3.78 (s, 3 H, OCH ₃),
b	4-ClC ₆ H ₄	55	111-12	CHCl ₃ / <i>n</i> -hexane	3060	1600	1540	1050	1000	6.78-7.98 (m,
c	3-NO ₂ C ₆ H ₄	60	160-62	C ₅ H ₅ N/MeOH	3040	1592	1510	1080	1010	14 H, ArH)
d	3,4-Cl ₂ C ₆ H ₃	65	104-06	CHCl ₃ / <i>n</i> -hexane	3060	1595	1515	1178	995	
e	4-FC ₆ H ₄	50	125-27	C ₅ H ₅ N/MeOH	3045	1590	1500	1165	1020	
R ¹ = 2-C ₄ H ₃ S; R ³ = 4-ClC ₆ H ₄										
f	4-NO ₂ C ₆ H ₄	50	176-78	CHCl ₃ / <i>n</i> -hexane	3070	1600	1495	1100	1000	
g	4-FC ₆ H ₄	65	153-55	CHCl ₃ / <i>n</i> -hexane	3060	1610	1510	1160	995	7.51-8.31 (m, 13
h	C ₆ H ₅	55	110-12	C ₅ H ₅ N/MeOH	3065	1600	1540	1090	1010	H, ArH)
i	3 NO ₂ C ₆ H ₄	70	217-19	C ₅ H ₅ N/MeOH	3040	1590	1540	1090	995	
R ¹ = R ³ = 2-C ₄ H ₃ S										
j	3-CH ₃ OC ₆ H ₄	60	90-92	C ₅ H ₅ N/MeOH	3060	1600	1550	1170	990	3.75 (s, 3 H, OCH ₃),
k	3-ClC ₆ H ₄	70	138-40	CHCl ₃ / <i>n</i> -hexane	3080	1598	1535	1090	970	6.84-7.82 (m,
l	3-NO ₂ C ₆ H ₄	60	123-25	CHCl ₃ / <i>n</i> -hexane	3070	1620	1500	1020	980	12 H, ArH)

^a All the compounds gave satisfactory elemental analysis for C, H, N. ν = stretching vibrations. φ = bending vibrations (out-of-plane vibrations). s = singlet; m = multiplet.

sulting solid mass was filtered, washed twice with water and methanol, dried, and then crystallized from appropriate solvents shown in Table I to give the desired pyridines (5a-l).

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Literature Cited

- (1) Frank, R. L.; Riever, E. F. *J. Am. Chem. Soc.* **1950**, *72*, 4182.
- (2) Tschitschibabin, A. E. *Bull. Soc. Chim. Fr.* **1936**, *4*, 1826.
- (3) Tschitschibabin, A. E. *J. Russ. Chem. Soc.* **1905**, *37*, 1229.
- (4) Tschitschibabin, A. E. *J. Prakt. Chem.* **1924**, *107*, 112.
- (5) Gupta, K. C.; Srivastava, N.; Nigam, R. K. *J. Organomet. Chem.* **1981**, *204*, 55.
- (6) Gupta, K. C.; Srivastava, N.; Nigam, R. K. *Indian J. Chem., Sect. B* **1981**, *20*, 802, 923.
- (7) Tewari, R. S.; Gupta, K. C. *Indian J. Chem.* **1975**, *13*, 864.
- (8) Tewari, R. S.; Gupta, K. C. *Indian J. Chem., Sect. B* **1976**, *14*, 419, 829.
- (9) Tewari, R. S.; Gupta, K. C.; Dube, A. K. *J. Indian Chem. Soc.* **1980**, *57*, 1135.
- (10) Tewari, R. S.; Gupta, K. C.; Dube, A. K. *Indian J. Chem., Sect. B* **1981**, *20*, 706.
- (11) King, L. C. *J. Am. Chem. Soc.* **1933**, *66*, 894.
- (12) Krohnke, F.; Zecher, W. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 626.
- (13) Krohnke, F. *Synthesis* **1976**, 1.

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Synthesis of New 2-Pyridylhydrazones and 2-Quinolyhydrazones Containing 2-Thiophene or 2-Furan Groups

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The synthesis of 18 new 2-pyridylhydrazone and 2-quinolyhydrazone compounds containing either 2-thiophene or 2-furan functionalities is described.

Continued interest still exists in the study of a variety of different hydrazones, particularly 2-pyridyl- and 2-quinolyhydrazones, in addition to many other derivatives, for possible use as complexation reagents for transition metals (1-7). Because of this interest, 18 new 2-pyridylhydrazones and 2-quinolyhydrazones containing either various 2-thiophene or

2-furan moieties have been synthesized. The method used to prepare these new hydrazones was the standard procedure where equimolar quantities of the appropriate hydrazine and aldehyde or ketone were refluxed in ethanol, the solid hydrazone formed precipitating out of solution, filtered, and recrystallized from the appropriate solvent.

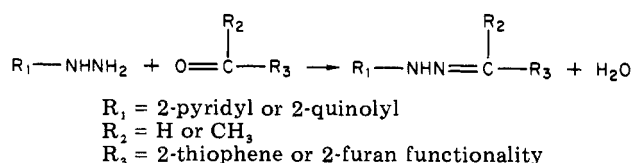


Table I. 2-Pyridyl- and 2-Quinolylhydrazones^a

hydrazone	hydrazine	carbonyl	mp, °C	reflux time, h	yield, %	formula
I ^b	2-pyridyl	2-thiophenecarboxaldehyde	155	1	35	C ₁₀ H ₉ N ₃ S
II ^b	2-pyridyl	2-acetylthiophene	102	3 ^e	40	C ₁₁ H ₁₁ N ₃ S
III ^b	2-pyridyl	3-methyl-2-thiophenecarboxaldehyde	142	4	37	C ₁₁ H ₁₁ N ₃ S
IV ^c	2-pyridyl	5-methyl-2-thiophenecarboxaldehyde	178	3 ^e	57	C ₁₁ H ₁₁ N ₃ S
V ^c	2-pyridyl	5-chloro-2-thiophenecarboxaldehyde	217	1	56	C ₁₀ H ₈ N ₃ SCl
VI ^c	2-pyridyl	5-bromo-2-thiophenecarboxaldehyde	219	1	57	C ₁₀ H ₈ N ₃ SBr
VII ^b	2-pyridyl	2-furaldehyde	140	2	49	C ₁₀ H ₉ N ₃ O
VIII ^c	2-pyridyl	5-methyl-2-furaldehyde	135	3.5	46	C ₁₁ H ₁₁ N ₃ O
IX ^c	2-pyridyl	5-nitro-2-furaldehyde	202	1	62	C ₁₀ H ₈ N ₄ O ₃
X ^b	2-quinolyl	2-thiophenecarboxaldehyde	151	2	63	C ₁₄ H ₁₃ N ₃ S
XI ^b	2-quinolyl	2-acetylthiophene	130	6.5 ^e	65	C ₁₅ H ₁₃ N ₃ S
XII ^b	2-quinolyl	3-methyl-2-thiophenecarboxaldehyde	140	4 ^e	39	C ₁₅ H ₁₃ N ₃ S
XIII ^c	2-quinolyl	5-methyl-2-thiophenecarboxaldehyde	163	3 ^e	55	C ₁₅ H ₁₃ N ₃ S
XIV ^c	2-quinolyl	5-chloro-2-thiophenecarboxaldehyde	196	1	65	C ₁₄ H ₁₀ N ₃ SCl
XV ^c	2-quinolyl	5-bromo-2-thiophenecarboxaldehyde	173	1	58	C ₁₄ H ₁₀ N ₃ SBr
XVI ^b	2-quinolyl	2-furaldehyde	143	2	51	C ₁₄ H ₁₃ N ₃ O
XVII ^b	2-quinolyl	5-methyl-2-furaldehyde	171	3.5	57	C ₁₅ H ₁₃ N ₃ O
XVIII ^d	2-quinolyl	5-nitro-2-furaldehyde	230, dec.	0.5	92	C ₁₄ H ₁₀ N ₄ O ₃

^a Elemental analyses in agreement with theoretical values were obtained and submitted for review. ^b Crystallizing solvent: C₂H₅OH-H₂O. ^c Crystallizing solvent: C₂H₅OH. ^d Triturated with C₂H₅OH. ^e Four drops of acetic acid added to reflux mixture.

All the resulting hydrazones were stable solids possessing sharp melting points.

Experimental Section

Preparation of 2-Hydrazinoquinoline. The reactant, 2-hydrazinoquinoline, was prepared by refluxing 2-chloroquinoline and hydrazine hydrate, with the procedure of Perkin and Robinson (8): mp 143 °C (lit. 142–3 °C).

Preparation of 2-Pyridyl- and 2-Quinolylhydrazones. A mixture of 0.025 mol of both the hydrazine and the carbonyl compound in 30 mL of ethanol was heated at reflux for the appropriate time (times are listed in the Table I; other procedural modifications are also shown). The reaction mixture was then cooled and the precipitate filtered and recrystallized from ethanol, or an ethanol–water solvent mixture.

Representative NMR Spectra. NMR spectral results for two representative hydrazones are given, where in one R₂ is H and in the other R₂ is CH₃: compound II, δ 2.1 (s, CH₃, 3), 6.5–7.6 (m, Ar–H, 6), 7.95–8.05 (d, py-6H, 1); 8.85 (s, NH, 1); compound III, δ 2.3 (s, CH₃, 3), 6.7–7.7 (m, Ar–H, 5), 8.0 (s, CH, 1), 8.1–8.2 (d, py-6H, 1), 9.85 (s, NH, 1).

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Literature Cited

- (1) Case, F. J. *Chem. Eng. Data* **1976**, *21*, 124.
- (2) Singh, R. B.; Jain, P.; Garg, B. S.; Singh, R. B. *Anal. Chim. Acta* **1979**, *104*, 191.
- (3) Kettrup, A.; Seshadri, T.; Jakobi, F. *Anal. Chim. Acta* **1980**, *115*, 383.
- (4) Otomo, M. *Anal. Chim. Acta* **1980**, *116*, 161.
- (5) Grases, F.; Garcia-Sanchez, F.; Volcarel, M. *Anal. Chim. Acta* **1980**, *119*, 359.
- (6) Schilt, A. A.; Quinn, P. C.; Johnson, C. L. *Talanta* **1979**, *26*, 373.
- (7) Schilt, A. A.; Case, F. *Talanta* **1980**, *27*, 55.
- (8) Perkin, W. H., Jr.; Robinson, R. *Chem. Soc. London, J. Trans.* **1913**, *103*, 1973.

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