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

compd	R^2	yield, %	mp, °C	recryst solvent	IR (KBr), cm^{-1} ν_{Ar-H}	$\nu_{C=C}$	$\nu_{C=N}$	$\nu_{C=S}$	ϕ_{C-H}	NMR data ($CDCl_3$), δ
$R^1 = 2\text{-}C_4H_3S$; $R^3 = C_6H_5$										
5a	4-$CH_3OC_6H_4$	65	93-95	$CHCl_3$/*n*-hexane	3040	1595	1510	1175	990	3.78 (s, 3 H, OCH_3), 6.78-7.98 (m, 14 H, ArH)
b	4-ClC_6H_4	55	111-12	$CHCl_3$/*n*-hexane	3060	1600	1540	1050	1000	
c	3-$NO_2C_6H_4$	60	160-62	C_5H_5N/MeOH	3040	1592	1510	1080	1010	
d	3,4-$Cl_2C_6H_3$	65	104-06	$CHCl_3$/*n*-hexane	3060	1595	1515	1178	995	
e	4-FC_6H_4	50	125-27	C_5H_5N/MeOH	3045	1590	1500	1165	1020	
$R^1 = 2\text{-}C_4H_3S$; $R^3 = 4\text{-}ClC_6H_4$										
f	4-$NO_2C_6H_4$	50	176-78	$CHCl_3$/*n*-hexane	3070	1600	1495	1100	1000	
g	4-FC_6H_4	65	153-55	$CHCl_3$/*n*-hexane	3060	1610	1510	1160	995	7.51-8.31 (m, 13 H, ArH)
h	C_6H_5	55	110-12	C_5H_5N/MeOH	3065	1600	1540	1090	1010	
i	3 $NO_2C_6H_4$	70	217-19	C_5H_5N/MeOH	3040	1590	1540	1090	995	
$R^1 = R^3 = 2\text{-}C_4H_3S$										
j	3-$CH_3OC_6H_4$	60	90-92	C_5H_5N/MeOH	3060	1600	1550	1170	990	3.75 (s, 3 H, OCH_3), 6.84-7.82 (m, 12 H, ArH)
k	3-ClC_6H_4	70	138-40	$CHCl_3$/*n*-hexane	3080	1598	1535	1090	970	
l	3-$NO_2C_6H_4$	60	123-25	$CHCl_3$/*n*-hexane	3070	1620	1500	1020	980	

[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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Registry No. **5a**, 85957-59-1; **5b**, 82613-22-7; **5c**, 82613-23-8; **5d**, 82613-25-0; **5e**, 85957-60-4; **5f**, 85957-61-5; **5g**, 85957-62-6; **5h**, 73910-99-3; **5i**, 85957-63-7; **5j**, 85957-64-8; **5k**, 85957-65-9; **5l**, 74441-39-7.

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

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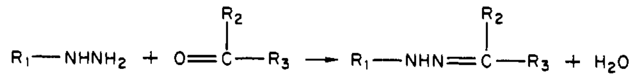
The synthesis of 18 new 2-pyridylhydrazone and 2-quinolylhydrazone compounds containing either 2-thiophene or 2-furan functionalities is described.

Continued interest still exists in the study of a variety of different hydrazones, particularly 2-pyridiyl- and 2-quinolylhydrazones, 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-quinolylhydrazones 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.



$$R_1{-}NHNH_2 + O{=}\overset{\overset{\displaystyle R_2}{|}}{C}{-}R_3 \longrightarrow R_1{-}NHN{=}\overset{\overset{\displaystyle R_2}{|}}{C}{-}R_3 + H_2O$$

R_1 = 2-pyridyl or 2-quinolyl
R_2 = H or CH_3
R_3 = 2-thiophene or 2-furan functionality

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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	$C_{10}H_9N_3S$
II[b]	2-pyridyl	2-acetylthiophene	102	3[e]	40	$C_{11}H_{11}N_3S$
III[b]	2-pyridyl	3-methyl-2-thiophenecarboxaldehyde	142	4	37	$C_{11}H_{11}N_3S$
IV[c]	2-pyridyl	5-methyl-2-thiophenecarboxaldehyde	178	3[e]	57	$C_{11}H_{11}N_3S$
V[c]	2-pyridyl	5-chloro-2-thiophenecarboxaldehyde	217	1	56	$C_{10}H_8N_3SCl$
VI[c]	2-pyridyl	5-bromo-2-thiophenecarboxaldehyde	219	1	57	$C_{10}H_8N_3SBr$
VII[b]	2-pyridyl	2-furaldehyde	140	2	49	$C_{10}H_9N_3O$
VIII[c]	2-pyridyl	5-methyl-2-furaldehyde	135	3.5	46	$C_{11}H_{11}N_3O$
IX[c]	2-pyridyl	5-nitro-2-furaldehyde	202	1	62	$C_{10}H_8N_4O_3$
X[b]	2-quinolyl	2-thiophenecarboxaldehyde	151	2	63	$C_{14}H_{11}N_3S$
XI[b]	2-quinolyl	2-acetylthiophene	130	6.5[e]	65	$C_{15}H_{13}N_3S$
XII[b]	2-quinolyl	3-methyl-2-thiophenecarboxaldehyde	140	4[e]	39	$C_{15}H_{13}N_3S$
XIII[c]	2-quinolyl	5-methyl-2-thiophenecarboxaldehyde	163	3[e]	55	$C_{15}H_{13}N_3S$
XIV[c]	2-quinolyl	5-chloro-2-thiophenecarboxaldehyde	196	1	65	$C_{14}H_{10}N_3SCl$
XV[c]	2-quinolyl	5-bromo-2-thiophenecarboxaldehyde	173	1	58	$C_{14}H_{10}N_3SBr$
XVI[b]	2-quinolyl	2-furaldehyde	143	2	51	$C_{14}H_{11}N_3O$
XVII[b]	2-quinolyl	5-methyl-2-furaldehyde	171	3.5	57	$C_{15}H_{13}N_3O$
XVIII[d]	2-quinolyl	5-nitro-2-furaldehyde	230, dec.	0.5	92	$C_{14}H_{10}N_4O_3$

[a] Elemental analyses in agreement with theoretical values were obtained and submitted for review. [b] Crystallizing solvent: $C_2H_5OH-H_2O$. [c] Crystallizing solvent: C_2H_5OH. [d] Triturated with C_2H_5OH. [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 R_2 is H and in the other R_2 is CH_3: compound II, δ 2.1 (s, CH_3, 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, CH_3, 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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