

**NITRILES IN HETEROCYCLIC SYNTHESIS: A NEW SYNTHESIS
OF SOME 4H-NAPHTHOPYRANS, 2H-BENZOTHIOPYRANS
AND THEIR FUSED DERIVATIVES**

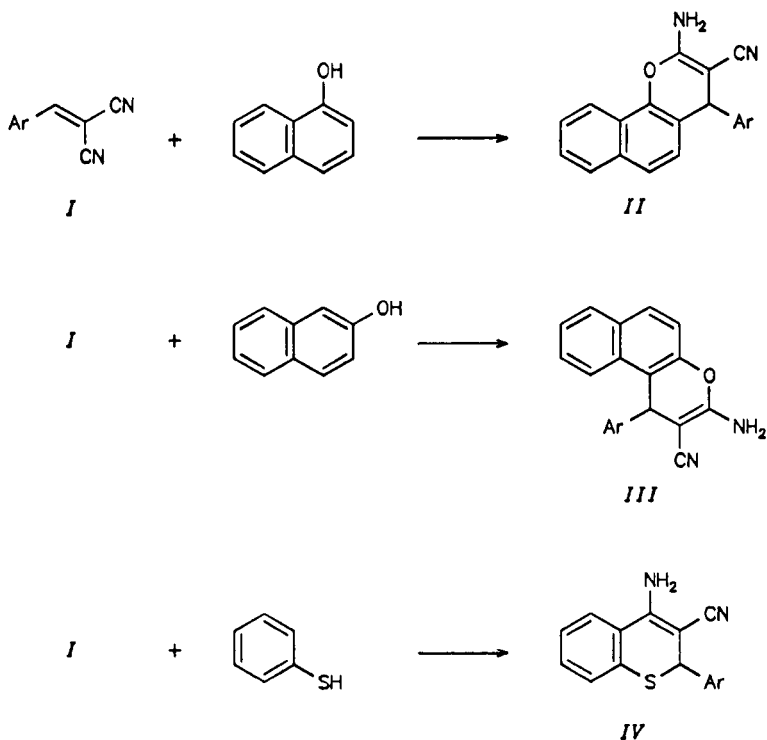
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α,β -Unsaturated nitriles are versatile reagents and their chemistry has received considerable attention^{1,2}. The reactivity of cinnamionitriles *I* toward active methylene reagents has been extensively utilised for synthesis of pyranes^{3,4}.

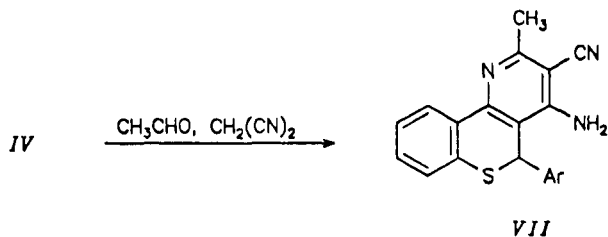
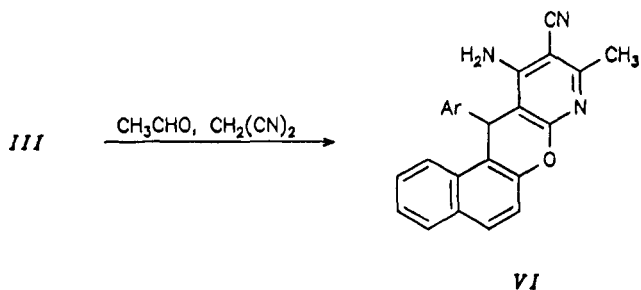
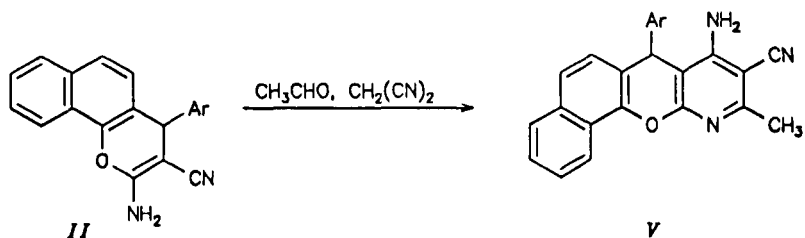


In formulae *I* - *IV*: a, Ar = *o*-Cl-C₆H₄,
b, Ar = *p*-CH₃-C₆H₄

We realized to explore the reactivity of aryl mercaptanes toward *I* with the aim of developing a new route to benzothiopyrans. The work enabled synthesis of several new naphtho[*b*]-4*H*-pyrans and benzo[*b*]-2*H*-thiopyrans.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were measured in KBr pellets. ^1H NMR spectra were measured in $(\text{CD}_3)_2\text{SO}$ using TMS as an internal standard on Varian EM 360 NMR spectrometer (90 MHz);



In formulae *II* - *VII*: a, Ar = *o*-Cl-C₆H₄
 b, Ar = *p*-CH₃-C₆H₄

chemical shifts are expressed as δ values (ppm). Microanalyses were performed by the microanalytical units at Cairo University and Assiut University.

Reaction of *Ia, Ib* with Naphthols and Thiophenol

A solution of *Ia, Ib* (0.01 mol) in ethanol (30 ml) was treated with equimolar amount of the appropriate naphthol or thiophenol and piperidine (0.5 ml). The reaction mixture was heated until precipitation was completed. The solid product formed was collected by filtration and recrystallized from a suitable solvent to give the corresponding *II, III* and *IV*. The physical constants and spectral data of the prepared compounds are presented in Tables I and II.

TABLE I
Characterization data of the newly synthesized compounds

Com- pound	M.p., °C	Yield, % Solvent	Formula (M. w.)	Calculated / Found			
				% C	% H	% N	% S
<i>IIa</i>	292	85	C ₂₀ H ₁₃ N ₂ OCl (332.8)	72.18	3.91	8.41	
		dioxane		72.1	4.0	8.5	
<i>IIb</i>	314	90	C ₂₁ H ₁₆ N ₂ O (312.4)	80.74	5.16	8.96	
		dioxane		80.6	5.3	9.1	
<i>IIIa</i>	287	90	C ₂₀ H ₁₃ N ₂ OCl (332.8)	72.18	3.91	8.41	
		dioxane		72.0	4.1	8.3	
<i>IIIb</i>	335	90	C ₂₁ H ₁₆ N ₂ O (312.4)	80.74	5.16	8.96	
		dioxane		80.3	5.0	8.7	
<i>IVa</i>	187	60	C ₁₆ H ₁₁ N ₂ SCl (298.8)	64.31	3.71	9.38	10.94
		ethanol		64.2	3.7	9.5	11.1
<i>IVb</i>	152	55	C ₁₇ H ₁₄ N ₂ S (278.3)	73.36	5.06	10.07	11.52
		ethanol		73.2	5.1	10.1	11.7
<i>Va</i>	215	65	C ₂₄ H ₁₆ N ₃ OCl (397.9)	72.45	4.05	10.56	
		ethanol		72.6	4.1	10.6	
<i>Vb</i>	261	65	C ₂₅ H ₁₉ N ₃ O (377.4)	79.55	5.07	11.13	
		ethanol		79.7	5.3	11.4	
<i>VIa</i>	210	72	C ₂₄ H ₁₆ N ₃ OCl (397.9)	72.45	4.05	10.56	
		ethanol		72.5	4.2	10.7	
<i>VIb</i>	276	80	C ₂₅ H ₁₉ N ₃ O (377.4)	79.55	5.07	11.13	
		ethanol		79.7	4.8	11.3	
<i>VIIa</i>	207	80	C ₂₀ H ₁₄ N ₃ SCl (363.9)	66.01	3.88	11.54	8.99
		ethanol		66.4	4.3	11.7	9.3
<i>VIIb</i>	207	80	C ₂₁ H ₁₇ N ₃ S (343.4)	73.44	4.99	12.24	9.34
		ethanol		73.1	5.2	12.3	9.5

Preparation of Naphthopyranopyridines *V*, *VI* and Benzothiopyranopyridines *VII*

A solution of equimolar amounts of acetaldehyde and malononitrile (0.01 mol) in ethanol (30 ml) was added to a suspension of the appropriate enamionitriles *II*, *III* and *IV* (0.01 mol) in ethanol (30 ml) and piperidine (0.5 ml). The reaction mixture was heated under reflux for about 3 h. The solvent was then evaporated under reduced pressure and the solid product was collected by filtration and recrystallized from the proper solvent to give the corresponding pyridine derivatives *V* – *VII*. The physical constants and spectral data of the prepared compounds are presented in Tables I and II.

TABLE II
Selected IR and ^1H NMR data for compounds listed in Table I

Compound	IR, cm^{-1}	^1H NMR (δ , ppm)
<i>Ila</i>	3 380, 3 320 (NH_2); 2 220 (CN)	4.8 s, 1 H (pyran 4-H); 6.8 – 7.9 m, 12 H (Ar and NH_2)
<i>Ilb</i>	3 380, 3 320 (NH_2); 2 220 (CN)	2.2 s, 3 H (CH_3); 4.8 s, 1 H (pyran 4-H); 6.8 – 7.8 m, 12 H (Ar and NH_2)
<i>IIla</i>	3 380, 3 330 (NH_2); 2 220 (CN)	5.85 s, 1 H (pyran 4-H); 6.7 – 7.8 m, 12 H (Ar and NH_2)
<i>IIlb</i>	3 380, 3 330 (NH_2); 2 220 (CN)	5.8 s, 1 H (pyran 4-H); 2.2 s, 3 H (CH_3); 6.7 – 7.9 m, 12 H (Ar and NH_2)
<i>IVa</i>	3 370, 3 320 (NH_2); 2 220 (CN)	6.1 s, 1 H (thiopyran 4-H); 6.8 – 7.5 m, 10 H (Ar and NH_2)
<i>IVb</i>	3 370, 3 320 (NH_2); 2 220 (CN)	6.05 s, 1 H (thiopyran 4-H); 2.2 s, 1 H (CH_3); 6.8 – 7.6 m, 10 H (Ar and NH_2)
<i>Va</i>	3 370, 3 310 (NH_2); 2 215 (CN)	2.4 s, 3 H (ring CH_3); 4.8 s, 1 H (pyran 4-H); 6.8 – 7.9 m, 12 H (Ar and NH_2)
<i>Vb</i>	3 370, 3 310 (NH_2); 2 215 (CN)	2.2 s, 3 H (CH_3); 2.4 s, 3 H (ring CH_3); 4.85 s, 1 H (pyran 4-H); 6.7 – 7.8 m, 12 H (Ar and NH_2)
<i>Vla</i>	3 380, 3 320 (NH_2); 2 220 (CN)	2.45 s, 3 H (ring CH_3); 5.85 s, 1 H (pyran 4-H); 6.8 – 7.7 m, 12 H (Ar and NH_2)
<i>Vlb</i>	3 380, 3 320 (NH_2); 2 220 (CN)	2.2 s, 3 H (CH_3); 2.45 s, 3 H (ring CH_3); 5.85 s, 1 H (pyran 4-H); 6.8 – 7.7 m, 12 H (Ar and NH_2)
<i>VIIa</i>	3 370, 3 310 (NH_2); 2 220 (CN)	2.4 s, 3 H (CH_3); 6.1 s, 1 H (thiopyran 4-H); 6.8 – 7.5 m, 10 H (Ar and NH_2)
<i>VIIb</i>	3 370, 3 310 (NH_2); 2 220 (CN)	2.2 s, 3 H (CH_3); 2.45 s, 3 H (ring CH_3); 6.1 s, 1 H (thiopyran 4-H); 6.7 – 7.5 m, 10 H (Ar and NH_2)

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