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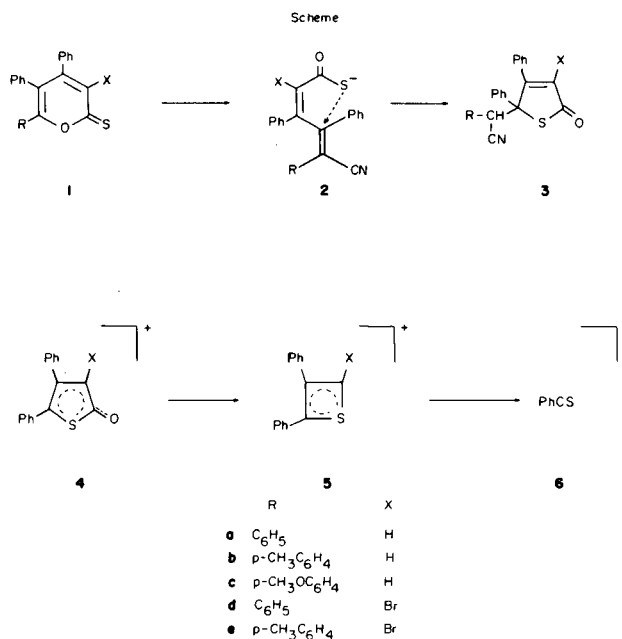
The reaction of sodium cyanide with 4,5,6-triaryl-2*H*-pyran-2-thiones and their 3-bromo derivatives led to the formation of 2,5-dihydrothiophenes.

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Nucleophilic attack on the 2*H*-pyran-2-one ring usually occurs at the carbonyl carbon (position 2) (1-5) or at position 6 (6-8). The reaction of cyanide ion with substituted 2*H*-pyran-2-one derivatives gave 5-cyano-2,4-pentadienoic acids assumed to be formed by attack at position 6 (8).

In the present study, the reaction of the 4,5,6-triaryl-2*H*-pyran-2-thiones **1a-c** and their 3-bromo derivatives **1d,e** with sodium cyanide in dimethylformamide led to the formation of the 2,5-dihydrothiophen-2-one derivatives **3a-c** and **3d,e**, respectively. The course of the reaction seems to be essentially the same as with the corresponding oxygen analogues. Initial attack of the cyanide ion at C-6 followed by ring opening at the 1,6 bond leading to the thiocarboxylate anion **2**. However, owing to the greater nucleophilicity of sulfur over oxygen, recyclization to the thiophene derivatives takes place. Such cyclization is assumed to proceed *via* an intramolecular attack of the thiocarboxylate anion at C-5 which is greatly facilitated by the electron attracting effect of the nitrile group. It should be noted that the exact stereochemistry of the thiocarboxylate anion **2** was not determined. However, cyclization to the thiophene derivatives necessitates a *cis* configuration about the double bond *alpha* to the thiocarboxylate (C₂-C₃). Moreover, spatial requirements make an *s-trans* conformation around the diene moiety (C₃-C₄) more likely (Scheme).

Consistent with the assigned structure, the infrared spectra of the parent 2,5-dihydrothiophen-2-one derivatives showed a cyclic carbonyl absorption at 1680-1700 cm⁻¹ and a cyanide band at 2240-2250 cm⁻¹. Their ¹H nmr spectra exhibited two singlets at δ 5.00-5.05 and δ



6.30-6.33 for the side chain methine and C-3 thiophene ring protons, respectively. This assignment is supported by the disappearance of the low field signal in the spectrum of the 3-bromo derivative **3d** (Table II). Their mass spectra gave the cation **4** as the base peak arising by elimination of RCHCN radical from the molecular ion. Loss of CO from the base peak **4** affords the moderately intense ion **5** which gives rise to the cation **6** at *m/e* 121 (Scheme).

Table I
Analytical Data of 2,5-Dihydrothiophen-2-one Derivatives

Mp °C	Formula	Calcd. %					Found %					
		C	H	N	Br	S	C	H	N	Br	S	
3a	155	C ₂₄ H ₁₇ NOS	78.4	4.7	3.8		8.7	78.6	4.8	3.8		8.9
3b	166	C ₂₅ H ₁₉ NOS	78.7	5.0	3.7		8.4	78.6	4.9	3.5		8.6
3c	131	C ₂₅ H ₁₉ NO ₂ S	75.5	4.8	3.5		8.1	75.8	5.0	3.4		8.2
3d	185	C ₂₄ H ₁₆ BrNOS	64.6	3.6	3.1	17.9	7.2	64.4	3.7	2.9	17.6	7.2
3e	152	C ₂₅ H ₁₈ BrNOS	65.2	3.9	3.0	17.4	7.0	64.9	3.9	3.2	17.1	6.9

Table II
Spectral Data of 2,5-Dihydrothiophen-2-one Derivatives

	IR (cm ⁻¹)		¹ H NMR Chemical Shift (δ/ppm) (a)			
	C=O	C≡N	H-3 (s)	CH (s)	Ar-H (m)	Others
3a	1680	2250	6.33	5.05	7.2	
3b	1700	2240	6.30	5.00	7.2	2.27 (s, CH ₃)
3c	1690	2250				
3d	1695			5.03	7.1	
3e	1690					

(a) s, Singlet, m, multiplet.

EXPERIMENTAL

Microanalyses were performed by Microanalysis Unit, Cairo University, Cairo. Infrared spectra were measured with a Unicam SP 1025 spectrophotometer on potassium bromide pellets or in Nujol. The ¹H nmr spectra were recorded on a Varian A-60 A instrument for solutions in deuteriochloroform with TMS as an internal standard. Mass spectra were recorded on an AEI MS902 instrument.

The 4,5,6-triaryl-2H-pyran-2-thiones **1a-c** (9,10) and their 3-bromo derivatives **1d,e** (9) were prepared according to the mentioned literature.

4,5-Diphenyl-5-(arylcyanomethyl)-2,5-dihydrothiophen-2-ones (Tables I, II).

A suspension of 4,5,6-triaryl-2H-pyran-2-thione (0.0015 mole) in dimethylformamide (5 ml) was kept with sodium cyanide (0.01 mole) at room temperature for 24 hours. The reaction mixture was then poured into water (20 ml) and extracted with ether. The ethereal solution after

washing with water, drying (sodium sulfate) and evaporation afforded the dihydrothiophenes (50-60% yield) which were crystallized from methanol or ethanol; ms: m/e (relative abundance) **3b** M 381 (12), 252 (21), 251 (100), 223 (18), 121 (9).

3-Bromo-4,5-diphenyl-5-(arylcyanomethyl)-2,5-dihydrothiophen-2-ones (Tables I, II).

They were prepared (50% yield) from the reaction of 3-bromo-4,5,6-triaryl-2H-pyran-2-thiones (0.001 mole) and sodium cyanide (0.01 mole) in dimethylformamide at room temperature for one hour; ms: m/e (relative abundance) **3d** 332, 330 (17), 331, 329 (100), 303; 301 (8), 281 (10), 250 (19), 221 (30), 121 (23), 111 (16), 109 (12), 98 (13), 97 (24), 95 (18).

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