SYNTHESIS OF A NEW TYPE OF PYRAZOLOTHIAZOLES*

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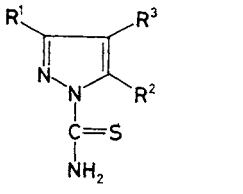
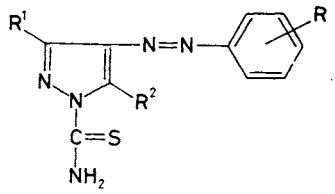
Pyrazolothiazoles *IV* have been synthesized by the condensation of appropriate 3,4,5-trisubstituted 1-thiocarbamoylpyrazoles *I*, *II* with various (ω-bromoacetyl)coumarins *III*.

In continuation of our work on the synthesis of heterocyclic systems derived from coumarin[1-3] we herein report the synthesis of 3-[2-(3,4,5-trisubstituted 1*H*-pyrazol--1-yl)-4-thiazolyl]-2*H*-1-benzopyran-2-ones *IV* in a single step from substituted 3-(ω-bromoacetyl)coumarin *III*.

3,4,5-Trisubstituted 1-thiocarbamoyl pyrazoles *I*, *II* on condensation with substituted 3-(ω-bromoacetyl)coumarins *III* in ethanol and N,N-dimethylformamide furnished the title compounds *IV*. Some of the hydroxy and N-arylamine analogues



I



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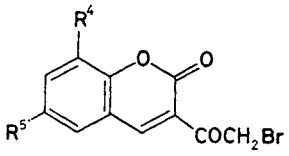
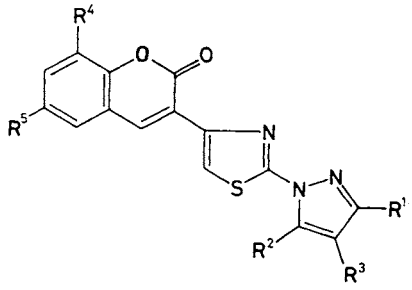


III



IV

* Part V in the series Studies on Coumarin Derivatives; Part IV see ref.[1].

TABLE I

3-[2-(3,4,5-Trisubstituted 1*H*-pyrazol-1-yl)-4-thiazolyl]-2*H*-1-benzopyran-2-ones *IV* and acetyl derivatives

Compound[a]	R^1 / R^2	R^3	R^4 / R^5	M.p. °C	Calculated/found	
					% N	% S
IVa	CH_3	H	H	220–222	13·00	9·90
	CH_3		H		13·02	9·88
IVb	CH_3	H	OCH_3	216–218	11·90	9·06
	CH_3		H		11·80	9·04
IVc	CH_3	H	H	260–262	10·45	7·96
	CH_3		Br		10·42	7·94
IVd	CH_3	H	Br	221–223	8·73	6·65
	CH_3		Br		8·74	6·68
IVe	CH_3	phenylazo	H	102–103	13·84	6·32
	CH_3		Br		13·82	6·30
IVf	CH_3	phenylazo	H	98–99	11·97	5·47
	CH_3		Br		11·94	5·48
IVg	CH_3	phenylazo	OCH_3	105–107	15·39	7·03
	CH_3		H		15·37	7·02
IVh	CH_3	*p*-methoxy-	H	80–82	13·06	5·97
	CH_3	phenylazo	Br		13·04	5·96
IVi	CH_3	*p*-methoxy-	Br	145–147	11·38	5·20
	CH_3	phenylazo	Br		11·36	5·22
IVj	*o*-HOC_6H_4	H	H	83–85	9·07	6·91
	C_6H_5		H		9·04	6·92
IVk	*o*-HOC_6H_4	H	H	120–122	7·75	5·90
	C_6H_5		Br		7·74	5·87
IVl	*o*-HOC_6H_4	H	Br	93–95	6·76	5·15
	C_6H_5		Br		6·74	5·12
IVm	*o*-$CH_3COOC_6H_4$	H	H	75–77	8·32	6·34
	C_6H_5		H		8·34	6·30
IVn	*o*-$CH_3COOC_6H_4$	H	H	250–251	14·00	8·00
	C_6H_5NH		H		14·00	7·90
IVo	CH_3	H	H	190–192	12·68	7·24
	$C_6H_5NCOCH_3$		H		12·66	7·22
IVp	CH_3	*p*-methoxy-	H	80–83	15·32	7·00
	CH_3	phenylazo	H		15·30	7·02
IVq	CH_3	*p*-methoxy-	OCH_3	105–107	14·38	6·57
	CH_3	phenylazo	H		14·36	6·56
IVr	CH_3	phenylazo	H	76–78	16·39	7·19
	CH_3		H		16·38	7·17

[a] All compounds were obtained in 70–80% yields and satisfactory C, H analysis have been obtained. Compounds *IVg*, *IVk*, *IVm*, *IVo*, *IVp*, *IVq*, and *IVr* were recrystallized from methanol, the others from benzene.

of these compounds on treatment with acetic anhydride and pyridine yielded the corresponding acetates.

Most of the title compounds exhibited three absorption bands in the UV region, at 250 ± 5 nm, 295 nm, and 340 nm. Compound *IVa* exhibited in IR spectra (KBr; ν_{max}, cm^{-1}) bands at 1 270, 1 610, 1 720 due to C—S—, C=N—, and lactone carbonyl of coumarin. ^1H NMR spectrum (C^2HCl_3) of *IVa* showed signals at δ 2·30 s, 3 H (C_3—methyl): 2·8 s, 3 H (C_5—methyl): 6·0 s, 1 H, (pyrazole proton at C_4): 7·2–7·7 m, 4 H (aromatic): 8·2 s, 1 H (thiazole proton at C_5) and 8·5 s, 1 H, (coumarin at C_4). Mass spectrum: *m/z* 323 (M^+, 100%), 308(8), 306(12), 295(5), 282(4), 202(4), 146(10), and 145(10).

Treatment of the hydroxy (*IVj*) and the N-arylamine (*IVn*) derivatives with hot acetic anhydride in the presence of a catalytic amount of pyridine gave the corresponding acetates *IVm* and *IVo*. IR spectrum (Nujol: ν_{max}, cm^{-1}) of these compounds showed the absence of bands corresponding to —O—H and —NH— while exhibiting absorption bands at 1 750 (—O—$COCH_3$) and at 1 770 cm^{-1} (—N—$COCH_3$) in addition to the other characteristic absorptions indicating the formation of the desired products.

EXPERIMENTAL

All the melting points are uncorrected. IR spectra (ν_{max}, cm^{-1}) were recorded on a Perkin–Elmer 282 instrument. ^1H NMR spectra were scanned on a Varian spectrometer using tetramethylsilane as internal standard. Mass spectrum was scanned on a Jeol-JMS-D300 (Japan) mass spectrometer at 70 eV.

The substituted 3-(ω-bromoacetyl)coumarins were prepared by bromination of the appropriate 3-acetylcoumarins[4] using bromine in chloroform. 3,5-Dimethyl-4-substituted-1-thiocarbamoylpyrazoles have been prepared by the known procedure[5].

3-[2-(3,4,5-Trisubstituted 1*H*-pyrazol-1-yl)-4-thiazolyl]-2*H*-1-benzopyran-2-ones *IV*

A mixture of the substituted 3-(ω-bromoacetyl)coumarin (1 mmol) and the appropriate 3,4,5-trisubstituted 1-thiocarbamoylpyrazole (1 mmol) was refluxed in ethanol (15 ml) and dimethylformamide (15 ml) for 4 h. The mixture was cooled and the separated solid filtered and crystallized from a suitable solvent.

Acetyl derivatives of IVj *and* IVn: The acetates of *IVj* and *IVn* were prepared by dissolving these compounds in the minimum amount of hot acetic anhydride and keeping the mixture at room temperature for 24 h in presence of a catalytic amount of pyridine. The mixture was digested with cold water and the separated solid filtered off and recrystallized from methanol. The analytical data are included in Table I.

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