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Short Communication

Synthesis of 3-Hetarylcoumarins from 3-Acetylcoumarins†

SUMMARY

Vilsmeier reaction ($DMF/POCl_3$) on the phenylhydrazones and semicarbazones of 3-acetylcoumarin derivatives led to a simple synthesis of 3-(4-formylpyrazol-3-yl)coumarins.

Fischer indole reaction on the phenylhydrazones of 3-acetylcoumarins gave rise to 3-indolylcoumarins.

The resulting pyrazolyl and indolylcoumarins were studied for their absorption–emission characteristics and they have been evaluated on polyester.

1. INTRODUCTION

In a previous paper[1] we reported a new approach to the synthesis of 3-hetarylcoumarins employing coumarin-3-acetic acids as starting materials. In this paper we report another approach to the synthesis of 3-hetarylcoumarins, utilising 3-acetylcoumarins as raw materials.

In contrast to the coumarin-3-acetic acids which are available only with difficulty and in moderate yields from salicylaldehydes, the use of 3-acetylcoumarins affords a considerable advantage as they are obtained in high yield by the condensation of salicylaldehydes with ethyl acetoacetate in the presence of a basic catalyst.

The Vilsmeier reaction on the phenylhydrazone and the semicarbazone

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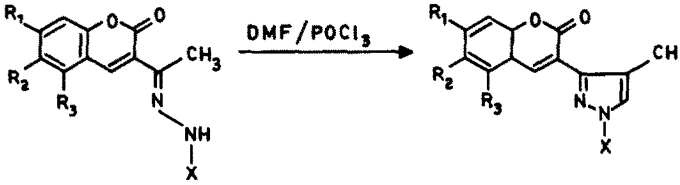
of acetophenone has been studied by Kira and co-workers;[2,3] the products were shown to be the 4-formylpyrazoles in good yield.

2. RESULTS

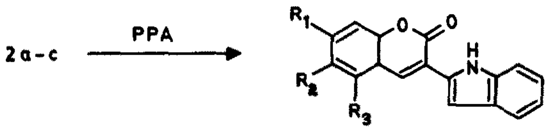
Vilsmeier reaction on the phenylhydrazones and semicarbazones of 3-acetylcoumarins gave the expected formylpyrazole derivatives. The products were identified by elemental analysis, chemical properties and infrared spectra (peaks at 1680 cm^{-1} and 1710 cm^{-1} assignable to the aldehyde and coumarin carbonyl functions). They were converted to the corresponding nitriles (**8a–c**, **9a–c**) via the oximes.

The phenylhydrazone derivatives were subjected to Fischer indole reaction in polyphosphoric acid leading to indolylcoumarin derivatives (**10a–c**). The structures of the products were established on the basis of elemental analysis, IR spectrum (NH peak at 3410 cm^{-1}) and strong fluorescence.



2a–c (X = Ph)
3a–c (X = CONH$_2$)

4a–c (X = Ph)
5a–c (X = H)



10a–c

	R1	R2	R3
a ⟹	H	H	H
b ⟹	Benzo		H
c ⟹	NEt$_2$	H	H

TABLE 1

Absorption–Emission Data and Dyeing Evaluation on Polyester

Compound	*Absorption*		*Emission* λ_{max} (*nm*)	*Grade*[a]	*Pick-up*[b]	*Xeno*	*Thermo*[c]	*Colour*
	λ_{max} (*nm*)	*log E*						
4b	370	4·53	450	1–2 (greenish)	—	—	—	Whitening
4c	405	4·50	—	—	3	1	4	Greenish yellow (dull)
5b	372	4·23	445	0 (greenish)	—	—	—	Whitening
5c	410	4·57	—	—	4	3	3–4(R)	Greenish yellow (bright)
8b	372	4·29	450	1–2	—	—	—	Whitening
8c	405	4·53	474	—	3–4	4–5	3–4	Greenish yellow (bright)
9b	372	4·44	448	0 (greenish)	—	—	—	—
9c	416	4·92	482	—	4	3–4	3–4	Greenish yellow (dull)
10b	414	4·38	—	—	—	—	—	—
10c	434	4·71	508	—	4	1	3–4	Reddish yellow

[a] The grading shown refers to the whitening effect produced on polyester fibre with respect to Uvitex ERN (grade 3) as reference.

[b] Pick-up values: 5, 2 × standard depth; 4, 1 × standard depth; 3, 0·5 × standard depth; 2, 0·33 × standard depth; 1, 0·16 × standard depth.

[c] R = Red: denotes change in tone on thermotest.

The products obtained were studied for their absorption–emission characteristics and whitening/dyeing properties on polyester (Table 1). The results show that only two of the compounds synthesised, **4b** and **8b**, had little whitening effect. On the other hand many of the compounds had appreciable tinctorial power and of these three compounds (**5c**, **8c** and **9c**) had moderate to good lightfastness properties.

3. EXPERIMENTAL PROCEDURE

All melting points are uncorrected. Ultraviolet spectra were recorded on a Beckmann DK-2 spectrophotometer, the fluorescence spectra on an Aminco–Bowman spectrophotometer and IR spectra on a Perkin–Elmer 397 spectrophotometer.

3-Acetylcoumarin (**1a**), 3-acetyl-5,6-benzocoumarin (**1b**), and phenylhydrazones (**2a**, **2b**) and semicarbazones (**3a**, **3b**) were prepared following the reported procedures.[4,5]

3-Acetyl-7-diethylaminocoumarin (**1c**)[6] was prepared from 4-diethylaminosalicylaldehyde and ethyl acetoacetate following a similar procedure reported for **1b**: yield 72%, m.p. 156–157 °C (EtOH). The phenylhydrazone[6] (**2c**), m.p. 162 °C (EtOH), and semicarbazone (**3c**),[6] m.p. 221 °C (aq EtOH), of **1c** were prepared following the usual procedures in 96% and 90% yields respectively.

3.1. Vilsmeier Reaction on the Phenylhydrazones and Semicarbazones of 3-Acetylcoumarins (2a–c, 3a–c)

To the Vilsmeier reagent prepared from DMF (17 ml) and $POCl_3$ (0·03 mol), the phenylhydrazone or semicarbazone derivative (0·01 mol) was added with stirring at 0–5 °C. The reaction mixture was slowly heated on a water bath for 6 h at 80–85 °C. The cooled reaction mixture was poured into ice cold water and neutralised with $NaHCO_3$ to pH 8–9. The product which separated was filtered, washed with water and dried. The yield, m.p., crystallisation solvent and molecular formula of the various products are given in Table 2.

3.2. Preparation of the Oxime Derivatives (6a–c, 7a–c)

A mixture of the aldehyde (0·05 mol) and neutralised $NH_2OH.HCl$ (0·07 mol) in DMF (5–7 mol) was refluxed for 1 h. The reaction mixture

TABLE 2
Physical Data of 3-Hetaryl Derivatives

Compound	*Yield* (%)	*M.p.* (°C)	*Recrystallisation solvent*	*Molecular formula*
Pyrazoles				
Formyl				
4a	90	222–223	HOAc	$C_{19}H_{12}N_2O_3$
4b	98	226–227	DMF:MeOH	$C_{23}H_{14}N_2O_3$
4c	95	198–199	EtOH	$C_{23}H_{21}N_3O_3$
5b	90	280	DMF:MeOH	$C_{17}H_{10}N_2O_3$
5c	95	199	EtOH	$C_{17}H_{17}N_3O_3$
Oximes				
6b	90	160	EtOH	—
6c	96	199	EtOH (aq.)	—
7c	98	154–155	EtOH	—
Nitriles				
8b	90	250	HOAc	$C_{23}H_{13}N_3O_2$
8c	92	156–157	EtOH	$C_{23}H_{20}N_4O_2$
9b	90	320	DMF:MeOH	$C_{17}H_9N_3O_2$
9c	95	162	EtOH	$C_{17}H_{16}N_4O_2$
Indoles				
10b	70	285	DMF:MeOH	$C_{21}H_{13}NO_2$
10c	92	231	acetone:H_2O	$C_{21}H_{20}N_2O_2$

was added to water and the product which separated was filtered and dried. The physical data of the products are given in Table 2.

3.3. Preparation of the Nitriles (8a–c, 9a–c)

The oxime derivative (0·025 mol) was refluxed in Ac_2O (6–8 ml) for 1 h and, after the usual work-up, the product was filtered, washed and dried. The physical characteristics of the nitrile derivatives are shown in Table 2.

3.4. Preparation of the Indole Derivatives (10a–c)

The phenylhydrazone derivative (**2**) (0·004 mol) was added to freshly prepared PPA (from 10·5 g P_2O_5 and 4·5 g H_3PO_4) at 80 °C and the temperature was raised slowly to 140–150 °C. The temperature was maintained for 1 h and the product obtained after the usual work-up was filtered, washed and dried. The physical characteristics of the various indolylcoumarins prepared are shown in Table 2.

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