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Attempted Synthesis of 3-Arylazo-4-methylcoumarins: An Unexpected Dimerisation of Ethyl α-Arylazoacetoacetates

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SUMMARY

Attempts to synthesise coumarin derivatives by condensation of ethyl α-arylazoacetoacetates with phenols failed, but gave rise to a facile formation of pyrazolone derivatives via a dimerisation reaction.

We have been investigating for some time the synthesis of various 3-substituted coumarins with a view to studying their fluorescence and dyeing properties. Our interest in this area prompted us to investigate the effect of a chromophore, namely an aryl azo group, on the coumarin fluorophore. All the azocoumarins so far reported in the literature have been synthesised by the coupling reaction of diazotised anilines with hydroxycoumarin derivatives.

For the synthesis of the coumarin derivatives **1**, the easily accessible β-keto ester derivative **2**, namely ethyl α-arylazoacetoacetate, was thought of as a suitable starting material (Scheme 1). All attempts to condense resorcinol (**3a**) or *m*-diethylaminophenol (**3b**) under Pechmann reaction conditions[1] using catalysts like H_2SO_4, $POCl_3$, $ZnCl_2$, NH_4OAc,[2] etc., resulted either in the recovery of the unchanged ketoester (**2**) or in the formation of highly impure reaction products. Surprisingly, however, the

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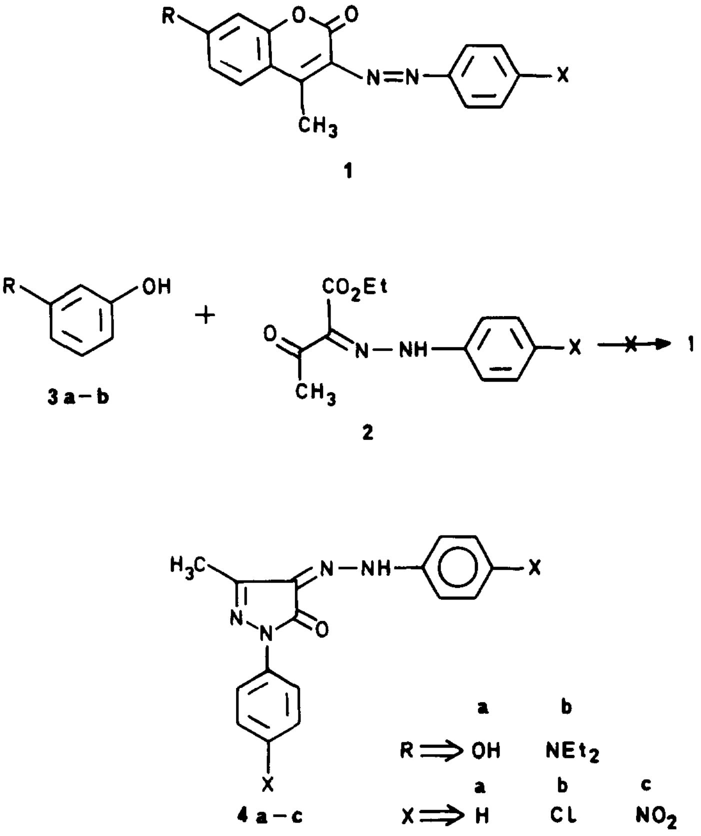
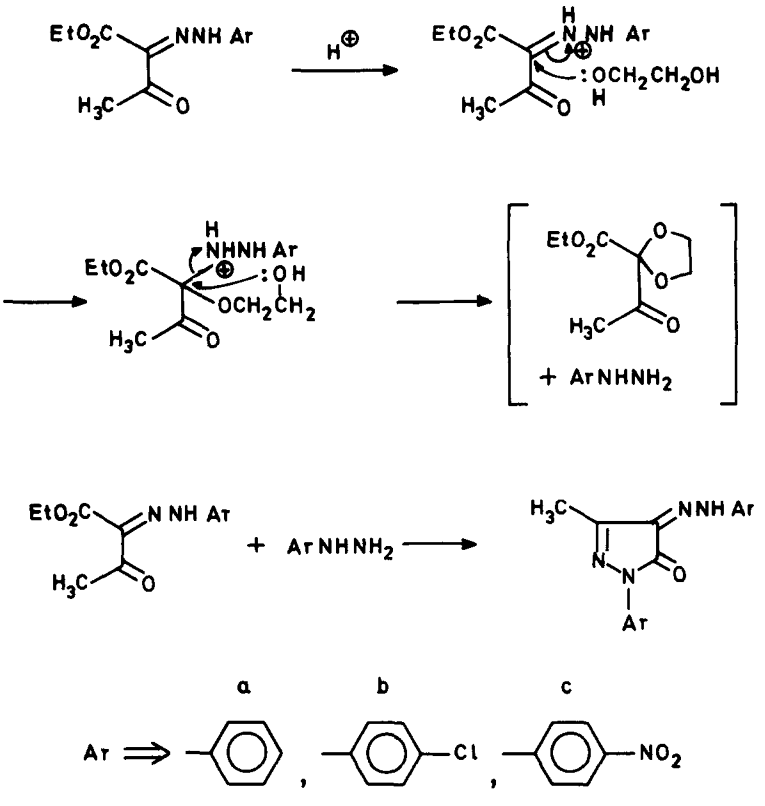


Scheme 1

formation of a single pure product, irrespective of the phenol used in the condensation, was observed when the reaction was carried out in refluxing ethanediol and *p*-toluenesulphonic acid, suggesting an intermolecular reaction of **2**. The same product was also formed in good yields when **2** was refluxed alone in ethanediol containing *p*-toluenesulphonic acid. It was shown on the basis of m.p., unambiguous synthesis, elemental analysis, PMR spectra (**4a** and **4b**) and mass spectra (**4a** and **4b**) to be the pyrazolone dye (**4**).

This method thus provides an efficient one-stage synthesis of 1,4-symmetrically aryl substituted pyrazolone dyes. A possible mechanism is presented in Scheme 2.



Scheme 2

EXPERIMENTAL PROCEDURE

All melting points are uncorrected. PMR spectra were recorded on a Varian EM-360 spectrometer using TMS as internal standard and mass spectra on a Varian Mat CH7 instrument.

The arylazoketoesters (**2a**,[3] **2b**[4] and **2c**[5]) were prepared following the reported procedures.

General procedure

A mixture of α-arylazoketoester (**2**) (0·01 mol), ethanediol (10 ml) and *p*-toluenesulphonic acid (0·015 mol) was refluxed for 3–4 h. The reaction

TABLE 1
Physical Data of the Pyrazolone Dyes (**4a–c**)

Compound	*X*	*Yield (%)*	*M.p. (°C)*	*Crystallisation solvent*	*Mol. formula*[a]	*PMR (δ,ppm)*	*MS M^+*
4a	H	65	153–5 (155–6)[6]	EtOH	$C_{16}H_{14}N_4O$	CCl_4 2·3 (s, 3H, CH_3) 7·6 (m, 11H, 10Ar—H, 1—NH)	278
4b	Cl	64	228–30 (232)[7]	EtOAc	$C_{16}H_{12}Cl_2N_4O$	TFA 2·8 (s, 3H, CH_3) 7·6 (m, 8H, Ar—H)	346
4c	NO_2	68	302–4 (298–300)[8]	EtOAc	$C_{16}H_{12}N_6O_5$	—	—

[a] Satisfactory elemental analyses were obtained.

mixture was cooled, then poured into ice-water; the solid was washed repeatedly with water, filtered and dried. The yield, m.p., crystallisation solvent, molecular formula and spectral data of the resultant pyrazolones are given in Table 1.

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