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Synthesis of Basic Hansa Yellow Analogs and their Butylamino Derivatives from *N*-Amino-3-acetoacetamidopyridinium 2,4-Dinitrophenate

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ABSTRACT

*In a multi-step synthesis, a series of new basic dyes (**4a–4g**, **5a–5g** and **8a–8g**) were prepared starting from 3-(acetoacetamido)pyridine. Whilst coupling of arene-diazonium salts with* N-*amino-3-(acetoacetamido)pyridinium 2,4-dinitrophenate afforded the* N-*aminopyridinium cationic dyes (**4a–4g**), which exist in the hydrazone configuration, the introduction of an alkylamino moiety into the latter dyes gave new basic arylazo dyes (**5a–5g**), in which double intramolecular hydrogen bonding is a principal structural feature. Reaction of these dyes with* p-*dimethylaminobenzaldehyde yielded a further series of basic dyes (**8a–8g**). The structure of the dyes was inferred from elemental and spectral analysis and, in some cases, by alternative synthetic routes.*

1 INTRODUCTION

One of the primary areas of importance of acetoacetarylamide coupling components is in the field of Hansa Yellow dyes and pigments;[1-3] of particular technical importance, are those embodying an alkylamino moiety in their structure.[4] Such compounds provide a fairly full range of hues, especially yellows, oranges and reds. They have very high all-round fastness properties, in particular towards light, heat, water, acids and alkalis, but they have inferior fastness to solvents and plasticizers. The presence of an alkylamino group converts part of the molecule to a more soluble and more deeply colored product which acts as a deflocculating agent in hydrocarbon media.[5]

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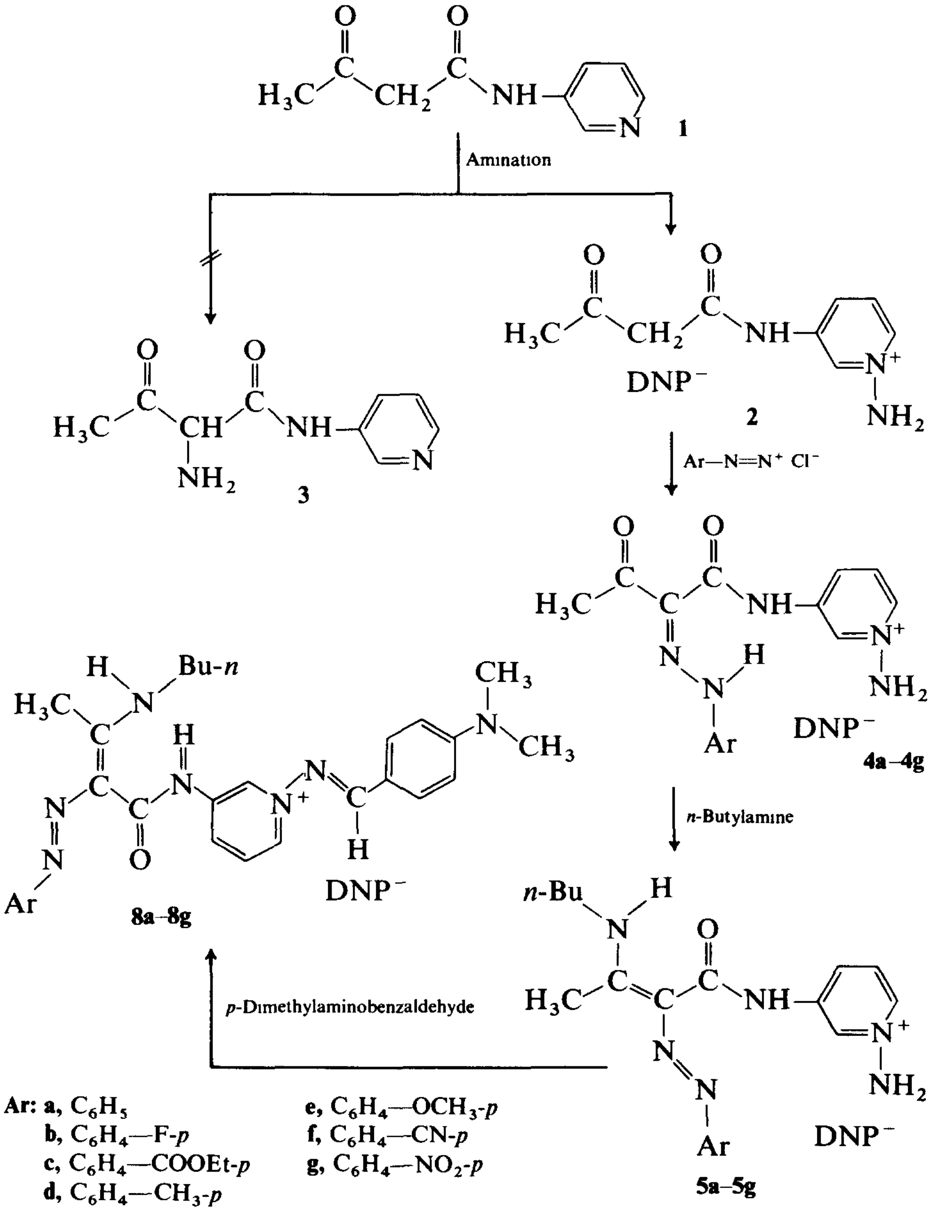


Ar: **a**, C_6H_5
b, C_6H_4—F-*p*
c, C_6H_4—COOEt-*p*
d, C_6H_4—CH_3-*p*
e, C_6H_4—OCH_3-*p*
f, C_6H_4—CN-*p*
g, C_6H_4—NO_2-*p*

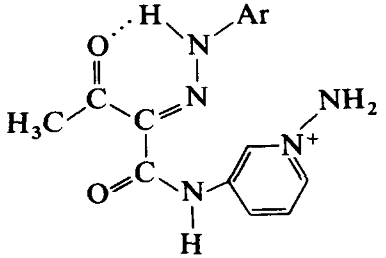
DNP$^-$ = Dinitrophenate anion

Scheme 1

As an extension of a program dealing with the synthesis and reactivity of heterocyclic analogs of Hansa Yellow dyes and pigments,[6-8] a new route is reported here for the synthesis of 3-acetoacetamido-*N*-aminopyridinium Hansa Yellow analogs, and their use in the further preparation of new heterocyclic cationic dyes.

2 RESULTS AND DISCUSSION

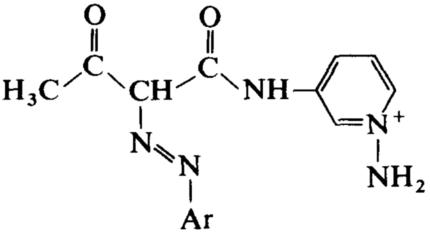
Sheradsky and co-workers[9,10] have described the use of *O*-(2,4-dinitrophenyl)hydroxylamine as an aminating agent for anionic-nitrogen and for carbanions, giving rise to *N*- and *C*-amino derivatives respectively. Yamamoto & Oae[11] later reported the use of the same reagent for the amination of uncharged nucleophiles. On this basis, amination of the previously prepared 3-acetoacetamidopyridine derivative (**1**) (Hanna, M. A. & Girges, M. M., unpublished) was accomplished using *O*-(2,4-dinitrophenyl)-hydroxylamine in the presence of dioxane and at ambient temperature, to give the *N*-amino-3-acetoacetamidopyridinium 2,4-dinitrophenate derivative (**2**) as the sole product in good yield (Scheme 1). The formation of this product, and not the 2-aminopyridine derivative (**3**), is in accord with the results of previous studies[11] on the amination of nitrogen heterocycles. Coupling of compound **2** with arene-diazonium chlorides yielded the 1-amino-3-(α-arylhydrazonoacetoacetamido)pyridinium 2,4-dinitrophenates (**4a**–**4g**) in high yield. In addition to typical absorption due to the amino group, the IR spectra of almost all the products showed a weak and broad absorption band in the 3325–3315 cm^{-1} region. By analogy to the pyridine derivative **1**, this broad absorption band could be ascribed to NH stretching vibrations of amide and hydrazone moieties; the large shift and broadening of absorption due to the latter moiety, as reported by Ramirez & Kirby[12] for simple hydrazones, can result from intramolecular hydrogen bonding as in structure **4-A**.



4-A

Moreover, the IR spectra also showed absorption bands in the region 1665–1620 cm^{-1}, which may be assigned to stretching vibrations of carbonyl groups. The higher frequency band near 1665 cm^{-1} is due to the amide I band, while the band at 1620 cm^{-1} corresponds to acetyl-carbonyl stretching vibrations.

The acetyl-carbonyl bands of the hydrazone derivatives (**4a**–**4g**) were at markedly lower frequency than those of the corresponding β-ketoanilides. This excludes the possibility of an azo–keto structure (**4-B**), which would require the acetyl-carbonyl stretching of the parent 3-acetoacetamidopyridine derivative and that of 1-amino-3-(α-arylazoacetoacetamido)pyridinium 2,4-dinitrophenate (**4-B**) to be at similar wavelengths.



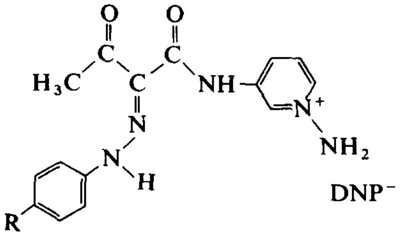
4-B

Among the structural factors which lead to a lowering of the stretching vibration of carbonyl groups are conjugation and hydrogen bonding. However, even if allowance is made for conjugation, the CO frequencies of the dyes under consideration are still much lower than those encountered in other α,β-unsaturated ketones. This suggests that the acetyl CO group of the dyes is involved in hydrogen bonding, as shown in the proposed structure **4-A**. Hence, conjugation of the acetyl-carbonyl group and possible intramolecular hydrogen bonding in the dyes probably result in shifting of the CO frequencies to lower wavelength. The shift in some cases, as in dyes **4a** and **4d**, is so large that the carbonyl band cannot be resolved from the aromatic C═C band near 1600 cm^{-1}.

That these diazonium coupling products of *N*-aminopyridinium derivatives exist exclusively in the hydrazone form can also be concluded from electronic spectral data, most of the dyes showing three main absorption bands at (24·40–34·00) × 10^3 cm^{-1}. Table 1 gives the spectral parameters for the longest-wavelength band of the dyes and Fig. 1 illustrates their electronic absorption spectra in methanol.

The electronic spectra of monophenylazo compounds differ from those of monophenylhydrazones.[13] The azo compounds have a strong conjugation band in the region of (35·7–37·0) × 10^3 cm^{-1}, hydrazones having a weak absorption (or none) at (33·90–35·20) × 10^3 cm^{-1} and an intense band at wave numbers lower than 31·3 × 10^3 cm^{-1}. Further, the spectra of arylhydrazones derived from the reaction of quinones with *N*-alkylarylhydrazines, unlike those of *ortho* and *para* hydroxyazo compounds which can tautomerize into the corresponding arylhydrazones, are largely independent

TABLE 1
Characterization Data of *N*-Aminopyridinium Hansa Yellow Cationic Dyes **4a–4g**



Dye no.	*R*	*M.p. (°C)*	*Formula (M. wt)*	*Analysis: calcd/found (%)*			$\bar{\nu}_{max} \times 10^{-3}$ *(cm^{-1})*[a]	*log ε*
				C	*H*	*N*		
4a	H	189	$C_{21}H_{19}N_7O_7$	52·4	4·0	20·4	24·40	4·37
			(481·42)	52·6	4·1	20·1	(24·40)[b]	4·44
4b	F	152	$C_{21}H_{18}N_7O_7F$	50·5	3·6	19·6	25·20	4·40
			(499·41)	50·7	3·5	19·3	(25·10)	4·16
4c	COOEt	201	$C_{24}H_{23}N_7O_9$	52·1	4·2	17·7	25·10	4·44
			(553·48)	52·4	4·0	17·5	(25·15)	4·44
4d	Me	206	$C_{22}H_{21}N_7O_7$	53·3	4·3	19·8	24·60	4·43
			(495·45)	53·1	4·4	20·0	(24·60)	4·38
4e	OMe	174	$C_{22}H_{21}N_7O_8$	51·7	4·1	19·2	24·65	4·46
			(511·45)	51·9	4·0	18·9	(24·70)	4·45
4f	CN	240	$C_{22}H_{18}N_8O_7$	52·2	3·6	22·1	25·60	4·48
			(506·42)	52·1	3·6	22·45	(25·50)	4·36
4g	NO_2	128	$C_{21}H_{18}N_8O_9$	47·9	3·45	21·3	25·00	4·50
			(526·41)	47·7	3·6	21·4	(24·80)	4·56

[a] $\bar{\nu}_{max}$ for longest-wavelength band.
[b] Values in parentheses are for $\bar{\nu}_{max}$ in cyclohexane.

of the polarity of the solvent.[14] The spectra of dyes **4a–4g** are similar to those of typical hydrazones. The relatively small differences observed are caused by solute–solvent interactions.[15]

Reactions of these coupling products with *n*-butylamine yielded the corresponding 1-amino-3-[α-arylazo-β-(*n*-butylamino)crotonamido]pyridinium 2,4-dinitrophenate dyes (**5a–5g**). The IR spectra of these products showed no absorption corresponding to the amide-carbonyl stretching vibrations (amide I and II bands), the double intramolecular hydrogen bonding of the amide moiety (structures **5-A** and **5-B**) accounting for this. The preference for the azo structure (**5-A**) over the hydrazone structure (**5-B**) is based not only on electronic spectral data of the products, which show three absorption bands in the region of (23·80–36·75) × 10^3 cm^{-1}

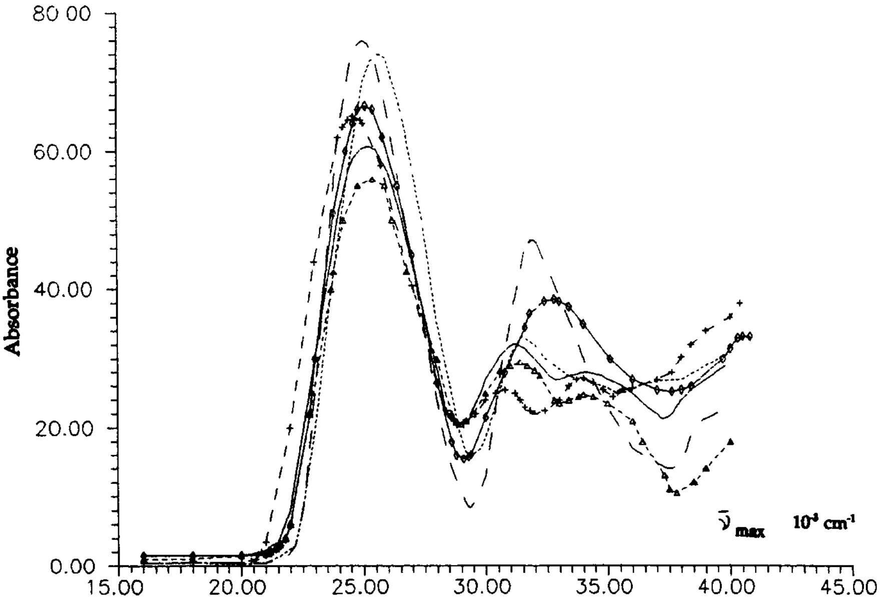
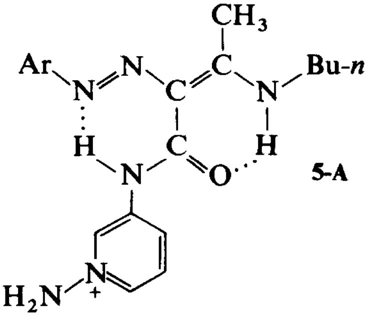
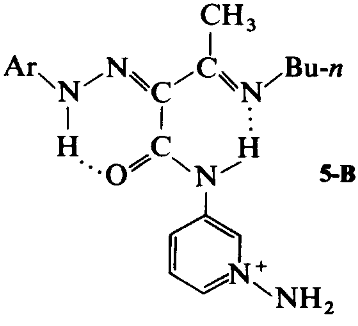


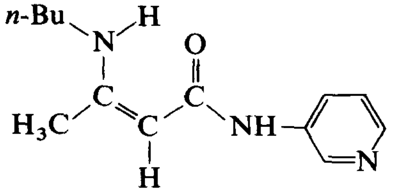
Fig. 1. Electronic absorption spectra of 1-amino-3-(α-arylhydrazonoacetoacetamido)-pyridinium Hansa Yellow cationic dyes in methanol: (△) **4a**; (——) **4b**; (◇) **4c**; (×) **4d**; (- - - -) **4f**; (– – –) **4g**.

(log $\varepsilon = 2{\cdot}98$, 4·41 and 4·63 respectively), in accordance with arylazo structures,[15] but also on their similarity to the previously reported structure of arylazo crotonanilide derivatives.[4,8]

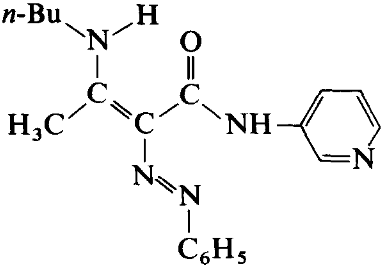
The structure of dyes **5a**–**5g** also follows from the fact that the products obtained by treating *N*-amino Hansa Yellow dyes with *n*-butylamine (through loss of a water molecule) were identical with the product obtained by coupling benzene diazonium chloride with the *n*-butylaminocrotonanilide derivative **6** followed by reaction with *O*-(2,4-dinitrophenyl)hydroxylamine. The structure of the substituted 3-aminocrotonanilide derivatives are well established.[4,8] In the synthesis involving coupling, it cannot be


5-A


5-B



6



7

assumed that the phenylazo aminocrotonanilide **7** is formed by hydrolysis of the aminocrotonanilide **6** to the pyridine, followed by coupling and then recombination with the amine, since the amines do not react with azoacetoacetanilides under the mild aqueous conditions used in coupling.

Mass spectra of representative dyes showed a base peak at 184 mass units, corresponding to the 2,4-dinitrophenol moiety.

Reaction of dyes **5a**–**5g** with *N*,*N*-dimethylaminobenzaldehyde was undertaken to explore their potential in the synthesis of new cationic dyes containing an extended conjugated chromophoric system. The presence of such a system in dyes **8a**–**8g** results in a considerable bathochromic effect in the π–π^* transitions, to the extent that the products exhibit an intense absorption band accompanied by a shoulder in the region of $(23{\cdot}25–21{\cdot}75) \times 10^3\,\text{cm}^{-1}$. The latter inflection might be ascribed to n–π^* transitions (R-bands) which are submerged by the more intense K-band.[16]

Dyeing parameters of the dyes are being investigated and will be reported later.

3 EXPERIMENTAL

All melting points are uncorrected. IR spectra (KBr) were recorded on an SP 2000 Pye–Unicam spectrometer. ^{1}H-NMR spectra ($CDCl_3$) were determined using a Varian EM 360 spectrophotometer at 80 MHz, using TMS as internal standard. EIMS were performed on a Varian 111 spectrometer operating at 70 eV. Ultraviolet and visible measurements were carried out using methanolic solutions on a Pye–Unicam SP 500 spectrophotometer.

3.1 Preparation of 3-acetoacetamido-1-aminopyridinium 2,4-dinitrophenate (2)

A mixture of equimolar quantities (0·01 mol) of 2-acetoacetamidopyridine (**1**) and *O*-(2,4-dinitrophenyl)hydroxylamine was dissolved in dioxane at room temperature and left overnight. Evaporation of solvent under reduced pressure afforded 2·9 g (76·2%) of **2** as a semi-solid residue, which was used as such in the following steps without further purification.

3.2 Preparation of 1-amino-3-(α-arylhydrazonoacetoacetamido)-pyridinium 2,4-dinitrophenate basic dyes (4a–4g)

To a cold and stirred solution of the pyridinium derivative **2** (3·8 g, 0·01 mol) in ethanol (25 ml) containing sodium acetate trihydrate (1 g), was added a cold solution of the appropriate diazonium salt (0·013 mol), at such a rate that the temperature was kept at 0–5°C. When addition was complete, the mixture was stirred for a further 2 h and then filtered. The product was washed with water and recrystallized from ethanol to give yellow to orange crystals in 76–91% yield. Characterization data for the products are given in Table 1.

IR spectra of **4a** (cm^{-1}): 3440–3315 (NH_2 and NH stretching vibrations), 1650 and 1540 (amide I and II bands), 1560 and 1350 (asym. and sym. stretching vibrations of nitro groups) and 1570 ($C{=}N$ group).

3.3 Preparation of 1-amino-3-[α-arylazo-β-(*n*-butylamino)-crotonamido]pyridinium 2,4-dinitrophenate basic dyes (5a–5g)

A solution of *n*-butylamine (5 ml) in ethanol (10 ml) was added to the appropriate *N*-aminopyridide derivative (**4**) (0·01 mol) in ethanol (20 ml). The resulting mixture was refluxed for 2 h, cooled and the product was filtered, washed with dilute ethanol, and recrystallized from ethanol or methanol to give the products as yellow to orange crystals in 80–85% yield. Physical data for the prepared dyes are given in Table 2.

^1H-NMR spectrum of **5a** (δ ppm): 9·52 (br, amide $N\underline{H}$), 8·71 (5, 1H, C_2—H), 8·67 (d, 1H, C_6—H), 8·48 (d, 1H, C_4—H), 8·16–6·38 (m, 9H, Ar—H and C_5—H of pyridine moiety), 4·92 (q, 2H, $NHC\underline{H}_2CH_2$), 4·02 (br, 2H, *N*-amino protons), 3·67 (s, 3H, $C\underline{H}_3C{=}C$), 2·55 (br, 1H, $\underline{H}N{-}CH_2$), 1·35–2·03 (br hump, 4H, $C\underline{H}_2CH_2$ and $CH_3C\underline{H}_2$) and 1·16 (t, 3H, $C\underline{H}_3CH_2$). EIMS of **5a** showed no parent peak. The highest two peaks were observed at *m/z* 337 (89·96%) and 338 (18·80%).

3.4 Alternative synthesis for the cationic arylazo dye (5a)

3.4.1 *Preparation of compound 6*

A solution of *n*-butylamine (3 ml) in ethanol (10 ml) was added to the pyridide derivative **1** (1 g) in ethanol (8 ml). Working up with reaction

TABLE 2
Characterization Data for Cationic Azo Dyes **5a–5g** and **8a–8g**

Dye no.	*R*	*M.p. (°C)*	*Formula (M. wt)*	*Analysis: calc/found (%)*		
				C	*H*	*N*
5a	H	179	$C_{25}H_{28}N_8O_6$	56·0	5·3	20·9
			(536·54)	56·3	5·0	21·1
5b	F	180	$C_{25}H_{27}N_8O_6F$	54·1	4·9	20·2
			(554·54)	54·5	5·2	20·4
5c	COOEt	192	$C_{28}H_{32}N_8O_8$	55·25	5·3	18·4
			(608·61)	55·3	5·2	18·7
5d	Me	191	$C_{26}H_{30}N_8O_6$	56·7	5·5	20·4
			(550·57)	56·8	5·4	20·4
5e	OMe	188	$C_{26}H_{30}N_8O_7$	55·1	5·3	19·8
			(566·57)	54·95	5·6	19·8
5f	CN	198	$C_{26}H_{27}N_9O_6$	55·6	4·85	22·45
			(561·57)	55·75	5·0	22·3
5g	NO_2	168	$C_{25}H_{27}N_9O_8$	51·6	4·7	21·7
			(581·56)	51·5	4·8	21·7
8a	H	129	$C_{34}H_{37}N_9O_6$	61·2	5·6	18·9
			(667·71)	61·35	5·6	19·0
8b	F	168	$C_{34}H_{36}N_9O_6F$	59·55	5·3	18·4
			(685·70)	59·4	5·4	18·6
8c	COOEt	188	$C_{37}H_{41}N_9O_8$	60·1	5·6	17·0
			(739·77)	60·0	5·6	16·8
8d	Me	130	$C_{35}H_{39}N_9O_6$	61·7	5·8	18·5
			(681·73)	61·7	5·9	18·6
8e	OMe	102	$C_{35}H_{39}N_9O_7$	60·25	5·6	18·1
			(697·73)	60·3	5·8	18·4
8f	CN	145	$C_{35}H_{36}N_{10}O_6$	60·7	5·2	20·2
			(692·72)	60·8	5·2	20·0
8g	NO_2	118	$C_{34}H_{36}N_{10}O_8$	57·3	5·1	19·65
			(712·71)	57·5	5·2	19·9

mixture as in Section 3.3 afforded a solid product which was filtered, washed with dilute ethanol and recrystallized from ethanol to give 3-(*n*-butyl)-*N*-(pyrid-3-yl)crotonamide (**6**), as yellow crystals of m.p. 168°C in 79% yield.

Calcd for $C_{13}H_{19}N_3O$ (233·30): C, 66·9; H, 8·2; N, 18·0. Found: C, 67·0; H, 8·3; N, 18·2%. IR spectrum (cm^{-1}): 3330–3305 (NH stretching vibrations), 1640, 1545 (amide I and II bands) and 1585 (C=N). EIMS revealed peaks at 233 (M$^+$, 20·02%); 176 (22·28%); 140 (100%); 135 (15·93%); 84 (35·93%) and 42 (35·57%).

*3.4.2 Coupling of benzenediazonium chloride with compound **6**: formation of compound 7*

A solution of **6** (1·1 g, 0·005 mol) in ethanol (20 ml) was stirred, cooled below 5°C and treated gradually with benzene diazonium chloride (prepared from 0·475 g aniline) over 15 min. Coupling was rapid and the product (**7**) was filtered, washed with water and recrystallized from ethanol as yellow crystals, m.p. 100–101°C in 74% yield.

Calcd for $C_{19}H_{23}N_5O$ (337·41): C, 67·6; H, 6·9; N, 20·8. Found: C, 67·55; H, 6·6; N, 21·1%. The IR spectrum showed absorption bands at 3330–3305 cm^{-1} (NH stretching vibrations) and 1585 cm^{-1} (C=N). ^1H-NMR spectrum (δ ppm): 8·84 (amide $N\underline{H}$), 8·15 (s, 1H, C_2—H), 7·56 (d, 1H, C_4—H), 7·42 (d, 1H, C_6—H), 7·37–7·25 (m, 6H, Ar—H and C_5—H), 5·20 (q, 2H, $HNC\underline{H}_2CH_2$), 3·43 (s, 3H, $C\underline{H}_3C{=}C$), 2·58 (br, 1H, Bu $N\underline{H}$), 1·06–2·26 (br hump, 4H, $CH_2C\underline{H}_2$ and $C\underline{H}_2CH_3$) and 0·99 (t, 3H, $C\underline{H}_3CH_2$). EIMS: *m/z* 337 (M^+, 100%); 233 (32·29%); 216 (15·42%); 135 (12·08%); 105 (48·59%); 57 (45·32%); 42 (80·56%) and 29 (50·42%).

*3.4.3 Amination of compound 7: formation of the basic dye **5a***

Equimolar quantities of derivative **7** and *O*-(2,4-dinitrophenyl)hydroxylamine were reacted together using the procedure described in Section 3.1 for preparation of compound **2**. The product was filtered and recrystallized from ethanol to give **5a** in 63% yield. No depression in m.p. was observed in admixture with the sample prepared by the method described in Section 3·3.

3.5 Preparation of 3-[α-arylazo-β-(*n*-butylamino)crotonamido]-1-(*p*-dimethylaminobenzylideneamino)pyridinium 2,4-dinitrophenate basic dyes (8a–8g)

A mixture of the *N*-aminopyridinium derivatives **5a**–**5g** (0·005 mol) and *p*-dimethylaminobenzaldehyde (0·006 mol) in ethanol (15 ml) was treated with a catalytic amount of 2,4-dinitrophenol and refluxed for 2–3 h. The precipitated dyes were filtered washed with water, dried and recrystallized from ethanol or *n*-butanol to give yellow to reddish orange crystals in an average yield of 63%. Physical data for these dyes are recorded in Table 2.

IR spectrum of **8a** (cm^{-1}): 3325–3305 (NH stretching vibrations), 1550 and 1345 (asym. and sym. stretching vibrations of nitro groups) and 1570 (C=N).

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