DERIVATIVES OF PIVALOYLACETANILIDE

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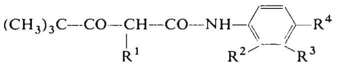
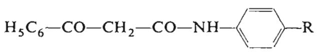
The azomethine dyestuffs prepared in gelatine layer by chromogeneous development of the couplers based on 4,4-dimethyl-3-oxo-N-phenylpentanamide (*I* to *XVII*) and 4,4-dimethyl-3-oxo-N-(sulphamoylphenyl)pentanamide (*XXI* to *XXVII*) have been found to have better light fastness than the correspondingly substituted dyestuffs based on 3-oxo-3,N-diphenylpropanamide (*XVIII* to *XX*). Spectral characteristics of the dyestuffs are given and preparation of the derivatives *XXI* to *XXVII* is described.

In the previous report[1] we described preparation of simple derivatives of 4,4-dimethyl-3-oxo-N-phenylpentanamide (pivaloylacetanilide) as two- or four-equivalent colour couplers and preparation of some azomethine dyestuffs thereof which were evaluated spectroscopically. The following couplers were prepared:



R^1 = H; $OCOCH_3$
R^2 = H; CH_3; Cl; OCH_3
R^3 = H; CH_3; Cl; OCH_3; NO_2
R^4 = H; CH_3; Cl; OCH_3; COOH

Coupler	R^1	R^2	R^3	R^4
I	H	H	H	H
II	H	CH_3	H	H
III	H	H	CH_3	H
IV	H	H	H	CH_3
V	H	Cl	H	H
VI	H	H	Cl	H
VII	H	H	H	Cl
VIII	H	OCH_3	H	H
IX	H	H	OCH_3	H
X	H	H	H	OCH_3
XI	H	H	NO_2	H
XII	H	H	H	COOH
XIII	$OCOCH_3$	CH_3	H	H
XIV	$OCOCH_3$	H	CH_3	H
XV	$OCOCH_3$	H	H	CH_3
XVI	$OCOCH_3$	H	NO_2	H
XVII	$OCOCH_3$	H	H	COOH



R = H; CH_3; Cl

Coupler	*XVIII*	*XIX*	*XX*
R	H	CH_3	Cl

The couplers of the both types were evaluated by the way of practical application. The simplest method of obtaining colour images by chromogenic way, *i.e.* colouration of black-and-white positive material by a colour coupler added to developer, did not give satisfactory results, because the disperse couplers *I* to *XI*, *XII* to *XVI*, *XVIII* to *XX* introduced into the developer by means of solvents separated from the solutions and gave dull colour images which could badly be evaluated. The dyestuffs from water-soluble couplers *XII* and *XVII* showed low substantivity for gelatine layer and passed to the developer solution. As the chromogenic development failed, the couplers were introduced into the gelatine layers. Mixture of cyclohexanone and tricresyl phosphate (1 : 1) proved to be the best solvent of the couplers. The couplers dissolved well in this mixture, they did not crystallize on cooling, and refractive index of the solutions varied within suitable limits. Sensitometric wedges were prepared from the coated sheets and developed with the following developing substances: N,N-diethyl-*p*-phenylenediamine sulphate (TSS), N,N-diethyl-1,4-(2-methyl)phenylenediamine sulphate (CD-2), 3-methyl-4-(N-ethyl-N-methylsulphamoylethyl)aniline (CD-3) and 3-methyl-4-(N-ethyl-N-2'-hydroxyethyl)aniline (CD-4). From the measured spectral values (Table I) it is obvious that the dyestuffs resulting from CD-4 are bathochromically shifted by 1 to 3 nm as compared with those from CD-2. On the contrary, the dyestuffs from TSS show considerable hypsochromic shift (8 to 13 nm) of the absorption maximum as compared with those from CD-2. Some of the couplers gave very weak colouration with the developers CD-4 and TSS and could not be measured spectrophotometrically. The best results were obtained with the developer CD-2.

When evaluating the solid azomethine dyestuffs we observed an only slight hypsochromic shift of the absorption maximum of pivaloylacetanilide as compared with benzoylacetanilide, the reverse shift being found for the corresponding *p*-methyl- and *p*-chloroanilides.

The colour images obtained with the CD-2 developer show less differences in the absorption maxima of the dyestuffs. In the proper series of the pivaloylacetanilide derivatives bathochromic effect is connected with *p*-methyl-, *o*- and *p*-chloro-, and especially *p*-nitrosubstituent. A marked hypsochromic shift is observed with the *p*-methoxy derivative.

The light fastness of the images was determined by xenotest. As the density logarithm is linearly proportional to the irradiation time, the former was plotted against the latter for each sample, and the irradiation time was determined which was necessary to reduce the decadic logarithm of density from zero value to the value −0·2, *i.e.* from the density 1·0 to 0·63. Table I gives these values for the individual dyestuffs obtained with the CD-2 developer. From the Table it follows that the light fastness of the pivaloyl derivatives *I* and *VII* is higher than that of the benzoyl derivatives *XVIII* and *XX* having the same substituents, being the same with the *p*-methyl derivatives *IV* and *XIX*. In the series of four-equivalent couplers the lowest light fastness was found with the azomethine dyestuff derived from the coupler *I*, the maximum being that of *X*. An amazingly strong decrease of light fastness was observed with the two-equivalent couplers *XIII* to *XVI* as compared with the corresponding four-equivalent ones. This decrease is so strong that it cannot be due to experimental error.

For better understanding of the effect of pivaloyl group on properties of the azomethine dyestuffs especially their light fastness we extended the series by couplers

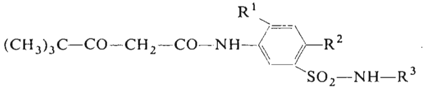
TABLE I

Absorption Maxima, (nm) of Azomethine Dyestuffs in the Layer and Light Fastness of the Dyestuffs formed with CD-2 Developer

Coupler	Developer			Time interval h
	TSS[a]	CD-2	CD-4[a]	
I	—	440	—	17·3
II	—	440	—	18·3
III	433	442	444	24·8
IV	433	446	—	23·9
V	438	452	453	24·8
VI	438	446	447	23·9
VII	—	450	453	28·9
VIII	—	441	—	17·8
IX	436	443	—	27·5
X	—	430	—	33·4
XI	—	449	—	23·5
XIII	—	440	—	14·6
XIV	434	442	—	16·3
XV	—	446	—	14·0
XVI	—	462	—	19·0
XVIII	438	449	450	13·5
XIX	—	439	—	23·3
XX	—	445	—	17·8

[a] The missing values could not be measured due to low density of the colour image.

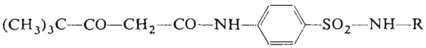
carrying sulfamoyl or alkylsulfamoyl groups in the aromatic ring, which makes the coupler molecule more soluble in aqueous alkaline solutions.



XXI, $R^1 = CH_3$; $R^2 = H$; $R^3 = n\text{-}C_4H_9$
XXII, $R^1 = CH_3$; $R^2 = H$; $R^3 = iso\text{-}C_4H_9$
XXIII, $R^1 = H$; $R^2 = CH_3$; $R^3 = n\text{-}C_3H_9$
XXIV, $R^1 = H$; $R^2 = CH_3$; $R^3 = iso\text{-}C_4H_9$

The compounds *XXI* to *XXIV* were prepared by condensation of methyl 4,4-dimethyl-3-oxopentanoate with 5-amino-4(2)-methylbenzene-N-n(iso)-butylsulphonamide (*XXXVII* to *XL*) in p-xylene in usual way.

The same procedures were applied for preparation of the compounds *XV* to *XXVII* by condensation of methyl 4,4-dimethyl-3-oxopentanoate with 4-aminobenzenesulphonamide or 4-aminobenzene-N-n(iso)-butylsulphonamide (*XXXV* and *XXXVI*).



XXV, $R = H$
XXVI, $R = n\text{-}C_4H_9$
XXVII, $R = i\text{-}C_4H_9$

TABLE II

Absorption Maxima and Light Fastness of Azomethine Dyestuffs with Sulphamoyl Group Prepared by Chromogenic Development with TSS Developer

Coupler	Absorption maximum nm	Fastness
XXII	446	32·9
XXIII	441	33·4
XXIV	439	40·6
XXV	443	17·6
XXVI	446	29·6
XXVII	443	25·6
1-Benzoyl-4′-sulphamoylacetanilide	451	10·3

The sulphonamide couplers were evaluated after chromogenic development. In the alkaline solution of developer only the coupler *XXV* was soluble. The other couplers separated from the solution at the pH of the developer, and, therefore, a greater amount of ethanol had to be added to keep them in solution. Even after this addition the solutions exhibited a slight opalescence, which obviously caused marked turbidity in the sensitograms. The sensitograms of all the couplers except for *XXV* had noticeable turbidity. The gelatine layer with the coupler *XXV* was clear and comparable with that of the corresponding benzoyl derivative. The couplers containing butyl residues caused a worse bleaching of silver, its complete removal being not achieved even after repeated bleaching in $K_2Cr_2O_7$ bath.

Light fastness of the colour images was evaluated in the same way as in the case of the above derivatives. The light fastness is far higher with the coupler *XXV* than with the benzoyl analogue. Also the butyl-carrying couplers exhibit higher light fastness as compared with non-substituted derivative. The absorption maxima and light fastness values of the azomethine dyestuffs prepared with the TSS developer are given in Table II.

EXPERIMENTAL

The melting points were determined with a Kofler apparatus and are not corrected.

Condensation of Acetaminobenzenesulphonyl Chlorides with Butylamine

Solution of 0·005 mol acetylated aminobenzenesulphonyl chloride in 30 ml butylamine was refluxed 3 h and poured in mixture of 100 ml conc. hydrochloric acid and 100 g ice. After 12 h standing the precipitated product was filtered off and dried in air. In this way the following substances were prepared: *XXIX* (3-acetamino-4-methylbenzene-N-butylsulphonamide; m.p. m.p. 111—112°C; yield 85%), *XXX* (3-acetamino-4-methylbenzene-N-isobutylsulphonamide; m.p. 144—148°C; yield 33%), *XXXI* (5-acetamino-2-methylbenzene-N-butylsulphonamide; m.p. 113 to 114°C; yield 51%), *XXXII* (5-acetamino-2-methylbenzene-N-isobutylsulphonamide; m.p. 156 to 158°C; yield 63%), *XXXIII* (4-acetaminobenzene-N-butylsulphonamide; m.p. 135—137°C; yield 65%), and *XXXIV* (4-acetaminobenzene-N-isobutylsulphonamide; m.p. 167—169°C; yield 64%).

Saponification of Acetaminobenzene-N-butylsulphonamides

Solution of 0·005 mol acetaminobenzene-N-butylsulphonamide in 22 ml methanol and 9 ml conc. hydrochloric acid was refluxed 3 h, cooled, and poured in 90 ml saturated sodium carbonate solution, whereupon the separated product was filtered off, washed with water until neutral, and dried in air. In this way the following substances were prepared: *XXXV* (4-aminobenzene-N-butylsulphonamide; m.p. 95—96°C; yield 93%), *XXXVI* (4-aminobenzene-N-isobutylsulphonamide; m.p. 133—134°C; yield 93%), *XXXVII* (3-amino-4-methylbenzene-N-butylsulphonamide; m.p. 97—98°C; yield 78%), *XXXVIII* (3-amino-4-methylbenzene-N-isobutylsulphonamide; m.p. 134—136°C; yield 86%), *XXXIX* (5-amino-2-methylbenzene-N-butylsulphonamide; m.p. 80—81°C; yield 75%), *XL* (5-amino-2-methylbenzene-N-isobutylsulphonamide; m.p. 116 to 117·5°C; yield 85%).

Preparation of Colour Couplers

0·1 mol Sulphonamide and 0·12 mol methyl 4,4-dimethyl-3-oxopentanoate in 100 ml xylene was heated 3 h with simultaneous distillation off of 75 ml of the solvent. After the end of the reaction the residue in the flask was cooled and kept at 0°C for 24 h. The separated crystalline product was collected by suction, washed with little ethanol, and dried in air. Properties and elemental analyses of the sulphonamidic couplers *XXI* to *XXVII* are given in Table III.

Preparation of Emulsion with Coupler

0·4 to 0·6 g of the coupler was dissolved in warm mixture of 1 ml tricresyl phosphate and 1 ml cyclohexanone. The hot solution was mixed with a solution containing 10 ml 10% gelatine in water, 8 ml water, and 2 ml 5% aqueous solution of Sandopan CBH (sodium dodecylbenzenesulphonate). After two minutes mixing the dispersion was mixed with 80 ml AgBr emulsion, coated on a triacetate support (using a laboratory coating device) in dark, and dried in air. It was kept in light-tight packing in refrigerator.

Baths for Processing of Sensitometric Wedges

Developer: Solution A — 1·2 g hydroxylamine sulphate and 5·0 g proper developing substance were dissolved in 500 ml water; solution B — 2·0 g chelaton III, 75 g potassium carbonate and 1·5 g potassium bromide were dissolved in water and the volume was adjusted at 500 ml. Before use the solution A and B were mixed, warmed, and 10 ml benzyl alcohol was dissolved therein.

TABLE III

Properties of Couplers with Sulphamoyl Groups and Results of their Elemental Analyses

Compound	Formula (m.wt.)	Yield m.p., °C	Calculated/Found % C	% H	% N
XXI	$C_{18}H_{27}N_2O_4S$ (368·4)	73 154—155	58·70 58·53	7·60 7·60	7·60 7·76
XXII	$C_{18}H_{27}N_2O_4S$ (368·4)	46 112—113·5	58·70 58·88	7·60 7·82	7·60 7·62
XXIII	$C_{18}H_{27}N_2O_4S$ (368·4)	70 121—121·5	58·70 58·56	7·60 7·70	7·60 7·80
XXIV	$C_{18}H_{27}N_2O_4S$ (368·4)	68 88·5—89	58·70 58·66	7·60 7·63	7·60 7·43
XXV	$C_{13}H_{18}N_2O_4S$ (298·3)	77 183—187	52·30 52·37	6·07 6·22	9·40 9·71
XXVI	$C_{17}H_{26}N_2O_4S$ (354·5)	89 161—162	57·70 57·84	7·30 7·46	7·90 8·06
XXVII	$C_{17}H_{26}N_2O_4S$ (354·5)	74 157—158·5	57·70 57·92	7·30 7·46	7·90 8·12

The bath for additional development: 2·0 g disodium pentaoxodisulphite and 1·0 g potassium bromide were dissolved in 800 ml water and the solution was adjusted at 1 000 ml volume.

Stop bath: 200·0 g crystalline dissodium thiosulphate, 10·0 g anhydrous disodium sulphite, 10 ml glacial acetic acid, 25·0 anhydrous sodium acetate and 15·0 g potassium aluminium sulphate were dissolved in 800 ml water, and the overall volume was adjusted at 1 000 ml by addition of water.

Bleaching bath: 20·0 g potassium bromide, 5·0 g potassium dichromate, 40·0 g potassium aluminium sulphate, 60·0 ml glacial acetic acid and 2·5 g anhydrous sodium acetate were dissolved in 800 ml water, the solution was adjusted at 1 000 ml volume with water and at pH 2·0 with sodium hydroxide.

Fixing bath: 3·0 g chelaton III and 200·0 g disodium thiosulphate (cryst.) were dissolved in 700 ml water, and the volume was adjusted at 1 000 ml with water.

The sensitometric wedges were processed in the following way: developing 6 min at 18°C, additional developing 5 min at 18°C, stop bath 5 min at 16—20°C, rinsing in running water 10—12 min, bleaching 5 min at 18°C, fixing 4 min at 18°C, and final rinsing in running water 15 min. The wedges were exposed in a sensitometer Joyce type 2L (Joyce-Loebl, Gateshead, GB).

Chromogenic Development of Couplers with Sulphamoyl Group

0·3 g Coupler was dissolved in 15 ml ethanol (only the coupler *XXV* was dissolved in the developer without ethanol), and the solution was adjusted at 300 ml volume by addition of Fomacolor negative developer. The sensitometric wedges on black-and-white material (Kinopositiv Foma) were exposed without filter with continuous wegde of the sensitometer Joyce 20 s and were developed by the process Fomacolor negative omitting the additional developer and stop-bath. N,N-Diethyl-*p*-phenylenediamine sulphate was used as developing substance (6 min at 18°C).

Determination of Light Fastness

The light fastness was determined in a Xenotest system Casulla, Hanau, xenon discharge lamp. All the samples were placed in the apparatus at the same time at 25°C at relative humidity 60%. The time decrease of dyestuff during irradiation was measured with a densitometer Macbeth type 504 at three different points of the sensitometric wedge having different density values at the beginning of irradiation. As logarithm of density is linearly dependent on the irradiation time, the dependence logarithm of density *vs* time was plotted for each sample, and the time interval was determined which was needed for irradiation of the sample to decrease its logarithm of density from the value zero to —0·2, *i.e.* from density 1·0 to 0·63.

The elemental analyses were carried out in Analytical Chemistry Department, Institute of Chemical Technology, Pardubice, under guidance of Mr J. Bulušek. The light fastness determination was carried out in Research Institute of Photographic Chemistry, Fotochema, Hradec Králové. The authors are indebted to Miss E. Česáková and Mrs P. Martincová for technical assistance.

REFERENCES

1. Kořínek J., Poskočil J., Arient J.: This Journal, in press.

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