1-PIVALOYLACETANILIDE DERIVATIVES

Josef KOŘÍNEK[a], Jaroslav POSKOČIL[a] and Josef ARIENT[b]

[a]*Institute of Chemical Technology, 532 10 Pardubice and*
[b]*Research Institute of Photographic Chemistry, 500 00 Hradec Králové*

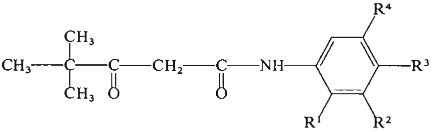
Received June 4th, 1978

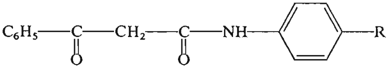
A series of couplers have been prepared on the basis of 4,4-dimethyl-3-oxo-N-phenylpentaneamide. Some of them have been converted into the respective azomethine dyestuffs the absorption maxima of which have been compared with those of the corresponding couplers based on 3-oxo-3,N-diphenylpropaneamide.

Recent patent literature[1-5] gives a great number of couplers based on 4,4-dimethyl-3-oxo-N-phenylpentaneamide (pivaloylacetanilide). Influence of the pivaloyl group on properties of the couplers is not given in literature except for a patent of Kodak[5] in which favourable effect of the pivaloyl group on light fastness of the corresponding azomethine dyestuffs is mentioned. Using simple compounds we tried to explain the influence of the pivaloyl group on properties of the respective azomethine dyestuffs.

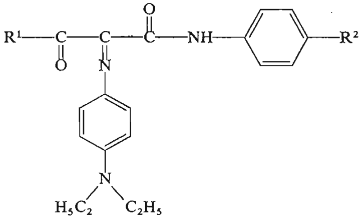
We prepared a series of derivatives of pivaloylacetanilide, 1-chloro-1-pivaloylacetanilide, and 1-acetoxy-1-pivaloylacetanilide. The couplers *I* to *XIV* were prepared by condensation of methyl pivaloylacetate with aniline, *o*-, *m*-, *p*-toluidine, *o*-, *m*-, *p*-chloroaniline, *m*-nitroaniline, *p*-aminobenzoic acid, dimethyl 5-aminoisophthalate, *o*-, *m*-, and *p*-anisidine. Condensation of methyl pivaloylacetate with *o*- and *p*-nitroaniline should have given 4,4-dimethyl-3-oxo-N-(2-nitrophenyl)pentaneamide and 4,4-dimethyl-3-oxo-N-(4-nitrophenyl)pentaneamide. However, these couplers could not be isolated from the reaction mixtures, because conversion to the respective products was very low. Chromatographic analysis of the reaction mixtures (Silufol thin layer, cyclohexane–acetone 1 : 1) showed that the 2-nitro derivative of pivaloylacetanilide was present in amounts of only about 5 to 10%, whereas the 4-nitro derivative was present in about the same amounts as the non-reacted *p*-nitroaniline. These mixtures could not be separated even by repeated crystallizations.

Chlorination of the compounds *Ia* to *IVa*, *VIa* to *XIa*, *XIIIa* and *XIVa* with sulphuryl chloride[6] gave the 2-chloro-4,4-dimethyl-3-oxo-N-phenylpentaneamide derivatives *Ib* to *IVb*, *VIb* to *XIb*, *XIIIb* and *XIVb*, respectively. The chloro derivative *Vb* could not be prepared in pure form. The coupler *XIIb* was prepared by chlorination of a mixture of *p*-nitroaniline and 4,4-dimethyl-3-oxo-N-(4-nitrophenyl)pentaneamide.





R = H, Cl, CH_3



R^1 = pivaloyl, benzoyl
R^2 = H, CH_3, Cl

Compound	R^1	R^2	R^3	R^4
I	H	H	H	H
II	CH_3	H	H	H
III	H	CH_3	H	H
IV	H	H	CH_3	H
V	Cl	H	H	H
VI	H	Cl	H	H
VII	H	H	Cl	H
VIII	OCH_3	H	H	H
IX	H	OCH_3	H	H
X	H	H	OCH_3	H
XI	H	NO_2	H	H
XII	H	H	NO_2	H
XIII	H	H	COOH	H
XIV	H	CO_2CH_3	H	CO_2CH_3

TABLE I

Properties of the Compounds *Ia—XIa*, *XIIIa*, *XIVa*, *Ib—IVb*, *VIb—VIIIb*, *Xb—XIVb*, *Ic—IVc*, *VIc*, *VIIc*, *Xc—XIVc*, *XXI—XXIII*

Compound	Formula (m. wt.)	Yield, % m.p., °C	Calculated/Found			
			% C	% H	% N	% Cl
Ia	$C_{13}H_{17}NO_2$	70·0	70·88	8·13	6·35	—
	(212·2)	76·5^{a}	71·15	7·96	6·32	—
IIa	$C_{14}H_{19}NO_2$	59·1	72·07	8·20	6·01	—
	(233.3)	83—84^{a}	72·04	8·02	6·27	—
IIIa	$C_{14}H_{19}NO_2$	70·1	72·07	8·20	6·01	—
	(233·3)	59·5—60·5^{a}	71·97	8·33	6·27	—
IVa	$C_{14}H_{19}NO_2$	81·0	72·07	8·20	6·01	—
	(233·3)	98·0^{a}	72·08	8·05	6·12	—
Va	$C_{13}H_{16}ClNO_2$	42·0	61·53	6·35	5·52	13·97
	(253·7)	52·5—53·5^{a}	61·44	6·34	5·70	13·83
VIa	$C_{13}H_{16}ClNO_2$	53·2	61·53	6·35	5·52	13·97
	(253·7)	38·5—43·5^{a}	61·90	6·20	5·33	13·71
VIIa	$C_{13}H_{16}ClNO_2$	66·3	61·53	6·35	5·52	13·97
	(253·7)	121·0^{a}	61·28	6·39	5·61	14·09
VIIIa	$C_{14}H_{19}NO_3$	31·0	67·44	7·68	5·61	—
	(249·3)	44·0—45·5^{a}	67·23	7·52	5·80	—
IXa	$C_{14}H_{19}NO_3$	46·2	67·44	7·68	5·61	—
	(249·3)	37·5—44·0^{a}	67·83	7·42	5·37	—
Xa	$C_{14}H_{19}NO_3$	75·5	67·44	7·68	5·61	—
	(249·3)	87·5^{a}	67·37	7·66	5·46	—
XIa	$C_{13}H_{16}N_2O_4$	37·8	59·08	6·10	10·60	—
	(264·3)	84·0^{b}	58·82	5·93	10·81	—
XIIIa	$C_{14}H_{17}NO_4$	51·8	63·86	6·50	5·31	—
	(263·3)	212·5^{c,d}	63·94	6·46	5·70	—
XIVa	$C_{17}H_{21}NO_6$	86·0	60·89	6·31	4·18	—
	(335·4)	112·0—113^{e}	60·82	6·52	4·36	—
Ib	$C_{13}H_{16}ClNO_2$	90·5	61·54	6·36	5·52	13·97
	(253·7)	152—153^{b}	61·86	6·31	5·41	14·08
IIb	$C_{14}H_{18}ClNO_2$	80·8	62·80	6·78	5·23	13·24
	(267·7)	90—91^{b}	62·56	6·61	5·48	13·40
IIIb	$C_{14}H_{18}ClNO_2$	75·9	62·80	6·78	5·23	13·24
	(267·7)	106—107^{b}	62·70	6·59	5·17	13·34
IVb	$C_{14}H_{18}ClNO_2$	72·6	62·80	6·78	5·23	13·24
	(267·7)	149—150^{b}	63·02	6·70	5·17	13·06

TABLE I
(*continued*)

Compound	Formula (m. wt.)	Yield, % m.p., °C	Calculated/Found			
			% C	% H	% N	% Cl
VIb	$C_{13}H_{15}Cl_2NO_2$	49·1	54·18	5·25	4·86	—
	(288·2)	115·5–116[b]	53·89	5·29	4·83	—
VIIb	$C_{13}H_{15}Cl_2NO_2$	70·5	54·18	5·25	4·86	24·61
	(288·2)	142·5–143[b]	54·19	5·19	4·81	24·55
VIIIb	$C_{14}H_{18}ClNO_3$	74·7	59·26	6·39	4·94	12·49
	(283·8)	97·0–97·5[b]	59·35	6·48	5·12	12·60
Xb	$C_{14}H_{18}ClNO_3$	66·6	59·26	6·39	4·94	12·49
	(283·8)	150·5[b]	59·41	6·38	5·16	12·53
XIb	$C_{13}H_{15}Cl_2NO_4$	42·9	52·25	5·06	9·41	—
	(298·7)	117·0[b]	52·57	5·30	9·46	—
XIIb	$C_{13}H_{15}ClN_2O_4$	38·4	52·25	5·06	9·41	—
	(298·7)	138–141[b]	51·98	5·14	9·56	—
XIIIb	$C_{14}H_{16}ClNO_4$	66·8	56·48	5·42	4·70	—
	(297·7)	190[b,c]	56·62	5·63	4·59	—
XIVb	$C_{17}H_{20}ClNO_6$	88·4	55·22	5·45	3·79	9·59
	(368·8)	164–166[b,c]	55·37	5·32	3·61	9·70
Ic	$C_{15}H_{19}NO_4$	64·0	64·97	6·91	5·05	—
	(277·3)	98·0–99·0[f]	64·87	6·86	4·96	—
IIc	$C_{16}H_{21}NO_4$	50·6	65·96	7·27	4·81	—
	(291·4)	79·5–80·0[f]	65·84	7·08	4·74	—
IIIc	$C_{16}H_{21}NO_4$	50·5	65·96	7·27	4·81	—
	(291·4)	77·0–78·0[f]	66·06	7·18	4·92	—
IVc	$C_{16}H_{21}NO_4$	57·2	65·96	7·27	4·81	—
	(291·4)	110·0[c,f]	66·08	7·14	4·73	—
VIIc	$C_{15}H_{18}ClNO_4$	51·6	57·78	5·81	4·49	—
	(311·8)	106–106·5[f]	57·58	5·94	4·36	—
Xc	$C_{16}H_{21}NO_5$	63·0	62·53	6·87	4·56	—
	(307·4)	121·0[f]	56·47	6·82	4·62	—
XIc	$C_{15}H_{18}N_2O_6$	30·9	55·90	5·63	8·69	—
	(322·3)	106·5–107[f]	56·04	5·48	8·60	—
XIIc	$C_{15}H_{18}N_2O_6$	47·5	55·90	5·63	8·69	
	(322·3)	115–118[f]	55·88	5·52	8·74	—
XIIIc	$C_{16}H_{19}NO_6$	42·8	59·81	5·96	4·36	—
	(321·3)	190·0[c,f]	59·64	6·08	4·45	—

TABLE I
(*continued*)

Compound	Formula (m. wt.)	Yield, % m.p., °C	Calculated/Found % C	 % H	 % N	 % Cl
XIVc	$C_{19}H_{23}NO_8$ (393·4)	81·5 138—139[f]	58·01 58·12	5·89 5·66	3·56 3·48	— —
XXI	$C_{15}H_{13}NO_2$ (239·3)	60·9 104·5—105[e]	75·30 75·15	5·48 5·15	5·87 5·91	— —
XXII	$C_{16}H_{15}NO_2$ (253·3)	56·3 132·5[g]	75·87 75·99	5·97 6·07	5·53 5·29	— —
XXIII	$C_{15}H_{12}ClNO_2$ (273·7)	55·3 157·0[b]	65·82 65·59	4·42 4·55	5·12 5·32	— —

[a] n-Hexane; [b] ethanol; [c] decomposition; [d] water; [e] 50% aqueous ethanol; [f] ethanol with addition of water until durable turbidity; [g] 75% aqueous ethanol.

Reaction of anhydrous sodium acetate in acetic acid with the chloro derivatives *Ib* to *IVb*, *VIIb*, *Xb* to *XIVb* gave the corresponding 1-acetoxy-4,4-dimethyl-3-oxo-N-phenylpentaneamides which, after development with a colour-forming developer, should give azomethine dyestuffs of the same properties as those from the couplers *I* to *XIII*.

Relations between structure of the both types of the prepared couplers and properties of the corresponding azomethine dyestuffs were evaluated from the colour images formed by chromogeneous development of gelatin layers containing the couplers. For the sake of comparison the solid azomethine dyestuffs *XV* to *XVII* were prepared from the four-equivalent couplers *Ia*, *IVa*, *VIIa* and from the two-equivalent couplers *IVc*, *VIIc* by oxidation condensation with N,N-diethyl-*p*-phenylenediamine hydrochloride. The dyestuffs *XVI* and *XVII* have identical elemental composition whether prepared from the four- or two-equivalent couplers. Also comparison of electronic absorption spectra (Table I) shows that the dyestuffs prepared from the couplers *IVa* and *IVc* are identical, the same being true of the dyestuffs prepared from *VIIa* and *VIIc*. Analogous dyestuffs *XVIII* to *XX* of the benzoyl series were prepared from the couplers *XXI* to *XXIII*, respectively, for comparison.

XXI, R = H *XXII*, $R = CH_3$ *XXIII*, R = Cl

Dyestuff	Starting coupler	R^1	R^2
XV	*Ia*	pivaloyl	H
XVI	*IVa, IVc*	pivaloyl	CH_3
XVII	*VIIa, VIIc*	pivaloyl	Cl
XVIII	*XXI*	benzoyl	H
XIX	*XXII*	benzoyl	CH_3
XX	*XXIII*	benzoyl	Cl

The absorption maxima of the visible band of the pivaloyl derivatives are somewhat shifted hypsochromically with the non-substituted (*XV*) and the *p*-methyl (*XVI*) derivatives, being bathochromically shifted with the *p*-chloro derivative (*XVII*) (all the cases compared with the corresponding derivatives of the benzoyl series *XVIII* to *XX*). The considerable difference in values of the molar absorption coefficients are due to conjugation of the benzoyl group which is a strong chromophore as compared with the pivaloyl group. However, cross-conjugation with the phenylenediamine system results in that the present benzoyl group does not have bathochromic effect on the electronic spectra.

EXPERIMENTAL

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

1-Pivaloylacetanilide Derivatives *Ia* to *XIIIa*

Mixture of 0·045 mol methyl pivaloylacetate (7·12 g), 0·040 mol aromatic amine and 10 ml xylene was heated at 135—140°C 5 h, the formed methanol being continuously distilled off. After the reaction the hot solution was cooled, the separated crystals were collected by suction and recrystallized from n-heptane or other solvent.

The same procedure was used for preparation of benzoylacetanilide (*XXI*) and its *p*-methyl (*XXII*) and *p*-chloro (*XXIII*) derivatives. Xylene was not used in preparations of the couplers *VIIIa*, *XXI* to *XXIII*, the starting compounds being heated without solvent (Table II).

1-Chloro-1-pivaloylacetanilide Derivatives

The suspension prepared from 0·00566 mol 1-pivaloylacetanilide derivative and 7 ml diethyl ether (cooling with brine bath) was treated with 0·00576 mol (0·472 ml) sulphuryl chloride added drop by drop at 0°C. The suspension dissolved partially, and, after 15 min stirring, a thick suspension was formed again. After another 15 min stirring the solid was collected by suction, washed with diethyl ether and crystallized twice from ethanol (Table I).

1-Acetoxy-1-pivaloylacetanilide Derivatives

0·00283 mol 1-chloro-1-pivaloylacetanilide derivative and 0·0061 mol anhydrous sodium acetate were dissolved in 15 ml acetic acid and heated to boil 18 h. After the reaction the mixture was poured in 100 ml cold water, the precipitated product was collected by suction, and the wet filter cake was dissolved in minimum amount of hot ethanol. The formed solution was slowly treated with water until first durable turbidity, whereupon it was cooled. The precipitated crystals were collected by suction and recrystallized in the same way with charcoal (Table I).

Azomethine Dyestuffs *XV* to *XX*

a) *From the couplers having non-substituted active group*: Solutions 0·50 g (0·00228 mol) coupler *Ia* in 10 ml ethanol, 0·55 g (0·00251 mol) N,N-diethyl-*p*-phenylenediamine hydrochloride in 8 ml water, and 0·55 g (0·01368 mol) NaOH in 10 ml water were poured simultaneously in a 800 ml beaker containing solution of 1·35 g (0·00502 mol) disodium octaoxodisulphate in 20 ml water. Volume of the mixture was adjusted at 600 ml. The separated yellow precipitate changed into black-brown solid on 20 min stirring, whereupon it was collected by suction and washed with water. The raw dyestuff was dissolved in minimum hot ethanol, and the solution was treated with

TABLE II

Properties of the Azomethine Dyestuffs *XV* to *XX* Prepared from Various Couplers

Dyestuff coupler	Formula (m. wt.)	Yield, % m. p., °C	Calculated/Found			λ_{max} [a]	ε
			% C	% H	% N		
XV	$C_{23}H_{29}N_3O_2$	42·3	72·79	7·72	11·07	415 heptan[e]	4 200
Ia	(379·5)	105–106	72·60	7·84	10·94	432 ethanol	4 600
XVI	$C_{24}H_{31}N_3O_2$	47·2	73·25	7·94	10·68	414 heptan	7 900
IVa	(393·5)	133–135	73·26	8·11	10·80	431 ethanol	8 500
XVII	$C_{23}H_{28}ClN_3O_2$[b]	51·7	66·74	6·82	10·15	417 heptan	6 200
VIIa	(413·9)	160–162	66·63	6·93	10·02	436 ethanol	6 500
XVI	$C_{24}H_{31}N_3O_2$	47·0	73·25	7·94	10·68	414 heptan	8 000
IVc	(393·5)	134–135	73·15	7·97	10·74	431 ethanol	8 600
XVII	$C_{23}H_{28}ClN_3O_2$[c]	49·8	66·74	6·82	10·15	418 heptan	6 200
VIIc	(413·9)	161–163	66·80	6·89	10·07	436 ethanol	6 500
XVIII	$C_{25}H_{25}N_3O_2$	46·3	75·16	6·31	10·52	– heptan[e]	–
XXI	(399·5)	212·0	75·28	6·48	10·74	438 ethanol	18 600
XIX	$C_{26}H_{27}N_3O_2$	53·0	75·52	6·31	10·16	– heptan[e]	–
XXII	(413·5)	186·0	75·58	6·48	10·30	438 ethanol	17 300
XX	$C_{25}H_{24}ClN_3O_2$[d]	54·5	69·20	5·57	9·68	– heptan[e]	–
XXIII	(433·9)	193·0	69·30	5·69	9·61	423 ethanol	17 800

[a] Measured with a spectrophotometer UV-VIS Specord (Zeiss, Jena); [b] calculated: 8·56% Cl; found: 8·49% Cl; [c] calculated: 6·56% Cl; found: 8·47% Cl; [d] calculated: 8·17% Cl; found: 8·32% Cl; [e] insoluble.

water until first durable turbidity. The yellow crystals formed on cooling were collected by suction. This procedure was repeated three times, the last crystallization was carried out with charcoal. Yield 0·383 g dyestuff *XV* (42·3%), m.p. 105—106°C. The same synthesis was applied for preparation of the dyestuffs *XVI* (from *IVa*), *XVII* (from *VIIa*), and dyestuffs of the benzoyl series *XVIII* to *XX* (from *XXI* to *XXIII*, respectively).

b) *From the couplers having substituted active group*: Solutions 0·5 g (0·0018 mol) compound *VIIc* in 30 ml ethanol, 0·45 g (0·0021 mol) N,N-diethyl-*p*-phenylenediamine hydrochloride in 10 ml water, 0·55 g (0·0021 mol) dipotassium octaoxodisulphate in 100 ml water, and 0·3 g (0·0075 mol) NaOH in 50 ml water were mixed, and the brown (originally yellow) precipitate was collected by suction after 20 min stirring. The solid was purified in the same way as in the above case. Yield 0·4 g (53·5%) dyestuff *XVII*, m.p. 165—167°C. The same procedure was used for preparation of the dyestuff *IIIc* from the coupler *VIIc* (Table II).

The elemental analyses were carried out in Analytical Department, Institute of Chemical Technology, Pardubice, under the guidance of Mr J. Bulušek.

REFERENCES

1. Fuji Photo: NSR 2, 213, 461 (1971); Chem. Abstr. *78*, 117602 (1973).
2. Kodak: Am. 3, 447, 928 (1965).
3. Konishiroku: NSR 2, 057, 941 (1971); Chem. Abstr. *75*, 110999 (1971).
4. Eastman Kodak: Am. 3, 644, 498 (1972); CHTR 21/30.
5. Kodak: Brit. 980, 507 (1957).
6. Konishiroku: NSR 2, 163, 812 (1972); Chem. Abstr. *79*, 37155 (1973).

Translated by J. Panchartek.