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Color Photographic Development Accelerators. Part III. Synthesis and Properties of a New Class of Selective Development Accelerators

Chen Shu-Ling, Zhu Zheng-Hua,* Yao Zu-Guang

Research Institute of Fine Chemicals,
East China University of Chemical Technology,
130 Meilong Road, Shanghai 200237, People's Republic of China

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Ji Su Xue

Institute of Photographic Chemistry, Academic Sinica,
Beijing 100101, People's Republic of China

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ABSTRACT

Several new selective development accelerators, viz. 2-[4-(2-acyl]hydrazino) anilinocarbonylmethyl] thio-5-alkylthio-1,3,4-thiadiazoles were synthesized. The structure of the compounds was confirmed by elemental analysis, MS, IR and ^{1}*H-NMR. Their effect on the photographic characteristics of color negative material was studied and it was found that the photographic speed can be greatly increased with the inclusion of these compounds in the color negative material.*

1 INTRODUCTION

Ideally, the developer selectively reduces exposed grains, and unexposed grains are unaffected. In reality, the image development is usually

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* To whom correspondence should be addressed.

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accompanied by an increase in fog formation during the normal development of a silver halide light sensitive material. In order to increase the rate of image development, development accelerators may be used.[1] However, some development accelerators usually accelerate fog formation, as well as image development, and hence decrease the development selectively.[2] Alternatively, in order to decrease fogging, various kinds of antifoggants may be used, but some antifoggants can inhibit the image development as well as the fog formation, and therefore decrease the maximum photographic speed.[1]

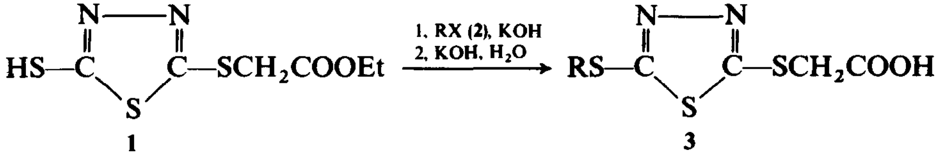
In order to improve the development selectivity and image quality, selective development accelerators have been widely investigated and applied in recent years. According to the mechanism of their action, the selective development accelerators may be classified into two types, viz. (i) those selectively releasing a development accelerator to the exposed area during development, such as development-accelerator-releasing (DAR) couplers,[2-8] and (ii) those introducing an antifoggant or development inhibitor in the molecule of a development accelerator.

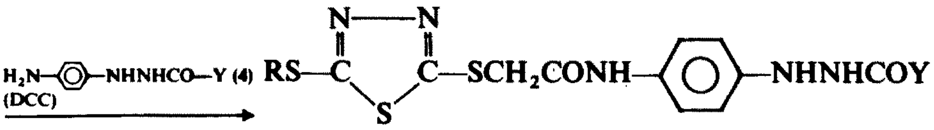
In continuation of our studies on selective development accelerators,[4,7-9] we now report the synthesis and application properties of some new hydrazine derivatives (**5**), which belong to the latter type of selective development accelerators mentioned above. In compounds **5**, the development accelerator hydrazine moiety is linked to the 1,3,4-thiadiazole heterocyclic system, which can decrease the reactivity of silver halide by forming an adsorption layer on the surface of unexposed silver halide grains and hence inhibit the fog formation. The mechanism of the action of compounds **5** and their adsorptivity on silver halides will be discussed in subsequent publications.

2 SYNTHESIS OF THE SELECTIVE PHOTOGRAPHIC DEVELOPMENT ACCELERATORS

2.1 Results and discussion

The selective development accelerators **5** were synthesized by a convenient two-step procedure:





5

2–5	R	*X*	*Y*
a	Me	$MeSO_4$	Me
b	Et	$EtSO_4$	Me
c	*n*-Bu	Br	Me
d	*n*-hexyl	Br	Me
e	*n*-Bu	Br	Ph

The alkylation of 2-ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (**1**) with one equivalent of the alkyl bromides or dialkyl sulfates (**2**) in refluxing ethanol in the presence of one equivalent of potassium hydroxide gave the 2-ethoxycarbonylmethylthio-5-alkylthio-1,3,4-thiadiazoles, which were not isolated, but hydrolyzed directly in alkaline aqueous ethanol at 40°C to give the 2-carboxymethylthio-5-alkylthio-thiadiazoles (**3**) in moderate yields. The selective development accelerators **5** were obtained in moderate yield by condensation of the 1,3,4-thiadiazoles (**3**) in *N*,*N*-dimethylformamide (DMF) at room temperature with one equivalent of 1-acyl-2-(4-aminophenyl) hydrazide (**4**), using *N*,*N*′dicyclohexylcarbodiimide (DCC) as condensing agent.

Relevant data on yields, melting points, elemental analysis and spectra of compounds **3** and **5** are given in Tables 1–3.

2.2 Experimental

2.2.1 General

Melting points were uncorrected. Elemental analyses were obtained using a Carlo Erba 1160R element analyzer. Mass spectra were recorded on a Hitachi M-80 spectrometer with either FD or EI ionization. IR spectra were recorded on a Nicolet FT-IR 20SX spectrometer. ^{1}H-NMR spectra were recorded on a Bruker WP-100SY spectrometer.

2-Ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (**1**) and 1-acetyl-2-(4-aminophenyl)hydrazide (**4a**) were prepared according to the literature procedures.[4]

2.2.2 2-Carboxymethylthio-5-alkylthio-1,3,4-thiadiazoles (3)

To a solution of 2-ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (**1**) (23·6 g, 100 mmol) in EtOH (100 ml) was added, at room temperature,

TABLE 1
Yields, Melting Points and Elemental Analysis for **3** and **5**

Compound	*Yield (%)*	*M.p. (solvent) (°C)*	*Molecular formula*	*Analysis: found/calculated (%)*		
				C	*H*	*N*
3a	40	140–142	$C_5H_6N_2O_2S_3$	26·90	2·81	12·50
		(H_2O–EtOH)	(222·3)	27·01	2·72	12·60
3b	41	98–100	$C_6H_8N_2O_2S_3$	30·49	3·46	12·01
		(H_2O–EtOH)	(236·3)	30·50	3·41	11·85
3c	76	54–56	$C_8H_{12}N_2O_2S_3$	36·26	4·55	10·66
		(CCl_4)	(264·4)	36·34	4·57	10·59
3d	51	64–66	$C_{10}H_{16}N_2O_2S_3$	41·38	5·55	9·76
		(CCl_4)	(292·4)	41·07	5·51	9·58
5a	60	216–218	$C_{13}H_{15}N_5O_2S_3$	42·01	3·95	18·70
		(EtOH–DMF)	(369·4)	42·27	4.09	18·96
5b	64	128–130	$C_{14}H_{17}N_5O_2S_3$	43·66	3·97	18·03
		(EtOH)	(383·4)	43·86	4·47	18·27
5c	71	148–150	$C_{16}H_{21}N_5O_2S_3$	46·63	5·14	16·92
		(EtOH)	(411·5)	46·70	5·14	17·02
5d	50	144–146	$C_{18}H_{25}N_5O_2S_3$	48·93	5·89	15·77
		(MeOH–DMF)	(439·5)	49·19	5·73	15·93
5e	64	183–185	$C_{21}H_{23}N_5O_2S_3$	52·91	4·88	14·52
		(ErOH–DMF)	(473·6)	53·26	4·89	14·79

Yield of isolated **3** based on **1**, and **5** based on **3**.
Alkylation conditions: reflux 2 h for **3a** and **3b**, and 5 h for **3c** and **3d**.

TABLE 2
Mass Spectra Data for Compounds **3**

Compound	*Mass spectra (70 eV) m/z (%)*
3a	222 (M^+, 60), 178 (100), 164 (10), 145 (34), 131 (8), 105 (26), 91 (95), 76 (29), 59 (36), 47 (36), 46 (63), 45 (74), 44 (15), 28 (10), 15 (19)
3b	236 (M^+, 99), 208 (29), 203 (28), 192 (73), 178 (22), 164 (27), 159 (33), 145 (9), 117 (12), 105 (43), 91 (24), 77 (43), 76 (38), 59 (65), 47 (31), 46 (60), 45 (61), 44 (31), 29 (100), 28 (50)
3c	264 (M^+, 28), 235 (9), 222 (17), 217 (94), 208 (100), 173 (46), 164 (42), 131 (7), 104 (12), 91 (4), 76 (12), 59 (20), 57 (46), 47 (18), 46 (26), 45 (30), 41 (50), 29 (56), 28 (9), 27 (19)
3d	292 (M^+, 22), 263 (5), 245 (48), 234 (14), 208 (60), 201 (21), 177 (12), 164 (23), 150 (18), 135 (4), 116 (9), 87 (13), 59 (23), 55 (24), 47 (13), 46 (19), 45 (26), 44 (7), 43 (100), 41 (49), 29 (43), 27 (20)

TABLE 3
Spectral Data for Compounds **5**

Product	*IR* *NH*	*(KBr),* *C=O*	*ν (cm^{-1})* *C=N*	*^{1}H-NMR (DMSO-d_6, TMS)* *δ, J (Hz)*	*MS (FD)* *(m/z)*
5a	3 450 3 295	1 675 1 655	1 615	1·85 (s, 3H, $COCH_3$), 2·71 (s, 3H, CH_3S), 4·16 (s, 2H, CH_2), 6·64–7·31 (m, 4Harom), 8·88 (s, 1H, NHN$\underline{H}$CO), 9·56 (s, 1H, CON$\underline{H}$Ar), 10·0 (s, 1H, N$\underline{H}$NHCO)	370 (M + 1)
5b	3 455 3 295 3 200	1 644 1 630	1 600	1·34 (t, 3H, J = 8, $C\underline{H}_3CH_2$), 1·87 (s, 3H, $COCH_3$), 3·24 (q, 2H, J = 8, CH_2S), 4·16 (s, 2H, CH_2CO), 6·64–7·30 (m, 4Harom), 8·88 (s, 1H, NHN$\underline{H}$CO), 9·52 (s, 1H, CON$\underline{H}$Ar), 10·0 (s, 1H, N$\underline{H}$NHCO)	384 (M + 1)
5c	3 430 3 320 3 280	1 650	1 610	0·87 (t, 3H, J = 8, $C\underline{H}_3CH_2$), 1·16–1·79 (m, 4H, $2CH_2$), 1·91 (s, 3H, $COCH_3$), 3·27 (t, 2H, J = 8·1, CH_2S), 4·22 (s, 2H, CH_2CO), 6·67–7·33 (m, 4Harom), 8·93 (s, NHN$\underline{H}$CO), 9·64 (s, 1H, CON$\underline{H}$Ar), 10·12 (s, 1H, N$\underline{H}$NHCO)	411 (M +)
5d	3 450 3 300 3 250	1 660 1 645	1 604	0·87 (t, 3H, J = 8, $C\underline{H}_3CH_2$), 0·96–1·76 (m, 8H, $4CH_2$), 1·85 (s, 3H, $COCH_3$), 3·21 (t, 2H, J = 8·2, CH_2S), 4·16 (s, 2H, CH_2CO), 6·61–7·28 (m, 4Harom), 8·96 (s, 1H, NHN$\underline{H}$CO), 9·52 (s, 1H, CON$\underline{H}$Ar), 10·0 (s, 1H, N$\underline{H}$NHCO)	440 (M + 1)
5e	3 430 3 315 3 245	1 645	1 610	0·87 (t, 3H, J = 8, $C\underline{H}_3CH_2$), 1·16–1·83 (m, 4H, $2CH_2$), 3·23 (t, 2H, J = 8·2, CH_2S), 4·25 (s, 2H, CH_2CO), 6·81–7·98 (m, 9Harom), 10·12 (s, 2H, both N$\underline{H}$CO), 10·42 (s, 1H, N$\underline{H}$NHCO)	473 (M +)

KOH (5·6 g, 100 mmol) and stirring was continued for 15 min. The appropriate alkyl bromide or dialkyl sulfate (**2**) (100 mmol) was then added and the mixture was refluxed with vigorous stirring for 2 to 5 h; it was then filtered immediately. The filtrate was cooled to 40°C and a solution of KOH (11·2 g, 200 mmol) in water (50 ml) was added, and stirring was continued for 30 min at 40°C. The solution was poured into a mixture of concentrated HCl (40 ml) and water (800 ml). The products precipitated readily and were filtered, washed several times with water and recrystallized, to give **3** as colorless crystals. The yields, melting points and analytical data are presented in Tables 1 and 2.

*2.2.3 1-Acetyl-2-(4-aminophenyl) hydrazide (**4e**)*

1-Acetyl-2-(4-nitrophenyl)hydrazide (10 g) was catalytically reduced by hydrogen at room temperature under a pressure of 20 Kg cm^{-2} in EtOH (100 ml) using 5% palladium–carbon (1·2 g) as catalyst. The solution was filtered, and the filtrate was evaporated to dryness under reduced pressure to give **4e** as a pale solid; yield: 6·6 g (75%); m.p. 142–143°C.

*2.2.4 2-[4-(Acylhydrazino)anilinocarbonylmethyl]thio-5-alkylthio-1,3,4-thiadiazoles (**5**)*

Compound **3** (50 mmol) and 1-acyl-2-(4-aminophenyl)hydrazide (**4**) (50 mmol) were dissolved in DMF (100 ml). A solution of DCC (10·3 g, 50 mmol) in DMF (20 ml) was added dropwise over 30 min at 0°C and stirring was continued at room temperature for 2 h. The solution was then filtered and the filtrate poured onto cold water (1000 ml). The products precipitated readily and were filtered, washed several times with water and recrystallized to give **5** as colorless crystalline solids. The yields, melting points and analytical data are presented in Tables 1 and 3.

3 EFFECT OF THE SELECTIVE PHOTOGRAPHIC DEVELOPMENT ACCELERATORS ON THE PHOTOGRAPHIC CHARACTERISTICS OF COLOR NEGATIVE MATERIAL

3.1 Experimental

In order to compare with the DAR colorless couplers,[7,8] the same experimental conditions used in the study of the DAR colorless couplers[8] were used here. The selective development accelerators were incorporated in the green- and red-sensitive coatings instead of the DAR colorless couplers as used previously[8] and the dye sensitometric data were also determined using the same conditions as those in the case of the DAR colorless couplers.[8]

TABLE 4

Effect of Selective Development Accelerators on the Photographic Characteristics of Green- and Red-sensitive Coatings of Color Negative Material

Compound no.	*Laydown* $+10^6$ *(mol m^{-2})*	*Relative sensitivity*	*Contrast*	*Fog*
Green-sensitive coatings				
—	0·0	100	1·84	0·62
5a	7·5	136	1·97	0·70
5b	7·5	132	2·02	0·77
5c	7·5	141	1·90	0·68
5d	7·5	117	2·16	0·64
5e	7·5	139	2·00	0·75
Red-sensitive coatings				
—	0·0	100	0·98	0·36
5a	4·2	200	0·97	0·50
5b	4·2	199	0·96	0·57
5c	4·2	199	0·96	0·57
5d	4·2	129	1·17	0·48
5e	4·2	187	1·00	0·60

3.2 Results and discussion

The dye sensitometric data for green-sensitive and red-sensitive coatings are given in Table 4.

It is apparent from Table 4 that the increase in sensitivity was excellent for the coatings incorporating the selective development accelerators, when compared with the coatings without these compounds, whilst virtually little increase of fogging was observed. The poor influence of compound **5e** on the photographic characteristics of the coatings shows that the introduction of a longer chain alkyl group in the type of compounds examined seems to offer advantages (Table 4).

Furthermore, Table 4 shows that compounds **5** are superior to the DAR colorless couplers[8] in improving the photographic characteristics of color negative material.

4 CONCLUSIONS

A new class of selective photographic development accelerators has been synthesized by a convenient two-step procedure.

Increase on the photograph speed was observed when these selective development accelerators were incorporated within the experimental bromo–iodide T-grain containing either cyan or magenta dye-forming image couplers. Under the same conditions, the selective development accelerators were more effective than DAR colorless couplers[8] in improving the photographic characteristics of color negative material.

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