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Color Photographic Development Accelerators. Part I: Synthesis of Novel Development–Accelerator–Releasing Colorless Couplers

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ABSTRACT

Several novel development–accelerator–releasing colorless couplers 2-[4-(2-acetylhydrazino)anilinocarbonylmethyl]thio-5-arylcarbonylmethylthio-1,3,4-thiadiazoles were synthesized by a simple and efficient three-step procedure starting from 2-ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole 1- and 2-bromo-4'-substituted acetophenones. The structure of the compounds was confirmed by elemental analysis, MS, IR and ^{1}H-NMR spectroscopy.

1 INTRODUCTION

It is known that hydrazine derivatives can be used to increase the photographic speed and contrast of a silver halide light-sensitive material during development.[1–3] A hydrazine derivative may be introduced, as a functional group, at the active position of a color coupler, and the resulting compound is called a development–accelerator–releasing (DAR) color coupler.[4–6] The photographic speed of a color negative material can be increased with the inclusion of the DAR color coupler.[4–8]

In the present paper, we report a class of novel DAR colorless couplers—2-[4-(2-acetylhydrazino)anilinocarbonylmethyl]thio-5-arylcarbonylmethylthio-1,3,4-thiadiazoles (**5**). The arylcarbonylmethyl group present in the DAR colorless coupler **5** is a noncoloring coupler residue which is capable of undergoing a coupling reaction with an oxidation product of an

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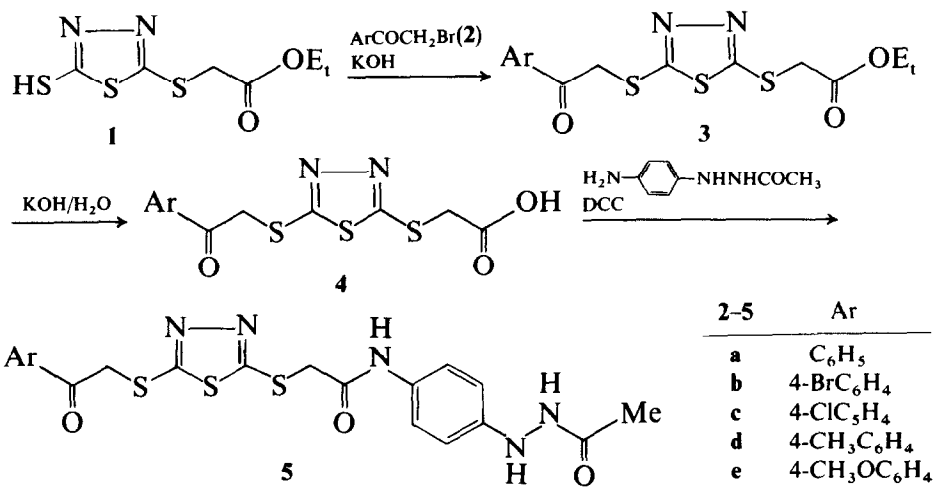
aromatic primary amine developing agent by the removal of one hydrogen atom from the active methylene group of the coupler residue to form a colorless coupling product. The 2-[4-(2-acetylhydrazino)anilinocarbonylmethyl]thio-1,3,4-thiadiazole-5-thio group is released as a coupling-off group by the coupling reaction and exhibits a development accelerating function. Because the coupling product of the DAR colorless coupler **5** with the color developing agent is colorless, it may be used, together with any one of the cyan, magenta and yellow imagewise couplers, in a color negative material. The convenience of practical application and the simplicity of the molecular structure are the advantages of the DAR colorless couplers **5** over the DAR color couplers.[4-6]

2 RESULTS AND DISCUSSION

The DAR colorless couplers **5** were synthesized by a simple and efficient three-step procedure.



The 2-ethoxycarbonylmethylthio-5-arylcarbonylmethylthio-1,3,4-thiadiazoles (**3**) were obtained in yields of 75–87% by the reaction of 2-ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (**1**) in refluxing absolute ethanol with one equivalent of 2-bromo-4′-substituted acetophenones (**2**) in the presence of one equivalent of potassium hydroxide, and were smoothly hydrolyzed in an alkaline aqueous methanol solution at 40°C to give 2-carboxymethylthio-5-arylcarbonylmethylthio-1,3,4-thiadiazoles (**4**) in high yields. The DAR colorless couplers **5** were prepared in moderate yields by the condensation of compounds **4** in *N*,*N*-dimethylformamide at room temperature with 1-acetyl-2-(4-aminophenyl)hydrazide, using *N*,*N*′-dicyclohexylcarbodiimide (DCC) as condensing agent.

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

Compound	*Yield*[a] *(%)*	*m.p. (solvent) (°C)*	*Molecular formula*	*Analysis: found/calculated (%)*		
				C	*H*	*N*
3a	87	90–92 (EtOH)	$C_{14}H_{14}N_2O_3S_3$ (354·4)	47·47 47·45	3·96 3·98	7·80 7·90
3b	84	95–97 (EtOH)	$C_{14}H_{13}BrN_2O_3S_3$ (433·3)	38·63 38·81	3·04 3·02	6·47 6·46
3c	81	91–93 (EtOH)	$C_{14}H_{13}ClN_2O_3S_3$ (388·8)	43·55 43·25	3·38 3·37	7·22 7·21
3d	80	113–114 (EtOH)	$C_{15}H_{16}N_2O_3S_3$ (368·4)	48·52 48·90	4·36 4·38	7·49 7·60
3e	75	109–111 (EtOH)	$C_{15}H_{16}N_2O_4S_3$ (384·3)	46·61 46·88	4·05 4·20	7·15 7·29
4a	93	169–171 (EtOH)	$C_{12}H_{10}N_2O_3S_3$ (326·4)	44·26 44·16	3·12 3·09	8·43 8·58
4b	91	163–164 (EtOH)	$C_{12}H_9BrN_2O_3S_3$ (405·3)	35·69 35·56	2·46 2·24	6·97 6·91
4c	94	162–164 (EtOH)	$C_{12}H_9ClN_2O_3S_3$ (360·8)	39·88 39·95	2·51 2·51	7·65 7·76
4d	90	176–178 (EtOH)	$C_{13}H_{12}N_2O_3S_3$ (340·4)	45·88 45·87	3·51 3·55	8·25 8·23
4e	85	186–188 (EtOH)	$C_{13}H_{12}N_2O_4S_3$ (356·4)	43·86 43·86	3·47 3·40	7·88 7·87
5a	64	199–201 (DMF–EtOH)	$C_{20}H_{19}N_5O_3S_3$ (473·5)	50·79 50·73	4·20 4·04	14·50 14·79
5b	51	207–209 (DMF–EtOH)	$C_{20}H_{18}BrN_5O_3S_3$ (552·4)	43·78 43·49	3·31 3·28	12·49 12·68
5c	61	198–200 (DMF–EtOH)	$C_{20}H_{18}ClN_5O_3S_3$ (507·9)	46·97 47·30	3·55 3·57	13·66 13·79
5d	53	190–192 (DMF–EtOH)	$C_{21}H_{21}N_5O_3S_3$ (487·5)	51·86 51·74	4·49 4·34	14·49 14·36
5e	55	202–204 (DMF–EtOH)	$C_{21}H_{21}N_5O_4S_3$ (503·5)	49·70 50·09	4·22 4·20	13·64 13·91

[a] The yields of **3** based on **1**, **4** based on **3**, and **5** based on **4**.

The relevant data on yields, melting points, and elemental analysis of the intermediates **3** and **4** and DAR colorless couplers **5** are given in Table 1, and the spectra data of the compounds **3–5** are given in Tables 2 and 3.

In the IR spectra of **5**, C=N vibrations of the thiadiazole ring are observed in the range 1600–1612 cm^{-1}.[9] The strongest absorption peaks in the range

TABLE 2
Mass Spectral Data of Compounds **3** and **4**

Compound	*Mass spectra (70 ev) m/z (%)*[a]
3a	354 (M^+, 74), 309 (17), 105 (100), 77 (22), 29 (8)
3b	434/432 (M^+, 15/13), 389/387 (3/3), 249 (10), 185/183 (97/100), 157/155 (9/9), 90 (7), 76 (6), 59 (3), 29 (7)
3c	390/388 (M^+, 33/100)
3d	368 (M^+, 100)
3e	384 (M^+, 100)
4a	326 (M^+, 70), 268 (86), 204 (92), 105 (100), 77 (20), 45 (8)
4b	406/404 (M^+, 12/14), 362/360 (8/8), 348/346 (13/14), 316/314 (22/19), 204 (3), 185/183 (96/100), 157/155 (6/6), 90 (7), 76 (8), 18 (5)
4c	362/360 (M^+, 8/22), 318 (10), 316 (11), 304/302 (11/25), 270 (7), 204 (5), 141/139 (31/100), 113/111 (8/26), 75 (14), 45 (6)
4d	340 (M^+, 16), 307 (6), 282 (20), 250 (4), 204 (4), 119 (100), 91 (26), 45 (3)
4e	356 (M^+, 100)

[a] **3c–3e** and **4e** measured using field desorption (FD) ionization.

1634–1678 cm^{-1} are caused by stretching vibrations of carbonyl groups and the N—H vibrations are observed in the range 3259–3450 cm^{-1}.

In the ^{1}H-NMR spectra of **5**, the singlet peaks in the ranges 9·97–10·12 and 8·83–8·92 ppm may be assigned to ArN—H and CON—H of the hydrazine group, respectively. The peaks in the range 9·50–9·60 ppm may be due to the N—H of the amido group. All the N—H protons are exchangeable with deuteroxide.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. Elemental analyses were obtained using a Carlo Erba 1160R element analyser. Mass spectra were obtained using a Hitachi M-80 spectrometer. IR spectra were recorded on a Nicolet FT-IR 20SX spectrometer. ^{1}H-NMR spectra were recorded on a Bruker WP-100SY spectrometer at 100 MHz.

2-Ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (**1**) and 1-acetyl-2-(4-aminophenyl)hydrazide,[5] 2-bromo-4′-substituted acetophenones (**2d**)[10] and (**2e**)[11] were prepared by the literature procedures; **2a–2c** are commercially available.

TABLE 3
Spectral Data of 1,3,4-Thiadiazoles (**5**) Prepared

Product	*IR (KBr), (cm^{-1})*			*^{1}H-NMR (DMSO-d_6, TMS) (δ)*	*Mass spectra (FD)*
	NH	*C=O*	*C=N*		*M^+, m/z*
5a	3420 3259	1668 1634	1605	1·9 (s, 3H, CH_3), 4·2 (s, 2H, CH_2), 5·07 (s, 2H, $ArCOCH_2$), 6·6–8·1 (m, 9Harom), 8·9 (s, 1H, NHNHCO) 9·6 (s, 1H, CONHAr), 10·1 (s, 1H, NHNHCO)	473
5b	3430 3336 3268	1670 1648	1606	1·92 (s, 3H, CH_3), 4·24 (s, 2H, CH_2), 5·09 (s, 2H, $ArCOCH_2$), 6·65–8·04 (m, 8Harom), 8·92 (s, 1H, NHNHCO), 9·6 (s, 1H, CONHAr), 10·12 (s, 1H, NHNHCO)	551, 553
5c	3440 3280	1678 1658 1646	1612	1·86 (s, 3H, CH_3), 4·13 (s, 2H, CH_2), 5·10 (s, 2H, $ArCOCH_2$), 6·55–8·0 (m, 8Harom), 8·83 (s, 1H, NHNHCO), 9·5 (s, 1H, CONHAr), 9·97 (s, 1H, NHNHCO)	507, 509
5d	3450 3295	1670 1660 1646	1604	1·85 (s, 3H, $COCH_3$), 2·38 (s, 3H, $ArCH_3$), 4·16 (s, 2H, CH_2), 5·11 (s, 2H, $ArCOCH_2$), 6·57–7·94 (m, 8Harom), 8·86 (s, 1H, NHNHCO), 9·53 (s, 1H, CONHAr), 10·0 (s, 1H, NHNHCO)	487
5e	3440 3290	1678 1660 1640	1600	1·87 (s, 3H, $COCH_3$), 3·84 (s, 3H, OCH_3), 4·16 (s, 2H, CH_2), 5·02 (s, 2H, $ArCOCH_2$), 6·58–8·04 (m, 8Harom), 8·88 (s, 1H, NHNHCO), 9·54 (s, 1H, CONHAr), 10·0 (s, 1H, NHNHCO)	503

3.2 2-Ethoxycarbonylmethylthio-5-arylcarbonylmethylthio-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 (200 ml) was added, at room temperature, solid KOH (5·6 g, 100 mmol), and stirring was continued for 15 min. The 2-bromo-4′-substituted acetophenone (**2**) (100 mmol) was then added and the

mixture was refluxed with vigorous stirring for 30 min and then filtered immediately. The filtrate was chilled overnight and a crystalline solid was formed. This was filtered to give **3** as colorless needles. The products were sufficiently pure for use in the next step. Yields, melting points and analytical data are shown in Tables 1 and 2.

3.3 2-Carboxymethylthio-5-arylcarbonylmethylthio-1,3,4-thiadiazoles (4)

A solution of KOH (5·6 g, 100 mmol) in water (30 ml) was added to a mixture of 2-ethoxycarbonylmethylthio-5-arylcarbonylmethylthio-1,3,4-thiadiazole (**3**) (50 mmol) and MeOH (50 ml) and stirring was continued at 40°C for 30 min. After cooling, the solution was poured into cold concentrated hydrochloric acid (20 ml) and water (400 ml). The products precipitated readily and were separated, washed several times with water and recrystallized from EtOH to give **4** as colorless needles. Yields, melting points and analytical data are shown in Tables 1 and 2.

3.4 Preparation of DAR colorless couplers (5)

2-Carboxymethylthio-5-arylcarbonylmethylthio-1,3,4-thiadiazole (**4**) (50 mmol) and 1-acetyl-2-(4-aminophenyl)hydrazide (8·3 g, 50 mmol) were dissolved in DMF (100 ml). A solution of DCC (10·3 g, 50 mmol) in DMF (20 ml) was added dropwise at 0°C over 30 min and stirring was continued at room temperature for 120 min. The solution was filtered, and the filtrate poured into cold water (1000 ml), when the products precipitated. They were filtered, washed several times with water and recrystallized from EtOH–DMF to give **5** as colorless crystalline solids. Yields, melting points and analytical data are shown in Tables 1 and 3.

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