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Development-Accelerator-Releasing(DAR) Couplers Part 3: Synthesis of Development-Accelerator-Releasing Couplers from Different Hydrazines

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ABSTRACT

Development-accelerator-releasing couplers were synthesized and used in the red layer of color film sensitizing medium in order to compare the effect of p-*hydrazide and inhydrazide compounds in accelerating development. the structure of the compounds was confirmed by elemental analysis MS, IR spectroscopy. © 1998 Elsevier Science Ltd*

Keywords: DAR coupler, synthesis, *p*-hydrazine structure, *m*-hydrazine structure.

INTRODUCTION

Several patents specifications relating to the development-accelerator-releasing(DAR) couplers have been issued e.g. [1–4] and Zhu and coworkers have carried out much work in this area [5–7]. DAR compounds are represented by the general formula Cp–L–A in which Cp represents a coupler residue, A represents a development accelerating functional group and L represents a divalent linking group. In Parts 1 and 2 of the investigation the effects of the A and L group have been studied [5–7]. In this present paper, we report the effect of the development accelerating functional group derived from hydrazine compounds. Five DAR compounds were synthesized containing *p*-hydrazide and m-hydrazide groups in order to compare the relative effect of such groups on the photographic characteristics of color negative material.

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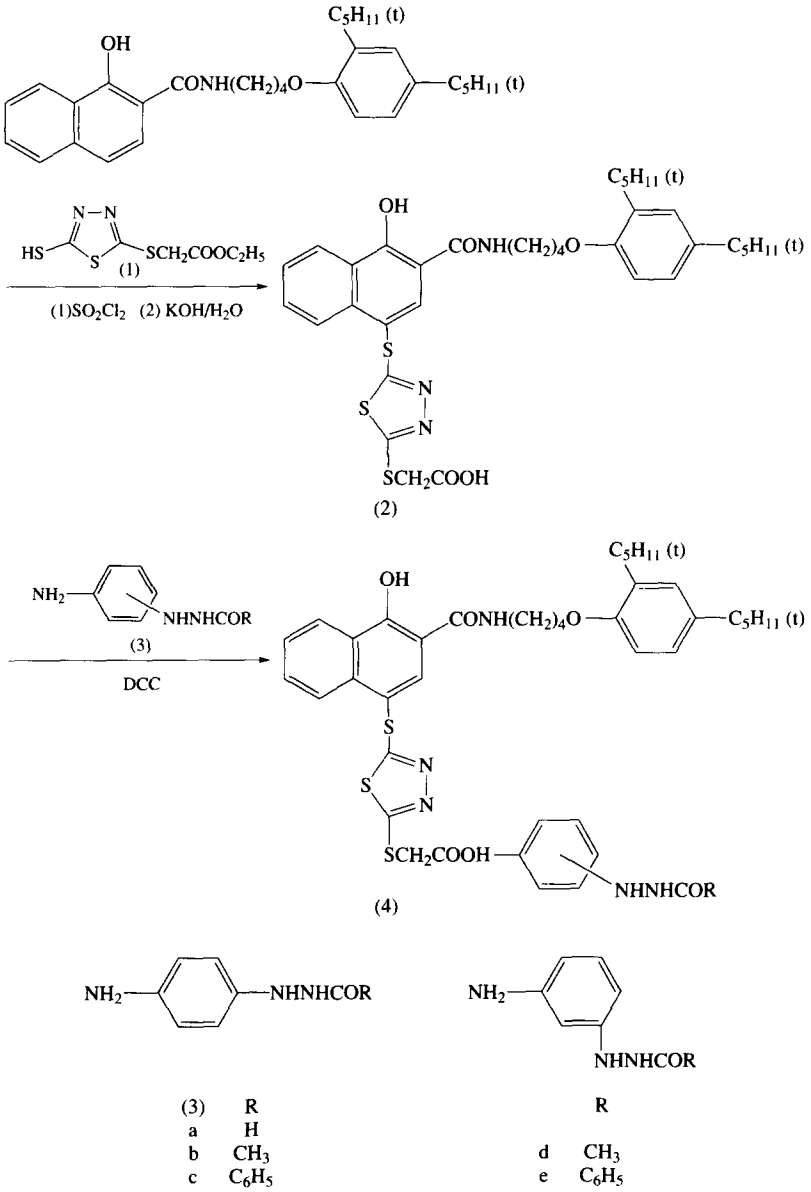
RESULTS AND DISCUSSION

The DAR couplers can be synthesized by various routes and typical synth eses are illustrated in Scheme 1.



Scheme 1. Relevant data on yields, melting, points, elemental analysis and spectra of the intermediates 2, 3 and the DAR couplers 4 are given in Tables 1–3

EXPERIMENTAL

General

Melting points are uncorrected. Elemental analyses were obtained using a Carlo Erba 1160R element analyzer. Mass spectra are recorded on a Hitachi M-80 spectrometer and IR spectra on a Nicolet FT-IR 20sx spectrometer. 2-Ethoxycarbonylmethylthio-5-mercapto-1.3.4-thiadiazole(1), 1-formyl-2-(4-amino-phenyl)-hydrazide, 1-acetyl-2-(4-aminophenyl)hydrazide and 1-benzoyl-2-(4-amino-phenyl) hydrazide were prepared according to literature procedures [5,8]. The other hydrazide derivatives were obtained using similar methods.

1-Hydroxy-4-{2-carboxymethylthio-1,3,4-thiadiazolyl-5-thio}-N-{4- (2,4-tert-pentyl phenyloxy)-butyl}-2-naphthamide(2).

A solution of sulfurylchloride (0.1 mol) in CH_2Cl_2 (40 ml) was added dropwise over 1h with ice cooling to a solution of 2-ethoxycarbonylmethylthio-5-mercapto-1,3,4-thiadiazole (1) (0.1 mol) in CH_2Cl_2 (200 ml) and stirring was continued for 1h at this temperature and then at room temperature for 30 min. A solution of 1-hydroxy-*N*-[4-(2,4-*tert*- pentylphenyloxy) butyl]-2-naphthamide (0.1 mol) in CH_2Cl_2 (50 ml) was then added, the mixture refluxed with vigorous stirring for 4h and after removal of CH_2Cl_2 the residue was dissolved in ethanol (80 ml). A solution of KOH (0.1 mol) in water was added, and stirring was continued at 60°C for 40 min. After cooling, the solution was poured into cold 10% hydrochloric acid (200 ml). The product precipitated readily and was filtered, washed several times with water, and recrystallized from EtOH to give compound 2 as colorless needles. Yield melting point and analytical data are shown in Tables 1, 2 and 3.

TABLE 1
Yields, Melting Points and Mass Spectra Data of Compound 3

Compound	*Yields (%)*	*Melting Points (°C) (recrystallization solvent)*	*Mass spectra (70ev) m/z(%)*
3(a)	94	184–186 (CH_3CN)	Literature 5
3(b)	82	140–142 (EtOH)	Literature 5
3(c)	73	142–144 (EtOH)	Literature 8
3(d)	71.3	140–142 (EtOH)	165 (M+) 123 (M+—$COCH_3$+1) 93 (M+—$NHNHCOCH_3$+1)
3(e)	50	160–162 (EtOH)	227 (M+) 122(M+—COC_6H_5)

TABLE 2
Yields Melting Points and Elemental Analysis for Compounds 2 and 4

Compound	*Yields (%)*	*m.p.(°C) (recrystallization solvent: EtOH)*	*Molecular formula*	*Analysis found/calculated (%)*		
				C	*H*	*N*
2	88	93–95	$C_{35}H_{43}N_3O_5S_3$	61.92	6.19	6.64
			(681.92)	61.65	6.36	6.61
4(a)	54	170–172	$C_{42}H_{50}N_6O_5S_3$	62.07	6.47	10.45
			(815.07)	61.91	6.18	10.31
4(b)	60	126–128	$C_{43}H_{52}N_6O_5S_3$	62.21	6.35	10.01
			(829.1)	62.23	6.32	10.14
4(c)	54.5	134–136	$C_{48}H_{54}N_6O_5S_3$	64.96	6.40	9.04
			(891.17)	64.69	6.11	9.43
4(d)	47.1	146–148	$C_{43}H_{52}N_6O_5S_3$	61.87	6.30	10.03
			(829.1)	62.23	6.32	10.14
4(e)	49.5	190–192	$C_{48}H_{54}N_6O_5S_3$	65.07	6.26	9.40
			(891.17)	64.69	6.11	9.40

TABLE 3
IR and Mass Spectra Data for Compounds 2 and 4

Compound	*IR(KBr)(cm^{-1})*					*Mass spectra (FD) M+, m/z*
	NH	*C=O*	*C=N*	*$(CH_2)_4$*	*Ph*	
2						22
4(a)	3298	1659	1578	1450	1040	
	3230	1632			810	815
					755	
4(b)	3295	1659	1588	1450	1040	
		1638			810	829
					760	
4(c)	3298	1659	1585	1460	1045	
		1638			810	892(M^+ + 1)
					760	
4(d)	3300	1670	1588	1465	1040	
					810	829
					760	
4(e)	3300	1659	1585	1475	1040	
					810	892(M^+ + 1)
					760	

Preparation of DAR couples (4)

Compound **2** and the appropriate hydrazide derivatives (0.05 mol) were dissolved in DMF (100 ml). A solution of N,N^1-dicyclohexylcarbdimide (0.55 mol) in DMF (20 ml) was added dropwise at 0°C over 30 min, and stirring was continued at room temperature for 2h. The solution was filtered, and the filtrate poured into cold water, when the products precipatated. They

were filtered, washed several times with water and recrystallized from EtOH to give compounds **4** as colorless solids. Yield melting points and analytical data are shown in Table 2

CONCLUSION

Five DAR couplers with different development accelerating functional group have been synthesized. The structure of the compounds was confirmed by elemental analysis. MS, IR spectroscopy. The effect of the DAR couplers on the photographic characteristics of color negative material is being evaluated and will be reported later.

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