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Synthesis and photographic properties of novel development accelerator releasing (DAR) coupler

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Abstract

Several novel DAR couplers were synthesized. The structures of the compounds were confirmed by elemental analysis, MS, IR and ^{1}H NMR.

Keywords: Coupler; DAR coupler; Synthesis; Structure

1. Introduction

The development-accelerator-releasing coupler(DAR) can be represented by the general formula Cp-L-A, in which "Cp" represents a coupler moiety (Cyan, Magenta or Yellow), "A" represents a development accelerating functional group and "L" represents a divalent linking group. With the inclusion of the DAR coupler the photographic speed of a color negative material can be increased [1–4]. The DAR coupler can release a development accelerator. They are added to silver halide emulsions in order to achieve an increase in speed or contrast brought about by the increased image development caused by the image-wise release of the development accelerator. Typically, these couplers release a hydrazide nucleor, which is activate by an oxidized color development agent and hydroxyl ions.

In this paper, three novel DAR couplers were synthesized, which contained a 1-phenyl-3-pyrazolidinone derivative as development accelerating group, 2-amino-5-thio-1,3,4-thiadiazole, Phenylthioltrinitrogenazole and 6-aminobenzimidazole as adsorption group. The photographic characteristics and mechanism of the action of these novel DAR couplers will be discussed in subsequent publications.

2. Experimental

2.1. Synthesis of the novel DAR couplers

2.1.1. General

Melting Points were uncorrected. Elemental analyses was obtained using a Carlo Erba 1160R element analyzer. Mass Spectra was recorded on a Hitachi M-80 Spectrometer with either ESI or EI ionization. IR Spectra was recorded on a Nicolet FT-IR 20sx spectrometer. ^{1}H NMR Spectra was recorded on a Bruker WP-500SY spectrometer. The intermediates were prepared by the literature procedure [5,6].

The DAR coupler a, b and c were synthesized as Schemes 1–3.

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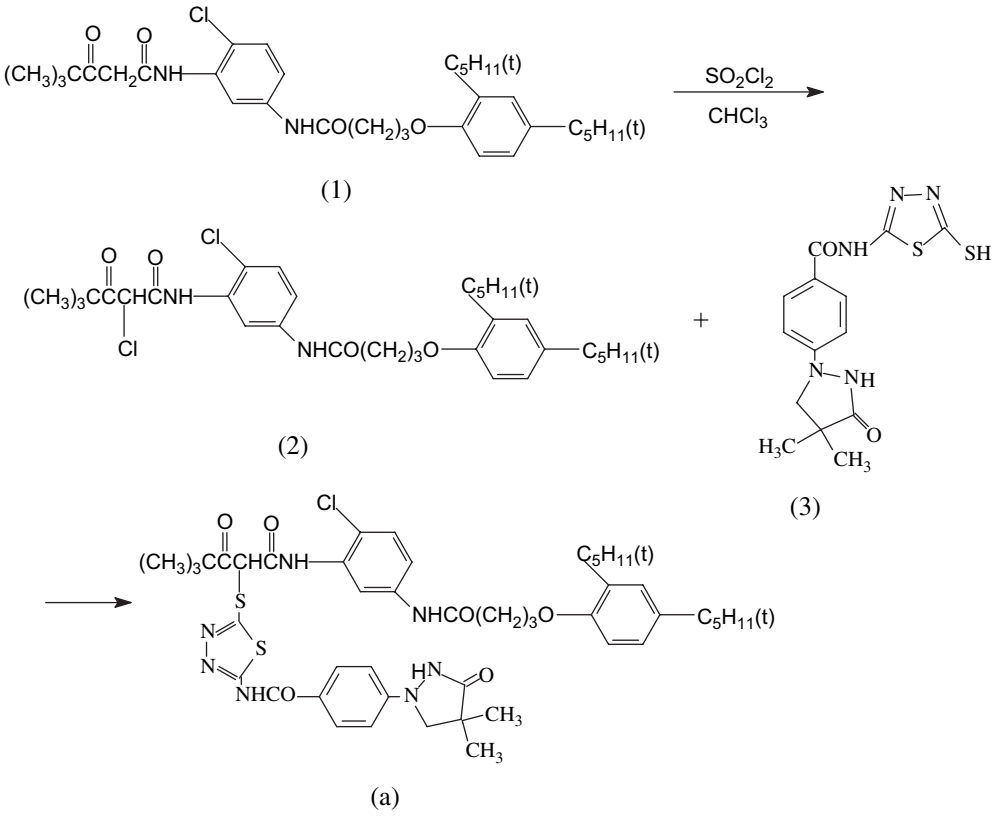
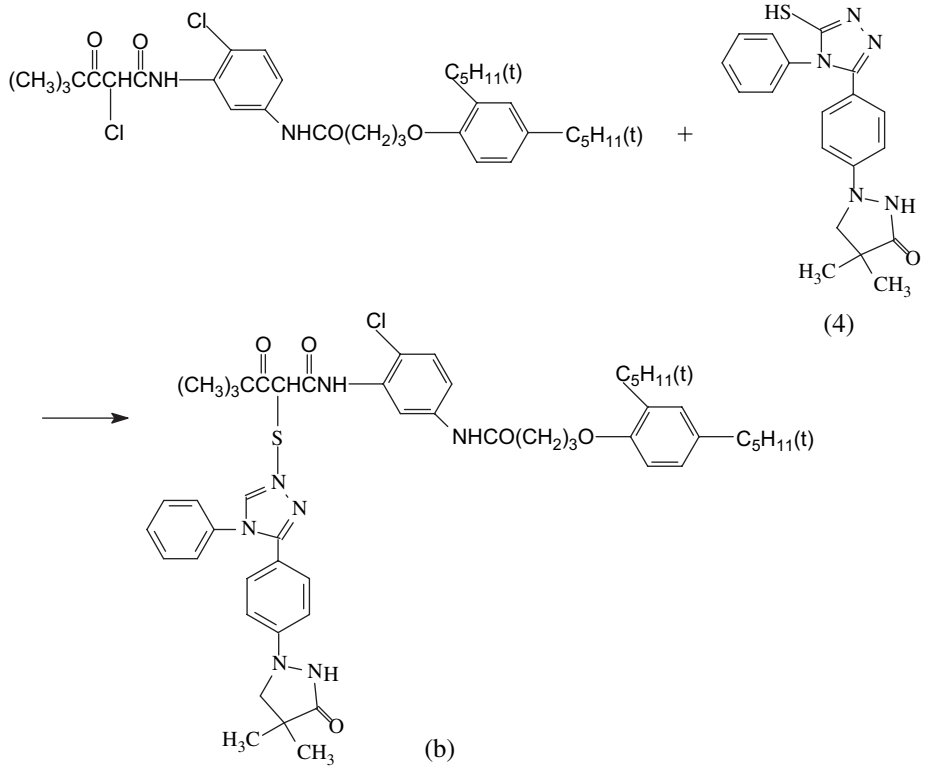
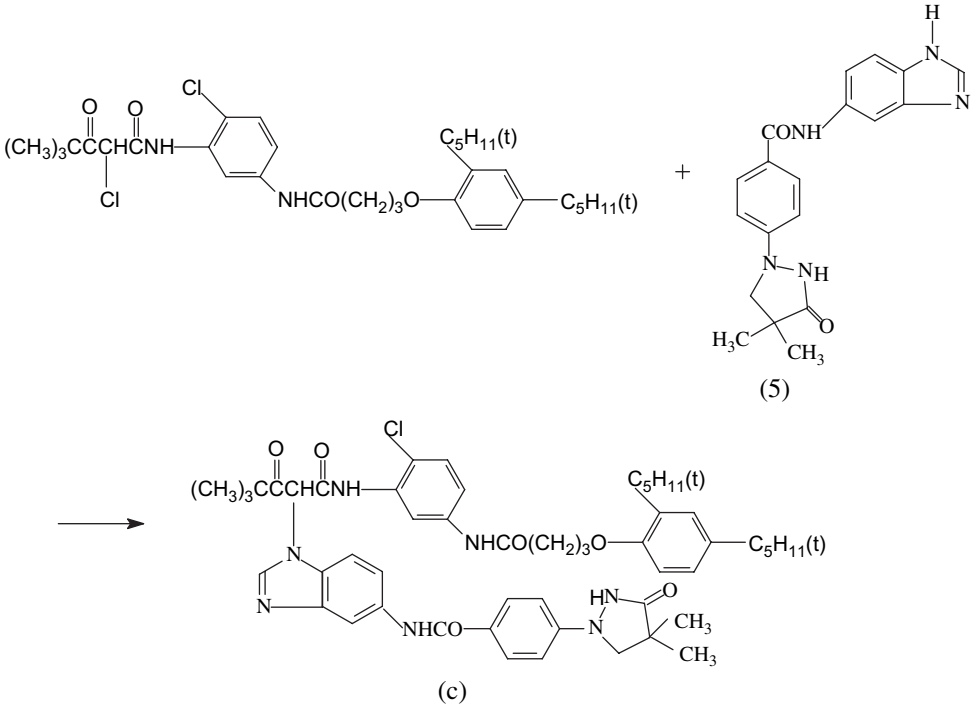


Scheme 1. The novel DAR coupler (a) was synthesized as follows.



Scheme 2. The DAR coupler (b) was synthesized as follows.



Scheme 3. The DAR coupler (c) was synthesized as follows.

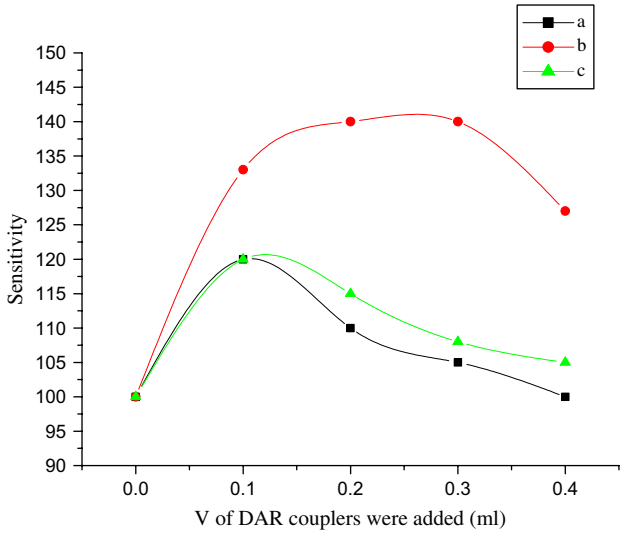
2.1.2. Synthesis of Compound (2)

A solution of 22.8 g (0.04 mol) compound (1) in 50 ml $CHCl_3$ was cooled to 0 °C, then a solution of 5.9 g (0.044 mol) SO_2Cl_2 in 20 ml $CHCl_3$ was added dropwise slowly. After stirring at 0 °C for 3 h, $CHCl_3$ was distilled off from the flask, then 50 mL petroleum ether was added and heated to solubilize, then cooled, 21 g compound (2) as white precipitate was formed.

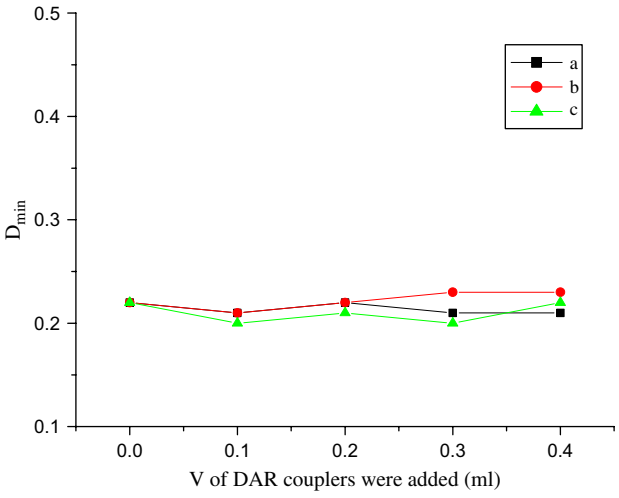
2.1.3. Synthesis of DAR coupler (a)

To a solution of development accelerator (3) (2.7 g, 0.008 mol) in dry DMF (30 mL) was added, triethylamine (0.97 g, 0.096 mol) at room temperature under nitrogen with stirring. A solution of compound (2) (5.4 g, 0.0088 mol) in dry DMF (20 mL) was then added dropwise to the above mixture over a period of 1 h. After stirring at room temperature for 6 h, the reaction mixture was poured into a rapidly stirring mixture of concentrated HCl (20 mL) and ice/water (1.25 L). The white precipitate formed was collected by filtration under suction.

After washing with water, the crude material was dried to give a white solid. Then recrystallized with ethanol and the product is white solid.



Scheme 4. The effect of DAR couplers to photosensitivity.



Scheme 5. The effect of DAR couplers to D_{min}.

The DAR coupler (b) and (c) were prepared as (a).

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

2.2. Photographic properties of DAR couplers

To examine the effect of DAR couplers on the photographic properties, a single-layer color negative coating structure was employed.

First, the amount of the DAR couplers on the color negative material was studied and this clarified that the effect of DAR couplers on photographic properties is the best with a 0.1 ml (a and c) or 0.2 ml (b) amount of 1% DAR coupler in methanol solution.

To obtain dye sensitometric response curves, the coatings were exposed stepwise to white light, followed by C-41-processing.

3. Results and discussion

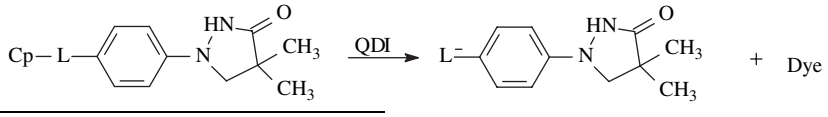
The dye sensitometric data for blue sensitive coating, according to the increase of photosensitivity for the coating is given in Table 4. The effect of DAR couplers to photosensitivity and D_{min} are given in Schemes 4 and 5.

It is apparent from the table that the increase of photosensitivity was considerably for the coating incorporating the DAR couplers, compared with coating without the DAR couplers. All DAR couplers had a considerable effect for the coating with different photosensitivity but fogging was not increase. Comparing the laydown of the three DAR couplers, 0.1 ml was the best in increasing photosensitivity for a and c, 0.2 ml was the best for b. Comparing these three DAR couplers in increasing photosensitivity, b was the best.

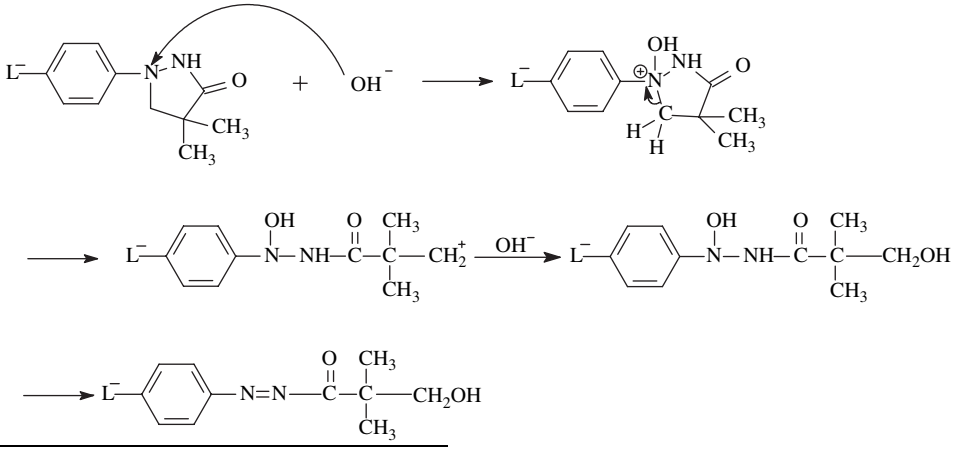
Comparing the structure of these three DAR couplers, the adsorption group was different, the adsorption group was most important to DAR coupler. The stronger the adsorbability of the adsorption group, the better of the DAR coupler's photographic properties when Cp and A are the same. For these three DAR couplers Phenylthioltrinitrogenazole was the strongest adsorption group. So it could increase photosensitivity significantly.

The sensitizing mechanism of DAR coupler which contain 1-phenyl-3-pyrazolidinone derivative as development accelerating group was as follows:

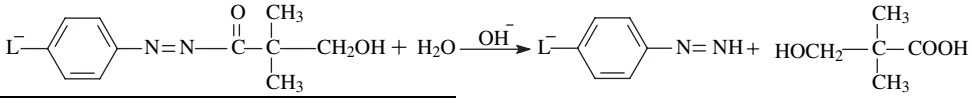
(1) In development DAR coupler react with QDI (Qxidized developer–quinondiimine) and make dye, at the same time release a development accelerator.



(2) Development accelerator is oxidized to 2-acyl-4-substituent phenylenediamide.



(3) 2-acyl-4-substituent phenyldiamide is hydrolyzed to 4-substituent phenyldiamide.



(4) The 4-substituent phenyldiamide is a very strong electron-donating group, it can make AgX (exposure or non-exposure) reduce to Ag.

Table 1
Yields, melting points, elemental analysis and ESI data for 3, 4 and 5

Compound	Yield (%)	M.P. (°C)	Molecular formula	Elemental analysis			EI (m/z)
				C	H	N	
				Found/calculated (%)			
2	86.8	96∼98	$C_{33}H_{46}N_2O_4Cl_2$	65.15	7.31	4.38	604.3
				65.45	7.60	4.63	
3	75.3	158∼160	$C_{14}H_{15}N_5O_2S_2$	48.23	4.29	19.98	349
				48.12	4.33	20.04	
4	77.6	>260	$C_{19}H_{19}N_5OS$	62.26	5.19	19.09	365
				62.44	5.24	19.16	
5	74	>260	$C_{19}H_{19}N_5O_2$	65.27	5.35	19.99	349
				65.32	5.48	20.04	

Table 2
Yields, melting points and elemental analysis data for a, b and c

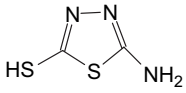
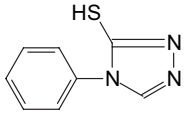
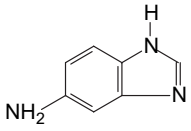
Product	Yield (%)	M.P. (°C)	Appearance	Molecular formula	Elemental analysis		
					C	H	N
					Found/calculated (%)		
a	69.1	100∼103	White solid	$C_{47}H_{59}N_7O_6S_2Cl$	61.19	6.23	11.01
					61.52	6.48	10.69
b	65.7	94∼96	White solid	$C_{52}H_{64}N_7O_5SCl$	66.46	6.74	10.36
					66.82	6.90	10.49
c	60.5	120∼122	White solid	$C_{47}H_{59}N_7O_6S_2Cl$	61.35	6.12	10.73
					61.52	6.48	10.69

Table 3
Spectral data for DAR coupler a, b and c

Product	IR(KBr), ν(cm^{-1})	^{1}H NMR(DMSO-d_6, TMS)	ESI(m/z)
a	3310.9 cm^{-1} (ν_{NH}, m), 2963.9 cm^{-1} (ν_{asCH}, s), 2872.7 cm^{-1} (νs_{CH}, s), 1700.4 cm^{-1} ($\nu_{C=O}$, s), 1603.2 cm^{-1} ($\nu_{C=C}$, m), 1514.0 cm^{-1} ($\nu_{C=C}$, m), 1462.8 cm^{-1} (νs_{CH}, m)	0.5–0.6(t,6H), 1.0–1.4(m,27H), 1.2(m,2H), 1.5(m,2H), 1.8(m,2H), 2.1(m,2H), 2.5(m,2H), 3.9(s,3H), 4.0(m,2H), 5.9(s,1H), 6.8–7.7(m,10H), 8.1(m,1H), 9.9–10.2(m,2H).	940.4(M^++Na)
b	3315.3 cm^{-1} (ν_{NH}, m), 2963.3 cm^{-1} (ν_{asCH}, s), 2872.7 cm^{-1} (νs_{CH}, s), 1689.4 cm^{-1} ($\nu_{C=O}$, s), 1601.5 cm^{-1} ($\nu_{C=C}$, m), 1562.0 cm^{-1} ($\nu_{C=N}$, m), 1461.5 cm^{-1}, 1381.3 cm^{-1} (νs_{CH}, m), 3325.5 cm^{-1} (ν_{NH}, m),	0.5–0.6(t,6H), 1.0–1.4(m,27H), 1.2(m,2H), 1.5(m,2H), 1.8(m,2H), 2.1(m,2H), 2.5(m,2H), 3.9(s,3H), 4.0(m,2H), 5.9(s,1H), 6.8–7.7(m,10H), 8.1(m,1H), 10.2(m,1H).	933.4(M^+)
c	2962.8 cm^{-1} (ν_{asCH}, s), 228.1 cm^{-1} (νs_{CH}, s), 1687.3 cm^{-1} ($\nu_{C=O}$, s), 1602.3 cm^{-1} ($\nu_{C=C}$, m), 1525.1 cm^{-1} ($\nu_{C=N}$, m), 1464.0 cm^{-1}, 1381.9 cm^{-1} (νs_{CH}, m).	0.5–0.6(t,6H), 1.0–1.4(m,27H), 1.2(m,2H), 1.5(m,2H), 1.8(m,2H), 2.1(m,2H), 2.5(m,2H), 3.9(s,3H), 4.0(m,2H), 5.9(s,1H), 6.8–7.7(m,10H), 8.1(m,1H), 9.9–10.2(m,2H).	940.4(M^++Na)

23 is the atom weight of Na.

Table 4
The photographic properties of DAR coupler a, b and c

DAR coupler	Adsorption group	V of DAR coupler was added	Photographic properties		
			D_{min}	γ	S_r
–	–	–	0.22	0.52	100
a		0.1	0.21	0.55	120
		0.2	0.22	0.56	110
		0.3	0.21	0.54	105
		0.4	0.21	0.50	100
b		0.1	0.21	0.55	133
		0.2	0.22	0.60	140
		0.3	0.23	0.57	140
		0.4	0.23	0.54	127
c		0.1	0.20	0.60	120
		0.2	0.21	0.55	115
		0.3	0.20	0.53	108
		0.4	0.22	0.56	105

To the sensitivity mechanism of these three DAR couplers OH^- was very important. So if increasing the pH of developer, the effect of these DAR couplers could be better.

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