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Synthesis of the novel photographic DIAR couplers

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Abstract

The synthesis and characterization of six novel photographic DIAR couplers are reported. They are based on yellow couplers which can react with an oxidized color-developing agent to form yellow dyes; *N*-(ethylamido)-methyl-4-nitrophenol and 2-(isopropylamino)phenthiol, synthesized by a new method from benzothiazole, are used as timing groups to control the release of the inhibitor. The substituted tetrazole, 1,2,3-thiadiazole, benzothiazole and 1H-benzotriazole are used as the inhibiting groups. Two of the six novel couplers are the hydrolyzable inhibitor type of DIAR coupler. During preparation of the intermediates, triphosgene was substituted for phosgene and good results were obtained.

Keywords: Color negative film; Image quality; DIAR coupler; Timing group; Development inhibitor; Synthesis

1. Introduction

Silver halide photographic DIAR (Development Inhibitor Archimeric Releasing) couplers were first invented and applied in color negative film to improve image quality in 1980s [1–3]. It can react with an oxidized color-developing agent to form dye and timing and inhibitor entities, which are able to react to release an inhibitor. Its structure character is that the coupler contains a timing group, joining a side coupler group and an inhibitor, which controls the time of release, rate of release, and rate of inhibitor. This type of coupler can enhance the effects since they can release a development inhibitor at a distance from the point at which the oxidized color-developing agent reacted with the coupler. They can be represented by the formula:

COUP–TIME–INT

where COUP is a coupler group, TIME is a timing group and INT is an inhibiting group.

DIAR couplers have been developed since its invention and some new compounds with good effects or new functions have been synthesized [4–14]. When color negative film is developed, the developing inhibitor released from the DIAR coupler will accumulate in the developing solution and make the efficiency of the developing solution drop. In order to overcome this limitation, the hydrolyzable inhibitor type of DIAR coupler has been invented [4–9]. This releases the inhibitor in color negative processes, which can diffuse within the film to exert its development inhibiting function. However, when the inhibitors enter the color-developing solution, the inhibitor hydrolyzes to a compound that has little or no development inhibiting properties, and so has no influence on the development of subsequent films processed in the same developer solution. For increased image sharpness and good inter-image results, some DIAR couplers have been synthesized with new inhibitors [10–14]. For example, where the new DIAR coupler contains a releasable

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development inhibitor group comprising an amide group containing a carbon that is di- or tri-fluorinated alpha to the amide. Application of these new compounds further improves image quality of the color negative film [10].

In the last few years, there has been an increase in color film with higher light-sensitivity, so that research and development of photographic higher light-sensitive materials, such as the DIAR coupler, are very necessary. In this paper, six new DIAR couplers are synthesized and new synthetic routes are developed.

2. Experimental

Melting points were measured on an X_4 micro-melting point apparatus. IR spectra were recorded with a Nicolet 5SXC instrument using KBr tabulating. The ^{1}H NMR spectra were recorded with a Brucker AVANCE500 at 500 MHz in deuterium solvent, with TMS as an internal reference. EI mass spectra (70 eV) were obtained with Micromass LCT spectrometer. An element vario EL III analyzer (made by Elementar Analysem Systeme, Germany) was used for element analysis. 2-(*N*-Ethyl-trifluoroacetamido)-methyl-4-nitrophenol, 1*H*-benzotriazole-5-carboxylic phenyl ester and 2-trifluoroacetamido-5-mercapto-1,3,4-thiadiazole were synthesized in the lab by previously described methods [1,14], other chemicals were purchased from commercial suppliers.

2.1. Synthesis of compound *3*

Compound **1** (15.2 g, 0.025 mol) and di-isopropyl ethylamine (7.10 g, 0.055 mol) were added to a solution of compound **2** (8.0 g, 0.025 mol) in acetone (50 cm^3). The mixture was refluxed for 5 h. After cooling to 5 °C, a solution of sodium hydroxide (10 g, 0.25 mol) in water (25 cm^3) was added dropwise. The reaction solution was stirred for 1 h and then the dark red solution was poured into 400 ml of ice water and 200 ml of concentrated hydrochloric acid. The solid was collected and recrystallized from ethyl acetate. Yield: 18 g (91.3%); m.p. 185–186 °C (Lit [15]: yield 89%; m.p. 184–186 °C).

2.2. Synthesis of compound *4*

A saturated solution of sodium bicarbonate (20 cm^3) was added dropwise to a mixture of compound **3** (8.0 g, 0.01 mol) suspended in ethyl acetate (20 cm^3) at room temperature. When the entire solid had been dissolved, the organic phase was separated and dried over magnesium sulfate. A solution of compound **4** was obtained (Solution A).

2.3. Synthesis of compounds *5A*, *5B*, *5C* and *5D*

(1) A solution of triphosgene (2.97 g, 0.01 mol) in absolute tetrahydrofuran (10 cm^3) was added dropwise to a solution of 2-mercaptobenzothiazole (5.1 g, 0.03 mol) and di-isopropyl ethylamine (3.9 g, 0.03 mol) in absolute tetrahydrofuran (20 cm^3) at 0 °C under nitrogen. After addition, the reaction mixture was stirred at room temperature for 3 h. The solvent was evaporated in vacuo and the solid residue was recrystallized from ethyl acetate. Yield of **5A**, 7.56 g (70%); m.p. 136–137 °C. IR/cm^{-1}: ∼ν: 1703.16 (C=O), 1622.16 (C=N), 1453.82, 1409.81, 992.65, 833.09, 763.39. Anal. Calcd. for $C_{15}H_4N_2OS_4$: C, 19.88; H, 2.03; N, 7.87. Found: C, 49.78; H, 2.23; N, 7.77; MS (EI): *m*/*z* (%) = 360(M^+), 194, 166 (100).

Using a similar reaction procedure, compounds of **5B** and **5C** were synthesized. Yield of **5B**% = 72%, m.p. 107–108 °C. IR/cm^{-1}: ∼ν: 1740.96 (C=O), 1705.24 (C=O), 1239.55, 1176.12. Anal. Calcd. for $C_{13}H_{14}N_4O_5S_6$: C, 31.33; H, 2.67; N, 11.05. Found: C, 31.31; H, 2.83; N, 11.24; MS (EI): *m*/*z* (%) = 498(M^+), 263, 235 (100), 190, 162; Yield of **5C**% = 78%; m.p. 168–170 °C; IR/cm^{-1}: ∼ν: 1775.73 (CF_3C=O), 1725.24 (C=O), 1559.98, 1217.96, 1163.08, 820.61. Anal. Calcd. for $C_9H_2F_6N_6O_3S_4$: C, 22.58; H, 0.39; N, 1726. Found: C, 22.32; H, 0.42; N, 17.35; MS (EI): *m*/*z* (%) = 484(M^+), 256, 228 (100), 131.

(2) A solution of triphosgene (2.97 g, 0.01 mol) in dichloromethane (15 cm^3) was added to a solution of phenoxycarbonylbenzotriazole (4.78 g, 0.02 mol) and dimethylaniline (2.42 g, 0.02 mol) in dichloromethane (20 cm^3) at 0 °C. After addition, the reaction mixture was stirred at 30 °C for 4 h. A solution of compound **5D** was obtained (Solution B).

2.4. Synthesis of compounds *6A*, *6B*, *6C* and *6D*[16–19]

(1) Solution A (20 cm^3) was added dropwise into a solution of compound **5A** (3.6 g, 0.01 mol) in tetrahydrofuran (20 cm^3) at 0 °C. After stirring for 1 h, the solvent was removed under reduced pressure. The solid residue was recrystallized from methanol. Yield of **6A**, 5.7 g (60%); m.p. 102–105 °C. IR/cm^{-1}: ∼ν: 3382.74, 3314.69(w, N–H), 1598, 1477.79(m, Ar–H), 1701.45, 1687.09,1667.71(s, CO), 1523.87, 1342.82(s, NO_2); ^{1}H NMR ($CDCl_3$): δ/ppm = 0.5–0.65(t, 6H, CH_3), 1.25(s, 21H, CH_3), 1.50 (t, 3H, N–CH_2–CH_3), 1.55(q, 2H, –C–CH_2–CH_3), 1.85(q, 2H, –C–CH_2–CH_3), 2.2(m, 2H, –CH_2–), 2.6(t, 2H, CO–CH_2–), 3.5(s, 2H, Ar–CH_2–), 4.0(t, 2H, CH_2–O), 4.7(q, 2H, N–CH_2–C), 5.8(t, 1H, COCHCO), 6.7–8.5(m, 14H, Ar–H); MS (EI) *m*/*z*: 957(M^+).

(2) Solution A (20 cm^3) was added dropwise into a solution of compound **5B** (5.0 g, 0.01 mol) in

tetrahydrofuran (20 cm^3) at 0 °C. After stirring for 4 h at room temperature, the solvent was removed under reduced pressure. The solid residue was recrystallized from methanol. Yield of **6B**, 6.4 g (62%); m.p. 98–99 °C. IR/cm^{-1}: ~ν: 3356.03(w, N–H), 3078.31, 2963.10, 2872.08(m, CH_3), 2928.12(m, CH_2), 1723.68, 1701.30(s, CO), 1668.68(s, C=N), 1598.89, 1523.95, 1477.38, 1343.25, 1241.50, 1185.81, 1054.26, 986.64, 810.96; ^{1}H NMR ($CDCl_3$): δ/ppm = 0.5–0.65(t, 6H, CH_3), 1.25(s, 21H, CH_3), 1.32(t, 3H, $COOCH_2CH_3$), 1.50 (t, 3H, N–CH_2–CH_3), 1.55(q, 2H, –C–CH_2–CH_3), 1.85(q, 2H, –C–CH_2–CH_3), 2.2(m, 2H, –CH_2–), 2.6(t, 2H, CO–CH_2–), 3.5(s, 2H, Ar–CH_2–), 3.9(s, 2H, SCH_2COO), 4.0(t, 2H, CH_2–O), 4.1(q, 2H, $COOCH_2CH_3$), 4.7(q, 2H, N–CH_2–C), 5.8(t, 1H, COCHCO), 6.7–8.5(m, 9H, Ar–H); MS (EI) m/z: 1026(M^+).

(3) Solution A (20 cm^3) was added dropwise into a solution of compound **5C** (4.8 g, 0.01 mol) in tetrahydrofuran (20 cm^3) at room temperature. After stirring for 4 h at 40 °C, the solvent was removed under reduced pressure. The solid residue was recrystallized from methanol. Yield of **6C**, 5.3 g (52%). IR/cm^{-1}: ~ν: 3384.94 (w, N–H), 2964.04, 2873.88(m, CH_3), 2933.47(m, CH_2), 1698.58(s, CO), 1674.02 (s, C=N), 1601.05, 1525.20, 1497.81, 1450.09, 1344.48, 1240.53, 1143.65; ^{1}H NMR ($CDCl_3$): δ/ppm = 0.5–0.65(t, 6H, CH_3), 1.25(s, 21H, CH_3), 1.50(t, 3H, N–CH_2–CH_3), 1.55(q, 2H, –C–CH_2–CH_3), 1.85(q, 2H, –C–CH_2–CH_3), 2.2(m, 2H, –CH_2–), 2.6(t, 2H, CO–CH_2–), 3.5(s, 2H, Ar–CH_2–), 4.0(t, 2H, CH_2–O), 4.7(q, 2H, N–CH_2–C), 5.8(t, 1H, COCHCO), 6.7–8.5(m, 9H, Ar–H); MS (EI) m/z: 1019(M^+).

(4) Solution B was added dropwise into Solution A and dimethylaniline (2.42 g, 0.02 mol) at 5–10 °C. The resultant solution was stirred for 2 h at 45 °C. The reaction solution was slowly added to hydrochloric acid solution (3%), and extracted with ethyl acetate (50 cm^3). The organic layer was washed with water, dried with magnesium sulfate, and concentrated at reduced pressure. The resultant material was recrystallized from the ethyl acetate and hexane (1:4) (Fig. 1). Yield of **6D**, 5.2 g (50%). IR/cm^{-1}: ~ν: 3388.06(w, N–H), 1597.88, 1478.67.79(m, Ar–H), 1736.65, 1702.52(s, CO), 1523.94, 1347.62(s, NO_2); ^{1}H NMR ($CDCl_3$): δ/ppm = 0.6–0.7(t, 6H, CH_3), 1.25–1.4(s, 21H, CH_3), 1.55–1.65(q, 2H, –C–CH_2–CH_3), 1.85(q, 2H, –C–CH_2–CH_3), 2.2(m, 2H, –CH_2–), 2.6(t, 2H, CO–CH_2–), 3.5(s, 2H, Ar–CH_2–), 4.0(t, 2H, CH_2–O), 4.7(q, 2H, N–CH_2–C), 5.8(t, 1H, COCHCO), 6.7–8.9(m, 17H, Ar–H); MS (EI): 1029(M^+).

2.5. Synthesis of compound *10*

(1) Compound **8** (17 g, 0.1 mol) was added to a solution of compound **7** (6.76 g, 0.05 mol) in toluene (20 cm^3). The reaction mixture was refluxed for 24 h. After cooling to 20 °C, the solid residue was filtered, washed several times with acetone and diethyl ether (1:1), and dried in the air to obtain the compound **9**. Yield 12.8 g (90%); m.p. 138–139 °C. ^{1}H NMR (DMSO-d_6): δ/ppm = 1.78(b, 6H,CH (CH_3)$_2$), 5.38(m, 1H, CH (CH_3)$_2$), 7.81–8.50(m, 4H, Ar–H), 10.52(s, 1H SCHN).

(2) A solution of sodium hydroxide (4.0 g, 0.1 mol) in water (5 cm^3) was added to compound **9** (6.1 g, 0.02 mol), the mixture was refluxed for 10 h under nitrogen. After cooling to room temperature, water (50 cm^3) was added and stirred for 1 h and the oil was extracted with toluene (50 cm^3). The solvent was removed at reduced pressure, compound **10** distils at 114–117 °C/1.21 × 10^3 Pa. Yield 3 g (90%). IR/cm^{-1}: ~ν: 3380.32(w, N–H), 3068.74, 2965.86(m, CH_3), 2520.36(w, S–H), 1589.57, 1503.10(Ar–H); ^{1}H NMR ($CDCl_3$) δ: 1.2–1.3(b, 6H, CH(CH_3)$_2$), 3.62–3.70(m, 1H, CH(CH_3)$_2$), 6.50–7.42(m, 4H, Ar–H).

2.6. Synthesis of compound *11*

Compound **10** (1.65 g, 0.01 mol) was added to a solution of compound **1** (6.05 g, 0.01 mol) and triethylamine (1.5 g, 0.015 mol) in tetrahydrofuran (20 cm^3). The mixture was stirred for 8 h at 50 °C and then poured into water. The crude solid was collected and recrystallized from diethyl ether. Yield 6.3 g (85%); m.p. 176–178 °C; ^{1}H NMR ($CDCl_3$): δ/ppm = 0.55–0.65(t, 6H, –CH_2H_3), 1.12(b, 6H, ArNHCH (CH_3)$_2$) 1.25(s, 21H, CH_3), 1.55(q, 2H, –C–CH_2–CH_3), 1.85(q, 2H, –C–CH_2–CH_3), 2.23(m, 2H, CH_2–CH_2–CH_2), 2.6(t, 2H, CO–CH_2–), 3.62(m, 1H, ArNHCH (CH_3)$_2$)), 4.0(t, 2H, CH_2–O), 6.51–8.5(m, 10H, Ar–H).

2.7. Synthesis of compounds *14A* and *14B*

A solution of triphosgene (1.5 g, 0.005 mol) in tetrahydrofuran (5 cm^3) was added dropwise into a solution of compound **11** (7.3 g, 0.01 mol) and dimethylaniline (1.22 g, 0.01 mol) in tetrahydrofuran (20 cm^3) at 0 °C. After addition, the reaction mixture was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the solid product compound **12** was obtained.

(1) Compound **12** as synthesized in the last step was dissolved in pyridine (10 cm^3), and compound **13A** (1.78 g, 0.01 mol) in pyridine (10 cm^3) was added. The reaction mixture was stirred for 3 h at 0–5 °C and then poured into ice water. The crude solid was collected and recrystallized from ethyl acetate and hexane (1:3). Compound **14A** was obtained. Yield 7 g (75%); m.p. 126–128 °C. IR/cm^{-1}: ~ν: 3340.33(w, N–H), 2964.44

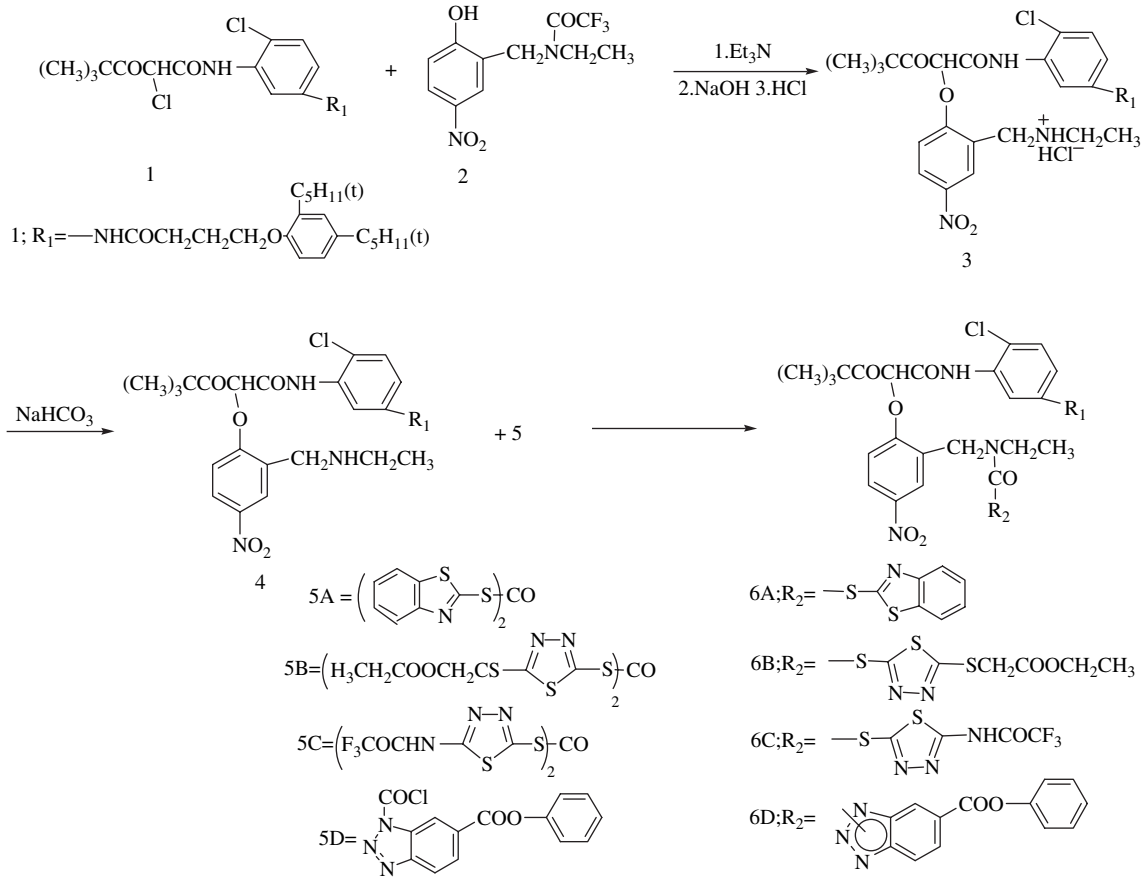

Fig. 1. Synthesis of the DIAR couplers **6A**, **6B**, **6C** and **6D**.

(m, CH_3), 2933.44(m, CH_2), 1700, 1688.69(s, CO), 1598.55, 1495.85(m, Ar–H); ^{1}H NMR ($CDCl_3$) $\delta = 0.55$–0.65(t, 6H, $-CH_2H_3$), 1.12(b, 6H, ArNHCH $(CH_3)_2$) 1.25(s, 21H, CH_3), 1.55(q, 2H, $-C-CH_2-CH_3$), 1.85(q, 2H, $-C-CH_2-CH_3$), 2.23(m, 2H, $CH_2-CH_2-CH_2$), 2.6(t, 2H, $CO-CH_2-$), 4.0(t, 2H, CH_2-O), 5.09(s, COCHCO), 6.72–8.5(m, 15H, Ar–H); MS (EI): 939(M^+).

(2) Compound **12** was dissolved in tetrahydrofuran (10 cm^3), and compound **13B** (1.52 g, 0.01 mol) in tetrahydrofuran (10 cm^3) was added dropwise at 0 °C. The reaction mixture was stirred for 3 h at room temperature and then poured into ice water. The crude solid was collected and recrystallized from ethyl acetate and hexane (1:2). Compound **14B** was obtained (Fig. 2). Yield 6.7 g (75%); m.p. 70–72 °C. IR/cm^{-1}: $\sim\nu$: 3329.07(w, N–H), 2962.74(m, CH_3), 29234.96(m, CH_2), 1710.23, 1689.86(s, CO), 1601.26, 1500.23(m, Ar–H); ^{1}H NMR ($CDCl_3$) $\delta = 0.55$–0.65(t, 6H, $-CH_2H_3$), 1.12(b, 6H, ArNHCH $(CH_3)_2$) 1.25(s, 21H, CH_3), 1.35(t, 3H, $NNCH_2CH_3$), 1.55(q, 2H, $-C-CH_2-CH_3$), 1.85(q, 2H, $-C-CH_2-CH_3$), 2.23(m, 2H, $CH_2-CH_2-CH_2$), 2.6(t, 2H, $CO-CH_2-$), 4.0(t, 2H, CH_2-O), 4.45(q, 2H $NNCH_2CH_3$), 5.09(s, COCHCO), 6.72–8.5(m, 9H, Ar–H); MS (EI): 891(M^+).

3. Results and discussion

Synthesis of compound **3** has been reported [1,15], but compared with the method in this paper, these methods were complex and used the environmentally unattractive acetonitrile as the reaction solvent. The pH range of the reaction solution is critical, and yield is lower if it is not controlled carefully. When the pH range is 8–9, better results are obtained.

The usual synthetic method of the compounds of **5A**, **5B**, **5C**, **5D** and **12** needs the use of phosgene. One of the serious drawbacks of the method is the gaseous and lethal nature of phosgene, which is required in considerable excess to affect the completion of reaction. It is dangerous and uneconomical to store and handle phosgene. In this paper, triphosgene has been substituted for phosgene and good results were obtained. Because triphosgene is solid and less poisonous, the reaction method is simple and safe. The pure compounds **5A**, **5B** and **5C** were obtained by recrystallization, so that they can be used in precise amount in the next reaction. Element analysis and the IR, ^{1}H NMR and MS spectra confirmed the structure of the synthesized compounds of **5A**, **5B** and **5C**. The infrared spectra revealed an intense band at 1700–1730 cm^{-1} assignable to (SC=OS)

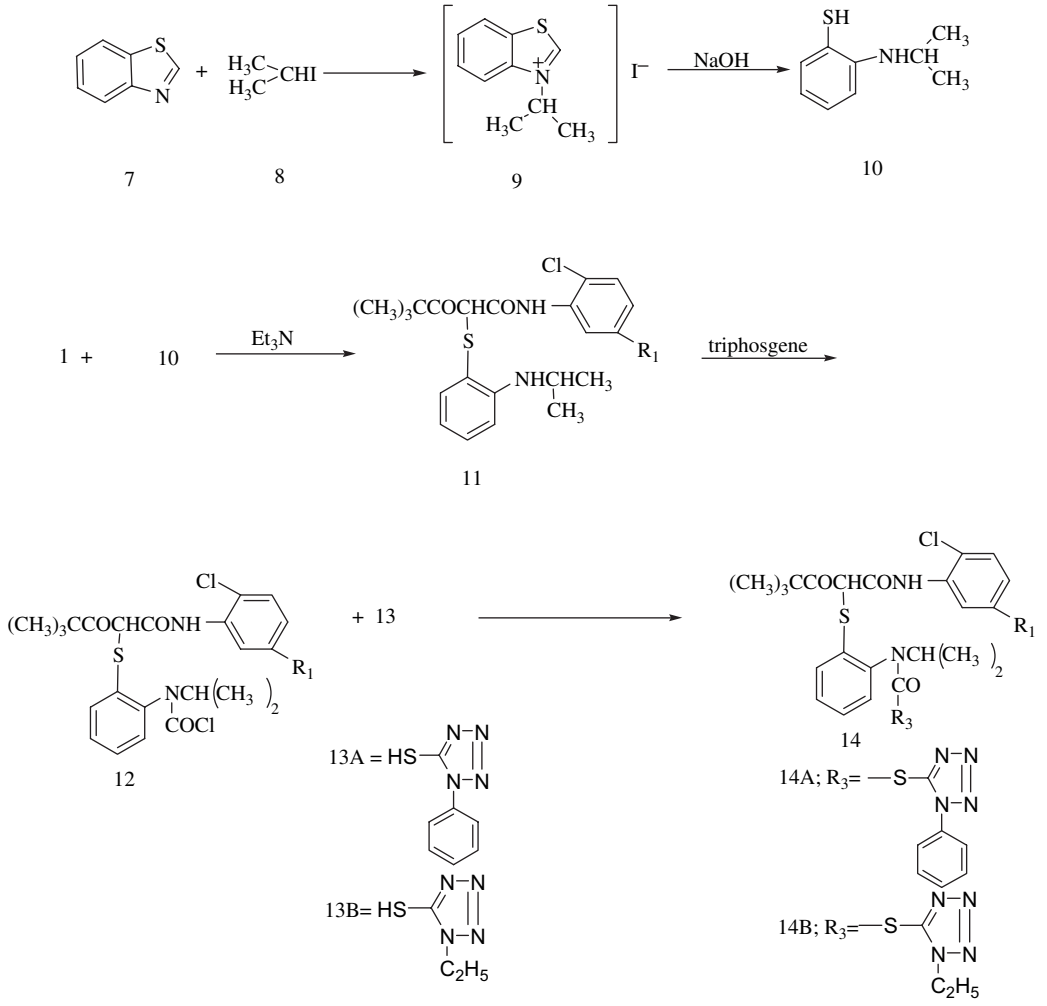

Fig. 2. Synthesis of the DIAR couplers **14A** and **14B**.

stretching. Compounds **5A**, **5B** and **5C** behave differently in subsequent reactions. Compound **5A** is able to react with compound **4** at 0 °C, but the reaction of compound **5C** and compound **4** needs heat. The compounds **5D** and **12** are very unstable, and so they are usually separated and purified in the reaction, and used in the next reaction.

A method for the preparation of 2-(isopropylamino)-benzenethiol is by the reaction of benzothiazole-2-one and 2-iodinepropane [20], but benzothiazole-2-one is not available commercially and must be synthesized by several steps in the lab. In this paper, benzothiazole was reacted with 2-iodinepropane to give iodine salt of (*N*-isopropylamino) benzothiazole and then 2-(isopropylamino)-benzenethiol was obtained by the reaction of the corresponding iodine salt and sodium hydroxide. A convenient procedure for the synthesis of 2-(isopropylamino)-benzenethiol is by utilizing commercially available benzothiazole. The reaction is operationally simple and offers high yields. Its structure was confirmed by IR and ^{1}H NMR. The infrared spectra revealed a band at 2520.36 cm^{-1} assignable to (S–H) stretching. The ^{1}H NMR spectrum of **10** showed two peaks at $\delta = 1.2–1.3$ for two CH_3 groups, a multiplet at $\delta = 3.62–3.70$ for

Table 1
Elemental analysis date

DIAR coupler	Molecular formula	C Calcd. (Found)	H Calcd. (Found)	N Calcd. (Found)
6A	$C_{50}H_{60}ClN_5O_8S_2$	62.67 (62.65)	6.30 (6.31)	7.33 (7.31)
6B	$C_{49}H_{63}ClN_6O_{10}S_3$	57.26 (57.27)	6.19 (6.18)	8.19 (8.18)
6C	$C_{47}H_{57}ClF_3N_7O_9S_2$	55.33 (55.31)	5.62 (5.63)	9.60 (9.61)
6D	$C_{56}H_{64}ClN_7O_{10}S$	63.28 (63.29)	6.09 (6.07)	9.26 (9.23)
14A	$C_{51}H_{66}ClN_7O_5S_2$	64.28 (64.03)	6.87 (6.95)	10.53 (10.25)
14B	$C_{47}H_{66}ClN_7O_5S_2$	62.33 (62.13)	7.31 (7.32)	10.95 (10.79)

CH group, a multiplet peak at $\delta = 6.50-7.42$ for four aromatic protons.

In this paper, six new DIAR couplers were synthesized and their structures were confirmed by element analysis (Table 1) and the IR, ^{1}H NMR and MS spectra. A yellow coupler was used as the coupler group of these DIAR couplers, substituted phenol and phezenethiol as the timing group, and six inhibitors were the inhibitor group.

References

[1] Phillip TSL. US patent, 4 248 962; 1981.
[2] Kumashiro Kenji. JP patent, 58-132 233; 1983.
[3] Ichijima Yasushi, Obayashi Keiji. 61-249 052; 1986.
[4] Ishige Osamu, Sato Naoki. JP patent, 9-160 189; 1997.
[5] Sato Naoki, Ishige Osamu. JP patent, 9-114 055; 1997.
[6] Yoshio Ishii, Akira Ikeda, Fumitaka Ueda, Hiroyuki Yamagaml, Yoshiharu Yabukl. US patent, 2001-6218 096.
[7] Avidano Mauro, Biavasco Raffaella, Brignone Diego, Rocca Giuseppe, Tavella Luisa. EP patent, 2000-1 055 967.
[8] Seki Hiroyuki, Ho Takayuki. JP patent, 2001-92 090.
[9] Ishige Osamu, Ikemizu Masaru, Kataoka Emiko, Tonishi Masakazu. JP patent, 2001-33 920.
[10] Gregor J Lestina, Davial T Southby, Wojiciech Slusarek. US patent, 1994-5 283 163.
[11] Allway Philip, Stanley Paul, Watts Chrisina. EP patent, 2000-1 014 182.
[12] Philip A Allway, Christina M Watts, Paul L Stanley. US patent, 2001-6 238 855.
[13] Paul B Merkel, Philip A Allway, David A Steele, Jerrold N Poslusny. US patent, 2001-6 146 820.
[14] Kiyoshi Murase, Todjoyasu Mase, Hiromu Hara, et al. JP patent, 1989-4 855 310.
[15] Philip Thiam Shin Lau. GB patent, 1979-2 010 818.
[16] Ito Takayuki, Mizukawa Hiroki. JP patent, 2001-147 510.
[17] Nishizeki Masato, Ishige Osamu. JP patent, 2001-60 000.
[18] Ikeda Akira. JP patent, 2001-83 671.
[19] Inder Pal Singh, Shradha Singh. US patent, 2002-6 455 702.
[20] Shulezhko AA, Rozhdestvenskaya IT, Kiprianov AI. Zh Org Khim 1970;6(10):2118–21.