Technology for their helpful discussion throughout this studies.

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Synthesis of 10-Oxo-β-rhodomycinone Derivatives

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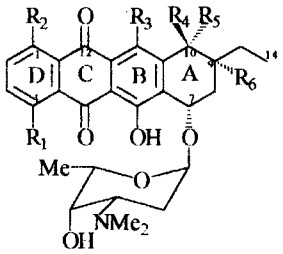
Regiospecific total syntheses of (±)-11-deoxy-4-methoxy-10-oxo-β-rhodomycinone (**21a**) and (±)-11-deoxy-1-methoxy-10-oxo-β-rhodomycinone (**21b**) are described. 2-(2-Bromoethyl)-1,3-dioxane (**6**) was transformed to naphthalenone **12**, which was condensed with (phenylsulfonyl)-isobenzofuranone **13** to afford 7,8-dihydro-9-ethyl-6-hydroxy-4-methoxynaphthacen-5,12-dione (**15**). Epoxide **16** prepared from olefinic compound **15**, reacted with HF/Pyr (7 : 3) to give **17**. Dihydroxylation of **17** with *t*-BuOK/$P(OMe)_3/O_2$, selective *cis*-diol protection of mixed compounds **18** with phenylboronic acid in toluene, separation of *cis*-boronate **19** and *trans*-diol **20** by column chromatography on silica gel, and cleavage of the boronate group of **19** with 2-methylpentane-2,4-diol in acetic acid completed the construction of **21**.

Introduction

Rhodomycins in anthracycline series were first discovered by Krassilnikov and Koreniakov.[1] Among these, rhodomycin and isorhodomycin family produced by *streptomyces purpurascens* were the first anthracycline compounds whose structures were elucidated by Brockmann and coworkers.[2] Rhodomycins like daunomycin and aklavin are well-known, clinically useful anticancer chemotherapeutic agents against acute leukemia and human cancer, as well as various experimental tumors. Since then, anthracyclines have been the objects of intensive clinical tests and synthetic studies for the last decade because of their strong antineoplastic activities.[3] Numerous synthetic approaches have been



	R_1	R_2	R_3	R_4	R_5	R_6
1	OH	H	OH	OH	H	OH
2	OH	OH	OH	OH	H	OH
3	OH	H	H	=O		F
4	OH	H	H	=O		OH
5	H	OH	H	=O		OH

Figure 1.

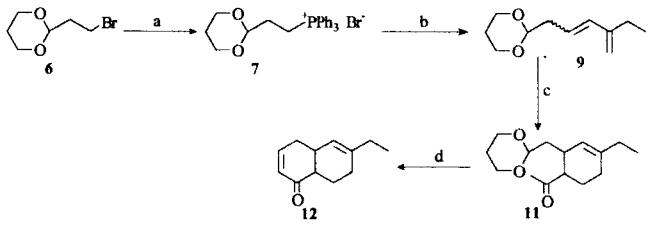
developed and a number of their derivatives have been synthesized.[4]

All rhodomycins have a hydroxyl group at C-11 position of the aglycone, and β-isorhodomycins (**2**) possess an additional hydroxyl group at C-1 position unlike β-rhodomycins (**1**). Cardiotoxicity studies by Tone and coworkers[5] have shown that the toxicity was reduced when aclacinomycin derivatives without hydroxyl group at C-11 position were used. Moreover, 11-deoxydaunorubicin isolated by Arcamone *et al.*[6] was found to have higher anticancer activity and less cardiotoxicity than daunorubicin having a hydroxyl group at C-11 position.

In a recent publication,[7] we reported the synthesis of novel 9-fluoroanthracycline derivatives and their isomeric glycosides. The first synthesized 9-fluoroanthracycline derivative **3** showed an improved anti-proliferative effect to Hepatoma cells (Hep 3B). Here, we report the synthesis of aglycones (±)-**21a** and (±)-**21b** for the synthesis of anthracycline derivatives **4** and **5**. The fluorine atom at C-9 position of **3** was replaced by an hydorxyl group.

Results and Discussion

The anthracyclines containing the tetracyclic polynuclear aromatic ring system in the aglycone have at least one sugar residue glycosidically linked[4] to the C-7 hydroxyl group. The regiospecific convergent syntheses of aglycones were accomplished through condensation of phthalide sulfone derivatives with α,β-unsaturated carbonyl system using the Michael type condensation reaction.[8] The key element of the synthesis was the use of naphthalenone **12**,[8a] which served as a synthon for the construction of tetracyclic ring system by condensing with phthalide sulfone in one step. In the earlier work,[8a] Rho reported the synthesis of 1(4*H*)-naphthalenone **12** through five steps involving Grignard reaction, acetylation, and elimination in the presence of palladium acetate as a catalyst. However, the Rho's route to prepare naphthalenone **12** took a long step. We have developed a short and efficient route for the preparation of the intermediate **9** in multigram quantities *via* direct Wittig reaction,[9] and have employed the method to accomplish the synthesis of 10-oxo-β-rhodomycinones. Unlike the result from Grignard reaction (*E*-isomer only), the diene **9** synthesis through Wittig reaction gave a mixture of *E*- and *Z*-isomer (1 : 1). Without further purification, Diels-Alder cycloaddition of **9** with methyl vinyl ketone **10** (neat, sealed tube, 150 °C) regiospecifically furnished the cyclohexene **11** as a mixture of *cis* and *trans* isomers. The desired naphthalenone **12** was successfully synthesized in 80% yield by the hydrolysis of acetal group

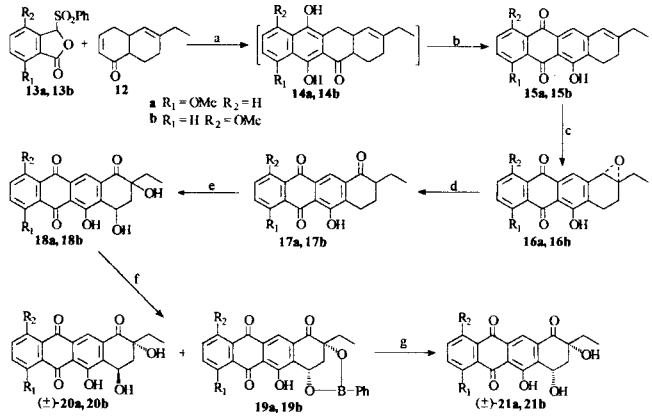


Scheme 1. (a) PPh_3/toluene, reflux, (b) *n*-BuLi/THF, acrolein (**8**), (c) methyl vinyl ketone (**10**) in seal tube, 150 °C, (d) 3 N $HClO_4$.

using 3 N aqueous $HClO_4$.

Naphthalenone **12** was condensed with phthalide sulfone **13** which had been converted to an anion with *t*-BuOLi at −78 °C to afford naphthacene **15** in 83-85% yield after oxygen bubbling in DMF, and then the double bond of **15** was subjected to epoxidation with *m*-CPBA to produce epoxide **16**.[10] From the previous studies on the syntheses of 9-fluoro-10-hydroxynaphthacene and 10-oxo compound **17**,[7,11] we found that the fluorinated compound was obtained as a major product when the epoxy compound **16** was treated with HF/pyridine (7 : 3) at 0 °C for 5 min. On the other hand, when the same reaction was performed at room temperature for 8 hr, the epoxide **16** was transformed to 10-oxo compound **17** in 70% yield. It appears that the epoxide **16** in HF/pyridine (7 : 3) generated the fluorinated compound within 5 min and then dehydrofluorination took place due to the pyridine base.

Now, the two hydroxyl groups have to be introduced at C-7 and C-9 position as *cis* form to obtain the final products **21**. Hydroxylation of 10-oxo-compound **17** at C-7 and C-9 position was achieved by Swenton's method[12] (O_2/*t*-BuOK/$P(OCH_3)_3$/DMF). 9-Hydroxyl compound and 7,9-dihydroxy compound **18** were obtained in 12% and in 53% yield respectively. Tanaka *et al.*[13] reported that the amount of *t*-BuOK was a critical factor to give the best result of *cis*/*trans* formation. After several trials, we obtained the 7,9-dihydroxy compound **18** in the best yield when using 4 equivalent of *t*-BuOK. The major product of the reaction



Scheme 2. (a) *t*-BuOLi/THF, −78 °C, rt. reflux, (b) O_2/DMF, (c) *m*-CPBA/CH_2Cl_2, rt, 5 hr., (d) HF/Pyr (7 : 3)/THF, 0 °C (5 min), rt (8 hr), (e) *t*-BuOK, $P(OMe)_3$, O_2/DMF, −15 °C, (f) PhB$(OH)_2$, *p*-TsOH/toluene, (g) 2-methyl-2,4-pentanediol, AcOH/CH_2Cl_2/acetone.

was *cis* compound: the *cis/trans* ratio was 9 : 1, which was determined by ^{1}H NMR spectrum analysis. The selective *cis*-diol protection of the isomers **18** with phenylboronic acid in dry toluene gave the benzene boronate (±)-**19** and the unreacted *trans*-diol (±)-**20**.[12] After purification by chromatography, the isolated *cis*-boronate (±)-**19** was easily converted to *cis*-diol (±)-**21** using 2-methylpentane-2, 4-diol in acetic acid.[14] The structures of **20** and **21** having a half-chair form[6] were analyzed based on the ^{1}H NMR spectra. The protons at C-7 and C-8 exhibited different scalar coupling patterns for *cis*-**21a** ($J_{7e,8a}$=3.91 Hz, $J_{7e,8e}$= 1.96 Hz) and *trans*-**20a** ($J_{7a,8a}$=8.79 Hz, $J_{7a,8e}$=5.86 Hz), which were similar to the results of Keay.[15] 1-Methoxy compound **21b** was readily prepared by the same procedure for the synthesis of 4-methoxy compound **21a**, and all the reactivities for the synthesis of **21b** were similar to those of **21a. 21b** ($J_{7e,8a}$=4.40 Hz, $J_{7e,8e}$=3.01 Hz) and **20b** ($J_{7a,8a}$=9.28 Hz, $J_{7a,8e}$=5.86 Hz) were also identified as *cis* and *trans* isomer, respectively, by comparing the coupling constants with those reported in the literature.[15]

In conclusion, we developted an efficient method for the synthesis of the title compound (±)-**21**, which was the precursor for the synthesis of the glycoside as a potential anticancer drug. The glycoside containing N-acetyl-D-glucosamine or L-fucose can be readily prepared in a few steps. The *in vitro* antitumor activity of the glycosides against adrimycin will be reported elsewhere.

Experimental

All reactions were carried out under nitrogen atmosphere with oven-dried glassware. All solvents were purified by distillation and dried, if necessary, prior to use. ^{1}H and ^{13}C spectra were obtained on a JEOL JNM EX-400 spectrometer. Chemical shifts were internally referenced to TMS for ^{1}H or to the solvent signals for ^{13}C. Mass spectra were obtained on a JEOL JMX-DX 300 spectrometer (EI and FAB+) and on a VG QUATTRO spectrometer (ESI). Melting points were obtained on a Buchi 510 melting point apparatus and were uncorrected. Products were purified by flash column chromatography on silica gel (60-200 mesh), and HPLC was carried out on a Waters 4000 instrument having a Waters PDA UV spectrophotometer and a Waters 410 differential refractometer.

2-(4-Methylene-2-hexenyl)-1,3-dioxane (9). 2-(2-bromoethyl)-1,3-dioxane **6** (4.91 g, 25.17 mmol) and triphenylphosphine (6.60 g, 25.17 mmol) in tolune (100 mL) were heated at reflux under dry nitrogen for 2 days. The cooled product was separated by filtration, washed well with dry ether, and dried under vacuum to afford phosphonium salt **7** (10.50 g, 91.2%).

7 (3.13 g, 6.85 mmol) was suspended in 20 mL of tetrahydrofuran under dry nitrogen and treated with a solution of *n*-buthyllithium in hexane (1.2 molar equiv., 5.9 mL of a 1.4 M solution) at −20 °C. After 15 min, the nearly clear, red solution was cooled to −78 °C, and acrolein **8** (0.71 mL, 6.16 mmol) was added, discoloring the solution. The solution was then warmed to room temperature. The solvent was evaporated, and the oil was dissolved in methylene chloride. This solution was rinsed with 5% aqueous sodium sulfate solution and concentrated to dienes **9** (0.99 g, 88.5%) as liquid. The physical and spectroscopic data of **9** are in accordance with the literature.[8a]

1-Acetyl-2-[(1,3-dioxa-2-cyclohexyl)methyl]-4-ethylcyclohex-3-ene (11). Diene 9 (4.5 g, 24.69 mmol) was treated with methyl vinyl ketone **10** (3.1 mL, 37.04 mmol) in a sealed tube according to our earlier procedure to give adduct **11** (5.98 g, 96%). The physical and spectroscopic data are in accordance with the literature.[8a]

6-Ethyl-4a,7,8,8a-tetrahydro-1(4*H*)-naphthalenone (12). Adduct **11** (5.0 g, 19.81 mmol) was hydrolyzed with 3 N $HClO_4$ (30 mL) according to our earlier procedure to give naphthalenone **12** (2.79 g, 80%). Less polar isomer: ^{1}H NMR ($CDCl_3$) δ 6.98 (ddd, J=10.2, 5.5, 2.4 Hz, 1H), 6.05 (ddd, J=10.2, 2.4, 1.9 Hz, 1H), 5.22 (dtt, J=3.4, 1.9, 1.5 Hz, 1H), 2.30-2.55 (m, 3H), 2.0-2.3 (m, 4H), 1.95 (q, J=7.0 Hz, 1H), 1.36 (m, 1H), 1.02 (t, J=7.0 Hz, 3H). More polar isomer: 6.86 (dt, J=10.2, 4.4 Hz, 1H), 5.99 (dt, J=10.2, 1.9 Hz, 1H), 5.30 (dtt, J=5.9, 2.4, 1.5 Hz, 1H), 2.8 (m, 1H), 2.45-2.63 (m, 2H), 2.15-2.25 (m, 1H), 2.0-2.10 (m, 3H), 1.95 (q, J=7.0 Hz, 2H), 1.68 (m, 1H), 0.97 (t, J=7.0 Hz, 3H).

7,8-Dihydro-9-ethyl-6-hydroxy-4-methoxynaphthacen-5,12-dione (15a). 7,8-Dihydro-9-ethyl-6-hydroxy-1-methoxynaphthacen-5,12-dione (15b). To cold (−78 °C) magnetically stirred solution of lithium *t*-Butoxide, prepared from *t*-butyl alcohol (6.13 mL, 64.06 mmol) and *n*-BuLi (45.76 mL, of 1.4 M solution, 64.06 mmol) in dry THF (70 mL) was added the sulfone **13a** (7.22 g, 23.73 mmol) in THF (50 mL), and the mixture was stirred for 30 min at −78 °C. Solution of **12** (3.76 g, 21.35 mmol) in THF (20 mL) was added by syringe, and the mixture was stirred at −78 °C for 2 h. The cooling bath was removed, and the reaction was stirred at r.t. for 3 h and then heated at reflux for 20 min. The mixture was cooled to 0 °C and acidified with 2 N HCl. The THF was evaporated under reduced pressure, and the aqueous mixture was extracted with methylene chloride. The combined methylene chloride extracts were washed successively with H_2O, brine, dried $MgSO_4$, filtered, and evaporated at reduced pressure to give crude naphthacenone **14a** (6.44 g, 89.2%). Oxygen was bubbled through a heated (100 °C) solution of **14a** (2.7 g, 7.98 mmol) in DMF (50 mL) for 6 h. The solution was cooled in an ice-water bath. Addition of H_2O to the solution precipitated **15a** as orange crystals, which were collected by filtration, washed with H_2O, and dried to give 2.23 g (83.6%) of pure **15a** with mp 156-158 °C.

15a: ^{1}H NMR ($CDCl_3$) δ 13.28 (s, 1H), 7.95 (dd, J=8.0, 1.9 Hz, 1H), 7.71 (t, J=8.0 Hz, 1H), 7.44 (s, 1H), 7.34 (dd, J=8.0, 1.0 Hz, 1H), 6.29 (s, 1H), 4.07 (s, 3H), 2.94 (t, J=8.8 Hz, 2H), 2.34 (t, J=8.8 Hz, 2H), 2.27 (q, J=7.6 Hz, 2H), 1.15 (t, J=7.6 Hz, 3H); MS m/z 334 (M^+).

By the above procedure, **15b** was obtained in a yield of 65% over two steps from **13b**.

15b: mp 168-170 °C; ^{1}H NMR ($CDCl_3$); δ 12.78 (s, 1H), 7.93 (d, J=7.8 Hz, 1H, ArH), 7.68 (t, J=8.1 Hz, 1H, ArH), 7.41 (s, 1H, ArH), 7.38 (d, J=8.3 Hz, 1H, ArH), 6.29 (s, 1H, =CH), 5.03 (s, 3H, OMe), 2.90 (t, J=8.1 Hz, 2H, CH_2), 2.34-2.27 (m, 4H), 1.16 (t, J=7.31 Hz, 3H, CH_3); MS (m/z) 334 (M^+).

9,10-Epoxy-9-ethyl-6-hydroxy-4-methoxy-7,8,9,10-tetrahydronaphthacen-5,12-dione (16a). 9,10-

Epoxy-9-ethyl-6-hydroxy-1-methoxy-7,8,9,10-tetrahydronaphthacen-5,12-dione (16b). A mixture of naphthacene **15a** (2.45 g, 7.33 mmol) and *m*-CPBA (70%, 2.71 g, 10.99 mmol) was dissolved in 50 mL of methylene chloride and stirred at r.t. for 5 h. The reaction mixture was diluted with 50 mL of methylene chloride and washed successively with 10% aqueous sodium carbonate solution and saturated brine, dried over Na_2SO_4. The residue was chromatographed on silica gel (CH_2Cl_2/EtOAc=95 : 5) to give 2.40 g (93.3%) of **16a** with mp 208-210 °C. **16a**: ^{1}H NMR ($CDCl_3$) δ 13.25 (s, 1H), 7.96 (dd, *J*=7.8, 0.9 Hz, 1H), 7.80 (s, 1H), 7.73 (t, *J*=7.8 Hz, 1H), 7.34 (d, *J*=7.8 Hz, 1H), 4.07 (s, 3H), 3.73 (s, 1H), 3.08 (m, 2H), 2.48 (m, 2H), 1.88 (q, *J*= 7.9 Hz, 2H), 1.06 (t, *J*=7.9 Hz, 3H); MS m/z 350 (M^+).

By the above procedure, **16b** was obtained from **15b** in 92.1% yield with mp 184-186 °C.

16b: ^{1}H NMR ($CDCl_3$) δ 12.67 (s, 1H, OH), 7.85 (d, *J*= 7.8 Hz, 1H, ArH), 7.68 (t, *J*=8.1 Hz, 1H, ArH), 7.41 (s, 1H, ArH), 7.39 (d, *J*=8.3 Hz, 1H, ArH), 6.29 (s,1H), 4.03 (s, 3H, OMe), 2.90 (t, *J*=8.5, 2H, CH_2), 2.34-2.27 (m, 4H), 1.16 (t, *J*=7.3 Hz, 3H, CH_3); MS (m/z) 350 (M^+).

9-Ethyl-6-hydroxy-4-methoxy-7,8,9,10-tetrahydronaphthacen-5,10,12-trione (17a). 9-Ethyl-6-hydroxy-1-methoxy-7,8,9,10-tetrahydronaphthacen-5,10,12-trione (17b). Using polyethylene equipment and under strict exclusion of moisture, to the cooled (0 °C) solution of HF/Pyr (7 : 3, 54 mL) was added the epoxide **16a** (1.70 g, 4.85 mmol) in THF (50 mL) in one portion, and the mixture was stirred for 5 min. The cooling bath was removed and the mixture was stirred for 8 h at r.t. The reaction mixture was poured into ice water (100 mL) and extracted with CH_2Cl_2. The combined organic phases were evaporated to dryness and the residue was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc, 2% → CH_2Cl_2 /EtOAc, 10%) to give **17a** (1.44 g, 84.7%) with mp 208-210 °C as light yellow powder. **17a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.37 (s, 1H, OH), 8.33 (s, 1H, ArH), 7.96 (d, 1H, *J*=8.1 Hz, ArH), 7.77 (t, 1H, *J*=8.1 Hz, ArH), 7.37 (d, 1H, *J*=8.1 Hz, ArH), 4.08 (s, 3H, OMe), 3.22 (dt, 1H, *J*=18.6, 4.9 Hz, C_{7eq}H), 2.89 (ddd, *J*=18.6, 9.7, 4.9 Hz, 1H, C_{7ax}H), 2.32 (ddd, 1H, *J*=13.6, 9.7, 4.7 Hz, 1H, C_{8eq}H), 2.02-1.90 (m, 2H), 1.63-1.53 (m, 1H, C_{13}H), 1.59-1.46 (m, 1H, C_{9ax}H), 1.03 (t, 3H, *J*= 7.3 Hz, 3H, C_{14}H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.91, 188.91, 181.88, 161.01, 160.69, 140.28, 137.34, 136.17, 135.95, 130.31, 120.71, 120.30, 119.21, 118.30, 116.93, 56.67, 48.41, 26.34, 22.14, 22.03, 11.34; MS: m/z=350 (M^+, 83%), 322 (100), 304 (32), 266 (27).

By the above procedure, **17b** was obtained from **16b** in 82.1% yield with mp 200-202 °C.

17b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.74 (s, 1H, OH), 8.27 (s, 1H, ArH), 7.87 (d, 1H, *J*=7.8 Hz, ArH), 7.66 (t, 1H, *J*=8.1 Hz, ArH), 7.30 (d, 1H, *J*=8.3 Hz, ArH), 4.00 (s, 3H, OMe), 3.11 (dt, 1H, *J*=18.1, 4.4 Hz, 1H, C_{7eq}H), 2.88 (ddd, 1H, *J*=18.1, 9.7, 4.9 Hz, 1H, C_{9ax}H), 2.30 (m, 1H, C_{9ax}H), 2.25 (ddd, *J*=13.2, 4.9, 4.4 Hz, 1H, C_{8eq}H), 1.96-1.80 (m, 1H), 1.56-1.46 (m, 1H, C_{13}H), 0.95 (t, *J*=7.3 Hz, 3H, C_{14}H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 198.91, 188.84, 180.94, 160.61, 160.12, 138.51, 138.11, 135.23, 135.06, 129.79, 121.71, 119.52, 118.83, 116.37, 56.61, 48.50, 29.67, 26.35, 22.13, 21.86, 11.36; MS: m/z=350 (M^+, 83%), 322 (100), 304 (32), 266 (27).

(±)-11-Deoxy-4-methoxy-10-oxo-β-rhodomycinone (20a). (±)-4,11-Dideoxy-1-methoxy-10-oxo-β-rhodomycinone (20b). Oxygen was bubbled to the cold (−15 °C) magnetically stirred solution of *t*-BuOK (95%, 1.43 g, 12.10 mmol) and trimethyl phosphite (0.79 mL, 6.66 mmol) in dry DMF (30 mL) for 15 min. Solution of **17a** (1.06 g, 3.03 mmol) in DMF (10 mL) was added, and the mixture was carefully maintained between −15 and −10 °C. After the color of the reaction mixture changed from yellow to dark blue, the reaction was quenched by the addition of 20 mL of water. The reaction mixture was stirred for 3 h at ambient temperature, the color of the mixture changing from dark blue to red-brown. The solvent was removed, and the resulting slurry was dissolved in CH_2Cl_2. The organic layer was then washed with water, filtered, and concentrated, and the trimethyl phosphate was removed under vacuum. The residue was chromatographed on silica gel (CH_2Cl_2/EtOAc 2%, → CH_2Cl_2/EtOAc 50%) to give **18a** (0.98 g, 85.1%).

The mixture of **18a** (0.72 g, 1.88 mmol), phenylboronic acid (97%, 0.31 g, 2.45 mmol) and anhydrous *p*-toluenesulfonic acid (51 mg, 0.30 mmol) in dry toluene (50 mL) was stirred at r.t. for 13 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The extract was washed with H_2O, dried, and concentrated *in vacuo* to give crude **19a**. Recrystallization from $CHCl_3$/hexane afforded **19a** (0.62 g, 70.8%) as red crystals.

The mixture of **19a** (0.54 g, 1.15 mmol), 2-methyl-2,4-pentanediol (1.47 mL, 11.53 mmol), AcOH (0.15 mL), CH_2Cl_2 (10 mL) and acetone (10 mL) was stirred at r.t. for 13 h. The reaction mixture was poured into a mixture of CH_2Cl_2 (30 mL) and saturated aqueous $NaHCO_3$ (15 mL). The organic layer was separated, washed with water, dried, and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (CH_2Cl_2/EtOAc 1% → CH_2Cl_2/EtOAc 5%), to give **21a** (0.38 g, 86.5%) with mp 175 °C as dark yellow powder. **21a**: ^{1}H NMR ($CDCl_3$+ CD_3OD) δ 13.78 (s, 1H, OH), 8.47 (s, 1H, ArH), 8.02 (dd, *J*=7.8, 1.0 Hz, 1H, ArH), 7.82 (t, *J*=8.3 Hz, 1H, ArH), 7.41 (dd, *J*=8.8, 1.0 Hz, 1H, ArH), 5.40 (ddd, *J*=5.9, 3.9, 2.0 Hz, 1H, C_{7eq}H), 4.10 (s, 3H, OMe), 3.71 (s, 1H, C_7OH), 2.99 (dd, *J*=15.6, 3.9 Hz, 1H, C_{8eq}H), 2.84 (dd, *J*=15.6, 5.9 Hz, 1H, C_{8ax}H), 2.23 (dq, *J*=15.1, 7.3 Hz, 1H, C_{13}H), 1.16 (t, *J*= 7.3 Hz, 3H, C_{14}H); ^{13}C NMR ($CDCl_3$) δ 189.75, 188.77, 181.49, 161.25, 161.12, 136.72, 136.56, 135.63, 133.99, 132.40, 120.53, 120.39, 119.22, 118.42, 117.90, 64.27, 61.10, 56.78, 40.89, 32.28, 9.82; MS (m/z) 282 (M^+).

20a: ^{1}H NMR ($CDCl_3$+CD_3OD) δ 14.06 (s, 1H, OH), 8.50 (s, 1H, ArH), 8.01 (dd, *J*=7.8, 1.0 Hz, 1H, ArH), 7.82 (t, *J*= 8.3 Hz, 1H, ArH), 7.41 (dd, *J*=8.8 Hz, 1H, ArH), 5.45 (ddd, *J*=8.8, 5.9, 1.9 Hz, 1H, C_{7ax}H), 4.54 (d, *J*=1.9 Hz, 1H, C_7OH), 4.10 (s, 3H, OMe), 3.01 (dd, *J*=14.7, 5.9 Hz, 1H, C_{8eq}H), 2.41 (dq, *J*=16.6, 7.3 Hz, 1H, C_{13}H), 2.28-2.22 (m, 2H, C_{8ax}H), 1.15 (t, *J*=7.3 Hz, 3H, C_{14}H); ^{13}C NMR ($CDCl_3$) δ 189.10, 188.85, 181.36, 161.23, 160.84, 138.44, 136.80, 135.60, 134.21, 131.94, 120.53, 120.28, 118.89, 118.48, 118.34, 65.09, 56.75, 40.78, 32.16, 9.71; MS (m/z) 282 (M^+).

By the above procedure, **21b** was obtained in a yield of 82.1% over three steps from **17b**.

21b: mp 155-158 °C; ^{1}H NMR ($CDCl_3$) δ 13.03 (s, 1H,

OH), 8.41 (s, 1H, ArH), 8.01 (dd, J=7.8, 1.0 Hz, 1H, ArH), 7.78 (t, J=8.3 Hz, 1H, ArH), 7.42 (d, J=8.8, 1.0 Hz, 1H, ArH), 5.06 (ddd, J=4.4, 3.0, 1.9 Hz, 1H, $C_{7eq}H$), 4.07 (s, 3H, OMe), 2.96 (s, 1H, C_7OH), 2.53 (dd, J=14.7, 3.0 Hz, 1H, $C_{8eq}H$), 2.24 (dd, J=14.7, 4.4 Hz, 1H, $C_{8ax}H$), 1.81-1.76 (m, 2H, $C_{13}H$), 0.92 (t, J=7.1 Hz, 3H, $C_{14}H$); ^{13}C NMR ($CDCl_3$) δ 199.91, 188.70, 180.40, 160.65, 160.42, 136.01, 135.56, 134.21, 133.03, 132.88, 121.79, 119.79, 118.92, 118.02, 117.84, 70.55, 63.52, 56.69, 40.18, 7.29; MS (m/z), 282 (M^+).

20b: ^1H NMR ($CDCl_3$) δ 13.36 (s, 1H, OH), 8.38 (s, 1H, ArH), 8.00 (dd, J=7.8, 1.0 Hz, 1H, ArH), 7.80 (t, J=8.0 Hz, 1H, ArH), 7.43 (dd, J=8.1, 1.0 Hz, 1H, ArH), 5.37 (ddd, J= 9.3, 6.1, 3.4 Hz, 1H, $C_{7ax}H$), 4.07 (s, 3H, OMe), 3.66 (d, J= 3.4 Hz, 1H, C_7OH), 2.79 (dd, J=13.7, 6.1 Hz, 1H, $C_{8eq}H$), 2.24 (dd, J=13.7, 9.3 Hz, 1H, $C_{8ax}H$), 1.76-1.56 (m, 2H, $C_{13}H$), 0.92 (t, J=7.3, Hz, 3H, $C_{14}H$); ^{13}C NMR ($CDCl_3$) δ 199.45, 189.17, 180.15, 160.81, 160.31, 137.47, 135.51, 135.19, 134.84, 132.56, 121.37, 119.70, 119.47, 119.35, 117.89, 76.19, 63.63, 40.28, 29.82, 7.24; MS (m/z) 282 (M^+).

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Rapid Energy Transfer Mechanism of F Electronic Excitation to the Vibration of Randomly Distributed OH^- in KCl

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The nature of F electronic excitation energy transfer to OH^- vibrational levels in KCl crystals is the exchange interaction, although the transfer process exhibits three temporally distinguishable components depending on the distance between excited F center and OH^-. The critical distance as well as rate of the major energy transfer process in randomly distributed samples increases rapidly as OH^- librational motions become active with temperature rise. The excited state character introduced into the OH^- ground electronic state by perturbation is essential for the exchange interaction. The perturbation is brought about by the expanded electron cloud of excited F center for OH^- associated to F center, whereas by librations and lattice vibrations perpendicular to the bond axis for isolated OH^-. F excitation quenching efficiency by OH^- is dependent on the variation of the critical distance rather than the rate as the rate is much faster than the normal F bleach recovery rate.

Introduction

This is the final paper concluding a series of studies[1-4] on the bleach recovery kinetics of F centers in alkali halides. F absorption bleach in OH^- doped crystals recovers with four temporally distinguishable components designated as super-