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SYNTHESES OF NEGATIVE PHOTOCHROMIC CROWNED SPIROBENZOPYRANS

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ABSTRACT: Two synthetic routes to negative photochromic spirobenzopyrans bearing a monoazacrown moiety at the 8-position were described and compared. Method B gives much higher total yield than method A.

Crowned spirobenzopyran derivatives are more effective than corresponding spirobenzopyrans without crown moiety for photochemical control of physical properties[1-3]. They possess great potential for application as a key material for photoresponsive membrane potential[4], photoinduced ionic-conductivity switching and metal ion spectrophotometry[2c]. We have designed and synthesized some new

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crowned spirobenzopyran derivatives. It is interesting to notice that these crowned spirobenzopyrans, unlike normal ones, exhibit negative photochromism. This paper describes the syntheses of these new compounds.

All the spirobenzopyrans bearing a monoazacrown moiety at the 8-position were synthesized by Kimura's route[2] (method A). We also followed this method to synthesize our compounds(**6**). However, we found that the yields of the cyclization reaction between Fischer's bases (**4c**, **4d**) and the compound **3** were very low, and the separation and purification of the final products were difficult. We think that it is attributed to the steric hinder resulted from the group R at 1'-position and the crown ether moiety at 8-position. Thus, we changed the synthetic route and employed the method B. The results showed that the total yields were improved dramatically. Total yields of two synthetic methods are summarized in Table 1. It is believed that the method B has two advantages over the method A: (1) the yield of cyclization in the first step is higher ,owing to the absence of bulky crown moiety which causes a steric hinder; (2) the separation of the final product is easier because of less by-product in the second step. So the method B is more effective and more convenient for the syntheses of crowned spirobenzopyran derivatives bearing bulky groups at 1'and 8 position. Two synthetic routes are outlined in the following scheme 1.

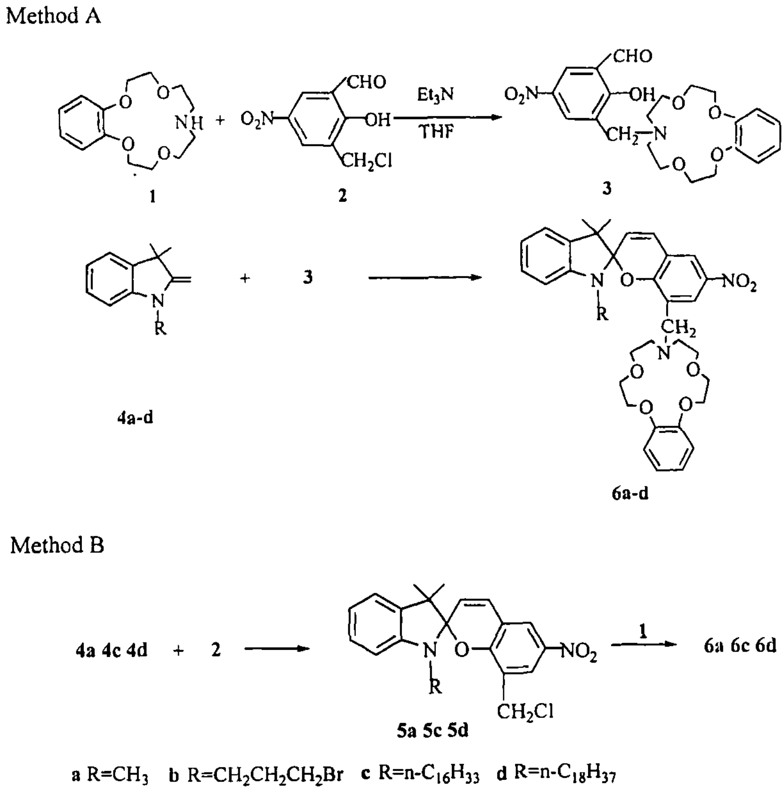
EXPERIMENTAL

The IR spectra were recorded on a Nicolet 170SX FT-IR spectrometer. The ^{1}HNMR spectra were measured on a Jeol FX-90Q spectrometer with TMS as an

Table 1 Total yields of two synthetic method

	6a(%)	6b(%)	6c(%)	6d(%)
method A	12.0	30.0	6.0	7.5
method B	46.8	—*	24.1	27.4

* **6b** was not obtained with method B owing to elimination of 3-bromopropyl and condensation of 3-bromopropyl with monoazacrown ether.



Scheme 1 Two synthetic routes for crowned spirobenzopyrans

interval standard. Elemental analyses were obtained on a Perkin-Elmer 204B elemental analyzer. The MS spectra were obtained on a ZAB-HF-3F spectrometer with FAB ionization mode.

Compound **1**[5], **2**[6], **4a**[7], **4b**[8],**4c**[9], **4d**[9], **5a**[10]were prepared according to the literature procedures.

Synthesis of 3-formyl-2-hydroxy-5-nitrobenzyl monoaza benzo-15-C-5(**3**)

To a dry THF solution (20mL) of monoazabenzo-15-C-5(**1**)(6.0mmol) and triethylamine(18.0mmol) was added a dry THF solution (20mL) of 3-chloromethyl-5-nitrosalicylaldehyde(**2**)(6.0mmol) dropwise while stirring on an ice bath. The stirring was continued overnight at room temperature and then under reflux for 3h. After filtration of triethylamine hydrochloride, evaporation of the THF afforded crude 3-formyl-2-hydroxy-5-nitrobenzyl monoazabenzo-15-C-5 (**3**), which was purified by column chromatography (silica gel, eluent: $CHCl_3$). Yield 59.8% (1600mg). ^1H NMR ($CDCl_3$)δ(ppm): 2.70-2.95(4H.t), 3.66-4.20(14H,m), 6.85(4H,s), 7.92 (1H,d), 8.42 (1H,d), 9.66(1H,s), 10.20 (1H,s). IR(KBr): 2927, 1684, 1607, 1562, 1503, 1441, 1313, 1287, 1256, 1123, 1085, 1057, 977, 937, 795, 751cm^{-1}. MS m/e (rel. intensity): 447 (MH^+,75). Anal. Calcd. for $C_{22}H_{26}N_2O_8$: C,59.19; H,5.83; N,6.28. Found: C,59.42; H,5.91; N,6.21.

Syntheses of spirobenzopyrans **5c** and **5d** (Exemplified with **5c**)

A benzene solution(60mL) of Fischer's base **4c**(1.0mmol) and 3–chloromethyl–5-

nitrosalicylaldehyde(**2**)(1.1mmol) was refluxed for 6h. The reaction mixture was washed with NaOH aqueous solution(30mL×3) and with water until the pH value of water layer was 7, then dried by anhydrous Na_2SO_4. After filtration and evaportion of the solvent, the residue was subjected to column chromatography(silica gel, eluent: AcOEt : petroleum ether=1 : 10) to give **5c**. Yield 37.0%(215mg); oil. ^{1}H NMR ($CDCl_3$)δ(ppm): 0.88(3H,t); 1.22(34H,s); 3.08(2H,t); 4.32(2H,s); 5.85(1H,d, J=10.8Hz); 6.50(1H,d,J=7.2Hz); 6.75-7.10(4H,m); 7.90(1H,d,J=2.6Hz); 8.10 (1H, d,J=2.6Hz). IR(KBr): 2924; 2853; 1610; 1524; 1457; 1339; 1281; 1094; 918; 744cm^{-1}. MS m/e (rel. intensity): 582(MH$^+$,35); 545(M$^+$-Cl,35). Anal. Calcd. for $C_{35}H_{49}N_2O_3Cl$: C, 72.35; H, 8.44; N, 4.82. Found: C, 72.05; H, 8.38; N, 4.87.

5d: Yield 44.5%; oil. ^{1}H NMR ($CDCl_3$)δ(ppm): 0.88(3H,t); 1.20(38H,s); 3.08(2H,t); 4.32(2H,s); 5.85(1H,d,J=10.8Hz); 6.50(1H,d,J=7.2Hz); 6.75-7.10 (4H,m); 7.90(1H,d,J=2.6Hz); 8.10(1H,d,J=2.6Hz). IR(KBr): 2926; 2852; 1608; 1520; 1459; 1335; 1278; 1089; 923; 746cm^{-1}. MS m/e (rel intensity): 610(MH$^+$,30); 574(MH$^+$-Cl,35). Anal. Calcd. for $C_{37}H_{53}N_2O_3Cl$: C, 72.94; H, 8.77; N, 4.60. Found: C, 72.83; H, 8.82; N, 4.55.

Syntheses of crowned spirobenzopyrans **6a-d** with method A(Exemplified with **6a**)

A dry ethanol solution (20mL) of 1,3,3-trimethyl-2-methylene indoline (**4a**) (3.0mmol) and 3-formyl-2-hydroxy-5-nitrobenzyl monoazabenzo-15-C-5(**3**) (3.0mmol) was heated under reflux for 20h. After evaporation of the ethanol, the residue was subjected to column chromatography (silica gel, eluent: AcOEt : petroleum ether=1 : 3) to yield crowned spirobenzopyran (**6a**). Yield 20.0% (360mg). ^{1}H NMR($CDCl_3$)δ(ppm): 1.16(3H,s), 1.24(3H,s), 2.66(7H,t), 3.38-4.10 (14H,m), 5.80(1H,d,J=10.8Hz), 6.50(1H,d,J=7.2Hz), 6.78-7.08(8H,m), 7.82(1H, d, J=2.6Hz), 8.12(1H,d,J=2.6Hz). IR (KBr): 2925, 2884, 1609, 1504, 1451, 1334, 1257, 1089,927, 744 cm^{-1}. MS m/e (rel intensity): 603(MH$^+$, 30), 335(MH$^+$-crown ether,100). Anal. Calcd. for $C_{34}H_{39}N_3O_7$: C,67.89; H,6.49; N,6.99. Found: C,68.12;H,6.41;N,7.08.

6b:Yield 50.0%. ^{1}H NMR(DMSO)δ(ppm): 1.42(6H, s), 2.15(2H,m), 2.92 (2H,t), 3.35(6H, m), 3.68-4.40(14H, m), 6.95(4H, S), 7.42-7.80(5H, m), 8.02 (1H,d,J=2.6Hz), 8.32(2H,t). IR (KBr): 2923, 2870, 1603, 1524, 1446, 1282, 1261, 1194, 1123, 1095, 930, 745cm^{-1}. MS m/e (rel intensity): 628 (M$^+$-Br, 35), 361(85). Anal. Calcd. for $C_{36}H_{42}BrN_3O_7$: C,61.02;H, 5.97; N,5.93. Found: C,60,78; H,6.05; N,5.84.

6c: Yield 10.0%; oil; ^{1}H NMR ($CDCl_3$)δ(ppm): 0.88(3H,t); 1.22(34H,s); 2.65(4H,t); 3.08(2H,t); 3.40-4.12(14H,m); 5.80(1H,d,J=10.8Hz); 6.50(1H, d, J=7.2 Hz); 6.75-7.10(8H,m); 7.90(1H,d,J=2.6Hz); 8.10(1H,d,J=2.6Hz). IR(KBr): 2924; 2853; 1608; 1521; 1454; 1334; 1258; 1130; 933; 742 cm^{-1}. MS m/e(rel intensity): 812(MH$^+$,10); 835(M$^+$+Na,5); 851 (M$^+$+K, 5); 545(M$^+$-crown ether, 65). Anal. Calcd. for $C_{49}H_{69}N_3O_7$: C, 72.47; H, 8.56; N, 5.17. Found: C, 72.27; H, 8.58; N, 5.12.

6d: Yield 12.5%; oil: ^{1}H NMR ($CDCl_3$)δ(ppm): 0.88(3H,t); 1.22(38H,s); 2.65(4H,t); 3.08(2H,t); 3.40-4.12(14H,m); 5.78(1H,d,J=10.8Hz); 6.47(1H,d, J= 7.2Hz); 6.72-7.20(8H,m); 7.82(1H,d,J=2.6Hz); 8.14(1H,d,J=2.6Hz). IR(KBr): 2921; 2852; 1608; 1504; 1484; 1455; 1335; 1257; 1131; 933; 743 cm^{-1}. MS m/e(rel intensity): 840(M^+,10); 863(M^++Na,5); 879(M^++K,5); 574(M^+-crown ether,50). Anal. Calcd for $C_{51}H_{73}N_3O_7$: C, 72.91; H, 8.76; N, 5.00. Found: C, 72.78; H, 8.80; N, 4.95.

Syntheses of crowned spirobenzopyrans **6a**,**6c**,**6d** with method B(Exemplified with **6a**)

A dry THF solution (25mL) of 1', 3', 3'-trimethyl-8-chloromethyl-6-nitro-spiro[2H-1-benzopyran-2, 2'-indolenine](**5a**) (1.0mmol), triethylamine(3.0mmol) and monoazabenzo-15-C-5 (**1**) (1.2mmol) was refluxed for 20h. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel; eluent: AcOEt : petroleum ether=1 : 3) to yield crowned spirobenzopyran (**6a**). Yield 52.0% (313mg).

6c: Yield 65.0%; **6d**:Yield 61.6%.

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