Synthesis of spironaphthopyrans containing an allyl group

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INTRODUCTION

Polymeric materials containing incorporated photochromic molecules have been given considerable attention due to their application in advanced technologies [1–3]. The synthesis of a relatively large number of indoline spirobenzopyrans and spironaphthoxazines bearing polymerizable allyl, methacryloxy and trimethoxysilyl organic functional groups have been reported [4–8]. However, very little documentation exists about preparation of polymerizable derivatives of indoline spironaphthopyrans. It is known that molecules of indoline spironaphthopyrans exhibit photochromic and thermochromic properties [9–11]. Therefore, their incorporation into the structure of polymeric materials could be of a considerable scientific and technological interest.

The purpose of the current investigation is development of the methods for the preparation of allyl group containing spironaphthopyrans.

RESULTS AND DISCUSSION

The most common route for the synthesis of spiroopyrans is based on condensation of 1-substituted 2,3,3-trimethyl-3H-indolium salts or the corresponding methylene bases with ortho-hydroxy aromatic aldehydes [12]. Our synthesis strategy was based on alkylation of the corresponding 3H-indoles with allyl bromide and the subsequent condensation of the obtained 1-allyl-3H-indolium salts with 2-hydroxy-1-naphthaldehyde. When 2,3,3-trimethyl-3H-indole 1a was heated with allyl bromide in acetone, the expected 1-allyl-3H-indolium bromide did not crystallize from the reaction mixture. However, treatment of the crude product with perchloric acid afforded perchlorate 2 with a yield 73%. Similar alkylation of 5-bromo-2,3,3-trimethyl-3H-indole 1b with allyl bromide gave crystalline bromide 3 directly (yield 56%). In the 1H NMR spectrum of perchlorate 2 the allyl group protons gave complex multiplets in the area of 5.06–6.12 ppm.

Condensation of 1-allyl-3H-indolium salts 2, 3 with 2-hydroxy-1-naphthaldehyde was carried out in ethanol in the presence of piperidine. Work-up of the reaction mixture with sodium acetate afforded spironaphthopyrans 4a,b. Their 1H NMR spectra are characterized by the presence of multiplets of the allyl group protons in the area of 5.06–6.12 ppm, and a doublet of the 3'-H at about 5.85 ppm with J = 10.2–10.5 Hz, which evidences the cis-allocation of the vinylic protons. Compound 4b was synthesized also by condensation of bromide 3 with 2-hydroxy-1-naphthaldehyde in acetic acid.
In order to synthesize spiro[5H-1-benzoxazepino[3,2-\(\gamma\)]indol-2-one] 6, an analogous product was obtained when the condensation was carried out in ethanol in the presence of piperidine. In both cases, the spiroannelation reaction proceeded via stages of the imidazoline ring opening of starting imidazo[1,2-\(\gamma\)]indole, intermolecular condensation of an active methyl group with formyl one, and finally in spiro[5H-1-benzoxazepino[3,2-\(\gamma\)]indole] 7 with a yield 50%. The presence of the pyrrolidine ring was confirmed by the \(\beta\) NMR spectrum of 6 were an AB-quadruplet of diastereotopic protons of NCH\(2\)CO moiety in the area of 3.54–3.83 (\(J = 16.8\) Hz), a doublet of 3'-H at 5.94 (\(J = 10.8\) Hz) and a broad NH singlet at 7.82 ppm.

Recently we have demonstrated that treatment of spiro[5H-1-benzoxazepino[3,2-\(\gamma\)]indole] 6 in ethanol containing potassium hydroxide afforded cis-7a,15-methanonaphth[1',2':6,7][1,3]oxazepino[3,2-\(\gamma\)]indole-14-(N-phenylcarboxamide) 7 with a yield 50%. The presence of the pyrrolidine ring aneled to the indole nucleus was confirmed by the \(\beta\) NMR spectrum of 7 that contained characteristic signals at 32.79 (C-16), 37.14 (C-15), 78.63 (C-14) ppm.

**EXPERIMENTAL**

Melting points were determined on a KLeinfeld melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrophotometer. \(\beta\) H NMR spectra were recorded at 300 MHz and \(\beta\) C NMR spectra were recorded at 75 MHz on a Varian Gemini 2000 instrument. Tetramethylsilane was used as an internal standard. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F254) were used.

1-Allyl-2,3,3-trimethyl-3H-indolium perchlorate (2). To a solution of 2,3,3-trimethyl-3H-indole (7.96 g, 0.05 mol) in acetone (15 ml) allyl bromide (12.1 g, 8.65 ml, 0.1 mmol) was added and the mixture was refluxed for 5 h and then left to cool to room temperature. The solvent was evaporated under reduced pressure, the residue was dissolved in ethanol (8 ml), and to the solution 42% HClO\(_4\) was added dropwise until pH 2. The mixture was left at 5 °C for 24 h, the separated crystalline material was filtered off, washed with cold ethanol (2 ml), ether (10 ml) and recrystallized from ethanol to yield 10.94 g (73%) of perchlorate 2 with m.p. 158–159 °C. \(\beta\) H NMR (CF\(_3\)COOH): 1.22 (6H, s, 3,3-CH\(_3\)); 2.40 (3H, s, 2-CH\(_3\)); 4.62–4.80 (2H, m, NCH\(_2\)); 4.92–5.18 (2H, m, CH = CH\(_2\)); 5.40–5.80 (1H, m, CH = CH\(_2\)); 7.12–7.28 ppm (4H, s, ArH). Found: C, 56.03; H, 5.64; N, 4.42%. Calculated for C\(_{18}\)H\(_{18}\)ClNO\(_3\)_2: C, 56.10; H, 5.62; N, 4.48%.

1-Allyl-5-bromo-2,3,3-trimethyl-3H-indolium bromide (3). To a solution of 5-bromo-2,3,3-trimethyl-3H-indole (1.60 g, 6.7 mmol) in acetone (5 ml) allyl bromide (1.62 g, 1.16 ml, 13.4 mmol) was added and the mixture was refluxed for 5 h, then cooled to room temperature and left at 5 °C for 24 h. The crystalline material was filtered off, washed with acetone (1 ml), ether (5 ml) and recrystallized from ethanol to yield 1.34 g (56%) of bromide 3 with m.p. 196–197 °C. \(\beta\) H NMR (300 MHz, DM SO-d\(_6\)): 1.57 (6H, s, 3,3-CH\(_3\)); 2.84 (3H, s, 2-CH\(_3\)); 5.06–5.22 (2H, m, NCH\(_2\)); 5.40–5.46 (2H, m, CH = CH\(_2\)); 5.97–6.12 (1H, m, CH = CH\(_2\)); 7.85–8.19 ppm (3H, \(\beta\) H).
m, ArH). Found: N, 4.09; Br, 44.67. Calculated for C_{23}H_{20}BrN: N, 3.90; Br, 44.50.

1-Allyl-1,3-dihydro-3,3-dimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b]pyran] (4a). To a solution of perchlorate 2 (1.00 g, 3.3 mmol) and 2-hydroxy-1-naphthaldehyde (0.59 g, 3.4 mmol) in ethanol (15 ml) three drops of piperidine were added. The reaction mixture was heated under reflux for 5 h, then cooled to room temperature and poured into 5% sodium acetate (150 ml). The mixture was extracted with ether (3 × 20 ml), the organic extract washed with water (20 ml), dried with Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was recrystallized from ethanol to yield 0.89 g (76%) of compound 4a with m.p. 125–126 °C. 1H NMR spectrum (300 MHz, DMSO-d_6): 1.17 (3H, s, CH_3); 1.26 (3H, s, CH_3); 3.60–3.95 (2H, m, NCH); 5.03–5.20 (2H, m, CH=C); 5.84 (1H, d, J = 4.8 Hz, 14-H); 6.84–8.20 ppm (m, 11H, 4'-H, ArH). Found: C, 84.88; H, 6.85%. Calculated for C_{25}H_{23}NO: C, 84.95; H, 6.71; N, 6.62.

1-Allyl-5-bromo-1,3-dihydro-3,3-dimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b]pyran] (4b). Method A. To a solution of bromide 3 (0.45 g, 1.26 mmol) and 2-hydroxy-1-naphthaldehyde (0.22 g, 1.30 mmol) in ethanol (15 ml) a catalytic amount of piperidine was added. The reaction mixture was heated under reflux for 5 h, then cooled to room temperature and poured into 5% sodium acetate (50 ml). The mixture was extracted with ether (3 × 20 ml), the organic extract washed with water (20 ml), dried over Na_2SO_4, solvent evaporated. The residue was recrystallized from ethanol to yield 0.33 g (62%) of compound 4b with m.p. 111–112 °C. 1H NMR spectrum (300 MHz, DMSO-d_6): 1.18 (3H, s, CH_3); 1.25 (3H, s, CH_3); 3.61–3.92 (2H, m, NCH); 5.03–5.19 (2H, m, CH=C); 5.70–5.83 (1H, m, CH = CH); 5.94 (1H, d, J = 10.8 Hz, 3'-H); 6.45–8.21 (11H, m, 4'-H, ArH); 7.82 ppm (1H, br.s, NH). Found: C, 79.10; H, 6.71; N, 6.79. Calculated for C_{25}H_{22}BrNO: C, 79.10; H, 6.71; N, 6.79.

Method B. To a mixture of 1-allylimidazo[1,2-a]indol-2-one 5 (0.90 g, 3.5 mmol) and 2-hydroxy-1-naphthaldehyde (0.65 g, 3.8 mmol) in ethanol (15 ml) a catalytic amount of piperidine was added. The reaction mixture was heated under reflux for 5 h, then cooled to room temperature, left at 5 °C for 24 h and the obtained crystalline material was filtered off. The filtrate was poured into 5% sodium acetate (100 ml), extracted with ether (3 × 20 ml), the organic layer was separated, washed with water (20 ml), dried with Na_2SO_4, and the solvent evaporated under reduced pressure. The residue was combined with the crystalline material obtained by filtration and recrystallized from ethanol to yield 0.85 g (59%) of spironaphthopyran 6 with m.p. 200–201 °C. 1H NMR spectrum (300 MHz, DMSO-d_6): 1.25 (3H, s, CH_3); 1.26 (3H, s, CH_3); 3.54–3.83 (2H, AB-syst., J = 16.8 Hz, NCH=CO); 3.68–3.74 (2H, m, NHCH_2); 4.99–5.09 (2H, m, CH = CH); 5.70–5.83 (1H, m, CH = CH); 5.94 (1H, d, J = 10.8 Hz, 3'-H); 6.45–8.21 (11H, m, 4'-H, ArH); 7.82 ppm (1H, br.s, NH). Found: C, 79.10; H, 6.71; N, 6.79. Calculated for C_{23}H_{22}BrNO: C, 79.00; H, 6.38; N, 6.82.

7aR^*,14S^*,15S^*)-14,15-Dihydro-7a,15-methano-8,8-dimethyl-8-H-naphth[1',2';6,7][1,3]oxazepino[3,2-a]indole-14-(N-allylcarboxamide) (7). To a solution of indoline 6 (2.05 g, 5 mmol) in ethanol (15 ml) fine-powdered potassium hydroxide (0.84 g, 15 mmol) was added and the mixture was refluxed for 2 hours. Then it was allowed to reach room temperature and left at 5 °C for 24 h. The precipitated crystalline material was filtered off, washed with water (5 ml) to remove remains of potassium hydroxide and recrystallized from ethanol to yield 1.02 g (50%) of compound 7 with m.p. 173–174 °C. 1H NMR spectrum (300 MHz, CDCl_3): 1.51 (3H, s, CH_3); 1.55 (3H, s, CH_3); 2.21 (1H, d, J = 11.4 Hz, ½ CH=bridge); 2.24 (1H, dd, J = 11.4 Hz, J = 3.6 Hz, ½ CH=bridge); 3.16–3.25 (1H, m, ½ NHCH_2); 3.47–3.56 (1H, m, ½ NHCH_2); 4.09 (1H, d, J = 4.8 Hz, 14-H); 4.34 (1H, dd, J = 16.8 Hz, J = 1.5 Hz, ½ CH = CH); 4.48–4.51
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(2H, m, ½ CH=CH₂, 15-H); 4.66–4.79 (1H, m, CH=CH₂); 6.56–8.04 (10H, m, ArH); 6.88 ppm (1H, br.s, NH). 13C NMR spectrum (CDCl₃): 23.17 (CH₃); 26.32 (CH₃); 32.79 (C-16); 37.14 (C-15); 40.82 (CH₂NH); 44.74 (C-8); 78.63 (C-14); 109.41 (C-7a); 110.53; 115.33; 117.35; 117.50; 122.0; 122.55; 122.92; 123.61; 126.68; 127.94; 128.29; 129.07; 129.30; 131.57; 133.44; 138.84; 149.22; 150.22; 170.34 ppm (C = O). Found: C, 78.74; H, 6.55; N, 6.59. Calculated for C₂₇H₂₆N₂O₂: C, 79.00; H, 6.38; N, 6.82%.

CONCLUSIONS

1. Practical and efficient methods for the synthesis of allyl group containing spironaphthopyrans were developed.
2. The main product of the rearrangement of 1-(N-allylcarbamoyl)methyl[indoline-spironaphthopyran] induced by a base is cis-7a,15-methanonaphth-[1',2':6,7][1,3]oxazepino[3,2-a]indole-14-(N-allylcarboxamide).

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References