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Synthesis of spironaphthopyrans containing an allyl group

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Alkylation of 2,3,3-trimethyl- and 5-bromo-2,3,3-trimethyl-3*H*-indole with allyl bromide afforded 1-allyl-3*H*-indolium salts. Their condensation with 2-hydroxy-1-naphthaldehyde gave 1-allylspiro[2*H*-indole-2,3'-[3*H*]naphth[2,1-*b*]pyrans]. When 2-hydroxy-1-naphthaldehyde was condensed with 1-allyl-9,9,9a-trimethylimidazo[1,2-a]indol-2-one, 1-(*N*-allylcarbamoyl)methylspiro[2*H*-indole-2,3'-[3*H*]naphth[2,1-*b*]pyran formed. Treatment of the latter with a strong base afforded a bridged oxazepino[3,2-*a*]indole derivative.

Key words: allyl group, 3*H*-indolium salt, imidazo[1,2-*a*]indole, spironaphthopyran

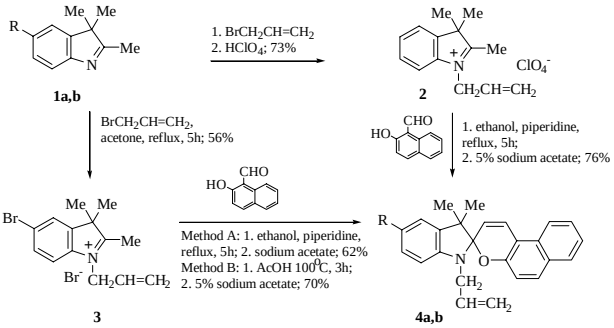
INTRODUCTION

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, methacroyloxy 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 exibit phtochromic 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 spiropyrans is based on condensation of 1-substituted 2,3,3-trimethyl-3*H*-indolium salts or the corresponding methylene bases with *ortho*-hydroxy aromatic aldehydes [12]. Our synthesis strategy was based on alkylation of the corresponding 3*H*-indoles with allyl bromide and the subsequent condensation of the obtained 1-allyl-3*H*-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-3*H*-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-3*H*-indole **1b** with allyl bromide gave crystalline bromide **3** directly (yield 56%). In the ^{1}H NMR spectrum of perchlorate **2** the allyl group protons gave complex multiplets in the area of 5.06–6.12 ppm.



1,4 a R = H, **b** R = Br

Condensation of 1-allyl-3*H*-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 1-allylspironaphthopyrans **4a,b**. Their ^{1}H 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.

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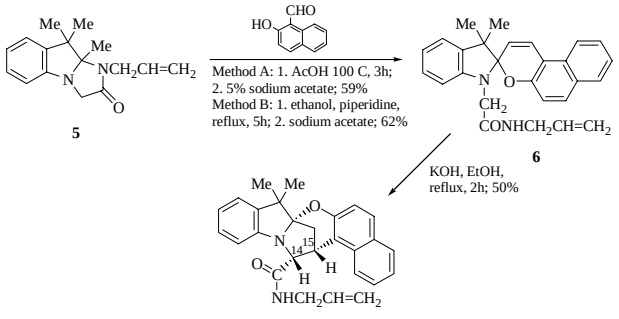
In order to synthesize spironaphthopyran containing (*N*-allylcarbamoyl)methyl moiety we investigated condensation of 2-hydroxy-1-naphthaldehyde with 1-allyl-9,9,9a-trimethylimidazo[1,2-*a*]indol-2-one **5** also. The starting compound **5** was obtained by the reaction of 9,9,9a-trimethylimidazo[1,2-*a*]indol-2-one with allyl chloride [13]. It is known that 1-substituted 9,9,9a-trimethylimidazo[1,2-*a*]indol-2-one derivatives promptly condensed with aromatic aldehydes in solution of acetic acid [14]. Heating of a solution of compound **5** and 2-hydroxy-1-naphthaldehyde in acetic acid and the following workup of the reaction mixture with sodium acetate afforded 1-(*N*-allylcarbamoyl)methylspiro[indoline-spironaphthopyran] **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 imidazolidine ring opening of starting imidazo[1,2-*a*]indole, intermolecular condensation of an active methyl group with formyl one, and finally in spiropyrane ring closure. Characteristic signals in the ^{1}H NMR spectrum of **6** were an *AB*-quadruplet of diastereotopic protons of NCH_2CO 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 spiropyrans containing at the indole ring nitrogen a (*N*-substitued carbamoyl)methyl group with a strong base generates short-living nitrogen ylides. The latter undergo easy cyclization to 5a,13-methano-1,3-benzoxazepino[3,2-*a*]indoles [13]. Our attempt to cyclize by a similar way 1-allylspiro[indoline-naphthopyran] **4a** was unsuccessful. However, heating of 1-(*N*-allylcarbamoyl)methyl[indoline-spironaphthopyran] **6** in ethanol containing potassium hydroxide afforded *cis*-7a,15-methanonaphth[1',2':6,7][1,3]oxazepino[3,2-*a*]indole-14-(*N*-allylcarboxamide) **7** with a yield 50%. The presence of the pyrrolidine ring annelated to the indole nucleus was confirmed by the ^{13}C NMR spectrum that contained characteristic signals at 32.79 (C-16), 37.14 (C-15), 78.63 (C-14) and 109.41 ppm (C-7a).



The assignment of *cis*-configuration for the compound **7** was based on comparisons with ^{1}H NMR spectra of the relevant structure compounds [13]. For example, the distinction between two diastereomers of 7a,15-methanonaphth[1',2':6,7][1,3]oxazepino[3,2-*a*]indole-14-(*N*-phenylcarboxamide) rested on the magnitute of the $^3J_{14,15}$ values: 4.5 Hz was characteristic of *cis* configuration and 0 Hz for *trans* configuration. In the case of compound **7** $^3J_{14,15}$ = = 4.8 Hz, allowing to assign relative *cis*-configuration at C_{14}–C_{15}.

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. ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz on a Varian Gemini 2000 instrument. Tetramethylsilane was used as an internal standart. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F254) were used.

1-Allyl-2,3,3-trimethyl-3*H*-indolium perchlorate (2). To a solution of of 2,3,3-trimethyl-3*H*-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. ^{1}H NMR (CF_3COOH): 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_2=C*H*); 7.12–7.28 ppm (4H, s, ArH). Found: C, 56.03; H, 5.64; N, 4.42%. Calculated for $C_{14}H_{18}ClNO_4$: C, 56.10; H, 6.05; N, 4.67%.

1-Allyl-5-bromo-2,3,3-trimethyl-3*H*-indolium bromide (3). To a solution of 5-bromo-2,3,3-trimethyl-3*H*-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. ^{1}H NMR (300 MHz, DMSO-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, C*H* = CH_2); 7.85–8.19 ppm (3H,

m, ArH). Found: N, 4.09; Br, 44.67. Calculated for $C_{14}H_{17}Br_2N$: N, 3.90; Br, 44.50%.

1-Allyl-1,3-dihydro-3,3-dimethylspiro[2*H*-indole-2,3'-[3*H*]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. ^{1}H 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_2); 5.03–5.20 (2H, m, CH=CH_2); 5.75–5.94 (1H, m, CH_2C*H*); 5.85 (1H, d, J = 10.2 Hz, 3'-H); 6.48–8.20 ppm (m, 11H, 4'-H, ArH). Found: C, 84.88; H, 6.85%. Calculated for $C_{25}H_{23}NO$: C, 84.95; H, 6.56%.

1-Allyl-5-bromo-1,3-dihydro-3,3-dimethylspiro[2*H*-indole-2,3'-[3*H*]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. ^{1}H NMR (300 MHz, DMSO-d_6): 1.18 (3H, s, CH_3); 1.25 (3H, s, CH_3); 3.61–3.92 (2H, m, NCH_2); 5.03–5.19 (2H, m, CH=CH_2); 5.75–5.87 (1H, m, C*H* = CH_2); 5.84 (1H, d, J = 10.5 Hz, 3'-H); 6.44–8.20 ppm (10H, m, 4'-H, ArH). Found: C, 69.32; H, 5.11; N, 3.31%. Calculated for $C_{25}H_{22}BrNO_4$: C, 69.45; H, 5.13; N, 3.24%.

Method B. A solution of 1-allyl-5-bromo-2,3,3-trimethyl-3H-indolium bromide **3** (0.45 g, 1.26 mmol) and 2-hydroxy-1-naphthaldehyde (0.22 g, 1.30 mmol) in acetic acid (3 ml) was heated at 100 °C for 3 h. Then the reaction mixture was cooled to room temperature, poured into 5% sodium acetate (100 ml) and extracted with ether (3 × 20 ml). The combined extract was washed with water (20 ml), dried with Na_2SO_4, the solvent evaporated under reduced pressure and the residue crystallized from ethanol to yield 0.38 g (70%) of compound **4b** with the same m.p. as the sample obtained by the Method A.

1-(N-Allylcarbamoyl)methyl-1,3-dihydro-3,3-dimethylspiro[2*H*-indole-2,3'-[3*H*]naphth[2,1-*b*]pyran] (6). Method A. A solution 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 acetic acid (5 ml) was heated at 100 °C for 3 h. Then the reaction mixture was cooled to room temperature, poured into 5% sodium acetate (100 ml) and the separated solid was filtered off. The filtrate was extracted with ether (3 × 20 ml), the extract was washed with water (20 ml), dried with Na_2SO_4, and the solvent was 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. ^{1}H NMR (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_2CO); 3.68–3.74 (2H, m, NHCH_2); 4.99–5.09 (2H, m, CH=CH_2); 5.70–5.83 (1H, m, C*H* =CH_2); 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 $C_{27}H_{26}N_2O_2$: C, 79.00; H, 6.38; N, 6.82%.

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 0.89 g (62%) of spironaphthopyran **6** with the m.p. identical to the sample obtained by Method A.

(7a*R,14*S**,15*S**)-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. ^{1}H NMR spectrum (300 MHz, $CDCl_3$): 1.51 (3H, s, CH_3); 1.55 (3H, s, CH_3); 2.21 (1H, d, ^{2}J = = 11.4 Hz, ½ CH_2-bridge); 2.24 (1H, dd, ^{2}J = = 11.4 Hz, ^{3}J = 3.6 Hz, ½ CH_2-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, ^{3}J = = 16.8 Hz, ^{2}J = 1.5 Hz, ½ CH=CH_2); 4.48–4.51

(2H, m, ½ CH=CH_2, 15-H); 4.66–4.79 (1H, m, CH=CH_2); 6.56–8.04 (10H, m, ArH); 6.88 ppm (1H, br.s, NH). ^{13}C NMR spectrum ($CDCl_3$): 23.17 (CH_3); 26.32 (CH_3); 32.79 (C-16); 37.14 (C-15); 40.82 (CH_2NH); 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 $C_{27}H_{26}N_2O_2$: 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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ALILO GRUPÆ TURINÈIØ SPIRONAFTPIRANØ SINTEZË

S a n t r a u k a

Alkilinant 2,3,3-trimetil- ir 5-brom-2,3,3-trimetil-3H-indolà alilbromidu susidarë atitinkamos 1-alil-3H-indolio druskos. Jas kondensuojant su 2-hidroksi-1-naftaldehidu buvo gauti 1-alilspiro[2*H*-indolo-2,3'-[3*H*]-naft[2,1-*b*]piranai]. Kondensuojant 2-hidroksi-1-naftaldehidà su 1-alil-9,9,9*a*-trimetilimidazo[1,2-a]indol-2-onu, susintetintas 1-(*N*-alilkarbamoil)metilspiro[2*H*-indolo-2,3'-[3*H*]naft[2,1-*b*]piranas]. Pastaràjá junginá paveikus stipria baze, jis persigrupavo á oksazepino[3,2-*a*]indolo dariná.