CHEMIJA. 2006. T. 17. Nr. 1. P. 16–20

Synthesis and cyclization of 1'-[(*N*-propylcarbamoyl) methyl]spiro[1-benzopyran-2,2'-indoles]

Neringa Kleizienė,

Vytas Martynaitis,

Sonata Krikštolaitytė and

Algirdas Šačkus*

Kaunas University of Technology,
Institute of Synthetic Chemistry,
Radvilėnų pl. 19,
LT-50270 Kaunas, Lithuania

Condensation of 1-propyl- and 1-(3-phenylpropyl)imidazo[1,2-*a*]indoles with *ortho*-hydroxy-substituted aromatic aldehydes afforded 1'-[*N*-propyl- and *N*-(3-phenylpropyl)carbamoyl]methylspiro[1-benzopyran-2,2'-indoles]. Treatment of the latter with potassium hydroxide gave bridged oxazepino[3,2-*a*]indole derivatives.

Key words: propyl group, indole, imidazo[1,2-*a*]indole, spirobenzopyran, oxazepino[3,2-*a*]indole

INTRODUCTION

The formation of heterocyclic rings on cyclization reactions of in situ generated azomethine ylides has emerged as a widely used synthetic method [1]. The attraction of this synthetic construction is the ease of generation of 1,3-dipoles and a high degree of molecular complexity provided in a single cyclization reaction step. Recent examples of this approach included the synthesis of a wide variety of fused [2], spiro [3] and bridged [4] heterocyclic ring systems.

We have recently developed a new method for the construction of the pyrrolo[2,1-*a*]isoquinoline ring system based on condensation of 2-carbamoylmetyl-1-methyl-3,4-isoquinolinium salts or their cyclic form 10b-methylimidazo[2,1-*a*]isoquinolines with aromatic and heteroaromatic aldehydes followed by intramolecular addition of the methylene carbon atom to the double bond of the ethenyl moiety [5]. The proposed mechanism of such transformation includes generation of an intermediate azomethine methylide. It was found also that condensation of 1-carbamoylmethyl-2,3,3-trimethyl-3*H*-indolium salts with benzaldehydes afforded 9a-styrylimidazo[1,2-*a*]indole derivatives, which did not undergo further transformation to pyrrolo[1,2-*a*]indole ring system [6]. However, similar condensation of 1-(*N*-substituted carbamoylmethyl)-2,3,3-trimethyl-3*H*-indolium salts with salicyl aldehydes produced 1-(*N*-substituted carbamoylmethyl)indoline spiropyrans which easily underwent rearrangement to the bridged oxazepino[3,2-*a*]indole derivatives under treatment with strong bases [7]. The latter found application in preparation of imprinted polymer stationary phases. It has been shown that the structure of a substituent at the nitrogen atom of the carbamoylmethyl group has a significant influence on enantiorecognition of chiral molecules [8].

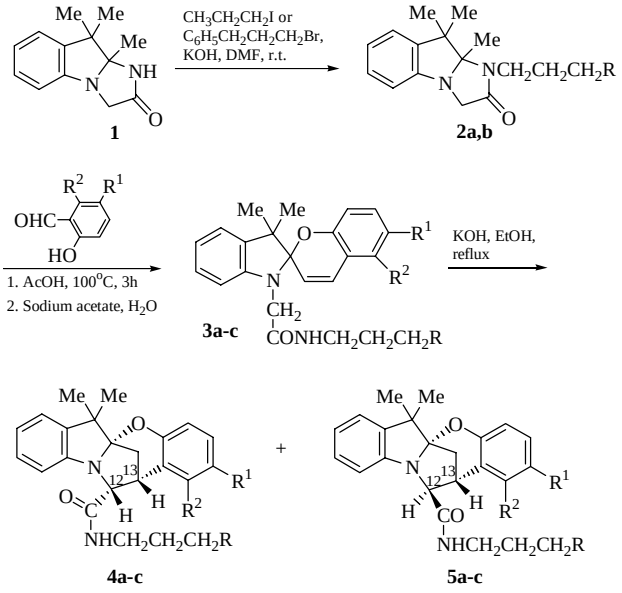
We now report further synthetically useful examples where indoline spiropyrans, bearing a substituted methylene group at the nitrogen atom, are transformed to bridged oxazepino[3,2-*a*]indole derivatives. In the present work, synthesis and base catalysed cyclization of 1'-[(*N*-propylcarbamoyl)methyl]-1',3'-dihydrospiro[1-benzopyran-2,2'-indole] have been explored.

RESULTS AND DISCUSSION

The starting 9,9,9a-trimethyl-1,2,3,9a-tetrahydro-9*H*-imidazo[1,2-*a*]indol-2-one **1** was prepared by the reaction of 2,3,3-trimethyl-3*H*-indole with α-chloroacetamide [9]. Alkylation of **1** with propyl iodide afforded 1-propylimidazo[1,2-*a*]indol-2-one **2a** [10], while the use 3-bromopropylbenzene gave new derivative **2b**.

Reaction of 1-substituted imidazo[1,2-*a*]indol-2-ones 2 a, b with 5-nitrosalicylaldehyde was carried out in acetic acid. Work-up of the reaction mixture with base gave 6-nitrospirobenzopyrans **3a, b**. The

* Corresponding author. E-mail: algirdas.sackus@ktu.lt



2a R = H, **b** R = C_6H_5; **3–5 a** R = R^2 = H, R^1 = NO_2; **b** R = C_6H_5, R^1 = NO_2, R^2 = H; **c** R = C_6H_5, R^1 + R^2 = CH=CH–CH=CH

^{1}H NMR spectra of **3a, b** contained a characteristic doublet of the methine proton in the area of 5.80-5.89 ppm with vicinal $^3J_{3,4}$ = 10.3–10.6 Hz, which evidences a *cis*-allocation of vinylic protons in the spiropyran system [11], while in the ^{13}C NMR spectra the signal of the spirocarbon C-2 was situated at 105.96 and 106.05 ppm, respectively.

When **3a, b** were treated with sodium hydroxide in boiling ethanol, formation of a mixture of *cis*- and *trans*-5a,13-methano-1,3-benzoxazepino[3,2-*a*]indoles **4a, b** and **5a, b** took place, from which the target products were isolated by fractional crystallization and methods of a column chromatography. Assignment of *cis*- and *trans*-configuration to **4a, b** and **5a, b** was based on comparisons with the ^{1}H NMR spectra of the relevant structure compounds [7] and results of MM3* calculations. For example, the experimental value of a vicinal coupling constant between protons 12-H and 13-H ($^3J_{12, 13}$) is 4.8 Hz for *cis*-**4b** and 0 Hz for *trans*-**5b**. Monte Carlo conformational searches using the MM3* force field of the optimized structures followed by energy minimizations gave for the dihedral angle H-$C_{(12)}$-$C_{(13)}$-H of the optimized structures of *cis*-4c and *trans*-5c 40.68° and 88.46°. In such case, $^3J_{12, 13}$ calculated by the *Karplus* equation [12] is 6.99 Hz for *cis*-**4b** and 1.98 Hz for *trans*-**5b**, and agrees satisfactorily with the experimental values.

Condensation of **2c** with 2-hydroxynaphthaldehyde afforded 1-(3-phenylcarbamoyl)methylindoline naphthopyran 3c, which was cyclized to bridged oxazepino[3,2-*a*]indoles **4c, 5c** by an analogous route as compounds **3a, b**. *Trans*-**5c** was isolated from the mixture by fractional crystallization.

EXPERIMENTAL

Melting points were determined on a *Kleinfeld* melting point apparatus. IR spectra were recorded on a Perkin Elmer Spectrum BXII spectrophotometer using KBr pellets. ^{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 the internal standard. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F254) were used. Separations by flash chromatography were performed on silica gel Merck, 9385, 230–400 mesh.

1,2,3,9a-Tetrahydro-9,9,9a-trimethyl-1-(3-phenylpropyl)-9*H*-imidazo[1,2-*a*]indol-2-one (2b). 1,2,3,9a-Tetrahydro-9,9,9a-trimethyl-9*H*-imidazo[1,2-*a*]indol-2-one **1** (1.52 g, 7.0 mmol) was dissolved in DMF (8 ml), and finely powdered potassium hydroxide (0.98 g, 17.5 mmol) was added to the solution. 3-Phenylpropyl bromide (2.78 g, 14.0 mmol) was added dropwise, and the solution was stirred for 2 h at room temperature. Then the mixture poured into water (100 ml) and extracted with ether (3 x 50 ml). The organic layer was separated, washed with water (20 ml) and dried with $CaCl_2$. Most the solvent was distilled off in *vacuo* and the residue kept at 4 °C overnight. The precipitated crystals were filtered off and recrystallized from ethanol. Yield of **2b** 1.06 g (45%), m.p. 84-85 °C. IR spectrum: 1710 cm^{-1} (C=O). ^{1}H NMR spectrum ($CDCl_3$): 0.98 (3H, s, 9-CH_3), 1.31 (3H, s, 9-CH_3), 1.39 (3H, s, 9a-CH_3), 1.81–1.99 (1H, m, ½ NCH_2**CH_2**), 2.15–2.32 (1H, m, ½ NCH_2**CH_2**), 2.56–2.80 (2H, m, **CH_2**C_6H_5), 2.88–3.00 (1H, m, ½ N**CH_2**CH_2), 3.51–3.63 (1H, m, ½ N**CH_2**CH_2), 3.86 (2H, AB-q, J = 15.4 Hz, CH_2CO), 6.72–7.33 ppm (9H, m, Ar-H). ^{13}C NMR spectrum ($CDCl_3$): 22.74 (9-CH_3), 23.68 (9-CH_3), 28.78 (9a-CH_3), 29.91, 33.38 (**CH_2**C_6H_5, NCH_2**CH_2**), 42.04 (1-CH_2), 49.52 (C-9), 54.78 (C-3), 91.93 (C-9a), 114.02 (CH), 122.00 (CH), 122.16 (CH), 125.97 (CH), 3 × 128.24 (3 × CH), 2 × 128.35 (2 × CH), 2 × 140.91 (2 × C), 148.40 (C), 171.15 ppm (C=O). Found: C, 79.20; H, 7.91; N, 8.22. $C_{22}H_{26}N_2O$ requires: C, 79.00; H, 7.84; N, 8.38%.

1',3'-Dihydro-3',3'-dimethyl-6-nitro-1'-[(*N*-propylcarbamoyl)methyl]spiro[1-benzopyran-2,2'-indole] (3a). A mixture of **2a** (1.29 g, 5.0 mmol) and 5-nitrosalicylaldehyde (0.92 g, 5.5 mmol) in acetic acid (10 ml) was heated at 100 °C for 3 h; then the mixture was poured into 5% sodium acetate (100 ml) and extracted with ether (2 × 15 ml). The combined organic extract was washed with water (20 ml) and dried with $MgSO_4$, the solvent was evaporated and the residue crystallized from ethanol to yield 1.02 g (50%) of **3a** with m.p. 127-128 °C. IR spectrum: 3390 (N-H), 1660 (C=O), 1515 (amid II), 1480, 1340 cm^{-1} (NO_2). ^{1}H NMR spectrum ($CDCl_3$): 0.87 (3H, t, J = 7.2 Hz, CH_2**CH_3**), 1.29 (3H, s, 3'-CH_3),

1.36 (3H, s, 3'-CH_3), 1.48 (2H, sext., J = 7.2 Hz, $NCH_2\mathbf{CH_2}$), 3.25 (2H, q., J = 7.2 Hz, $N\mathbf{CH_2}CH_2$), 3.82 (2H, AB-q, J = 17.7 Hz, CH_2CO), 5.89 (1H, d, J = 10.3 Hz, **CH**=CH), 6.54-8.08 ppm (9H, m, ArH, CH=**CH**, NH). ^{13}C NMR spectrum ($CDCl_3$): 11.11 ($CH_2\mathbf{CH_3}$), 19.91 (3'-CH_3), 22.66 ($\mathbf{CH_2}CH_3$), 25.94 (3'-CH_3), 40.80 ($N\mathbf{CH_2}CH_2$), 48.06 (C-3'), 52.49 (1'-CH_2), 105.96 (C-2'), 107.63, 115.34, 118.11, 120.31, 121.14, 121.93, 122.78, 125.98, 127.95, 129.13, 135.77, 141.26, 145.71, 158.48 (14 $C_{(Ar,\ CH=CH)}$), 168.87 ppm (C=O). Found: C, 68.10; H, 6.42; N, 10.50. $C_{23}H_{25}N_3O_4$ requires: C, 67.80; H, 6.18; N, 10.31%.

1',3'-Dihydro-3',3'-dimethyl-6-nitro-1'-[*N*-(3-phenylpropyl)carbamoyl]methylspiro[1-benzopyran-2,2'-indole] (3b) was synthesized from **2b** (1.67 g, 5.0 mmol) and 5-nitrosalicylaldehyde (0.92 g, 5.5 mmol) by a similar method as compound **3a**. Yield 1.01 g (42%), m.p. 140–141 °C (from ethanol). IR spectrum: 3240 (N-H), 1660 (C=O), 1515 (amid II), 1490, 1350 cm^{-1} (NO_2). ^{1}H NMR spectrum ($CDCl_3$): 1.24 (3H, s, 3'-CH_3), 1.34 (3H, s, 3'-CH_3), 1.79 (2H, p., J = 7.2 Hz, $NHCH_2\mathbf{CH_2}$), 2.55 (2H, t., J = 7.2 Hz, $\mathbf{CH_2}C_6H_5$), 3.27 (2H, q., J = 6.8 Hz, $NH\mathbf{CH_2}$), 3.80 (2H, AB-q, J = 18 Hz, CH_2CO), 5.80 (1H, d, J = 10.6 Hz, **CH** = CH), 6.48–8.08 ppm (14 H, m, Ar-H, CH = **CH**, NH). ^{13}C NMR spectrum ($CDCl_3$): 20.05 (CH_3), 26.13 (CH_3), 31.12 ($NHCH_2\mathbf{CH_2}$), 32.97 ($\mathbf{CH_2}C_6H_5$), 38.71 ($NHCH_2$), 48.16 (C-3'), 52.68 (1'-CH_2), 106.05 (C-2'), 107.75, 115.47, 118.17, 120.35, 121.36, 122.11, 122.93, 126.07, 126.17, 128.14, 128.26, 4 × 128.46, 129.33, 135.88, 141.02, 141.30, 145.71 (20 $C_{(Ar,\ C=C)}$), 168.99 ppm (C=O). Found: C, 72.16; H, 6.13; N, 8.53. $C_{29}H_{29}N_3O_4$ requires: C, 72.03; H, 6.04; N, 8.69%.

1,3-Dihydro-3,3-dimethyl-1-[*N*-(3-phenylpropyl)carbamoyl]methylspiro[indol-2,3'-naphtho[2,1-*b*]pyran] (3c) was synthesized from 2b (1.67 g, 5.0 mmol) and 2-hydroxy-1-naphthaldehyde (0.95 g, 5.5 mmol) by a similar method as for compound 3a. Yield 1.34 g (55%), m.p. 197–198 °C (from ethanol). IR spectrum: 3360 (N-H), 1660 (C=O), 1525 cm^{-1} (amid II). ^{1}H NMR spectrum ($CDCl_3$): 1.25 (3H, s, 3-CH_3), 1.32 (3H, s, 3-CH_3), 1.75 (2H, p., J = 7.4 Hz, NCH_2CH_2), 2.53 (2H, t., J = 7.4 Hz, $CH_2C_6H_5$), 3.25 (2H, q., J = 6.6 Hz, $NHCH_2$), 3.73–3.99 (2H, AB-q, J = 17.5 Hz, 1-CH_2), 5.73 (1H, d, J = 10.4 Hz, CH=CH), 6.50–8.05 ppm (17 H, ArH, CH=CH, NH). ^{13}C NMR spectrum ($CDCl_3$): 19.82 (CH_3), 25.49 (CH_3), 30.63 (NCH_2CH_2), 32.44 ($CH_2C_6H_5$), 38.11 ($NHCH_2$), 47.69 (C-3), 51.49 (1-CH_2), 103.79 (C-2), 106.88, 109.72, 116.00, 116.51, 120.20, 121.83, 123.16, 2 × 125.56, 125.60, 126.49, 127.34, 4 × 128.00, 128.02, 128.60, 129.14, 130.13, 135.88, 140.67, 145.43, 151.04 (24 $C_{(Ar,\ C=C)}$), 169.14 ppm (C=O). Found: C, 81.21; H, 6.92; N, 5.64. $C_{33}H_{32}N_2O_2$ requires: C, 81.12; H, 6.60; N, 5.73%.

(5*aR,12*S**,13*S**)-12,13-Dihydro-5a,13-methano-6,6-dimethyl-2-nitro-6*H*-1,3-benzoxazepino[3,2-*a*]indole-12-(*N*-propylcarboxamide) (*cis*-4a) and (5*aR**,12*R**,13*S**)-Isomer (*trans*-5a)**. To a solution of compound **3a** (1.01 g, 2.5 mmol) in ethanol (8 ml) fine powdered potassium hydroxide (0.42 g, 7.5 mmol) was added, the mixture was refluxed for 3 h and then the bulk of the solvent was distilled off. The concentrated solution was poured into water (20 ml), the precipitated crystalline material was collected by filtration and washed with water (5 ml). The obtained product mixture was two times recrystallized from ethanol to afford *cis*-**4a**. The combined ethanol filtrate was concentrated *in vacuo* and the residue purified by column chromatography (silica gel, eluent: acetone/hexane = 1/3) to give *trans*-**5a**. The yield of compound *cis*-**4a** is 0.42 g (42%), m.p. 215–216 °C. IR spectrum: 3380 (NH), 1673 (C=O), 1515 (amid II), 1478, 1345 cm^{-1} (NO_2). NMR spectrum ($CDCl_3$): 0.57 (3H, t, J = 7.2 Hz, $CH_2\mathbf{CH_3}$), 1.06 (2H, sext, J = 7.2 Hz, $\mathbf{CH_2}CH_3$), 1.50 (3H, s, 6-CH_3), 1.52 (3H, s, 6-CH_3), 2.14–2.24 (2H, m, 14-H_2), 2.74-2.85 (1H, m, ½ $NH\mathbf{CH_2}$), 3.06–3.18 (1H, m, ½ $NH\mathbf{CH_2}$), 3.81–3.84 (1H, m, 13-H), 3.96 (1H, d, J = 4.9 Hz, 12-H), 6.51–8.10 ppm (8H, m, Ar-H, NH). ^{13}C NMR spectrum ($CDCl_3$): 11.03 ($\mathbf{CH_3}CH_2$), 23.21, 22.63 (6-CH_3, $CH_3\mathbf{CH_2}$), 26.43 (6-CH_3), 32.82 (C-14), 40.49 ($NHCH_2$), 42.13 (C-13), 45.13 (C-6), 77.64 (C-12), 110.39 (CH), 110.91 (C-5a), 116.17 (CH), 122.43 (CH), 122.57 (CH), 124.58 (CH), 124.99 (CH), 125.72 (C), 128.46 (CH), 138.31 (C), 141.30 (C), 148.45 (C), 158.14 (C), 169.10 ppm (C=O). Found: C, 67.71; H, 6.27; N, 9.98. $C_{23}H_{25}N_3O_4$ requires: C, 67.80; H, 6.18; N, 10.31%. The yield *trans*-**5a** 0.18 g (18%), m.p. 164-165 °C (from acetone). IR spectrum: 3350 (NH), 1673 (C=O), 1520 (amid II), 1480, 1340 cm^{-1} (NO_2). ^{1}H NMR spectrum (DMSO-d_6): 0.89 (3H, t, J = 7.2 Hz, $CH_2\mathbf{CH_3}$), 1.26 (3H, s, 6- CH_3), 1.27 (3H, s, 6-CH_3), 1.42–1.52 (2H, m, $\mathbf{CH_2}CH_3$), 1.85-2.01 (2H, m, 14-H_2), 3.05–3.14 (2H, m, $NH\mathbf{CH_2}$), 3.86–4.03 (2H, m, 13-H, 12-H), 5.90–7.71 (7H, m, Ar-H), 8.17 ppm (1H, br s, NH). ^{13}C NMR spectrum (DMSO-d_6): 12.24 ($CH_2\mathbf{CH_3}$), 23.37, 24.40, 27.43, 41.27, 45.68, 45.68, 67.70 (CH_3, CH_3, C-14, CH_2CH_2, C-13, C-6), 71.83 (C-12), 107.37 (CH), 110.63 (C-5a), 120.14, 120.70, 123.41, 126.18, 127.09, 128.46, 128.47, 128.56, 130.30, 140.00, 151.25 (11 $C_{(Ar)}$), 174.30 ppm (C=O). Found: C, 67.68; H, 6.22; N, 10.27. $C_{23}H_{25}N_3O_4$ requires: C, 67.80; H, 6.18; N, 10.31%.

(5*aR,12*S**,13*S**)-12,13-Dihydro-5a,13-methano-6,6-dimethyl-2-nitro-6*H*-1,3-benzoxazepino[3,2-*a*]indole-12-[*N*-(3-phenylpropyl)carboxamide] (*cis*-4b) and (5*aR**, 12*R**, 13*S**)-Isomer (*trans*-5b)**. Compounds **4b** and **5b** were synthesized from **3b** (0.91 g, 1.9 mmol) by a similar method as compounds **4a**, **5a**. The yield of *cis*-**4b** 0.25 g (28%), m.p.: 180–182 °C (from ethanol). IR spectrum: 3380 (NH), 1650 (C=O), 1510 (amid II), 1475, 1325 cm^{-1} (NO_2). ^{1}H NMR spectrum ($CDCl_3$): 1.480–1.54 (2H, m, $\mathbf{CH_2}CH_2NH$), 1.66 (3H, s, CH_3), 1.69 (3H, s, CH_3), 2.34–2.47 (4H, m,

14-H_2, C_6H_5**CH_2**), 2.98–3.09 (1H, m, ½ NH**CH_2**), 3.30–3.42 (1H, m, ½ NH**CH_2**), 3.99–4.01 (1H, m, 13-H), 4.14 (1H, d, **J** = 4.8 Hz, 12-H), 6.66–8.17 ppm (13H, m, ArH, NH). ^{13}C NMR spectrum ($CDCl_3$): 23.80 (CH_3), 27.09 (CH_3), 31.49 (**CH_2**CH_2NH), 33.29 (C_6H_5**CH_2**) , 33.49 (C-14), 38.90 (NHCH_2), 42.76 (C-13), 45.80 (C-6), 78.26 (C-12), 111.10 (CH), 111.65 (C-5a), 116.89 (CH), 123.20 (CH), 123.32 (CH), 125.33 (CH), 125.80 (CH), 126.44 (C), 126.65 (CH), 128.76 (2 × CH), 129.11 (2 × CH), 129.21 (CH), 139.02 (C), 141.62 (C), 142.03 (C), 149.18 (C), 158.88 (C), 169.98 ppm (C=O). Found: C, 71.94; H, 6.17; N, 8.41. $C_{29}H_{29}N_3O_4$ requires: C, 72.03; H, 6.04; N, 8.69%. The yield of compound *trans*-**5b** is 0.32 g (36%), m.p. 153–155 °C (from acetone). IR spectrum: 3425 (NH), 1650 (C=O), 1510 (amid II), 1475, 1325 cm^{-1} (NO_2). ^{1}H NMR spectrum (DMSO-d_6): 1.23 (3H, s, CH_3), 1.24 (3H, s, CH_3), 1.68–1.98 (4H, m, **CH_2**CH_2NH, 14-H_2), 2.56–2.61 (2H, m, C_6H_5**CH_2**), 3.06–3.15 (2H, m, NH**CH_2**), 3.90–4.01 (1H, m, 13-H), 3.97 (1H, s, 12-H), 5.89–8.20 ppm (13H, m, ArH, NH). ^{13}C NMR spectrum (DMSO-d_6): 27.93 (CH_3), 28.15 (CH_3), 31.03, 32.50, 38.04, 39.28, 44.61, 52.21, 66.52 (**CH_2**CH_2NH, C_6H_5**CH_2,** C-14, NHCH_2, C-13, C-6, C-12), 106.33, 116.95, 118.35, 121.37, 123.77, 125.43, 125.88, 126.85, 128.02, 128.12, 128.12, 128.19, 128.19, 128.66, 132.72, 140.03, 141.65, 144.57, 161.48 (19 $C_{(Ar)}$), 170.89 ppm (C=O). Found: C, 71.90; H, 6.23; N, 8.42. $C_{29}H_{29}N_3O_4$ requires: C, 72.03; H, 6.04; N, 8.69%.

(7*aR*,*14*R*,*15*S)-14,15-Dihydro-8,8-dimethyl-8*H*-7*a*,15-methanonaphth[1',2':6,7][1,3]oxazepino[3,2-*a*]indole-14-[*N*-(3-phenylpropyl)carboxamide] (*trans*-5c)**. The compound **3c** (0.98 g, 2 mmol) was dissolved in ethanol (8 ml), and finely powdered potassium hydroxide (0.34 g, 6.0 mmol) was added to the solution. The mixture was refluxed for 4 h and was poured into water (30 ml) and extracted with ether (2 × 15 ml). The organic layer was washed with water (5 ml) and dried over $CaCl_2$. The sovent was evaporated under reduced pressure and the residue crystallized from ethanol to afford *trans*-**5c**. Yield of 0.37 g (38%), m.p. 129–131 °C. IR spectrum: 3320 (NH,)1650 (C=O), 1520 cm^{-1} (amid II). ^{1}H NMR spectrum ($CDCl_3$): 1.32 (3H, s, CH_3), 1.62 (3H, s, CH_3), 1.70–1.77 (2H, m, **CH_2**CH_2NH), 2.16 (1H, d, J = 11.0 Hz, 16-H), 2.47–2.54 (3H, m, C_6H_5**CH_2,** 16-H), 3.23–3.32 (2H, m, NH**CH_2**), 4.43 (1H, s, 14-H), 4.43–4.46 (1H, m, , 15-H), 5.85 (1H, br t, NH), 6.28 (1H, d, J = 7.5 Hz, 12-H), 6.77–8.09 ppm (14H, m, ArH). ^{13}C NMR spectrum ($CDCl_3$): 20.03 (CH_3), 27.75 (CH_3), 27.78, 30.69, 32.48 (C-16, **CH_2**CH_2NH, C_6H_5**CH_2**,), 38.39 (NHCH_2), 41.18 (C-15), 44.03 (C-8), 67.02 (C-14), 106.41, 106.45 (C-7a, C-12), 118.18, 118.95, 120.76, 122.40, 122.76, 125.55, 126.31, 127.40, 127.78, 2 × 127.95, 128.04, 3 × 128.14, 128.25, 130.04, 140.47, 140.47, 141.35, 150.20 (21 $C_{(Ar)}$), 169.51 ppm (C=O). Found: C, 81.34; H, 6.98; N, 5.76. $C_{33}H_{32}N_2O_2$ requires: C, 81.12; H, 6.60; N, 5.73%.

CONCLUSIONS

1. Indoline spiropyrans possessing *N*-propyl- and *N*-(3-phenylpropyl)carbamoylmethyl moieties at the indole ring nitrogen atom can be easily prepared by condensation of 1-propyl- and 1-(3-propylphenyl)imidazo[1,2-*a*]indol-2-one derivatives with *ortho*-hydroxy-substituted aromatic aldehydes.

2. 1'-[*N*-Propyl- and *N*-(3-phenylpropyl)carbamoylmethyl]spiro[1-benzopyran-2,2'-indoles] rearrange to bridged oxazepino[3,2-*a*]indole derivatives on treatment with postassium hydroxide in ethanol solution.

Received 02 December 2005
Accepted 02 January 2006

References

1. O. Tsuge and S. Kanemasa, *Advances in Heterocyclic Chemistry*; Katritzky A. R. Ed.; Academic Press: New York, 1989; Vol. 45, pp. 232–349; J. S. Clark, *Nitrogen, Oxygen and Sulfur Ylide Chemistry*; Oxford University Press: Oxford, 2002, pp. 57–76.
2. M. Nyerges, Į. Pintér, A. Virćnyi, I. Bitter and L. Tõke, *Tetrahedron Lett*., **46**, 377 (2005); M. Nyerges, A. Viriņyi, W. Zhang, P. W. Groundwater, G. Blaskó and L. Tõke, *Tetrahedron,* **60**, 9937 (2004); H. Okada, T. Akaki, Y. Oderaotoshi, S. Minakata and M. Komatsu, *Tetrahedron*, **59**, 197 (2003); R. Grigg, A. Hodgson, J. Morris and V. Sridharan, *Tetrahedron Lett*., **44**, 1023 (2003); Į. Pintér, M. Nyerges, A. Viriņyi and L. Tõke, *Tetrahedron Lett*., **44**, 2343 (2003); M. Noguchi, M. Shirai, K. Nakashima, I. Arai, A. Nishida, H. Yamamoto and A. Kakehi, *Tetrahedron*, **59**, 4581 (2003); M. Nyerges, A. Virćnyi, Į. Pintér and L. Tõke, *Tetrahedron Lett*., **44**, 793 (2003).
3. A. A. Raj, R. Raghunathan, M. R. SrideviKumari and N. Raman, *Bioorg. Med. Chem*., **11**, 407 (2003); A. A. Raj and R. Raghunathan, *Tetrahedron*, **59**, 2907 (2003); G. Subramaniyan, R. Raghunathan and M. Nethaji, *Tetrahedron*, **58**, 9075 (2002); P. R. Sebahar, H. Osada, T. Usui and R. M. Williams, *Tetrahedron*, **58**, 6311 (2002); R. Grigg, E. L. Millington and M. Thornton-Pett, *Tetrahedron Lett*., **43**, 2605 (2002).
4. G. Pandey, J. K. Laha and G. Lakshmaiah, *Tetrahedron*, **58**, 3525 (2002); P. Blaney, R. Grigg, Z. Rankovic, M. Thornton-Pett and J. Xu, *Tetrahedron*, **58**, 1719 (2002).
5. R. Degutytė, A. Šačkus and U. Berg. *J. Chem. Res.* (*S*), 540 (2001). N. Kleizienė, R. Degutytė, U. Berg and A. Šačkus. *J. Chem. Res.* (*S*), 370 (2004).
6. Šačkus A., Amankavičienė V. *Chem. Heterocycl. Compd*., 931 (2002).
7. V. Martynaitis, A. Šačkus and U. Berg, *J. Heterocycl. Chem*., **39**, 1123 (2002); N. Kleizienė, V. Amankavičienė, U. Berg, C. Schicktanz, K. Schlothauer and A. Šačkus, *Monatsch. Chem*. (in press).

8. E. Machtejevas, B. Sellergren, V. Martynaitis, P. K. Owens and A. Maruška, *J. Sep. Sci*., **27**, 547 (2004).
9. Yu. A. Degutis, A. A. Shachkus and A. G. Urbonavichyus, *Chem. Heterocycl. Compd.* (*Engl. Transl.)*, 774 (1986).
10. A. A. Shachkus and Yu. A. Degutis, *Chem. Heterocycl. Compd.* (*Engl. Transl.*), 41 (1988).
11. A. A. Bothner-By, *Adv. Magn. Res*., **1**, 195 (1965).

Neringa Kleizienė, Vytas Martynaitis,
Sonata Krikštolaitytė, Algirdas Šačkus

1-[(*N*-PROPILKARBAMOIL)METIL]SPIRO [1-BENZPIRAN-2,2'-INDOLŲ] SINTEZĖ IR CIKLIZACIJA

Kondensuojant 1-propil- ir 1-(3-fenilpropil)imidazo[1,2-a]indolus su *orto*-hidroksigrupe pakeistais aromatiniais aldehidais, susidarė 1'-[*N*-propil- ir *N*-(3-fenilpropil)karbamoilmetil]spiro[1-benzopiran-2,2'-indolai]. Pastarieji junginiai, kaitinami su stipria baze etanolyje, ciklizavosi į tiltelinius oksazepino[3,2-*a*]indolo darinius.