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BISINDOLES. 38.* SYNTHESIS OF SOME DERIVATIVES OF 1H,6H-INDOLO[7,6-*g*]INDOLE

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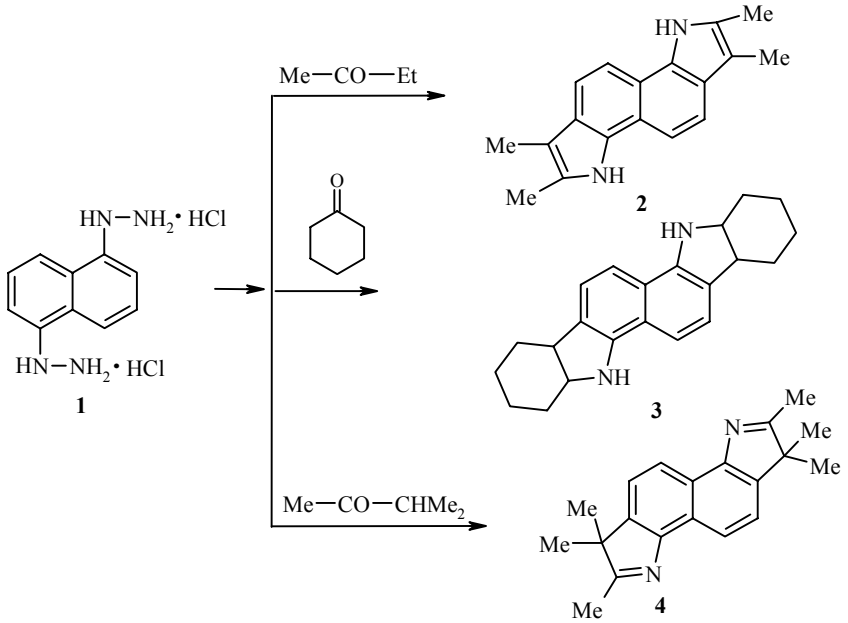
1H,6H,2,3,7,8-Tetramethylindolo[7,6-g]indole and 1H,8H,2,3,4,5,9,10,11,12-octahydrocarbazolo-[3,2-c]carbazole were synthesized by the condensation of 1,5-naphthylenedihydrazine with alkyl ketones followed by cyclization of the obtained hydrazones without isolation. The respective N,N-dibenzyl derivatives were obtained by benzylation of the alkyl-substituted compounds. A new spirocyclic system was synthesized by nucleophilic addition of 2,3,3,7,8,8-hexamethylindolenino[7,6-g]-indolenine to 2',3'-dimethoxycarbonylspirofluorenecyclopropene.

Keywords: indoloindole, carbazolocarbazole, spirocyclopropene, photochrome, benzylation, indolization.

The present paper describes the synthesis of alkyl-substituted indolo[7,6-*g*]indoles, their benzyl derivatives, and a new bisspirocyclic system based on the obtained indolenino[7,6-*g*]indolenine.

The alkyl-substituted indolo[7,6-*g*]indoles were synthesized in a single stage by the condensation of 1,5-naphthylenedihydrazine (**1**) with alkyl ketones followed by cyclization of the obtained dihydrazones by boiling in acetic acid according to the following scheme:



* For Communications 34-37, see [1-4].

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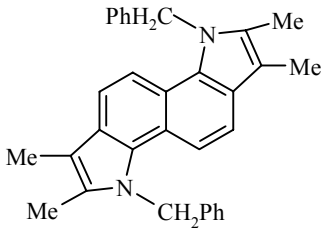
As a result of these reactions we isolated the following products: 1H,6H,2,3,7,8-tetramethylindolo-[7,6-*g*]indole (**2**); 1H,8H,2,3,4,5,9,10,11,12-octahydrocarbazolo[3,2-*c*]carbazole (**3**); 2,3,3,7,8,8-hexamethyl-indolenino[7,6-*g*]indolenine (**4**), described in [5].

Earlier [6, 7] we studied the benzylation of unsubstituted indoloindoles. In the search for physiologically active substances in the present work we undertook the benzylation of the obtained substituted indolo[7,6-*g*]indoles **2** and **3** by benzyl chloride under the conditions of phase-transfer catalysis. The corresponding N,N-dibenzyl derivatives **5** and **6** were isolated by column chromatography.



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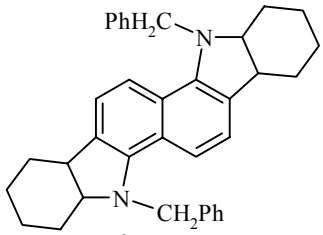

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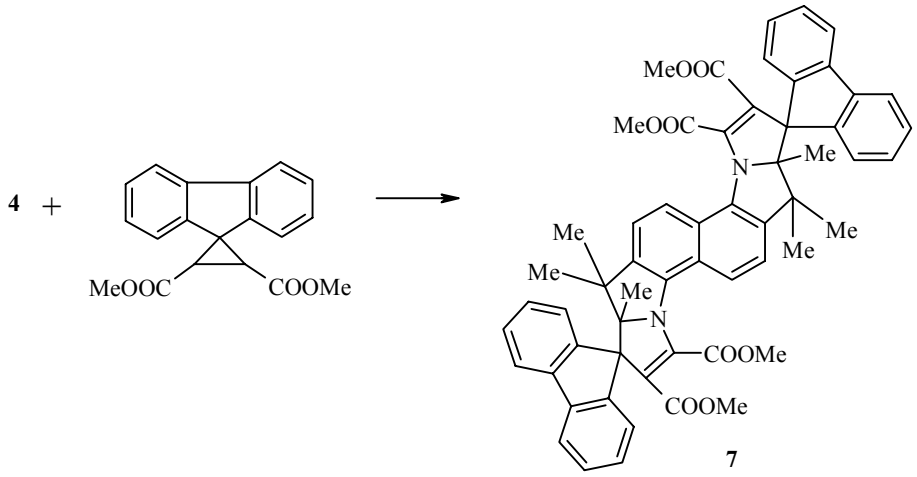
In order to obtain photochromic compounds based on bisindoles a new spirocyclic system was synthesized by the condensation of bisindolenine **4** with 2',3'-dimethoxycarbonylspirofluorenecyclopropene.



7

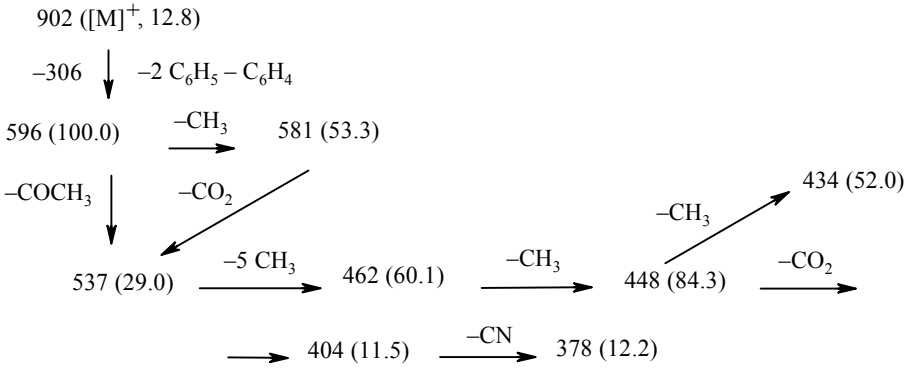
The photochemical characteristics of the isolated bis[2',3'-dimethoxycarbonyl-5',6',6'-trimethylspirofluorene-9,4'-(1'-aza-2'-cyclopentene)[1',5'-*a*]indolino[7,6-*g*]indoline] (**7**) were studied on the basis of the data from the electronic spectra. The formation of the corresponding betaine was not observed. However, it can be supposed that compound **7** is a quickly transformed photochromic system and that it is not possible to detect the equilibrium 1,5-electrocyclic photochromic transformation.

In the IR spectra of compounds **2** and **3** an absorption band for the indole NH groups is observed in the region of 3420 and 3400 cm^{-1}. These bands disappear in the IR spectra of their benzylation products **5** and **6**. The IR spectrum of the spiro compound **7** does not contain the absorption band of the C=N bond of the initial bisindolenine **6** (1570 cm^{-1}), and absorption bands for the C=C bond of the pyrrolizidine ring at 1690 and the C=O group at 1620 cm^{-1} appear.

The ^{1}H NMR spectra of compounds **2**, **3**, **6**, and **7** correspond to symmetrical structures. They contain one set of signals for both indole rings. The most downfield signal in the spectra of compounds **2** and **3** was assigned to the protons of the NH group (11.22 and 11.24 ppm). In the upfield region there are singlets for the

CH_3 groups (compound **2**) and triplets for the CH_2 groups of the cyclohexane ring (compounds **3** and **6**). In the spectrum of compound **6** there is no signal for NH protons, and the singlet signal of the protons of the N–CH_2 groups appears at 4.53 ppm. The spectra also contain signals for the protons of the naphthalene ring in the form of doublets. In the spectrum of compound **7** there are singlets for the protons of the $COOCH_3$ and CH_3 groups in the upfield region, and the doublet and triplet signals of the naphthalene and fluorene rings appear in the region of the aromatic protons. The full assignment of the proton signals is given in the experimental section.

In the mass spectrum of compound **7** there is a molecular ion peak of low intensity, and the fragmentation of the molecular ion does not contradict the proposed structure. The fragmentation scheme is as follows:



EXPERIMENTAL

The course of the reaction and the purity of the compounds were monitored on Silufol UV-254. Preparative chromatography was conducted on silica gel with particle size of 100-250 μm. The IR spectra were recorded on a UR-20 instrument in vaseline oil. The UV spectra were obtained on a Specord instrument in ethanol. The ^{1}H NMR spectra were obtained on a Bruker AM-400 spectrometer (400 MHz) in DMSO with TMS as internal standard. The mass spectra were recorded on a Varian MAT-31 instrument.

1H,6H,2,3,7,8-Tetramethylindolo[7,6-*g*]indole (2). To solution of 1,5-naphthylenedihydrazine (1 g, 4 mmol) in acetic acid we added methyl ethyl ketone (0.2 ml, 8 mmol). The mixture was boiled for 1 h, and the product was filtered off, dried, and purified on a column with benzene as eluent. Yield 0.2 g (35%); mp 233-234°C, R_f 0.2 (benzene). UV spectrum, λ_{max} (log ε), nm: 207 (4.10), 280 (4.59). IR spectrum, ν, cm^{-1}: 3420 (NH). ^{1}H NMR spectrum, δ, ppm, J (Hz): 2.22 (3H, s, 3-CH_3); 2.39 (3H, s, 2-CH_3); 7.50 (1H, d, J_{45} = 8.0, 4-H); 7.80 (1H, d, J_{54} = 8.0, 5-H); 11.22 (1H, s, NH). Found, %: C 82.72; H 6.55; N 1.32. $C_{18}H_{18}N_2$. Calculated, %:C 82.44; H 6.87; N 10.68.

1H,8H,2,3,4,5,9,10,11,12-Octahydrocarbazolo[3,2-*c*]carbazole (3). The compound was obtained similarly to compound **2** from 1,5-naphthylenedihydrazine (1 g, 4 mmol) and cyclohexanone (0.8 ml, 8 mmol). It was purified on a column with heptane–ether as eluent. Yield was 0.4 g (48%); mp 278-179°C, R_f 0.9 (benzene). UV spectrum, λ_{max} (log ε), nm: 206 (4.37), 277 (4.88). IR spectrum, ν, cm^{-1}: 3400 (NH). ^{1}H NMR spectrum, δ, ppm, J (Hz): 1.86 (4H, q, 3-CH_2, 4-CH_2); 2.70 (2H, t, 5-CH_2); 2.80(2H, t, 2-CH_2); 7.47 (1H, d, J_{67} = 8.0, 6-H); 7.80 (1H, d, J_{76} = 8.0, 7-H); 11.24 (1H, s, NH). Found, %: C 84.37; H 7.03; N 8.23. $C_{22}H_{22}N_2$. Calculated, %: C 84.07; H 7.00; N 8.91.

2,3,3,7,8,8-Hexamethylindolenino[7,6-*g*]indolenine (4). This compound was obtained similarly to compound **3** from 1,5-naphthylenedihydrazine (1 g, 1.5 mmol) and methyl isopropyl ketone (0.9 ml, 0.8 mmol) and was purified on a column with 1:4 heptane–ether as eluent. Yield 0.3 g (38%); mp 267-268°C; published data [5], mp 269°C (benzene).

N,N-Dibenzyl-2,3,7,8-tetramethylindolo[7,6-*g*]indole (5). To solution of compound **2** (0.2 g, 5 mmol) in benzene we added 50% solution of potassium hydroxide (20 ml), benzyl chloride (9 ml, 15 mmol), and catalyst (tetrabutylammonium bromide). The mixture was stirred for 5 h at 80°C, extracted with ether, and chromatographed on a column with 1:4 heptane–ether as eluent. Yield 0.3 g (39%); mp 245-246°C, R_f 0.4 (benzene). UV spectrum, λ_{max} (log ε), nm: 279 (4.91), 304.5 (4.31). Mass spectrum, *m/z* (*I*, %): 442 $[M]^+$ (96.7), 352 (100), 351 (84.7), 259 (53.6). Calculated: M 442. Found, %: C 86.03; H 6.91; N 6.29. $C_{32}H_{30}N_2$. Calculated, %: C 86.88; H 6.79; N 6.33.

N,N-Dibenzyl-2,3,4,5,9,10,11,12-octahydrocarbazolo[3,1-*c*]carbazole (6). The compound was obtained similarly to compound **5** from compound **3** (0.2 g, 0.6 mmol), 50% solution of potassium hydroxide (15 ml), benzyl chloride (1.1 ml, 1.8 mmol), and catalyst (tetrabutylammonium chloride). The product was chromatographed on a column with 3:1 benzene–ether as eluent. Yield 0.4 g (42%); mp 285-286°C, R_f 0.1 (benzene). UV spectrum, λ_{max} (log ε), nm: 284 (4.58), 312.5 (3.89). ^{1}H NMR spectrum, δ, ppm: 0.95 (2H, m, 4-CH_2); 1.72 (2H, t, 5-CH_2); 1.91 (2H, t, 3-CH_2); 2.74 (2H, t, 2-CH_2); 4.53 (2H, s, N–CH_2); 7.33 (1H, d, 7-H); 7.52 (1H, d, 6-H). Found, %: C 88.72; H 5.72; N 7.79. $C_{36}H_{26}N_2$. Calculated, %: C 88.88; H 5.34; N 7.76.

Bis[2',3'-dimethoxycarbonyl-5',6',6'-trimethylspirofluorene-9,4'-(1'-aza-2'-cyclopentene)[1',5'-*a*]-indolino[7,6-*g*]indoline (7). To solution of compound **6** (0.1 g, 0.3 mmol) in absolute ether we added 2',3-dimethoxycarbonylspirocyclopropene (0.2 g, 0.7 mmol). The mixture was stirred in the dark at 44°C for 36 h. The precipitate was filtered off, dried, and chromatographed on a column with 1:5 heptane–ether as eluent. Yield 0.08 g (17%); mp 182-183°C, R_f 0.3 (benzene). UV spectrum, λ_{max} (log ε), nm: 320 (4.12). IR spectrum, ν, cm^{-1}: 1690 (C=C); 1620 (C=O). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.39 (3H, s, 6'-CH_3); 1,58 (3H, s, 6'-CH_3); 2.21 (3H, s, 5'-CH_3); 3.60 (3H, s, $COOCH_3$); 3.83 (3H, s, $COOCH_3$); 6.20 (1H, d, J_o = 8.8, 1-H); 6.48 (1H, t, 2-H); 6.75 (1H, t, 7-H); 7.20 (1H, d, $J_{8'7'}$ = 7.5, 8'-H); 7.30 (1H, d, J_o = 8.2, 8-H); 7.42 (1H, t, 6-H); 7.54 (1H, t, 3-H); 7.73 (1H, d, J_o = 8.2, 5-H); 7.75 (1H, d, J_o = 8.2, 4-H); 7.81 (1H, d, $J_{7'8'}$ = 7.5, 7'-H). Mass spectrum, *m/z* (*I*, %): 920 $[M]^+$ (12.8), 596 (100.0), 581 (53.3), 537 (29.0), 462 (60.1), 448 (84.3), 434 (52.0), 404 (15.5), 378 (12.2). Calculated: M 920. Found, %: C 77.46; H 5.87; N 3.72. $C_{58}H_{50}N_2O_8$. Calculated, %: C 77.16; H 5.54; N 3.10.

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