Russian Journal of Organic Chemistry, Vol. 37, No. 9, 2001, pp. 1289–1296. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 9, 2001, pp. 1357–1363.
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Reactions of *N*- and *C*-Alkenylanilines: II.* Halocyclization of 2-(2-Cycloalkenyl)anilines

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Received November 15, 2000

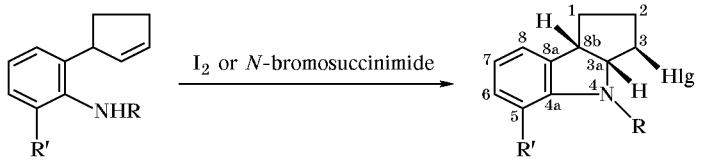
Abstract—The reaction of 2-(2-cyclopentenyl)anilines with I_2 in the presence of $NaHCO_3$ results in formation of 3-iodocyclopenta[*b*]indoles in high yields. Under similar conditions 2-(2-cyclohexenyl)anilines give rise to cyclization products whose structure depends on the solvent and substituents in the aromatic ring and on the nitrogen atom.

Halocyclization reactions [2] are characterized by high stereo- and regioselectivity; these reactions also ensure subsequent ready functionalization of intermediates. Halocyclizations are widely used in the synthesis of nitrogen-containing heterocycles from unsaturated aliphatic amines [3, 4] and carbamates [5, 6], but only a few examples of halocyclizations involving *ortho*-alkenylanilines have been reported [7]. In continuation of our studies [8–10] on heterocyclization of *ortho*-alkenylanilines with the goal of obtaining intermediate products for preparation of potential biologically active substances [11–13], in the present work we examined iodocyclization of 2-(2-cyclopentenyl)- and 2-(2-cyclohexenyl)anilines and -methoxyanilines which were synthesized by condensation of 3-chlorocyclopentene and 3-bromocyclohexene with anilines [14].

The reaction of 2-(2-cyclopentenyl)anilines **I** and **II** with I_2 in different solvents afforded 3-iodo-5-R-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indoles **III** and **IV** in 85–88% yield (Scheme 1). By reaction of *N*-acetyl-2-(2-cyclopentenyl)-6-methoxyaniline (**V**) with *N*-bromosuccinimide in $CHCl_3$ we obtained 91% of 3-bromohexahydrocyclopenta[*b*]indole (**VI**) (Table 1). The structure of the products indicates that the process follows the 5-*exo*-cyclization path [15].

The reactions of 2-(2-cyclohexenyl)anilines **VII** and **VIII** with I_2, depending on the solvent, gave only 1-iodo-1,2,3,4,4a,9a-hexahydrocarbazoles **IX** and **X** or their mixtures with 13-iodo-8-azatricyclo[7.3.1.$0^{2,7}$]-trideca-2,4,6-trienes **XI** and **XII** (Scheme 2; Tables 1 and 2). When the cyclization of amines **VII** and **VIII** was performed in acetonitrile, the major products were azatricyclodecatrienes **XI** and **XII**, while in carbon

Scheme 1.



I, II, V **III, IV, VI**

I–**IV**, R = H; **V, VI**, R = Ac; **I**, **III**, R′ = Me; **II**, **IV**–**VI**, R′ = OMe; **III**, **V**, Hlg = I; **VI**, Hlg = Br.

* For communication I, see [1].

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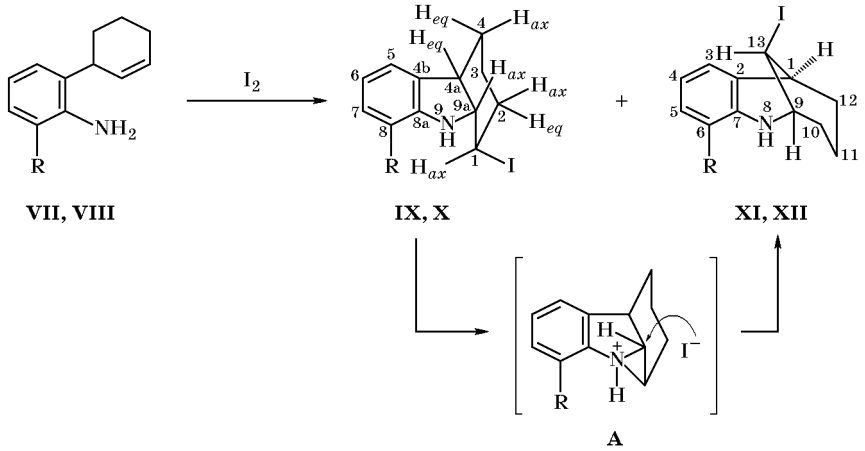
Scheme 2.



VII, **IX**, **XI**, R = H; **VIII**, **X**, **XII**, R = OMe.

tetrachloride hexahydrocarbazoles **IX** and **X** were formed exclusively (Table 2). Although acetonitrile is hardly suitable for preparation of hexahydrocarbazoles **IX** and **X**, conditions can be found under which azatricyclotridecatrienes **XI** and **XII** are formed as the sole products. We have found that compounds **IX** and **X** in acetonitrile at room temperature undergo a fairly fast rearrangement into isomeric azatricyclotridecatrienes **XI** and **XII** in quantitative yield. The complete conversion of **IX** takes ~10 days, and its methoxy analog **X** rearranges in ~30 days. In chloroform, the same transformations require ~90 and 240 days, respectively. The only known example of ring expansion of (1-iodoalkyl)pyrrolidines into 3-iodopiperidine was reported in [16]. The isomerization occurred on heating in acetonitrile under reflux, and it was characerized by poor yield and low selectivity. Presumably, the intramolecular isomerization of hexahydrocarbazoles **IX** and **X** into azatricyclotridecatrienes **XI** and **XII** follows the same mechanism as that proposed in [16], i.e., through intermediate formation of aziridinium salt **A** (Scheme 2). In the reactions of amines **VII** and **VIII** with I_2, the carbazole structure is likely to result from the transformation of complex **B**, shown in Scheme 3. The 6-*endo*-cyclization product, azatricyclotridecatriene, may be formed by both intramolecular isomerization of heterocycles **IX** and **X** and directly through further transformation of complex **B**. The cyclization of amine **VII** by the action of I_2 in methylene chloride is complete in 12 h, and the products are hexahydrocarbazole **IX** and azatricyclotridecatriene **XI** at a ratio of ~7 : 1 (Table 2). This ratio almost does not change on storage of the reaction mixture for 30 days. The large fraction of tricyclic product **XI** in the reaction mixture by the end of the process can be explained by considerable contribution of the 6-*endo*-cyclization pathway.

Cyclohexenylaniline derivatives **XIII**–**XV** reacted with iodine in acetonitrile to afford exclusively hexahydrocarbazoles **XVI**–**XVIII** (Scheme 4). Hexahydrocarbazole **XX** was obtained in 78% yield by treatment with iodine of substituted urea **XIX** which was synthesized by heating of amide **XIV** in a 16% solution of ammonia in methanol under pressure.

Scheme 3.

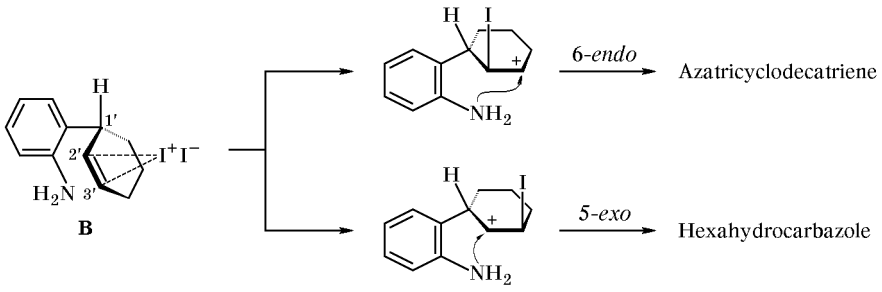


Table 1. Yields, R_f values, and IR and ^{13}C NMR spectra of compounds **IV**–**VI** and **IX**–**XXII**

Comp. no.	Yield, %	R_f[a]	IR spectrum, ν, cm^{-1}	^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm
IV	87	0.5 (A)	3400 (N–H)	33.0 (C^1), 35.1 (C^2), 36.9 (C^3), 45.9 (C^{8b}), 54.8 (OCH3), 73.9 (C^{3a}), 108.8 (C^6), 116.5 (C^7), 132.6 (C^{4a}), 138.3 (C^{8a}), 143.7 (C^5)
V	98	0.5 (A)	3280 (N–H)	
VI	91	0.7 (B)	648 (C–Br)	20.9 (CH_3); 30.0 (OCH_3); 30.9 (C^1); 34.8 (C^2); 45.4 (C^{8b}); 55.5 (C^3); 74.8 (C^{3a}); 121.1 , 125.7 , 128.3, 130.3, 136.2, 140.5 (C_{arom})
IX	90	0.6 (B)	3472 (N–H)	23.2 (C^3), 23.5 (C^4), 36.3 (C^2), 39.0 (C^1), 42.6 (C^{4a}), 69.5 (C^{9a}), 110.5 (C^8), 119.2 (C^6), 122.7 (C^5), 127.4 (C^7), 129.5 (C^{4b}), 149.7 (C^{8a})
X	90	0.6 (B)	3470 (N–H)	23.4 (C^3), 23.9 (C^4), 35.5 (C^2), 38.4 (C^1), 42.3 (C^{4a}), 55.8 (OCH_3), 69.2 (C^{9a}), 109.0 (C^7), 114.7 (C^5), 119.3 (C^6), 130.4 (C^{4b}), 138.2 (C^{8a}), 145.4 (C^8)
XI	73	0.6 (B)	3475 (N–H)	16.7 (C^{11}), 30.0 (C^{12}), 30.1 (C^{10}), 33.2 (C^{13}), 41.3 (C^1), 51.7 (C^9), 112.5 (C^6), 118.1 (C^4), 123.4 (C^2), 127.2 (C^3), 127.8 (C^5), 144.3 (C^7)
XII	75	0.5 (B)	3473 (N–H)	16.9 (C^{11}), 29.9 (C^{12}), 30.5 (C^{10}), 33.1 (C^{13}), 41.3 (C^1), 51.6 (C^9), 55.2 (OCH_3), 107.9 (C^5), 115.5 (C^3), 120.1 (C^4), 123.7 (C^7), 134.2 (C^2), 145.1 (C^6)
XIII	89	[b]	3290 (N–H)	
XIV	93	[c]	3280 (N–H)	14.2 (CH_3), 20.9 ($C^{5'}$), 24.5 ($C^{6'}$), 29.6 ($C^{4'}$), 39.3 ($C^{1'}$), 50.7 (OCH_2), 126.5 (C^6), 128.4 ($C^{3'}$), 128.7 (C^5), 128.9 (C^4), 129.3 ($C^{2'}$), 129.6 (C^5), 131.3 (C^2), 135.0 (C^1), 154.0 (C=O)
XV	93	0.4 (A)	3280 (N–H)	21.4 ($C^{5'}$), 24.1 (CH_3), 24.8 ($C^{6'}$), 29.8 ($C^{4'}$), 39.1 ($C^{1'}$), 121.4 (C^6), 125.7 ($C^{3'}$), 127.9 (C^4), 128.2 ($C^{2'}$), 129.5 (C^5), 129.8 (C^3), 136.4 (C^2), 138.5 (C^1), 168.5 (C=O)
XVI	86	0.6 (B)	564 (C–I)	22.7 (C^3), 24.5 (C^4), 31.0 (C^1), 36.1 (C^2), 38.3 (SCH_3), 42.6 (C^{4a}), 71.7 (C^{9a}), 118.8 (C^8), 123.3 (C^6), 125.3 (C^5), 128.1 (C^7), 135.2 (C^{4b}), 141.3 (C^{8a})
XVII	62	0.6 (B)	542 (C–I)	
XVIII	74	0.6 (B)	588 (C–I)	21.2 (CH_3), 22.5 (C^3), 23.6 (C^4), 29.8 (C^1), 34.6 (C^2), 38.3 (C^{4a}), 73.7 (C^{9a}), 115.9 (C^8), 124.8 (C^5), 125.4 (C^6), 126.6 (C^7), 135.0 (C^{4b}), 137.5 (C^{8a}), 168.5 (C=O)
XIX	89	0.2 (C)	3300–3450 (NH, NH_2)	
XX	46	0.3 (B)	3400 (NH_2)	22.8 (C^3), 23.0 (C^4), 31.2 (C^1), 37.2 (C^2), 43.3 (C^{4a}), 70.2 (C^{9a}), 118.2 (C^8), 122.5 (C^6), 127.4 (C^5), 128.2 (C^7), 133.7 (C^{4b}), 142.1 (C^{8a}), 147.0 (C=O)
XXI	83	0.6 (B)	3400 (NH, NH_2)	22.4 (C^3), 28.9 (C^2), 29.2 (C^4), 42.4 (C^{4a}), 55.2 (OCH_3), 64.2 (C^1), 70.6 (C^{9a}), 109.2 (C^7), 115.7 (C^5), 119.5 (C^6), 136.3 (C^{4b}), 138.4 (C^{8a}), 145.9 (C^8)
XXII	44	0.6 (B)	558 (C–I)	16.6 (C^{11}), 27.5 (C^{12}), 28.3 (C^{13}), 29.6 (C^{10}), 39.4 (SCH3), 42.1 (C^1), 56.5 (C^9), 117.3 (C^6), 122.9 (C^4), 128.0 (C^3), 128.4 (C^7), 129.3 (C^5), 137.1 (C^2)

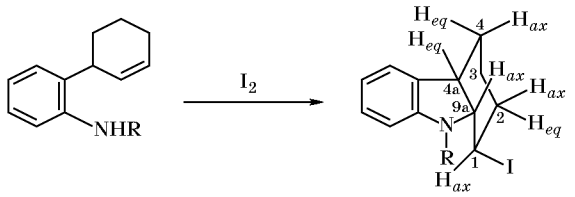
[a] Eluent CCl_4 (A), CH_2Cl_2 (B), C_6H_6 (C).
[b] mp 115–116°C.
[c] bp 98°C (1 mm).

Table 2. Product ratio in the reactions of compounds **VII** and **VIII** with iodine in various solvents

Reaction time, h	Initial compound	Solvent	ε	*B*	Products (ratio)
108	**VII**	MeCN	37.4	160	**IX**, **XI** (1 : 4)
48	**VII**	CCl_4	2.23	0	**IX**
12	**VII**	CH_2Cl_2	9.08	23	**IX**, **XI** (7 : 1)
48	**VIII**	CCl_4	2.23	0	**X**
72	**VIII**	MeCN	37.4	160	**X**, **XII** (1 : 2)

It is known [2] that kinetically controlled cyclization of unsaturated acids or amides by the action of I_2 yields mainly thermodynamically less favored product due to different rates of formation of stereo- or regioisomers. The above experiments were carried out under conditions (I_2/$NaHCO_3$/solvent) corresponding to kinetic control. When the reaction of **XIII** with I_2 was performed under conditions of thermodynamic control (I_2/MeCN), hexahydrocarbazole **XVI** was the only reaction product. Presumably, compound **XVI** is the only thermodynamically stable structure or the presence of the methylsulfonyl group hampers formation of the *endo*-6 isomer.

Scheme 4.



XIII–XV, XIX **XVI–XVIII, XX**

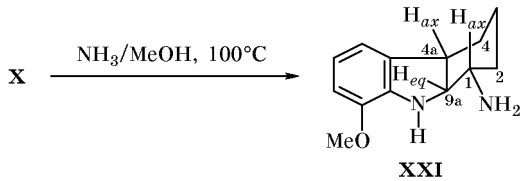
XIII, **XVI**, R = $MeSO_2$; **XIV**, **XVII**, R = CO_2Et; **XV**, **XVIII**, R = Ac; **XIX**, **XX**, R = $NH_2C(O)$.

The structure of compounds **II**–**XXI** was derived from their IR and NMR spectra and analytical data (Tables 3, 4). The spectral parameters of dihydroindole **III** were reported in [17], and those of compounds **IV** and **VI** are given in Experimental. The position of the 8b-H and 3a-H protons in molecules **III**, **IV**, and **VI** was proved by the large values of the corresponding vicinal coupling constants ($J_{3a,8b}$ = 8–9 Hz) which were determined by the double-resonance technique and by observation of intramolecular nuclear Overhauser effect. Saturation of the 3a-H signal induces a 8% increase of the 8b-H signal in the spectrum of **III**, whereas the 3-H signal remains unchanged. These data indicate that the 3a-H and 8b-H protons are located close to each other, which is possible when these protons are oriented axially and the five-membered rings are fused *cis* (the 3a-H and 3-H protons are arranged *trans*).

The 1-H signal in the spectra of carbazoles **IX**, **X**, **XVI**–**XVIII**, and **XX** is characterized by two large coupling constants, $J_{1,2\text{-}ax}$ = ~11–12 Hz and $J_{1,9a} \approx$ 8–9 Hz, indicating two axial–axial interactions, i.e., both 1-H and 9a-H protons are axial (Table 3). The coupling constant for the 9a-H and 4a-H protons (~7–8 Hz) suggests their *cis* arrangement and hence *cis* junction of the rings [18]. Irradiation at a frequency corresponding to the C^4H_2 protons results in transformation of the 4a-H multiplet into a doublet with J = 7–7.5 Hz. The 1-H proton is coupled with 2-H_{ax} and 2-H_{eq} through constants of ~12.0 (large) and ~4.0 Hz (small) [18, 19]. Analogous coupling constants were given in [20] for structurally related carbazole derivative.

Replacement of the iodine atom in **X** by NH_2 group on heating in a methanolic ammonia solution (Scheme 5) gives product **XXI** which exists in a *chair* conformation with the axial 4a-H proton. The 9a-H proton of **XXI** shows in the ^{1}H NMR spectrum two coupling constants, $J_{9a,1}$ = 4.6 and $J_{9a,4a}$ = 6.5 Hz which indicate equatorial orientation of 9a-H. Suppression of the 9a-H signal in the double-resonance spectrum gives rise to a doublet of doublets from the 4a-H proton, $J_{4a,4\text{-}eq}$ = 6.2 and $J_{4a,4\text{-}ax}$ = 11.5 Hz [18] (Table 3).

Scheme 5.



XXI

The 4a-H signal appears as a doublet of doublets, $J_{4a,9a}$ = 6.5 and $J_{4a,9a}$ = 11.5 Hz, on irradiation of the equatorial 4-H proton. The 1-H proton is axial. Its signal is a doublet of triplets with J_1 = 4.6 Hz (the coupling constants for 2-H_{eq}–1-H and 9a-H–1-H

Table 3. ^{1}H NMR spectra of compounds **IV**, **VI**, **IX**–**XIV**, **XVI**–**XVIII**, and **XX**–**XXII**

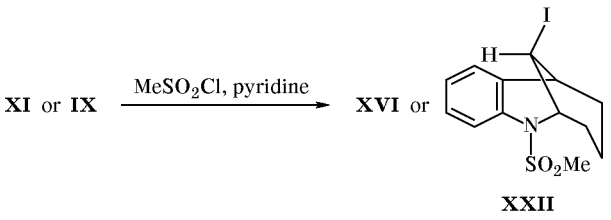
Comp. no.	Chemical shifts δ, ppm (*J*, Hz)
IV	1.5–2.7 m [$(CH_2)_2$], 3.9 s (OCH_3), 4.1 t (8b-H, *J* = 8.8), 4.3 m (3-H), 4.4 s (NH), 4.8 d (9a-H, *J* = 8.8,), 6.7–6.9 m (3H, Ar)
VI	1.7–2.3 m [$(CH_2)_2$], 2.2 s (CH_3), 2.4 s (OCH_3), 4.0 t (8b-H, *J* = 8.0), 4.3 m (3-H), 4.9 d.d, (9a-H, *J* = 8.0), 6.9–7.3 m (3H, Ar)
IX	1.1–2.2 m [$(CH_2)_3$], 3.2 m (9a-H), 3.9 d.d (9a-H, J_1 = 9.0, J_2 = 7.1), 4.0 d.d.d (1-H, J_1 = 3.9, J_2 = 11.97, J_3 = 9.0), 4.2 br. s (NH), 6.7 t (6-H), 6.8 d (8-H, 7.6), 7.1 d (5-H, 7.5), 7.2 t (7-H)
X	1.3–2.3 m [$(CH_2)_3$], 3.4 m (9a-H), 3.8 s (OCH_3), 3.9 d.d (9a-H, J_1 = 8.0, J_2 = 7.0), 4.0 d.d.d (1-H, J_1 = 3.9, J_2 = 12.0, J_3 = 8.0), 4.5 br. s (NH), 6.7–6.9 (3H, H_{arom})
XI	1.5–2.6 m [$(CH_2)_3$], 3.2 m (1-H), 3.7 d.d.d (13-H, J_1 = 1.6, J_2 = 1.9, J_3 = 2.0), 4.2 br.s (NH), 4.9 m (9-H), 6.6 d (*J* = 8.0, 6-H), 6.8 t (4-H, *J* = 7.3), 7.0 d (3-H, *J* = 7.3), 7.2 t (5-H)
XII	1.3–2.6 m [$(CH_2)_3$], 3.1 m (1-H), 3.7 m (13-H), 4.4 br.s (NH), 4.7 m (9-H), 6.5–6.7 m (3H, H_{arom})
XIII	1.3–2.2 m [$(CH_2)_3$], 3.0 s (CH_3), 3.8 m (1′-H), 5.6–5.9 m (2′-H, 3′-H), 7.1–7.4 m (4H, Ar), 7.4 s (NH)
XIV	1.3 t (CH_3), 1.5–2.1 m [$(CH_2)_3$], 3.5 m (1′-H), 5.6 d.d.d (3′-H, J_1 = 2.0, J_2 = 6.2, J_3 = 10.0), 6.0 m (2′-H), 7.0–7.2 m (4H, H_{arom}), 7.7 s (NH)
XVI	1.3–2.3 m [$(CH_2)_3$], 3.0 s (CH_3), 3.7 m (9a-H), 4.3 d.d.d (1-H, J_1 = 4.0, J_2 = 11.5, J_3 = 8.5), 4.7 d.d (9a-H, J_1 = 8.5, J_2 = 7.5), 7.2–7.6 m (4H, H_{arom})
XVII	1.3–2.3 m [$(CH_2)_3$], 1.4 t (CH_3, 7.2), 3.6 m (9a-H), 4.1 d.d.d (1-H, J_1 = 4.0, J_2 = 12.1, J_3 = 8.8), 4.3 q (CH_2), 4.9 d.d (9a-H, J_1 = 8.8, J_2 = 8.0), 6.9–7.5 m (4H, H_{arom})
XVIII	1.3–2.3 m [$(CH_2)_3$], 1.4 s (CH_3), 3.7 m (9a-H), 4.1 d.d.d (1-H, J_1 = 4.0, J_2 = 11.2, J_3 = 8.7), 4.7 d.d (9a-H, J_1 = 8.7, J_2 7.4), 6.9–7.5 m (4H, H_{arom})
XX	1.2–2.3 m [$(CH_2)_3$], 3.5 m (9a-H), 3.9 d.d.d (1-H, J_1 = 4.0, J_2 = 11.3, J_3 = 9.0), 4.6 d.d (9a-H, J_1 = 9.0, J_2 = 7.0), 5.9 s (NH_2), 6.9–7.5 m (4H, H_{arom})
XXI	1.1–1.9 m [$(CH_2)_3$], 3.1 d.d.d (9a-H, J_1 = 6.5, J_2 = 6.2, J_3 = 11.2), 3.8 s (OCH_3), 3.9 d.d.d (1-H, J_1 = 10.5, J_2 = 4.6, J_3 = 4.6), 4.5 br.s (NH, NH_2), 4.6 d.d (9a-H, J_1 = 4.6, J_2 = 6.56), 6.6–6.8 (3H, H_{arom})
XXII	1.1–2.5 m [$(CH_2)_3$], 3.0 s (SCH_3), 3.1 m (1-H), 3.6 m (13-H), 4.2 m (9-H), 6.9–7.7 m (3H, H_{arom})

coincided with each other) and $J_{1,2\text{-}ax}$ = 10.5 Hz. Had the 1-H proton been oriented equatorially, the coupling constant $J_{1,2\text{-}ax}$ would be much smaller. In the JMOD ^{13}C NMR spectra of carbazoles **IX**, **X**, **XVI**–**XVIII**, and **XX** the C^2 signal is displaced downfield (δ_C 34–36 ppm) due to β-effect of iodine [21] (Table 1).

Signals in the ^{13}C NMR spectra of azatricyclotridecatrienes **XI** and **XII** were assigned on the basis of their multiplicity, taking into account increments of ^{13}C chemical shifts given in [18]. Also, published data for substituted bicyclo[3.1.1]heptanes [22] and related bridged systems [23] were used. The *anti* orientation of the iodine atom with respect to the phenyl group was proved by the ^{1}H NMR data. The 13-H proton in the bridging group gives rise to eight lines or four doublets with coupling constants *J* not exceeding 2 Hz. Such values correspond to the *syn* orientation of 13-H with respect to the phenyl group [17]. Moreover, using the double resonance technique we have found that the 13-H proton is coupled with the two protons in the bridgehead positions (1-H and 9-H) and two equatorial protons (12-H_{eq} and 10-H_{eq}) whose signals appear in the region δ 2.3–2.6 ppm (*W*-coupling). The 12-H_{ax} and 10-H_{ax} signals are observed at δ 1.6–1.8 ppm.

In order to prove that hexahydrocarbazole **IX** and methylsulfonyl derivative **XVI** have the same struc-

Scheme 6.



XXII

Table 4. Elemental analyses of compounds **IV**–**VI**, **IX**–**XIV**, and **XVI**–**XXII**

Comp. no.	Found, %				Formula	Calculated, %			
	C	H	Hlg	N		C	H	Hlg	N
IV	45.30	4.21	39.79	3.93	$C_{12}H_{14}INO$	45.73	4.48	40.27	4.44
V	72.32	7.14		5.71	$C_{14}H_{17}NO_2$	72.70	7.41		6.05
VI	57.29	5.51	27.13	4.62	$C_{14}H_{16}BrNO_2$	57.16	5.48	27.16	4.76
IX	47.67	4.86		3.92	$C_{12}H_{14}IN$	48.18	4.72		4.68
X	47.07	4.54	38.97	3.87	$C_{13}H_{16}INO$	47.43	4.90	39.46	4.25
XI	48.42	4.23	41.94	4.00	$C_{12}H_{14}IN$	48.18	4.72	42.42	4.68
XII	47.12	4.47	38.87	3.69	$C_{13}H_{16}INO$	47.43	4.90	39.46	4.25
XIII	61.91	6.54		5.30	$C_{13}H_{17}NO_2S$[a]	62.15	6.77		5.58
XIV	73.08	7.61		5.19	$C_{15}H_{19}NO_2$	73.44	7.81		5.71
XVI	40.94	3.98	33.17	3.32	$C_{13}H_{16}INO_2S$[b]	41.39	4.27	33.64	3.71
XVII	48.17	4.32	33.74	3.28	$C_{15}H_{18}INO_2$	48.53	4.89	34.19	3.77
XVIII	48.87	4.29	36.76	3.68	$C_{14}H_{16}INO$	49.28	4.73	37.19	4.10
XIX	71.87	7.13		12.48	$C_{13}H_{16}N_2O$	72.19	7.46		12.95
XX	45.19	4.01	36.65	7.81	$C_{13}H_{15}IN_2O$	45.63	4.42	37.09	8.19
XXI	71.14	8.11		12.41	$C_{13}H_{18}N_2O$	71.53	8.31		12.83
XXII	40.81	4.16	33.15	3.45	$C_{13}H_{16}INO_2S$[c]	41.39	4.27	33.64	3.71

[a] Found S: 12.29%; calculated S: 12.75%.
[b] Found S: 8.08%; calculated S: 8.50%.
[c] Found S: 8.19%; calculated S: 8.50%.

ture of the tricyclic fragment, amines **IX** and **XI** were treated with methanesulfonyl chloride in pyridine. Compounds **XVI** and **XXII** were thus obtained (Scheme 6). Comparison of the ^{13}C NMR spectra of the products showed that carbazole **IX** obtained from amine **VII** and compound **XVI** obtained from **XIII** have similar structures. The presence of methylsulfonyl group on the nitrogen exerts shielding effect on C^1 in **XVI** and C^{13} in **XXII**, so that the corresponding signals appear more upfield relative to those observed for **IX** and **X**.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM300 instrument at 300 and 75 MHz, respectively; $CDCl_3$ was used as solvent, and Me_4Si, as internal reference. The IR spectra were obtained on a UR-20 spectrometer. The progress of reactions was monitored by TLC on Silufol UV-254 plates.

***N*-Acetyl-6-(2-cyclopentenyl)-2-methoxyaniline (V) and *N*-acetyl-2-(2-cyclohexenyl)aniline (XV)** [1]. Acetic anhydride, 2.04 g, was added to a solution of 10 mmol of amine **II** or **VII** in 10 ml of methylene chloride, and the mixture was kept for 18 h, treated with water, and extracted with 100 ml of methylene chloride. The extract was washed with a 5% aqueous solution of $NaHCO_3$ (until CO_2 no longer evolved) and with 20 ml of water, dried over $MgSO_4$, and evaporated under reduced pressure. Anilide **XV** was described in [1].

4-Acetyl-3-bromo-5-methoxy-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (VI). A mixture of 0.5 g of anilide **V** and 0.45 g of *N*-bromosuccinimide in 10 ml of chloroform was stirred for 48 h at 20°C. It was then filtered, and the filtrate was washed with 20 ml of a 10% aqueous solution of $NaHCO_3$ and evaporated under reduced pressure. The residue was filtered through a thin layer of silica gel (2 g; eluent methylene chloride.

***N*-Methylsulfonyl-2-(2-cyclohexenyl)aniline (XIII).** 2-(2-Cyclohexenyl)aniline (**VII**), 0.52 g, was dissolved in 4 ml of pyridine, and 0.6 ml of methanesulfonyl chloride was added dropwise. The mixture was kept for 24 h at room temperature, diluted with 20 ml of water, stirred for 30 min, and extracted with 40 ml of $CHCl_3$. The organic phase was washed with 20 ml of a 10% aqueous solution of $NaHCO_3$ and 20 ml of water, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was recrystallized from benzene.

2-(2-Cyclohexenyl)-*N*-(ethoxycarbonyl)aniline (XIV). A solution of 20 mmol of ethyl chloroformate

in 10 ml of methylene chloride was added dropwise with stirring to a mixture of 10 mmol of amine **VII**, 80 mmol of K_2CO_3, and 30 ml of methylene chloride. The mixture was kept for 18 h at 20°C and treated with water. It was then stirred for 30 min and extracted with 100 ml of methylene chloride. The extract was washed with 20 ml of water, dried over $MgSO_4$, and the solvent was evaporated under reduced pressure. The product was isolated by vacuum distillation.

***N*-[2-(2-Cyclohexenyl)phenyl]urea (XIX).** A 17-ml high-pressure reactor was charged with 2 g of compound **XIV** and 15 ml of a 16% solution of NH_3 in methanol, and the mixture was heated for 24 h at 100°C. It was then cooled to 20°C, and the precipitate was filtered off.

Hexahydrocarbazoles IX and X. A mixture of 1 mmol of substituted aniline **VII** or **VIII**, 1.5 g of $NaHCO_3$, and 0.51 g of I_2 in 10 ml of CCl_4 was shaken for 48 h at 20°C. The progress of the reaction was monitored by TLC using hexane–methanol (9.8 : 0.2) as eluent. The solvent was decanted from the precipitate, the latter was washed with 5 ml of CCl_4 and dissolved in 40 ml of methylene chloride, 30 ml of a 5% aqueous solution of $Na_2S_2O_3$ was added, the mixture was stirred for 5 min, and the organic phase was separated, washed with 20 ml of water, and dried over Na_2SO_4. The solvent was removed under reduced pressure to obtain pure hexahydrocarbazole **IX** or **X**.

Hexahydrocyclopenta[*b*]indoles III and IV, azatricyclotridecatrienes XI and XII, and hexahydrocarbazoles XVI–XVIII and XX. A mixture of 1 mmol of aniline **I**, **II**, **VII**, **VIII**, **XIII**–**XV**, or **XIX**, 1.5 g $NaHCO_3$, and 0.51 g of I_2 in 10 ml of appropriate solvent (methylene chloride, 1,2-dichloroethane, or acetonitrile for amines **I** and **II**; acetonitrile for compounds **VII**, **VIII**, **XIII**–**XV**, and **XIX**) was shaken for 24–130 h at 20°C. The progress of the reaction was monitored by TLC using hexane–MeOH (9.8 : 0.2) as eluent. The mixture was diluted with 50 ml of 1,2-dichloroethane, and the precipitate was filtered off and washed with 1,2-dichloroethane (3 × 10 ml). The organic phase was washed with a 5% aqueous solution of $Na_2S_2O_3$ (3 × 10 ml) and with water (20 ml), dried over Na_2SO_4, and evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel (2 g) to isolate indole **III** or **IV** or hexahydrocarbazole **XVI**–**XVIII** or **XX** (eluent CCl_4). In the synthesis of azatricyclotrienes **XI** and **XII** the residue obtained after evaporation of the solvent was dissolved in acetonitrile, and the solution was kept for 10 or 20 days, respectively. When the isomerization was complete, the solvent was removed under reduced pressure, and products **XI** and **XII** were purified by chromatography on silica gel as described above.

1-Amino-8-methoxy-1,2,3,4,4a,9a-hexahydrocarbazole (XXII). A mixture of 1 mmol of compounds **XI** and 15 ml of a 16% solution of ammonia in methanol was heated for 24 h at 100°C in a high-pressure reactor. The mixture was cooled, the solvent was distilled off, the residue was dissolved in chloroform (30 ml), and the solution was washed with a 5% aqueous solution of $NaHCO_3$ (20 ml) and with water (20 ml). The organic phase was dried over Na_2SO_4 and evaporated under reduced pressure, and the residue was subjected to chromatography on silica gel (10 g) using CCl_4 as eluent.

REFERENCES

1. Gataullin, R.R., Afon'kin, I.S., Fatykhov, A.A., Spirikhin, L.V., and Abdrakhmanov, I.B., *Russ. J. Org. Chem.*, 2001, vol. 37, no. 6, pp. 834–840.
2. Cardillo, C. and Orena, M., *Tetrahedron,* 1990, vol. 46, no. 10, pp. 3321–3407.
3. Bongini, A., Cardillo, G., Orena, M., Porzi, G., and Sandri, S., *Chem. Lett.*, 1988, no. 1, p. 87.
4. Wilson, S.R. and Sawicki, R.A., *J. Org. Chem.*, 1979, vol. 44, no. 2, pp. 287–291.
5. Reitz, A.B., Nortey, S.O., and Maryonoff, B.E., *Tetrahedron Lett.*, 1985, vol. 26, no. 33, pp. 3915–3918.
6. Hirama, M., Iwashita, M., and Yamazaki, Y., *Tetrahedron,* 1984, vol. 25, no. 23, pp. 4963–4964.
7. Raner, D. and Ward, A.D., *Aust. J. Chem.*, 1991, vol. 44, no. 12, pp. 1749–1760.
8. Gataullin, R.R., Afon'kin, I.S., Pavlova, I.V., Abdrakhmanov, I.B., and Tolstikov, G.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1999, no. 2, pp. 398–401.
9. Gataullin, R.R., Kazhanova, T.V., Il'yasova, L.T., Fatykhov, A.A., Spirikhin, L.V., and Abdrakhmanov, I.B., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 1999, no. 5, pp. 975–978.
10. Gataullin, R.R., Afon'kin, I.S., Fatykhov, A.A., Spirikhin, L.V., and Abdrakhmanov, I.B., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, no. 1, pp. 118–121.
11. Andreeva, N.I., Bogdanova, G.A., Bokanov, A.I., Ivanov, P.Yu., Mashkovitskii, M.D., and Shvedov, V.I., *Khim.-Farm. Zh.*, 1992, vol. 26, no. 1, pp. 4–7.
12. Russian Patent no. 1 830 069, 1993; *Byull. Izobret.*, 1993, no. 27.
13. Mashkovskii, M.D., Glushkov, R.G., Shvedov, V.I., Andreeva, N.I., and Golovina, S.M., *Eksp. Klin. Farmakol.*, 1993, vol. 56, no. 2, pp. 3–6.

14. Abdrakhmanov, I.B., Sharafutdinov, V.M., and Tolstikov, G.A., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, no. 9, pp. 2160–2162.
15. Baldwin, J.E., *J. Chem. Soc., Chem. Commun.*, 1976, no. 18, pp. 734–736.
16. Williams, D.R., Osterhout, M.H., and McGill, J.M., *Tetrahedron Lett.*, 1989, vol. 30, no. 21, pp. 1331–1334.
17. Gataullin, R.R., Kazhanova, T.V., Minnigulov, F.F., Fatykhov, A.A., Spirikhin, L.V., and Abdrakhmanov, I.B., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2000, no. 10, pp. 1789–1793.
18. Pretsch, E., Clerk, T., Seible, J., and Simon, W., *Tables of Spectral Data for Structure Determination of Organic Compounds*, Berlin: Springer, 1983.
19. Jackman, L.M. and Sternhell, S., *Application of Nuclear Magnetic Resonance in Organic Chemistry*, Oxford: Pergamon, 1969.
20. Clive, D.L.J., Wong, C.K., Kiet, W.A., and Menchen, S., *J. Chem. Soc., Chem. Commun.*, 1978, no. 2, pp. 379–380.
21. Watanabe, M., Okada, H., Teshima, T., Noguchi, M., and Kakehi, A., *Tetrahedron*, 1996, vol. 52, no. 8, p. 2827.
22. Whitersell, J.K. and Minton, M.A., *Stereochemical Analysis of Alicyclic Compounds by C-13 NMR Spectroscopy*, London: Chapman and Hall, 1987, pp. 114–116.
23. Sindler-Kulyk, M. and Laarhoven, W.H., *J. Am. Chem. Soc.*, 1978, vol. 100, no. 12, p. 3819.