ISSN 1070-4280, Russian Journal of Organic Chemistry, 2006, Vol. 42, No. 8, pp. 1131–1136. © Pleiades Publishing, Inc. 2006.
Original Russian Text © V.A. Glushkov, T.N. Vetoshkina, D.V. Kolgashev, O.A. Maiorova, S.N. Shurov, Yu.V. Shklyaev, 2006, published in Zhurnal Organicheskoi Khimii, 2006, Vol. 42, No. 8, pp. 1153–1158.

Spirocyclohexadienones: VIII.* 1-R-3,3-Dimethyl-2-azaspiro[5.5]undeca-1,7,10-trien-9-ones

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Received April 25, 2005

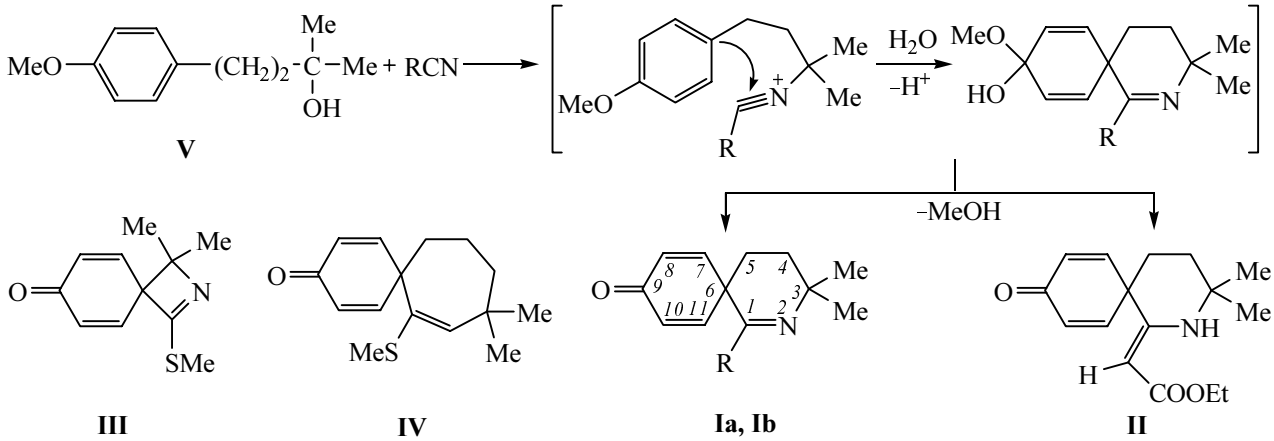
Abstract—1-R-3,3-Dimethyl-2-azaspiro[5.5]undeca-1,7,10-trien-9-ones were synthesized by condensation of 4-(*p*-methoxyphenyl)-2-methylbutan-2-ol with nitriles RCN in the presence of a concn. sulfuric acid.

DOI: 10.1134/S1070428006080045

Heterocyclic spirocyclohexa-2,5-dien-1-ones represent a specific heterocyclic class attracting lately the interest of researchers. We formerly carried out a three-component condensation of anisole, isobutyric aldehyde, and nitriles RCN in the presence of concn. H_2SO_4 to obtain spirocyclohexadienepyrrolines (1-R-3,3-dimethyl-2-azaspiro[4.5]-deca-1,6,9-trien-8-ones) [2, 3]. In this study we attempted to prepare homologs of these compounds with a piperidine ring instead of pyrroline one. The structural unit of a spirocyclohexadienepiperidine is encountered in some natural compounds of a high physiological activity, for instance, in nitramin, an alkaloid of plants from the genus *Nitraria* (2-azaspiro[5.5]undecane) [4, 5], in histrionicotoxin, the poison of arrow-poison South-American frogs (*Dendrobatidae*) (1-azaspiro-[5.5]undecane) [6, 7], in sponge alkaloids 3-azaspiro-[5.5]undecane [8, 9], and also in the recently described plankton toxins, gymnodimine (2-azaspiro[5.5]undecane) and spirolides A-D (2-azaspiro[6.5]dodecane) [10].

The synthetic approaches to this type compounds besides the classical oxidative coupling of phenols [9, 11–14] include an intramolecular Mannich reaction [5], an intramolecular ene reaction [6], acyliminium ions cyclization [15], spirofusion of tricarbonyl-1,3-cyclohexadiene iron [16], and also the metathesis reaction using Grubbs catalyst [10, 17]. The synthesis of seven-

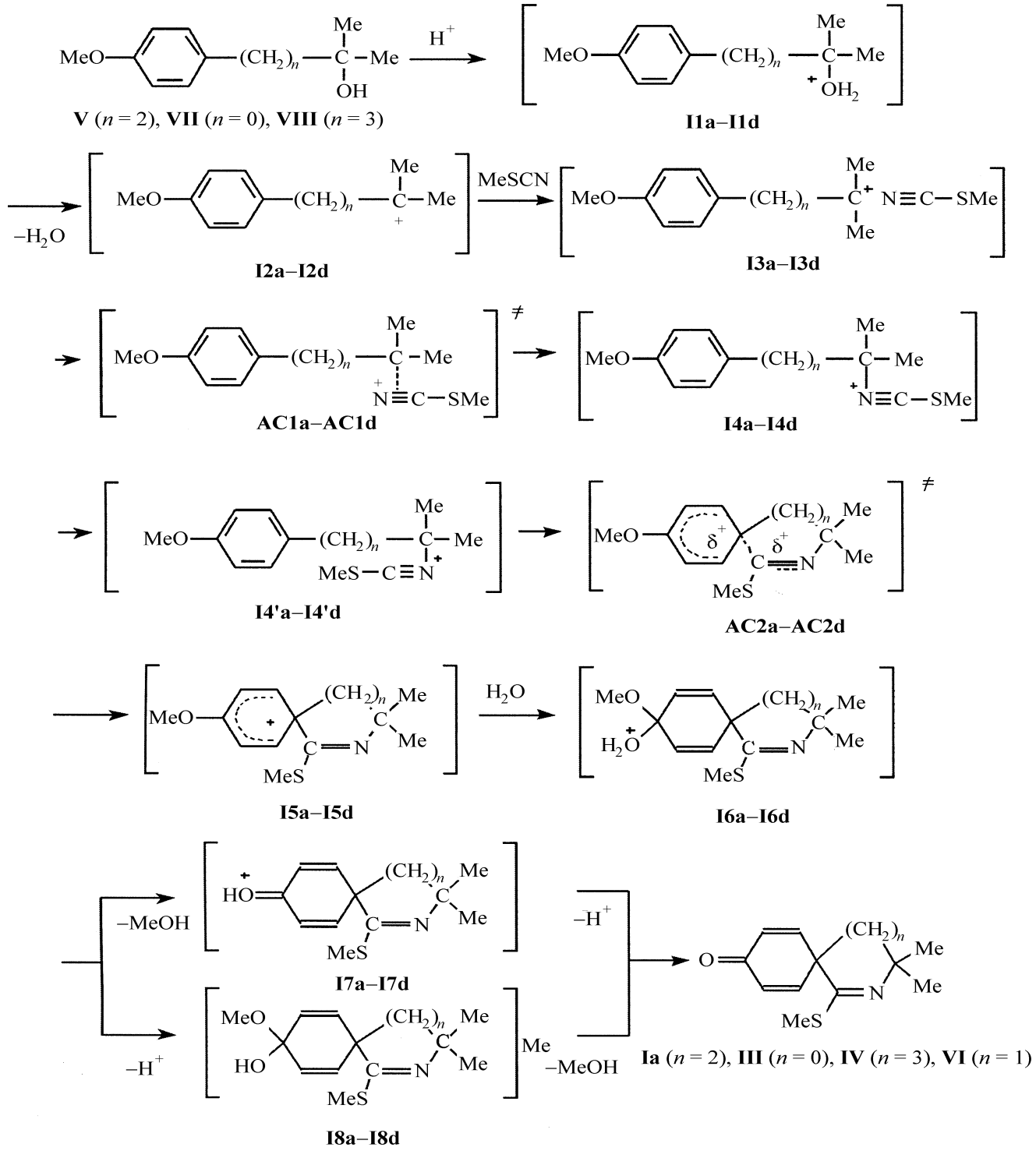
Scheme 1.



R = SMe (**a**), SCH_2Ph (**b**).

* For communication VII, see [1].

Scheme 2.



membered spirohexadienoazepines is also possible (a system of 2-azaspiro[6.5]dodecane) [10–13].

To synthesize 1-R-3,3-dimethyl-2-azaspiro[5.5]-undeca-1,7,10-triene-9-ones we carried out the Ritter reaction between 4-(*p*-methoxyphenyl)-2-methylbutan-2-ol and nitriles RCN in the presence of the concn. sulfuric acid (Scheme 1). In the case of R = SMe, SCH_2Ph, or CH_2COOEt we succeeded in preparation of spirocycliza-tion products, the corresponding 1-R-3,3-dimethyl-2-azaspiro[5.5]undeca-1,7,10-trien-9-ones **Ia**,

Enthalpy of formation ΔH_f (kJ mol^{-1}) of intermediates **I2-I8** and activated complexes **AC1, AC2** in spirocyclization reaction

n	I2	I3	AC1	I4	I4'	AC2	I5	I7	I8	Reaction product
0	623.7	689.5	672.9	708.5	–	931.6	900.0	–30.8	–	233.8
1	663.1	716.6	763.3	672.3	–	782.0	738.6	–188.4	724.4	64.8
2	639.9	690.2	736.2	651.8	643.5	755.1	695.5	–225.9	680.0	27.1
3	613.4	663.2	707.6	622.7	633.8	749.1	671.2	–220.7	651.4	26.0

Ib, and **II**, whereas at R = Me, Ph no spirocompounds formed under the same conditions. We formerly mentioned the favorable effect of alkylsulfanyl groups on the stability of spirocompounds **I** and **II** [18, 19].

In the ^{1}H NMR spectra of compounds **Ia** and **Ib** the protons at C^{8}H and C^{10}H give rise to doublets in the region 6.25–6.30 ppm (*J* 9.6 Hz). The signals of protons C^{7}H and C^{11}H appear as doublets in the region 6.8 ppm (7.2 ppm for compound **II**) with the same coupling constant. Compound **II** exists in an enamine form as proved by the olefin proton singlet at 4.20 ppm and the singlet of the NH group at 8.75 ppm. In the ^{13}C NMR spectra of compounds **Ia**, **Ib**, and **II** a signal from the spiro atom C^{6} is observed in the region δ 93–94 ppm.

We estimated the opportunity and limits of the spirocyclization under study by simulation of the formation of compound **Ia** and its four-membered (**III**, *n* = 0) and seven-membered (**IV**, *n* = 3) analogs. The probable path of 4-(*p*-methoxyphenyl)-2-methyl-2-butanol (**V**) transformation into 1-substituted 3,3-dimethyl-2-azaspiro[5.5]-undeca-1,7,10-trien-9-ones is presented in Scheme 2 by an example of compound **Ia**. The probability of the realization of the suggested scheme was evaluated by simulating separate stages of the process with the use of semiempirical method SCF MO LCAO in the AM1 approximation [20], and also by calculation of the enthalpy of formation (ΔH_f) for the possible intermediates and the preceding activated complexes. The calculated ΔH_f values are given in the table.

The reaction apparently starts by the protonation of the oxygen atom in alcohol **V** followed by water elimination from oxonium cation **I1c**. In the most stable conformation of alcohol **V** the carbon atoms of the main chain are located actually in the same plane, and the bonds C^{1}–C^{2} and C^{3}–C^{4} are directed *trans* with respect to the C^{2}–C^{3} bond.

The proton addition to the oxygen virtually does not affect the geometry of the main carbon–carbon chain, but the charge on the C^{2} atom grows from 0.076 to 0.116 a.u. The geometry of the main carbon chain also is not considerably affected in carbocation **I2c,** and the charge on the C^{2} becomes equal to 0.332 a.u. Just this electrophilic site of intermediate **I2c** is attacked by the nitrogen of the methyl thiocyanate molecule. We simulated this process by the reaction coordinate method selecting as the coordinate the interatomic distance $l_{C^2\ldots N}$. On the curve in the coordinates ΔH_f–$l_{C^2\ldots N}$ appeared two minima with characteristic interatomic distances $l_{C^2\ldots N}$ 2.943 and 1.451 Å, and a maximum ($l_{C^2\ldots N}$ 1.998 Å). The first minimum corresponds to ion-dipole complex **I3c** which governs the character of the reagents approach, and the second minimum is nitrilium cation **I4c**.

The maximum on the potential curve corresponds to activated complex **AC1c** that is the transition state of the reaction. The activation energy of nitrilium ion formation E_a was estimated from the difference ΔH_f(**AC1c**) – ΔH_f (**I1c**) at 46.0 kJ mol^{-1}.

The geometry of the main carbon chain is retained in going from intermediate **I3c** to intermediate **I4c**, the aromatic substituent in the latter is turned with respect to virtually planar main carbon chain through 70.1°, the spatial position of the nitrogen atom can be described with a dihedral angle $\Theta_{NC^2C^3C^4}$ 59.9°. The interatomic distance between the future reaction centers, the *sp*-hybridized carbon of the methyl thiocyanate fragment and C$^{1'}$ atom of the benzene ring, amounts to 5.070 Å. The direct approach of the reaction centers looks impossible for the *trans*-orientation of the bonds C^{1}–C^{2} and C^{3}–C^{4} with respect to the C^{2}–C^{3} bond is also conserved in intermediate **I4c**. Therefore we suggested that cation **I4c** could take a form more convenient for the electrophilic attack of the C$^{1'}$ atom by a rotation of fragments around the C^{2}–C^{3} bond. Actually, on the potential curve in the ΔH_f–$\Theta_{C^1C^2C^3C^4}$ coordinates a minimum was found at the dihedral angle value $\Theta_{C^1C^2C^3C^4}$ –68.6° corresponding to one more stable conformer of nitrilium cation **I4'c**. The transformation of nitrilium cation **I4c** into **I4'c** requires going over a low activation barrier (2.7 kJ mol^{-1}). The reaction centers in cation **I4'c** are at

a distance 3.533 Å. Their further approach results in the formation of a carbon-carbon bond in a cation of arenonium type **I5c**. According to calculations performed analogously the activation energy of the process equals 111.6 kJ mol^{-1}. The activation energy of the reverse process is 59.6 kJ mol^{-1}.

Arenonium cation **I5c** is likely attacked further by water, but we failed to detect oxonium cation **I6c** on the reaction coordinate. No minimum was found on the potential curve describing this process, and at the optimization of its geometry occurred "water ejection". The attack of $C^{4'}$ atom of the aromatic ring probably involves either a proton transfer to the oxygen of the methoxy group and methanol elimination leading to the formation of intermediate **I7c**, or a proton elimination giving rise to neutral intermediate **I8c**. The deprotonation of intermediate **I7c** or methanol ejection from intermediate **I8c** results in 2-azaspiro[5.5]-undeca-1,6,9-trien-8-one (**I**).

We believe that the scheme of compound **I** formation (**I5c** → **I7c** → **I**) is more reasonable since the water dissociation in the course of arenonium ion attack seems, firstly, unprobable (the reaction occurs in acid medium) and, secondly, the neutral intermediate is sufficiently stable as shows its ΔH_f value.

The calculations show, that the stage of the arenonium cation formation has the largest activation energy and thus controls the rate of the total process.

We performed further the simulation of formation of four-membered (**III**, $n = 0$) and seven-membered (**IV**, $n = 3$) compound **I** analogs. We performed by analogous procedure a parallel calculation of the formation path for 3,3-dimethyl-1-methylsulfanyl-2-azaspiro[4.5]-deca-1,6,9-trien-8-one (**VI**), which we had synthesized before [2, 3, 21].

The calculation shows that the activation parameters of formation of nitrilium cation **I4'b** are virtually similar to those for the above discussed reaction: the calculated activation energy E_a is 46.7 kJ mol^{-1}. However the position of the reaction centers in the cation (interatomic distance 3.568 Å) made possible its direct transformation into arenonium cation **I5b**. The calculated value of E_a was 109.7 kJ mol^{-1} also close to the corresponding value for cation **I5c**. The activation energy of the reverse process turned out to be 43.4 kJ mol^{1}.

The protonation of 2-methyl-2-(*p*-methoxyphenyl)-2-propanol (**VII**), a presumable initial compound for the synthesis of hypothetical 2-azaspiro[3.5]nona-1,5,8-trien-7-one (**III**), and water elimination from oxonium cation **I1a** should lead to the formation of a benzyl type cation **I1a**, which is more efficiently stabilized by the presence of the electron-donor *p*-methoxyphenyl group. It is evidenced partly by a smaller positive charge on the C^2 atom (0.225 a.u.) and shorter bond MeO–$C^{4'}$ compared with cations **I1b** and **I1c**. Apparently due to this stabilization the reactivity of cation **I1a** with respect to methyl thiocyanate is reduced, and the calculated activation energy of formation for nitrilium cation **I2a** rises to 73.4 kJ mol^{-1}. The spatial arrangement of the reaction centers in this species (interatomic distance 2.635 Å) should not in principle hamper the *ipso*-attack, but the higher calculated activation energy of formation of cation **I5a** equal to 223.0 kJ mol^{-1} suggests that this process is considerably less probable than those already discussed. Arenonium type cation **I5a** is characterized by a high positive value of the enthalpy of formation and a too long C^3–C^4 bond (1.681 Å) evidencing its possible instability. The activation barrier to the reverse process **I5a** → **AC2a** equal 31.6 kJ mol^{-1}, considerably lower than for the similar reactions at $n = 1, 2$. Therefore intermediate **I5a** should form with greater difficulty but easier transforms into the initial nitrilium cation. Intermediate **I7a** apparently does not exist: the attempts at optimization of its geometry resulted in the cleavage of the C^3–C^4 bond and to formation of methylsulfanyl-*p*-methoxyphenyl(2-propylidene)-aminomethyl cation. Thus the synthesis of 1-methylthio-2-azaspiro[3.5]nona-1,5,8-trien-7-one (**III**) by the above described procedure is most unlikely.

To obtain 3,3-dimethyl-1-methylsulfanyl-2-azaspiro-[6.5]dodeca-1,8,10-trien-9-one (**IV**) 2-methyl-5-(*p*-methoxyphenyl)-2-pentanol (**VIII**) can be used as a source of a carbocation of **I1d** type. The calculations suggest that the carbon atoms of the main carbon chain in this molecule are also located practically in one plane. The bonds C^1–C^2, C^3–C^4, and $C^{1'}$–C^5 are *trans*-oriented relative to C^2–C^3 and C^4–C^5 respectively. The geometry of the main chain is retained in going to carbocation **I2d** and nitrilium cation **I4'd**. The distance between the reaction centers in the latter is 5.081 Å. The calculated activation energy of formation of nitrilium cation **I4d** from carbocation **I3d** and methyl isocyanate equals 44.4 kJ mol^{-1}. Cation **I4d** can transform into **I4'd** by the rotation of fragments around C^3–C^4 and C^4–C^5 bonds; the distance between the reaction centers in the latter is smaller (3.098 Å). Unlike the previously considered cases cation **I4'd** proved to be less stable than cation **I4d** (the difference in the enthalpy of formation was 11.1 kJ mol^{-1}).

Consequently the activation barrier to the conversion of these cataions cannot be less than this value which is obviously larger than the activation barrier to the transition **I4c → I4'c**. The calculated value of the activation energy for reaction **I4'd → I5d** amounts to 115.3 kJ mol^{-1}, also exceeding the E_a values for the really occurring reactions.

Thus the conversion of compound **VIII** into 3,3-dimethyl-1-methylsulfanyl-2-azaspiro[6.5]dodeca-1,8,10-trien-9-one (**IV**), is apparently less probable due to the high activation barrier to the transformation of a nitrilium cation into arenonium type cation. However the nitrilium cation whose energy cosumption at the formation is comparable with those of cations **I2b, I2c** can participate in the other processes, for instance, in the classical Ritter reaction.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer UR-20 from mulls in mineral oil. ^{1}H NMR spectra were registered at 30°C on a spectrometer Bruker DRX-500 (500 MHz) in DMSO-d_6, internal reference HMDS. ^{13}C NMR spectra were registered on a spectrometer Varian Mercury Plus at 75 MHz. Mass spectrum of compound **I** (electron impact, 70 eV) was measured on Finnigan MAT instrument. The reaction progress was monitored and the purity of compounds obtained was checked by TLC on Silufol plates in the system chloroform–acetone, 9:1, development with 1% chloranil solution in toluene. 3-(*p*-Methoxyphenyl)propionic acid was a commercial product. Its methyl ester was prepared by a standard procedure by treating the acid with methanol in the presence of sulfuric acid, mp 36–38°C (from hexane) (publ.: mp 38°C [22]). 4-(*p*-Methoxyphenyl)-2-methylbutan-2-ol (**V**) was obtained by reaction of methyl 3-(*p*-methoxyphenyl)propionate with excess methylmagnesium iodide in ether, yield 82%, mp 35–36°C (from a mixture ethanol–water), {publ.: bp. 133°C (2 mm Hg) [23]}. Quantum-chemical calculations were performed with the use of MOPAC 7.0 software[24] on PC Pentium IV. The transition states were localized using algorithm NLLSQ. The validity of localization of each transition state was proved by a single negative eigenvalue of the Hesse matrix.

3,3-Dimethyl-1-methylsulfanyl-2-azaspiro-[5.5]-undeca-1,7,10-trien-9-one (**Ia**). A solution of 3.02 g (15.6 mmol) of 4-(*p*-methoxyphenyl)-2-methylbutan-2-ol (**V**) and 1.1 ml (15.6 mmol) of methyl thiocyanate in 40 ml of dichloromethane was added dropwise at vigorous stirring to 4 ml of concn. sulfuric acid (at cooling with a water bath). The reaction mixture was stirred for 30 min and poured into 200 ml of cold water. The organic layer was separated, the water layer was extracted with dichloromethane (50 ml). The combined organic solutions were washed with a saturated NaCl solution and dried with $MgSO_4$. On evaporating the solvent the residue was recrystallized from ethanol. Yield 0.79 g (26%), colorless crystals, mp 84–85°C. IR spectrum, cm^{-1}: 1665 (C=O), 1630 (C=N), 1610 (C=C), 1260, 1235, 1220. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 1.20 s (6H, 2Me), 1.67 m (2H, C^4H_2), 1.84 m (2H, C^5H_2), 2.13 C (3H, SMe), 6.31 d (2H, H^8, H^{10}, J 9.9 Hz), 6.78 d (2H, H^7, H^{11}, J 9.9 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 182.5 (C=O), 155.4 (C=N), 149.1 (C^7, C^{11}), 127.1 (C^8, C^{10}), 93.5 (C^6), 54.3 (C^5), 45.5 (C^3), 28.3* (C^4), 28.2* (CH_3), 27.3* (CH_3), 9.8 (SCH_3). Mass spectrum, *m/z* (I_{rel}, %): $[M]^+$ 235 (4), 162 (43), 147 (52), 120 (19), 107 (100), 91 (20). Found, %: C 66.23; H 7.36; N 5.76. $C_{13}H_{17}NOS$. Calculated, %: C 66.35; H 7.38; N 5.95.

1-Benzylsulfanyl-3,3-dimethyl-2-azaspiro-[5.5]-undeca-1,7,10-trien-9-one (**Ib**). A solution of 3.74 g (19.3 mmol) of carbinol **V** and 2.88 g (15.6 mmol) of benzyl thiocyanate in 40 ml of toluene was added dropwise at vigorous stirring to 6 ml of concn. sulfuric acid (at cooling with a water bath). The reaction mixture was stirred for 30 min and poured on a mixture of 100 ml of ice, 25 ml of 25% NH_4OH, and 25 ml of saturated NaCl solution. The water layer was separated and extracted with toluene (50 ml). The combined organic solutions were washed with a saturated NaCl solution and dried with $MgSO_4$. On evaporating the solvent the residue was twice re-crystallized from hexane. Yield 2.65 g (71%), colorless crystals, mp 122–124°C. IR spectrum, cm^{-1}: 1660 (C=O), 1625 (C=C), 1600 (C=C), 1260, 1240, 1220, 1185, 1135, 1095, 1070, 1045 w, 1030, 990, 970 s, 930, 895, 860 s, 810. ^{1}H NMR spectrum (300 MHz, $CDCl_3$), δ, ppm: 1.23 s (6H, 2Me), 1.65 m (2H, C^4H_2), 1.82 m (2H, C^5H_2), 4.00 s (3H, SCH_3), 6.28 d (2H, H^8, H^{10}), 6.75 d (2H, H^7, H^{11}), 7.16 m (5H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 182.4 (C=O), 154.6 (C=N), 148.8 (C^7, C^{11}), 136.2 ($C^{1'}$), 127.3 ($C^{2'}$, $C^{6'}$), 126.9 ($C^{3'}$, $C^{5'}$), 126.1 (C^8, C^{10}), 124.7 ($C^{4'}$), 93.5 (C^6), 54.6 (C^5), 45.4 (C^3), 30.3 (C^4), 28.2* (SCH_2), 28.1* (CH_3), 27.3* (CH_3). Found, %: C 73.19; H 6.85; N 4.37. $C_{19}H_{21}NOS$. Calculated, %: C 73.27; H 6.80; N 4.50.

3,3-Dimethyl-1-ethoxycarbonylmethylene-2-azaspiro[5.5]undeca-7,10-dien-9-one (II) was prepared

* The precise assignment of these signals was not performed.

similarly to compound **Ib** from 3.74 g (19.3 mmol) of carbinol **V**, 2.1 ml (2.23 g, 19.5 mol) of ethyl cyanoacetate, and 60 ml of dichloromethane in the presence of 5 ml of concn. sulfuric acid. Yield 0.6 g (16%), colorless crystals, mp 113–115°C. IR spectrum, cm^{-1}: 3250 br (NH), 1640 br (O–C=O and C=O), 1605 (C=C), 1280, 1215. ^1H NMR spectrum, δ, ppm: 1.12 t (3H, CH_3), 1.31 s (6H, 2Me), 1.85 m (2H, C^4H_2), 1.91 m (2H, C^5H_2), 3.95 q (2H, OCH_2), 4.13 s (1H, CH=), 6.20 d (2H, H^8, H^{10}), 7.19 d (2H, H^7, H^{11}), 8.74 C (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 183.2 (C=O), 168.6 (O–C=O), 156.3 (C^1), 149.1 (C^7, C^{11}), 126.3 (C^8, C^{10}), 94.2 (C^6), 80.7 (–HC=), 56.8 (OCH_2), 49.2 (C^3), 41.7 (C^5), 30.4 (C^4), 28.9 (CH_3), 27.6 (CH_3), 12.5 ($CH_2\underline{C}H_3$). Found, %: C 70.03; H 7.55; N 5.18. $C_{16}H_{21}NO_3$. Calculated, %: C 69.79; H 7.69; N 5.09.

The study was carried out under a financial support by the Russian Foundation for Basic Research (grant Ural 04-03-96045), and by a grant of the Presidium of the Russian Academy of Sciences "Purposeful synthesis of substances with desired properties, and creation of functional materials thereof".

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