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Reactions of Substituted 2,3,7-Triazabicyclo[3.3.0]oct-2-enes and 1,2,7-Triazaspiro[4.4]non-1-enes with Halogens

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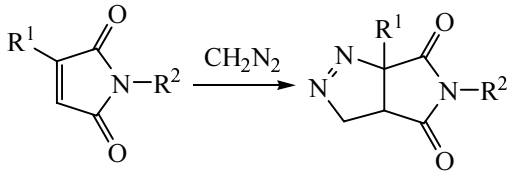
Abstract—Halogenation of 1-substituted 7-aryl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-diones gives different products, depending on the substituent in position *1* (R^1): when R^1 = Ar, 6-chloro-3-azabicyclo[3.1.0]hexanes are formed, while compounds with R^1 = H or Me give rise to 2- or 4-chloro-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-diones whose thermolysis leads to formation of the corresponding 6-chloro-3-azabicyclo[3.1.0]hexanes. Chlorination of 7-aryl-1,2,7-triazaspiro[4.4]non-1-ene-6,8-diones yields 3-chloro-1,2,7-triazaspiro[4.4]non-1-ene-6,8-diones, and thermolysis of the latter affords 1-chloro-5-azaspiro[2.4]heptanes.

We previously showed that esters derived from substituted 6,8-dioxo-2,3,7-triazabicyclo[3.3.0]oct-3-ene-4-carboxylic, 6,8-dioxo-1,2,7-triazaspiro[4.4]non-2-ene-3-carboxylic, and 4,5-dihydro-1*H*-pyrazole-3,5,5-tricarboxylic acids react with halogens (Cl_2, Br_2) or halogenating agents (*N*-iodosuccinimide, iodine–silver trifluoroacetate, *N*-fluoropyridinium tetrafluoroborate) to give1-halo-1-cyclopropanecarboxylic acid esters [1–7].

In the present work we examined reactions of substituted 2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-diones **IIa**–**IIg** and 1,2,7-triazaspiro[4.4]non-1-ene-6,8-diones **IVa**–**IVj** with halogens (Cl_2, Br_2) and *N*-iodosuccinimide. Bicyclic compounds **IIa**–**IIg** were synthesized by the action of diazomethane on maleic, citraconic, and arylmaleic acid imides (Scheme 1). Compounds **IIa**–**IIc** with no substituent in position *1* were reported previously; however, their spectral parameters were not given, and they were assigned different structures [8–10]. The ^{1}H NMR spectra of **IIa**–**IIc** contain signals from protons on C^1 and C^5 at δ 6.0 (d, *J* = 9 Hz) and 3.5 ppm (m), respectively, methylene protons on C^4 at δ 5.0 ppm (m), and aromatic protons. In the ^{13}C NMR spectrum of **IIa**, the C^1 signal is located at δ_C 94.9 ppm, and the C^4 signal appears at δ_C 80.8 ppm. Compounds **IId**–**IIg** showed in the ^{1}H NMR spectra an intricate signal from the methylene group (C^4H_2) at δ 5.0 ppm and a signal from the 5-H proton at δ, ppm: **IId**, **IIe**: 3.2 d.d (*J* = 8, 4 Hz); **IIe**, **IIg**: 3.9 d.d (*J* = 9, 3 Hz); these data are consistent with the assumed structures. We can conclude that diazomethane adds to citraconic and arylmaleic acid imides in a regioselective fashion, yielding fused 4,5-dihydro-3*H*-pyrazole derivatives **IId**–**IIg**, regardless of the R^1 substituent.

Spirocyclic compounds **IVa**–**IVj** were obtained by reaction of diazomethane with itaconic acid imides **IIIa**–**IIIj** (Scheme 2). The addition of diazomethane to imides **IIIa**–**IIIj** was also regioselective, and the products were

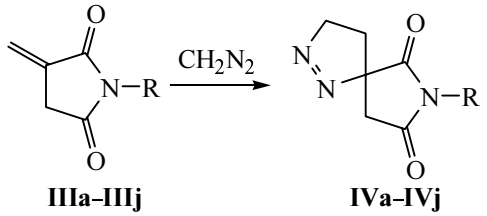
Scheme 1.



Ia–**Ig** **IIa**–**IIg**

R^1 = H, R^2 = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOCOC_6H_4$ (**c**); R^1 = Me, R^2 = 4-BrC_6H_4 (**d**), 4-MeC_6H_4 (**e**); R^1 = 4-ClC_6H_4, R^2 = 4-MeC_6H_4 (**f**); R^1 = 4-MeC_6H_4, R^2 = 4-ClC_6H_4 (**g**).

Scheme 2.



IIIa–**IIIj** **IVa**–**IVj**

R = Ph (**a**), 4-MeC_6H_4 (**b**), 3-Cl-4-MeC_6H_3 (**c**), 4-ClC_6H_4 (**d**), 4-BrC_6H_4 (**e**), 4-FC_6H_4 (**f**), 3,4-$Me_2C_6H_3$ (**g**), 3,5-$Cl_2C_6H_3$ (**h**), 4-$EtOC_6H_4$ (**i**), 3-ClC_6H_4 (**j**).

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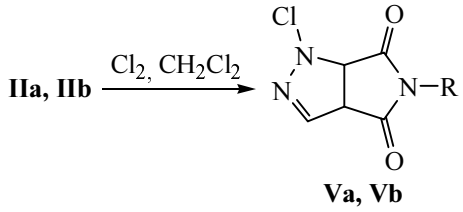
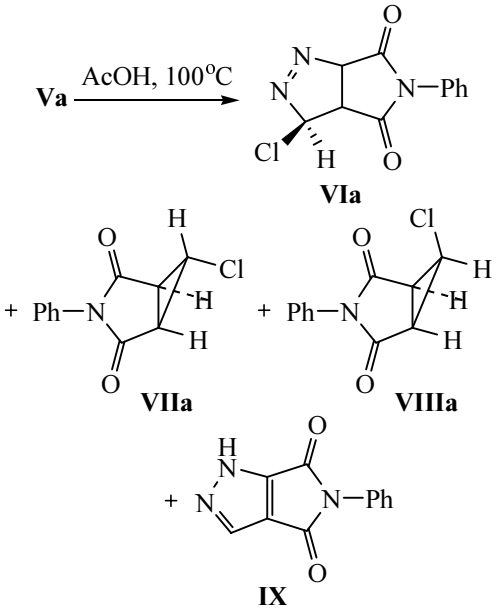
Scheme 3.



IIa, IIb → **Va, Vb**

R = Ph (**a**), 4-ClC_6H_4 (**b**).

Scheme 4.



Va → **VIa**; + **VIIa**; + **VIIIa**; + **IX**

VI–**VIII**, R^1 = Me, R^2 = 4-BrC_6H_4 (**b**), 4-MeC_6H_4 (**c**); **X**, R^1 = 4-ClC_6H_4, R^2 = 4-MeC_6H_4 (**a**); R^1 = 4-MeC_6H_4, R^2 = 4-ClC_6H_4 (**b**).

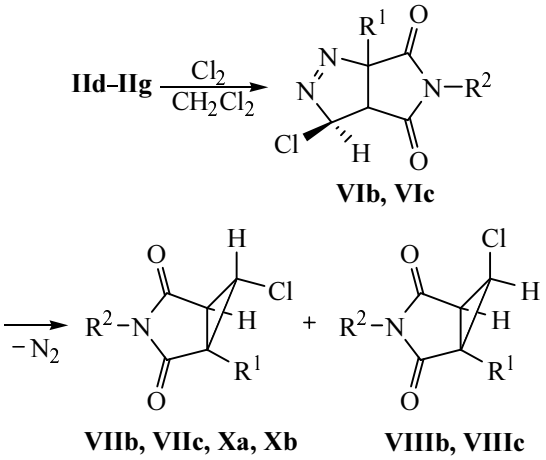
1,2,7-triazaspiro[4.4]non-1-ene-6,8-diones **IVa**–**IVj**. The ^{1}H NMR spectra of **IVa**–**IVj** contain signals from methylene protons in the dihydropyrazole ring [δ, ppm: 1.7 m (1H) and 2.5 m (1H, C^4H_2), 4.9 m (2H, C^3H_2)] and doublet signals from methylene protons in the pyrrolidine ring [δ, ppm: 2.9 (1H, J = 18 Hz) and 3.5 (1H, J = 18 Hz)]. The C^5 signal in the ^{13}C NMR spectrum of **IVa** is observed at δ_C 94 ppm, and the C^3 signal is located about δ_C 80 ppm.

The reaction of bicyclic compounds **IIa** and **IIb** with chlorine in methylene chloride at room temperature gave 7-aryl-2-chloro-2,3,7-triazabicyclo[3.3.0]oct-3-ene-6,8-diones **Va** and **Vb** in up to 67% yield (Scheme 3). Compounds **Va** and **Vb** showed in the ^{1}H NMR spectra signals from protons in the bridgehead positions [δ, ppm: 4.55 d.d (J = 10, 2 Hz), 4.73 d (J = 10 Hz)] and 4-H [δ, ppm: 6.86 d (J = 2 Hz)].

By heating compound **Va** in acetic acid at 100°C we obtained a complex mixture of products which were separated by column chromatography. As a result, we isolated compound **VIa** (6%), isomeric fused chlorocyclopropane derivatives **VIIa** (9%) and **VIIIa** (11%), and pyrrolopyrazole **IX** (10%) (Scheme 4). The structure of compounds **VIa**–**VIIIa** was confirmed by their spectral data. The ^{1}H NMR spectrum of **VIa** contains signals from protons in the bridgehead positions at δ 3.81 (d.d, 5-H, J = 8, 2 Hz) and 6.43 ppm (d.d 1-H, J = 8, 1.5 Hz) and from 4-H at δ 6.83 ppm (t, J = 2 Hz). The coupling constant between 4-H and 5-H (2 Hz) indicates their *trans* orientation with respect to each other, i.e., compound **VIa** has *exo* configuration. In the ^{13}C NMR spectrum of **VIa**, signals from C^1 and C^4 were located at δ_C 93.2 and 95.1 ppm, respectively, in keeping with the proposed structure. The ^{1}H NMR spectra of isomeric cyclopropane derivatives **VIIa** and **VIIIa** contain signals from protons in the three-membered ring at δ, ppm: **VIIa**: 2.69 d (2H, J = 2 Hz), 3.71 t (1H, J = 2 Hz); **VIIIa**: 2.53 d (2H, J = 8 Hz), 3.46 t (1H, J = 8 Hz). The formation of pyrrolopyrazole **IX** in the reaction of fused dihydropyrazole with bromine was described previously [8]. The physical constants and spectral parameters of compound **IX** obtained from **Va** coincided with published data.

In the chlorination of compounds **II** having a substituent (R^1) in position *1*, intermediate *N*-chloro derivative could not be isolated, while the product structure depends on the nature of R^1. From compounds **IId** and **IIe** (R^1 = Me) we isolated 4-chloro derivatives **VIb** and **VIc** in up to 87% yield. In the ^{1}H NMR spectra of **IId** and **IIe**, the coupling constant between 4-H (δ 6.6 ppm) and 5-H (δ 3.3 ppm) is 1.5 Hz, indicating *trans* orientation of these

Scheme 5.



IId–IIg → **VIb, VIc**; → **VIIb, VIIc, Xa, Xb** + **VIIIb, VIIIc**

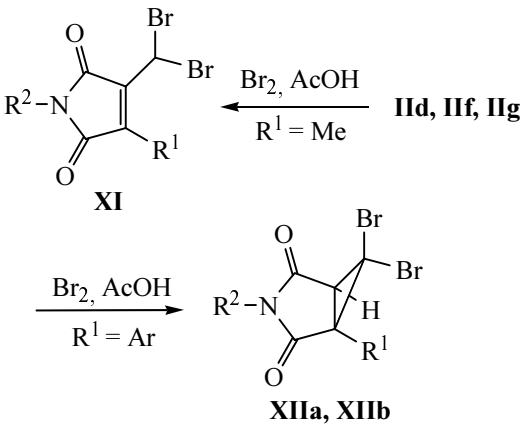
protons with respect to each other and hence *exo* orientation of the chlorine atom. Thermolysis of compounds **VIb** and **VIc** is not selective. As a result, 2 : 1 mixtures of isomeric chlorocyclopropanes **VIIb**/**VIIIb** and **VIIc**/**VIIIc** were obtained (Scheme 5). In the ^{1}H NMR spectra of these mixtures we observed doublet signals from the cyclopropane ring protons at δ 2.57 and 3.70 ppm (J = 1.5 Hz) for *exo* isomers **VIIb** and **VIIc** and at δ 2.80 and 3.81 ppm (J = 8 Hz) for *endo* isomers **VIIIb** and **VIIIc**. The chlorination of 1-aryl derivatives **IIf** and **IIg** afforded exclusively *exo*-chlorocyclopropanes **Xa** and **Xb** in up to 91% yield. Initially formed 4-chloro derivative is unstable and it readily loses nitrogen molecule to give compound **X**. The ^{1}H NMR spectra of **Xa** and **Xb** contain a doublet signal from the cyclopropane ring proton at δ 3.18 and 3.99 ppm (J = 2 Hz), respectively.

As noted above, the reaction of fused dihydropyrazole **IIa** with bromine yields only the corresponding fused pyrazole derivative. We expected that the presence of a substituent at the bridgehead carbon atom should change the reaction direction so that fused cyclopropane system should be formed. However, the bromination of compound **IId** (R^1 = Me) resulted in formation of a complex mixture of products. By column chromatography we succeeded in isolating only substituted maleimide **XI** in 31% yield. Bromo-substituted cyclopropane derivatives **XIIa** and **XIIb** were obtained only from compounds **IIf** and **IIg** (R^1 = Ar) in up to 68% yield (Scheme 6).

The structure of compounds **XI**, **XIIa**, and **XIIb** was determined on the basis of their spectral and analytical data. In the ^{1}H NMR spectra of dibromocyclopropanes **XIIa** and **XIIb** we observed a signal at δ 3.6 ppm due to proton on C^5; protons of the methyl group in **XI** gave a signal at δ 2.2 ppm, indicating that the methyl group is located at the double bond; the signal from the dibromomethyl group appears in a weak field, at δ 5.12 ppm.

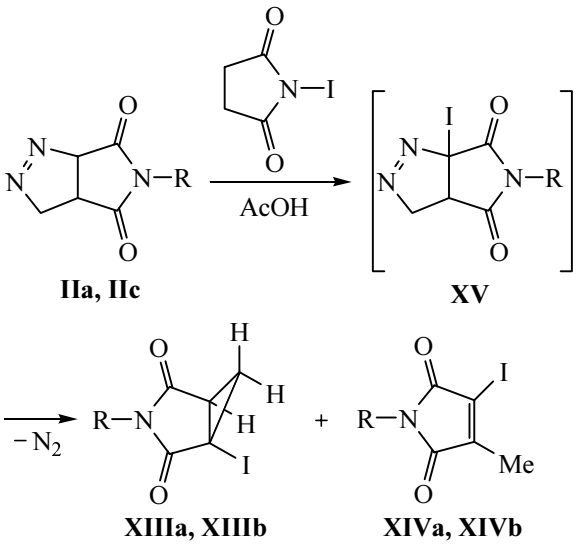
Compounds **II** reacted with *N*-iodosuccinimide much more difficultly, and we succeeded in obtaining iodine-containing products only from derivatives with no substituent in position *1*. In reactions with compounds **II** substituted at the bridgehead position, only decomposition products were detected. The reactions of fused dihydropyrazoles **IIa** and **IIc** with *N*-iodosuccinimide in acetic acid at 110°C were accompanied by strong tarring, and the products were 1-iodo-3-azabicyclo[3.1.0]hexane-2,4-diones **XIIIa** and **XIIIb** and iodinated imides **XIVa** and **XIVb** (yield 13 and 9%, respectively; Scheme 7). The structure of compounds **XIII** and **XIV** was confirmed

Scheme 6.



XI, R^1 = Me, R^2 = 4-BrC_6H_4; **XII**, R^1 = 4-ClC_6H_4, R^2 = 4-MeC_6H_4 (**a**); R^1 = 4-MeC_6H_4, R^2 = 4-ClC_6H_4 (**b**).

Scheme 7.

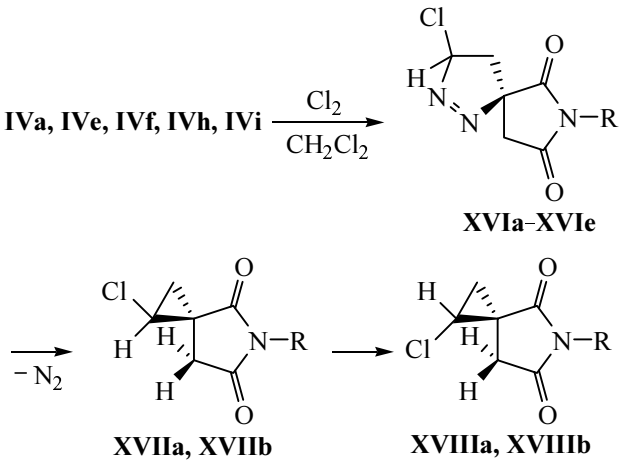


R = Ph (**a**), 4-$MeOCOC_6H_4$ (**b**).

by spectral and analytical data. Protons in the three-membered ring of compounds **XIIIa** and **XIIIb** appeared in their ^{1}H NMR spectra at δ 2.0 (d.d, J = 8, 3 Hz), 2.1 (t, J = 3 Hz), and 2.8 ppm (d.d, J = 8, 3 Hz); also, signals from aromatic protons were present. Presumably, the mechanism of formation of compounds **XIII** and **XIV** involves initial electrophilic iodination at position *1* to give iodo derivative **XV** which is converted into final products **XIII** and **XIV** via elimination of nitrogen molecule (Scheme 7).

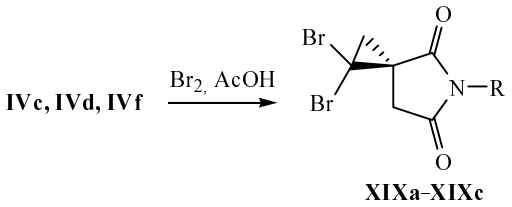
Spiro compounds **IVa**, **IVe**, **IVf**, **IVh**, and **IVi** reacted with chlorine in methylene chloride at room temperature to afford in high yields substituted 3-chloro-1,2,7-

Scheme 8.



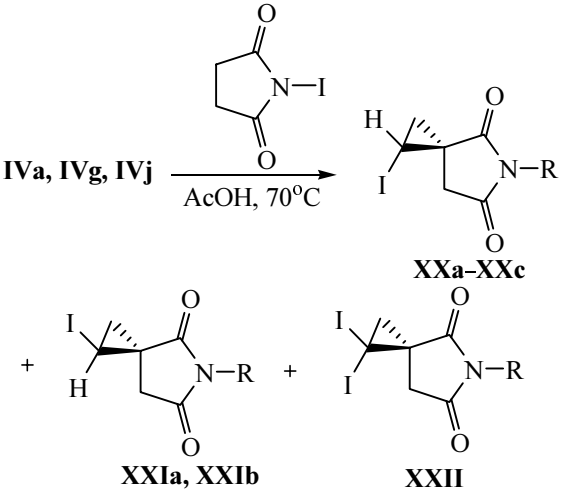
XVI, R = Ph (**a**), 3,5-$Cl_2C_6H_3$ (**b**), 3-Cl-4-$EtOC_6H_3$ (**c**), 4-FC_6H_4 (**d**), 4-BrC_6H_4 (**e**); **XVII**, **XVIII**, R = Ph (**a**), 3-Cl-4-$EtOC_6H_3$ (**b**).

Scheme 9.



R = 4-ClC_6H_4 (**a**), 3-Cl-4-MeC_6H_4 (**b**), 4-FC_6H_4 (**c**).

Scheme 10.



XX, R = Ph (**a**), 3,4-$Me_2C_6H_3$ (**b**), 3-ClC_6H_4 (**c**); **XXI**, R = Ph (**a**), 3,4-$Me_2C_6H_3$ (**b**); **XXII**, R = 3-ClC_6H_4.

triazaspiro[4.4]non-1-ene-6,8-diones **XVIa**–**XVIe** as *anti* isomers (Scheme 8). The ^{1}H NMR spectra of **XVIa**–**XVIe** contain signals from protons in the dihydropyrazole ring as doublets of doublets at δ 1.9 (J = 14, 6 Hz) and 3.0 ppm (J = 14, 7 Hz) (C^4H_2) and at δ 6.4 ppm (J = 6, 7 Hz); protons of the methylene group in the pyrrolidine ring give rise to two doublets at δ 3.1 and 3.6 ppm (J = 18 Hz). In the ^{13}C NMR spectrum of **XVIa**, signals from the C^3 and C^5 are located at δ_C 93.7 and 95.2 ppm, respectively. The reaction of **IVi** with chlorine was accompanied by chlorination of the aromatic ring with formation of compound **XVIc**.

On heating at 130–140°C under reduced pressure, compounds **XVIa** and **XVIc** lose nitrogen molecule, thus being converted into 1-chloro-5-azaspiro[2.4]heptane-4,6-diones as mixtures of *anti* (**XVIIa**, **XVIIb**) and *syn* isomers (**XVIIIa**, **XVIIIb**) in an overall yield of up to 96% [ratio (1.6–2.1) : 1; Scheme 8]. Their ^{1}H NMR spectra contain signals from protons in the cyclopropane ring [δ, ppm: *anti* isomers **XVIIa** and **XVIIb**: 1.4 t (J = 6 Hz), 2.0 d.d (J = 6, 1.5 Hz), 3.5 d.d (J = 6, 1.5 Hz); *syn* isomers **XVIIa** and **XVIIb**: 1.7 t (J = 7 Hz), 2.1 d.d (J = 7, 2.5 Hz), 3.7 d.d (J = 7, 2.5 Hz)] and methylene protons in the pyrrolidine ring [a singlet at δ 2.9 ppm for the *anti* isomers and two doublets at δ 2.9 and 3.2 ppm (J = 19 Hz) for the *syn* isomers]. In the spectra of *syn* isomers **XVIIIa** and **XVIIIb**, signal from one proton on C^7 is displaced downfield due to deshielding effect of the chlorine atom. We failed to separate isomeric products **XVII** and **XVIII**.

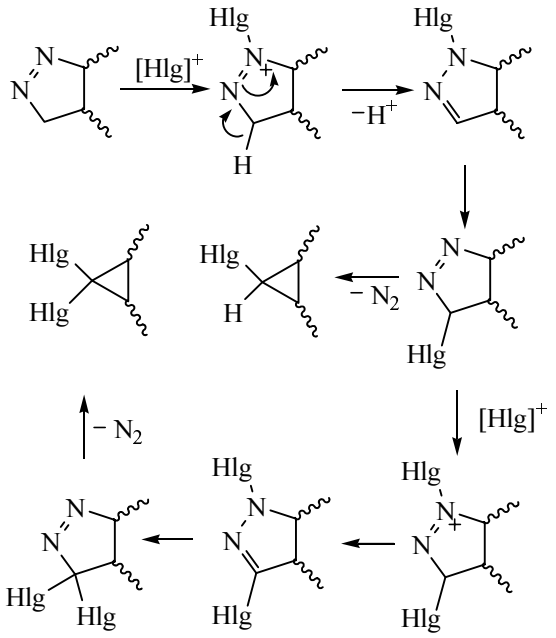
The bromination of compounds **IVc**, **IVd**, and **IVf** with bromine in acetic acid at 70°C led to formation of a complex mixture of products, from which we isolated only 5-aryl-1,1-dibromo-5-azaspiro[2.4]heptane-4,6-diones **XIXa**–**XIXc** in 18–22% yield (Scheme 9). Compounds **XIXa**–**XIXc** showed in the IR spectra an absorption band at 1720 cm^{-1}, which corresponds to stretching vibrations of the carbonyl groups. Their ^{1}H NMR spectra contained doublet signals from the methylene protons in the three-membered ring at δ 2.2 and 2.7 ppm (J = 8 Hz) and signals from the methylene protons in the pyrrolidine ring at δ 3.0 and 3.5 ppm (J = 19 Hz).

Compounds **IVa**, **IVg**, and **IVj** reacted with *N*-iodosuccinimide in acetic acid at 70°C to give a mixture of products. The mixture was subjected to column chromatography to isolate 1-iodo-5-azaspiro[2.4]heptane-4,6-diones as mixtures of *syn* (**XXa**–**XXc**) and *anti* isomers (**XXIa**, **XXIb**) in 35–42 and 16–19% yield, respectively. No corresponding *syn*-isomeric product was isolated in the reaction with compound **IVj**; in this case, the minor product was 5-(3-chlorophenyl)-1,1-diiodo-5-azaspiro[2.4]heptane-4,6-dione (**XXII**; yield 7%). No

transformation products were detected in the reaction of compounds **IVa**, **IVg**, and **IVj** with *N*-iodosuccinimide in chloroform at 60°C. However, compound **IVa** reacted with the system iodine–silver trifluoroacetate in dichloroethane at 80°C to give isomeric iodocyclopropane derivatives **XXa** and **XXIa** in poor yields (9 and 13%, respectively), the substrate conversion being 38% (Scheme 10). In the ^{1}H NMR spectra of compounds **XX** and **XXI**, signals from protons in the cyclopropane ring appeared as δ, ppm: *syn* isomers **XXa**–**XXc**: 1.4 t (J = 6 Hz), 2.4 d.d (J = 6, 3 Hz), 3.4 d.d (J = 6, 3 Hz); *anti* isomers **XXIa** and **XXIb**: 1.9 m (2H), 3.0 t (J = 7 Hz). The 1-H signal in the spectra of the *anti* isomers is located in a stronger field (δ 3.0 ppm) relative to the corresponding signal of the *syn* isomers (δ 3.4 ppm) due to shielding by the methylene group in the pyrrolidine ring. The C^1 signal in the ^{13}C NMR spectra of **XXa**–**XXc**, **XXIa**, and **XXIb** is displaced strongly upfield: it is located at δ_C –4.4 (**XXa**–**XXc**) or –8.8 ppm (**XXIa**, **XXIb**) due to strong shielding effect of heavy iodine atom. The ^{1}H NMR spectrum of geminal diiodocyclopropane derivative **XXII** contains doublet signals from the cyclopropane methylene protons at δ 2.4 and 2.8 ppm (J = 8 Hz) and doublets at δ 3.0 and 3.3 ppm (J = 9 Hz), which belong to methylene protons in the pyrrolidine ring.

Presumably, the formation of cyclopropane derivatives from fused or spirobicyclic 4,5-dihydro-3*H*-pyrazoles involves initial electrophilic attack on one of the N=N nitrogen atoms to give dihydropyrazolium ion. Proton abstraction from the latter yields the corresponding 1-halo-4,5-dihydro-1*H*-pyrazole which undergoes isomerization into 3-halo-4,5-dihydro-3*H*-pyrazole, followed by elimination of nitrogen molecule. Geminal dihalocyclopropanes are likely to be formed in two consecutive steps (Scheme 11).

Scheme 11.



EXPERIMENTAL

The elemental compositions were determined on a Hewlett–Packard 185B CHN analyzer. The melting points were determined on a Boetius device. The IR spectra were recorded on a UR-20 spectrophotometer from 2% solutions in chloroform. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-300 instrument (300.13 MHz for ^{1}H) from 2% solutions in $CDCl_3$ or DMSO-d_6. The UV spectra were measured on a Specord UV-Vis spectrophotometer from (0.2–1.4) × 10^{-4} M solutions in dichloroethane. The purity of compounds was checked, and the progress of reactions was monitored, by thin-layer chromatography on Silufol UV-254 plates. Column chromatography was performed on silica gel L (100–160 and 40–100 μm).

Maleic acid imides [11], arylmaleic anhydrides [12], itaconic anhydride [13], *N*-arylitaconimides [14], and *N*-arylcitraconimides [9] were synthesized by known methods.

1-Substituted 7-aryl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-diones IId–IIg. A solution of diazomethane in diethyl ether was added to a solution of the corresponding substituted citraconic or arylmaleic acid imide in methylene chloride. The mixture was kept for 2 h at room temperature and evaporated, and the residue was washed with diethyl ether.

7-(4-Bromophenyl)-1-methyl-2,3,7-triazabicyclo-[3.3.0]oct-2-ene-6,8-dione (IId) was synthesized from 0.5 g (2.5 mmol) of imide **Id**. Yield 0.56 g (93%), mp 191–193°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.68 s (3H, CH_3), 3.25 d.d (1H, CH, J = 8, 4 Hz), 4.92–5.12 m (2H, CH_2), 7.27 d (2H, C_6H_4, J = 9 Hz), 7.69 d (2H, C_6H_4, J = 9 Hz). Found, %: C 46.65; H 3.37; N 13.47. $C_{12}H_{10}BrN_3O_2$. Calculated, %: C 46.78; H 3.27; N 13.64.

1-Methyl-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]-oct-2-ene-6,8-dione (IIe) was synthesized from 0.5 g (1.9 mmol) of imide **Ie**. Yield 0.53 g (91%), mp 182–183°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.67 s (3H, CH_3), 2.33 s (3H, CH_3), 3.25 d.d (1H,

CH, J = 8, 4 Hz), 4.92–5.08 m (2H, CH_2), 7.15 d (2H, C_6H_4, J = 8 Hz), 7.15 d (2H, C_6H_4, J = 8 Hz). Found, %: C 64.09; H 5.47; N 17.27. $C_{13}H_{13}N_3O_2$. Calculated, %: C 64.19; H 5.39; N 17.27.

1-(4-Chlorophenyl)-7-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione (IIf) was synthesized from 0.5 g (1.7 mmol) of imide **If**. Yield 0.51 g (89%), mp 109–110°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.34 s (3H, CH_3), 3.95 d.d (1H, CH, J = 9, 2 Hz), 5.13 d.d (1H, CH, J = 18, 9 Hz), 5.32 d.d (1H, CH, J = 18, 2 Hz), 7.21 d (2H, C_6H_4, J = 8 Hz), 7.30 d (2H, C_6H_4, J = 8 Hz), 7.57 d (2H, C_6H_4, J = 9 Hz), 7.72 d (2H, C_6H_4, J = 9 Hz). Found, %: C 63.51; H 4.06; N 12.19. $C_{18}H_{14}ClN_3O_2$. Calculated, %: C 63.63; H 4.15; N 12.37.

7-(4-Chlorophenyl)-1-(4-tolyl)-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione (IIg) was synthesized from 0.5 g (1.7 mmol) of imide **Ig**. Yield 0.47 g (81%), mp 114–116°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.32 s (3H, CH_3), 3.91 d.d (1H, CH, J = 9, 2 Hz), 5.16 d.d (1H, CH, J = 18, 9 Hz), 5.29 d.d (1H, CH, J = 18, 2 Hz), 7.26 d (2H, C_6H_4, J = 8 Hz), 7.34 d (2H, C_6H_4, J = 8 Hz), 7.51 d (2H, C_6H_4, J = 9 Hz), 7.68 d (2H, C_6H_4, J = 9 Hz). Found, %: C 63.65; H 4.13; N 12.23. $C_{18}H_{14}ClN_3O_2$. Calculated, %: C 63.63; H 4.15; N 12.37.

7-Aryl-1,2,7-triazaspiro[4.4]non-1-ene-6,8-diones IVa–IVj. A solution of diazomethane in diethyl ether was added to a solution of the corresponding substituted itaconic acid imide in methylene chloride. The mixture was kept for 3 h at room temperature and evaporated, and the residue was recrystallized from methanol.

7-Phenyl-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVa) was synthesized from 0.5 g (2.6 mmol) of *N*-phenylitaconimide (**IIIa**). Yield 0.45 g (75%), mp 114–116°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.65–1.72 m (2H, CH_2), 2.40–2.50 m (2H, CH_2), 2.92 d (1H, CH_2, J = 18 Hz), 3.46 d (1H, CH_2, J = 18 Hz), 7.36–7.54 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 27.2 (C^4); 39.8 (C^9); 79.9 (C^5); 94.1 (C^3); 126.7, 129.4, 129.7, 131.9 (C_{arom}); 173.6, 173.7 (CO). Found, %: C 62.73; H 4.67; N 18.17. $C_{12}H_{11}N_3O_2$. Calculated, %: C 62.87; H 4.84; N 18.33.

7-(4-Tolyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVb) was synthesized from 0.5 g (2.5 mmol) of *N*-(4-tolyl)itaconimide (**IIIb**). Yield 0.42 g (75%), mp 147–149°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62–1.71 m (2H, CH_2), 2.24 s (3H, CH_3), 2.40–2.49 m (2H, CH_2), 2.95 d (1H, CH_2, J = 18 Hz), 3.46 d (1H, CH_2, J = 18 Hz), 7.12 d (2H, C_6H_4, J = 8 Hz), 7.23 d (2H, C_6H_4, J = 8 Hz). Found, %: C 64.11; H 5.33; N 17.16. $C_{13}H_{13}N_3O_2$. Calculated, %: C 64.19; H 5.39; N 17.27.

7-(4-Chloro-3-methylphenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVc) was synthesized from 0.5 g (2.1 mmol) of *N*-(4-chloro-3-methylphenyl)itaconimide (**IIIc**). Yield 0.48 g (83%), mp 125–127°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.75–1.84 m (2H, CH_2), 2.16–2.25 m (2H, CH_2), 3.11 d (1H, CH_2, J = 18 Hz), 3.23 d (1H, CH_2, J = 18 Hz), 7.18–7.43 m (3H, C_6H_3). Found, %: C 56.17; H 4.38; N 15.05. $C_{13}H_{12}ClN_3O_2$. Calculated, %: C 56.23; H 4.36; N 15.13.

7-(4-Chlorophenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVd) was synthesized from 0.5 g (2.3 mmol) of *N*-(4-chlorophenyl)itaconimide (**IIId**). Yield 0.53 g (88%), mp 134–136°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.76–1.85 m (2H, CH_2), 2.18–2.27 m (2H, CH_2), 3.12 d (1H, CH_2, J = 18 Hz), 3.24 d (1H, CH_2, J = 18 Hz), 7.42 d (2H, C_6H_4, J = 8 Hz), 7.61 d (2H, C_6H_4, J = 8 Hz). Found, %: C 54.53; H 3.88; N 15.87. $C_{12}H_{10}ClN_3O_2$. Calculated, %: C 54.66; H 3.82; N 15.94.

7-(4-Bromophenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVe) was synthesized from 0.5 g (1.9 mmol) of *N*-(4-bromophenyl)itaconimide (**IIIe**). Yield 0.44 g (76%), mp 152–154°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.76–1.85 m (2H, CH_2), 2.18–2.26 m (2H, CH_2), 3.13 d (1H, CH_2, J = 18 Hz), 3.24 d (1H, CH_2, J = 18 Hz), 7.15 d (2H, C_6H_4, J = 8 Hz), 7.63 d (2H, C_6H_4, J = 8 Hz). Found, %: C 46.71; H 3.33; N 13.59. $C_{12}H_{10}BrN_3O_2$. Calculated, %: C 46.78; H 3.27; N 13.64.

7-(4-Fluorophenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVf) was synthesized from 0.5 g (2.4 mmol) of *N*-(4-fluorophenyl)itaconimide (**IIIf**). Yield 0.42 g (71%), mp 96–98°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.76–1.85 m (2H, CH_2), 2.18–2.27 m (2H, CH_2), 3.12 d (1H, CH_2, J = 18 Hz), 3.24 d (1H, CH_2, J = 18 Hz), 7.34–7.44 m (4H, C_6H_4). Found, %: C 58.37; H 3.99; N 16.93. $C_{12}H_{10}FN_3O_2$. Calculated, %: C 58.30; H 4.08; N 17.00.

7-(3,4-Dimethylphenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVg) was synthesized from 0.5 g (2.3 mmol) of *N*-(3,4-dimethylphenyl)itaconimide

(**IIIg**). Yield 0.41 g (67%), mp 105–107°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62–1.72 m (2H, CH_2), 2.21 s (6H, $2CH_3$), 2.41–2.51 m (2H, CH_2), 2.94 d (1H, CH_2, J = 18 Hz), 3.46 d (1H, CH_2, J = 18 Hz), 7.10–7.28 m (3H, C_6H_3). Found, %: C 65.37; H 5.69; N 16.18. $C_{14}H_{15}N_3O_2$. Calculated, %: C 65.36; H 5.88; N 16.33.

7-(3,5-Dichlorophenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVh) was synthesized from 0.5 g (1.9 mmol) of *N*-(3,5-dichlorophenyl)itaconimide (**IIIh**). Yield 0.53 g (92%), mp 144–146°C (decomp.). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.78–1.86 m (2H, CH_2), 2.19–2.27 m (2H, CH_2), 3.14 d (1H, CH_2, J = 18 Hz), 3.25 d (1H, CH_2, J = 18 Hz), 7.33 s (2H, C_6H_3), 7.44 s (1H, C_6H_3). Found, %: C 48.23; H 3.12; N 14.02. $C_{12}H_9Cl_2N_3O_2$. Calculated, %: C 48.35; H 3.04; N 14.04.

7-(4-Ethoxyphenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVi) was synthesized from 0.5 g (2.2 mmol) of *N*-(4-ethoxyphenyl)itaconimide (**IIIi**). Yield 0.45 g (75%), mp 153–155°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (3H, CH_3, J = 7 Hz), 1.62–1.72 m (2H, CH_2), 2.41–2.51 m (2H, CH_2), 2.94 d (1H, CH_2, J = 18 Hz), 3.46 d (1H, CH_2, J = 18 Hz), 4.07 q (2H, $CH_3C\mathbf{H}_2O$, J = 7 Hz), 7.00 d (2H, C_6H_4, J = 8 Hz), 7.27 d (2H, C_6H_4, J = 8 Hz). Found, %: C 61.39; H 5.61; N 15.22. $C_{14}H_{15}N_3O_3$. Calculated, %: C 61.53; H 5.53; N 15.38.

7-(3-Chlorophenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (IVj) was synthesized from 0.5 g (2.3 mmol) of *N*-(3-chlorophenyl)itaconimide (**IIIj**). Yield 0.48 g (81%), mp 105–107°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.62–1.73 m (2H, CH_2), 2.42–2.51 m (2H, CH_2), 2.96 d (1H, CH_2, J = 18 Hz), 3.47 d (1H, CH_2, J = 18 Hz), 7.30–7.49 m (4H, C_6H_4). Found, %: C 54.59; H 3.71; N 15.79. $C_{12}H_{10}ClN_3O_2$. Calculated, %: C 54.66; H 3.82; N 15.94.

2-Chloro-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-3-ene-6,8-dione (Va). A stream of gaseous chlorine was carefully passed through a solution of 0.54 g (2.5 mmol) of compound **IIa** in methylene chloride until a solid began to separate from the solution. The chlorine supply was turned off, and the mixture was kept for 1 h at room temperature in a closed vessel. The precipitate was filtered off and washed with diethyl ether. Yield 0.48 g (77%), mp 127–129°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.55 d.d (1H, CH, J = 10, 2 Hz), 4.73 d (1H, CH, J = 10 Hz), 6.86 d (1H, N=CH, J = 2 Hz), 7.22–7.50 m (5H, C_6H_5). Found, %: C 52.81; H 3.26; N 16.70. $C_{11}H_8ClN_3O_2$. Calculated, %: C 52.92; H 3.23; N 16.83.

2-Chloro-7-(4-chlorophenyl)-2,3,7-triazabicyclo-[3.3.0]oct-3-ene-6,8-dione (Vb) was synthesized in a similar way from 0.30 g (1.2 mmol) of compound **IIb**. Yield 0.24 g (72%), mp 143–145°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.57 d.d (1H, CH, J = 10, 2 Hz), 4.73 d (1H, CH, J = 10 Hz), 6.86 d (1H, N=CH, J = 2 Hz), 7.18 d (2H, C_6H_4, J = 8 Hz), 7.53 d (2H, C_6H_4, J = 8 Hz). Found, %: C 46.39; H 2.43; N 14.67. $C_{11}H_7Cl_2N_3O_2$. Calculated, %: C 46.51; H 2.48; N 14.79.

4-Chloro-7-phenyl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione (VIa) and 6-chloro-3-phenyl-3-azabicyclo[3.1.0]hexane-2,4-dione (VIIa/VIIIa). A mixture of 0.30 g (1.2 mmol) of compound **Va** and 5 ml of glacial acetic acid was heated for 2 h at 100°C. The solvent was distilled off, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (2 : 1, by volume) as eluent. We isolated 0.02 g (6%) of compound **VIa** and 0.04 g (20%) of a mixture of compounds **VIIa** and **VIIIa**.

Compound **VIa**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.81 d.d (1H, 5-H, J = 8, 2 Hz), 6.43 d.d (1H, 1-H, J = 8, 1.5 Hz), 6.83 d.d (1H, 4-H, J = 2, 1.5 Hz). Found, %: C 52.74; H 3.18; N 16.78. $C_{11}H_8ClN_3O_2$. Calculated, %: C 52.92; H 3.23; N 16.83.

Isomer mixture **VIIa**/**VIIIa**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **VIIa**: 2.69 d (2H, CH, J = 2 Hz), 3.71 t (1H, CH, J = 2 Hz), 7.19–7.45 m (5H, C_6H_5); **VIIIa**: 2.53 d (2H, CH, J = 8 Hz), 3.46 t (1H, CH, J = 8 Hz), 7.19–7.45 m (5H, C_6H_5). Found, %: C 59.68; H 3.46; N 6.29. $C_{11}H_8ClNO_2$. Calculated, %: C 59.61; H 3.64; N 6.32.

7-(4-Bromophenyl)-4-chloro-1-methyl-2,3,7-triazabicyclo[3.3.0]oct-2-ene-6,8-dione (VIb). A stream of dry gaseous chlorine was passed through a solution of 0.40 g (1.3 mmol) of compound **IId** in 10 ml of methylene chloride until the mixture turned light yellow. The mixture was kept in a closed vessel for 1 h at room temperature and evaporated, and the residue was washed with cold diethyl ether. Yield 0.36 g (82%), mp 130–132°C (decomp.). UV spectrum (dichloroethane): λ_{max} 333 nm (log ε 2.42). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.93 s (3H, CH_3), 3.34 d (1H, CH, J = 1.5 Hz), 6.60 d (1H, CH, J = 1.5 Hz), 7.14 d (2H, C_6H_4, J = 8 Hz), 7.61 d (2H, C_6H_4, J = 8 Hz). Found, %: C 41.98; H 2.56; N 12.29. $C_{12}H_9BrClN_3O_2$. Calculated, %: C 42.07; H 2.65; N 12.27.

4-Chloro-1-methyl-7-(4-tolyl)-2,3,7-triazabicyclo-[3.3.0]oct-2-ene-6,8-dione (VIc) was synthesized as described above for compound **VIb** from 0.40 g (1.64 mmol) of **IIe**. Yield 0.36 g (79%), mp 137–141°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.93 s (3H, CH_3), 2.40 s (3H, CH_3), 3.32 d (1H, CH, J = 1.5 Hz), 6.58 d (1H, CH, J = 1.5 Hz), 7.11 d (2H, C_6H_4, J = 8 Hz), 7.28 d (2H, C_6H_4, J = 8 Hz). Found, %: C 56.25; H 4.29; N 14.97. $C_{13}H_{12}ClN_3O_2$. Calculated, %: C 56.23; H 4.36; N 15.13.

3-(4-Bromophenyl)-6-chloro-1-methyl-3-azabicyclo[3.1.0]hexane-2,4-dione (VIIb/VIIIb). Compound **VIb**, 0.2 g (0.6 mmol), was heated for 3 min at 140°C under reduced pressure (20 mm). The resulting material was cooled and recrystallized from methanol to obtain 0.12 g (62%) of a mixture of *exo* and *endo* isomers **VIIb** and **VIIIb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *exo* isomer **VIIb**: 1.73 s (3H, CH_3), 2.57 d (1H, CH, J = 1.5 Hz), 3.70 d (1H, CH, J = 1.5 Hz), 7.14–7.50 m (4H, C_6H_4); *endo* isomer **VIIIb**: 1.83 s (3H, CH_3), 2.80 d (1H, CH, J = 8 Hz), 3.81 d (1H, CH, J = 8 Hz), 7.14–7.50 m (4H, C_6H_4). Found, %: C 45.71; H 2.86; N 4.29. $C_{12}H_9BrClNO_2$. Calculated, %: C 45.82; H 2.88; N 4.45.

6-Chloro-1-methyl-3-(4-tolyl)-3-azabicyclo-[3.1.0]hexane-2,4-dione (VIIc/VIIIc). Compound **VIc**, 0.2 g (0.7 mmol), was heated for 5 min at 140°C under reduced pressure (20 mm). The resulting material was cooled and recrystallized from methanol to obtain 0.12 g (68%) of a mixture of *exo* and *endo* isomers **VIIc** and **VIIIc**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: *exo* isomer **VIIc**: 1.71 s (3H, CH_3), 2.34 s (3H, CH_3), 2.53 d (1H, CH, J = 1.5 Hz), 3.67 d (1H, CH, J = 1.5 Hz), 7.09–7.34 m (4H, C_6H_4); *endo* isomer **VIIIc**: 1.82 s (3H, CH_3), 2.37 s (3H, CH_3), 2.77 d (1H, CH, J = 8 Hz), 3.79 d (1H, CH, J = 8 Hz), 7.09–7.34 m (4H, C_6H_4). Found, %: C 62.61; H 4.89; N 5.48. $C_{13}H_{12}ClNO_2$. Calculated, %: C 62.53; H 4.84; N 5.61.

6-Chloro-1-(4-chlorophenyl)-3-(4-tolyl)-3-azabicyclo[3.1.0]hexane-2,4-dione (Xa). A stream of dry gaseous chlorine was passed through a solution of 0.5 g (1.5 mmol) of compound **IIf** in 15 ml of methylene chloride until the solution turned light yellow. The mixture was kept for 30 min at room temperature and evaporated, and the residue was recrystallized from ethanol. Yield 0.47 g (91%), mp 187–188°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.40 s (3H, CH_3), 3.18 d (1H, CH, J = 2 Hz), 3.99 d (1H, CH, J = 2 Hz), 7.10–7.51 m (8H, C_6H_4). Found, %: C 62.38; H 3.66; N 4.09. $C_{18}H_{13}Cl_2NO_2$. Calculated, %: C 62.45; H 3.78; N 4.05.

6-Chloro-3-(4-chlorophenyl)-1-(4-tolyl)-3-azabicyclo[3.1.0]hexane-2,4-dione (Xb). A stream of dry gaseous chlorine was passed through a solution of 0.5 g (1.5 mmol) of compound **IIg** in 15 ml of methylene chloride until the solution turned light yellow. The mixture was kept for 40 min at room temperature and evaporated, and the residue was recrystallized from ethanol. Yield 0.41 g (79%), mp 179–181°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.40 s (3H, CH_3), 3.18 d (1H, CH, J = 2 Hz), 3.99 d (1H, CH, J = 2 Hz), 7.15–7.63 m (8H, C_6H_4). Found, %: C 62.44; H 3.59; N 3.98. $C_{18}H_{13}Cl_2NO_2$. Calculated, %: C 62.45; H 3.78; N 4.05.

1-(4-Bromophenyl)-3-dibromomethyl-4-methyl-2,5-dihydro-1*H*-pyrrole-2,5-dione (XI). A mixture of 0.50 g (1.6 mmol) of compound **IId**, 0.3 ml of bromine, and 8 ml of glacial acetic acid was heated for 2 h at 70°C. The solvent was distilled off under reduced pressure, the residue was dissolved in a diethyl ether–ethyl acetate mixture, and the solution was washed with a solution of sodium sulfite. The solvent was distilled off, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (3 : 1, by volume) as eluent). Yield 0.18 g (38%), mp 110–111°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.22 s (3H, CH_3), 5.15 s (1H, CH), 7.25 d (2H, C_6H_4, J = 8 Hz), 7.66 d (2H, C_6H_4, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 24.5 (CH_3); 49.0 ($CHBr_2$); 122.1, 123.6 (=C); 127.8, 130.1, 133.0, 142.9 (C_{arom}); 169.6, 171.8 (CO). Found, %: C 32.83; H 1.86; N 3.06. $C_{12}H_8Br_3NO_2$. Calculated, %: C 32.91; H 1.84; N 3.20.

6,6-Dibromo-1-(4-chlorophenyl)-3-(4-tolyl)-3-azabicyclo[3.1.0]hexane-2,4-dione (XIIa). A mixture of 0.30 g (0.9 mmol) of compound **IIf**, 0.15 ml of bromine, and 6 ml of glacial acetic acid was heated for 1 h at 60°C. The solvent was distilled off under reduced pressure, the residue was treated with ethanol, and the precipitate was filtered off and recrystallized from ethanol. Yield 0.26 g (68%), mp 157–158°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.40 s (3H, CH_3), 3.60 s (1H, CH), 7.21–7.49 m (8H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: 21.7 (CH_3); 41.1 (C^5); 46.8 (C^6); 48.5 (C^1); 126.3, 129.5, 130.3, 131.5, 136.3, 139.7 (C_{arom}); 168.8, 169.3 (CO). Found, %: C 45.92; H 2.69; N 2.87. $C_{18}H_{12}Br_2ClNO_2$. Calculated, %: C 46.04; H 2.58; N 2.98.

6,6-Dibromo-3-(4-chlorophenyl)-1-(4-tolyl)-3-azabicyclo[3.1.0]hexane-2,4-dione (XIIb). A mixture of 0.30 g (0.9 mmol) of compound **IIg**, 0.15 ml of bromine,

and 6 ml of glacial acetic acid was heated for 1 h at 60°C. The solvent was distilled off under reduced pressure, the residue was treated with ethanol, and the precipitate was filtered off and recrystallized from ethanol. Yield 0.24 g (64%), mp 166–167°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 s (3H, CH_3), 3.62 s (1H, CH), 7.19–7.54 m (8H, C_6H_4). Found, %: C 46.08; H 2.49; N 2.71. $C_{18}H_{12}Br_2ClNO_2$. Calculated, %: C 46.04; H 2.58; N 2.98.

Reaction of compound IIa with *N*-iodosuccinimide. A mixture of 0.20 g (0.9 mmol) of compound **IIa** and 0.31 g of *N*-iodosuccinimide in 5 ml of glacial acetic acid was heated for 3 h at 110°C. The solvent was distilled off under reduced pressure, the residue was dissolved in ethyl acetate, and the solution was washed with a solution of sodium sulfite. The organic phase was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (2 : 1, by volume) as eluent to isolate 0.03 g (11%) of 1-iodo-3-phenylazabicyclo[3.1.0]hexane-2,4-dione (**XIIIa**) and 0.025 g (9%) of 3-iodo-4-methyl-1-phenyl-2,5-dihydro-1*H*-pyrrole-2,5-dione (**XIVa**).

Compound **XIIIa**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.01 d.d (1H, CH_2, J = 8, 3 Hz), 2.11 t (1H, CH_2, J = 3 Hz), 2.81 d.d (1H, CH, J = 8, 3 Hz), 7.18–7.41 m (5H, C_6H_5). Found, %: C 42.11; H 2.62; N 4.29. $C_{11}H_8INO_2$. Calculated, %: C 42.20; H 2.58; N 4.47.

Compound **XIVa**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.19 s (3H, CH_3), 7.22–7.49 m (5H, C_6H_5). Found, %: C 42.09; H 2.71; N 4.31. $C_{11}H_8INO_2$. Calculated, %: C 42.20; H 2.58; N 4.47.

Reaction of compound IIc with *N*-iodosuccinimide. A mixture of 0.20 g (0.7 mmol) of compound **IIc** and 0.4 g of *N*-iodosuccinimide in 5 ml of glacial acetic acid was heated for 4 h at 110°C. The solvent was distilled off under reduced pressure, the residue was dissolved in ethyl acetate, and the solution was washed with a solution of sodium sulfite. The organic phase was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (2 : 1, by volume) as eluent to isolate 0.034 g (13%) of 1-iodo-3-(4-methoxycarbonylphenyl)-3-azabicyclo[3.1.0]hexane-2,4-dione (**XIIIb**) and 0.016 g (6%) of 3-iodo-1-(4-methoxycarbonylphenyl)-2,5-dihydro-1*H*-pyrrole-2,5-dione (**XIVb**).

Compound **XIIIb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.09 d.d (1H, CH_2, J = 8, 3 Hz), 2.15 t (1H, CH_2, J = 3 Hz), 2.8 d.d (1H, CH, J = 8, 3 Hz), 3.94 s (3H, OCH_3), 7.37 d (2H, C_6H_4, J = 8 Hz), 8.13 d (2H, C_6H_4, J = 8 Hz). Found, %: C 42.03; H 2.80; N 4.00. $C_{13}H_{10}INO_4$. Calculated, %: C 42.07; H 2.72; N 3.77.

Compound **XIVb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.19 s (3H, CH_3), 3.95 s (3H, OCH_3), 7.50 d (2H, C_6H_4, J = 8 Hz), 8.14 d (2H, C_6H_4, J = 8 Hz). Found, %: C 41.82; H 2.11; N 3.76. $C_{13}H_{10}INO_4$. Calculated, %: C 42.07; H 2.72; N 3.77.

7-Substituted 3-chloro-1,2,7-triazaspiro[4.4]non-1-ene-6,8-diones XVIa–XVId. A stream of chlorine was passed through a solution of the corresponding compound **IV** in methylene chloride until the mixture turned light yellow. The mixture was kept in a closed vessel for 2 h at room temperature and evaporated, and the residue was recrystallized from methanol.

3-Chloro-7-phenyl-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (XVIa) was synthesized from 0.40 g (1.7 mmol) of compound **IVa**. Yield 0.37 g (83%), mp 131–132°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.90 d.d (1H, CH_2, J = 14, 6 Hz), 3.01 d.d (1H, CH_2, J = 14, 6 Hz), 3.10 d (1H, CH_2, J = 19 Hz), 3.55 d (1H, CH_2, J = 19 Hz), 6.40 t (1H, CH, J = 6 Hz), 7.34–7.52 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: 37.8 (C^4); 39.3 (C^9); 93.7 (C^3); 95.2 (C^5); 126.6, 129.7, 129.8, 131.6 (C_{arom}); 172.2, 172.6 (CO). Found, %: C 54.59; H 3.86; N 16.05. $C_{12}H_{10}ClN_3O_2$. Calculated, %: C 54.66; H 3.82; N 15.94.

3-Chloro-7-(3,5-dichlorophenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (XVIb) was synthesized from 0.3 g (1.0 mmol) of compound **IVh**. Yield 0.27 g (86%), mp 132–134°C (decomp.). IR spectrum, ν, cm^{-1}: 1030, 1080, 1260, 1390, 1410, 1510, 1720 v.s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.93 d.d (1H, CH_2, J = 14, 6 Hz), 3.00 d.d (1H, CH_2, J = 14, 6 Hz), 3.11 d (1H, CH_2, J = 19 Hz), 3.58 d (1H, CH_2, J = 19 Hz), 6.43 t (1H, CH, J = 6 Hz), 7.35 d (2H, C_6H_3, J = 2 Hz), 7.46 s (1H, C_6H_3). Found, %: C 43.27; H 2.36; N 12.55. $C_{12}H_8Cl_3N_3O_2$. Calculated, %: C 43.34; H 2.42; N 12.63.

3-Chloro-7-(3-chloro-4-ethoxyphenyl)-1,2,7-triazaspiro[4.4]non-1-ene-6,8-dione (XVIc) was synthesized from 0.40 g (1.5 mmol) of compound **IVi**. Yield 0.38 g (72%), mp 124–125°C (decomp.). UV spectrum (dichloroethane): λ_{max} 330 nm (log ε 2.52). IR spectrum, ν, cm^{-1}: 1030, 1070, 1260, 1390, 1500, 1720 v.s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.51 t (3H, CH_3), 1.91 d.d (1H, CH_2, J = 14, 6 Hz), 3.02 d.d (1H, CH_2, J = 14, 6 Hz), 3.09 d (1H, CH_2, J = 19 Hz), 3.57 d (1H, CH_2, J = 19 Hz), 4.18 q (2H, $CH_3C\mathbf{H}_2O$, J = 7 Hz), 6.42 t (1H,

CH, J = 6 Hz), 7.01 d (1H, C_6H_3, J = 8 Hz), 7.22 d.d (1H, C_6H_3, J = 8, 2 Hz), 7.40 d (1H, C_6H_3, J = 2 Hz). Found, %: 49.10; H 3.82; N 12.10. $C_{14}H_{13}Cl_2N_3O_3$. Calculated, %: C 49.14; H 3.83; N 12.28.

3-Chloro-7-(4-fluorophenyl)-1,2,7-triazaspiro-[4.4]non-1-ene-6,8-dione (XVId) was synthesized from 0.30 g (1.0 mmol) of compound **IVf**. Yield 0.25 g (89%), mp 118–120°C (decomp.). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.94 d.d (1H, CH_2, J = 14, 6 Hz), 3.01 d.d (1H, CH_2, J = 14, 6 Hz), 3.10 d (1H, CH_2, J = 19 Hz), 3.60 d (1H, CH_2, J = 19 Hz), 6.43 t (1H, CH, J = 6 Hz), 7.19–7.36 m (4H, C_6H_4). Found, %: C 51.06; H 3.16; N 14.79. $C_{12}H_9ClFN_3O_2$. Calculated, %: C 51.17; H 3.22; N 14.92.

7-(4-Bromophenyl)-3-chloro-1,2,7-triazaspiro-[4.4]non-1-ene-6,8-dione (XVIe) was synthesized from 0.30 g (0.97 mmol) of compound **IVe**. Yield 0.27 g (83%), mp 121–123°C (decomp.). IR spectrum, ν, cm^{-1}: 1030, 1090, 1250, 1390, 1400, 1510, 1720 v.s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.92 d.d (1H, CH_2, J = 14, 6 Hz), 2.99 d.d (1H, CH_2, J = 14, 6 Hz), 3.10 d (1H, CH_2, J = 19 Hz), 3.57 d (1H, CH_2, J = 19 Hz), 6.42 t (1H, CH, J = 6 Hz), 7.19 d (2H, C_6H_4, J = 8 Hz), 7.65 d (2H, C_6H_4, J = 8 Hz). Found, %: C 41.98; H 2.69; N 12.14. $C_{12}H_9BrClN_3O_2$. Calculated, %: C 42.07; H 2.65; N 12.27.

1-Chloro-5-phenyl-5-azaspiro[2.4]heptane-4,6-dione (XVIIa/XVIIIa). Compound **XVIa**, 0.20 g (0.76 mmol), was heated for 5 min at 140°C under reduced pressure (20 mm). The resulting material was cooled and recrystallized from ethanol. Yield of **XVIIa**/**XVIIIa** (isomer mixture) 0.11 g (61%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **XVIIa**: 1.37 t (1H, CH_2, J = 6 Hz), 1.99 d.d (1H, CH_2, J = 6, 1.5 Hz), 2.90 s (2H, CH_2), 3.45 d.d (1H, CH, J = 6, 1.5 Hz), 7.22–7.48 m (5H, C_6H_5); **XVIIIa**: 1.73 t (1H, CH_2, J = 7 Hz), 2.11 d.d (1H, CH_2, J = 7, 2.5 Hz), 2.86 d (1H, CH_2, J = 19 Hz), 3.22 d (1H, CH_2, J = 19 Hz), 3.71 d.d (1H, CH, J = 7, 2.5 Hz), 7.22–7.48 m (5H, C_6H_5). Found, %: C 61.20; H 4.22; N 5.77. $C_{12}H_{10}ClNO_2$. Calculated, %: C 61.16; H 4.28; N 5.94.

1-Chloro-5-(3-chloro-4-ethoxyphenyl)-5-aza-spiro[2.4]heptane-4,6-dione (XVIIb/XVIIIb). Compound **XVIc**, 0.20 g (0.58 mmol), was heated for 5 min at 130°C under reduced pressure (20 mm). The resulting material was cooled and recrystallized from ethanol. Yield of **XVIIb**/**XVIIIb** (isomer mixture) 0.13 g (72%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: **XVIIb**: 1.39 t (1H, CH_2, J = 6 Hz), 2.01 d.d (1H, CH_2, J = 6, 1.5 Hz), 2.93 s (2H, CH_2), 3.48 d.d (1H, CH, J = 6, 1.5 Hz), 7.00 d (1H, C_6H_3, J = 8 Hz), 7.16–7.28 m (1H, C_6H_3), 7.39 d.d (1H, C_6H_3, J = 8, 2 Hz); **XVIIIb**: 1.75 t (1H, CH_2, J = 7 Hz), 2.13 d.d (1H, CH_2, J = 7, 2.5 Hz), 2.86 d (1H, CH_2, J = 19 Hz), 3.23 d (1H, CH_2, J = 19 Hz), 3.73 d.d (1H, CH, J = 7, 2.5 Hz), 7.00 d (1H, C_6H_3, J = 8 Hz), 7.16–7.28 m (1H, C_6H_3), 7.39 d.d (1H, C_6H_3, J = 8, 2 Hz). Found, %: C 53.40; H 4.12; N 4.27. $C_{14}H_{13}Cl_2NO_3$. Calculated, %: C 53.52; H 4.17; N 4.46.

1,1-Dibromo-5-(4-chlorophenyl)-5-azaspiro-[2.4]heptane-4,6-dione (XIXa). A mixture of 0.40 g (1.5 mmol) of compound **IVd** and 0.1 ml of bromine in 6 ml of glacial acetic acid was heated for 2 h at 70°C. The solvent was distilled off under reduced pressure, the residue was dissolved in diethyl ether, and the solution was washed with a solution of sodium sulfite, dried over $MgSO_4$, and evaporated. The residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (2 : 1, by volume) as eluent. Yield 0.13 g (22%), mp 156–158°C. IR spectrum, ν, cm^{-1}: 1020, 1040, 1090, 1160, 1380 s, 1490, 1720 v.s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.15 d (1H, CH_2, J = 8 Hz), 2.67 d (1H, CH_2, J = 8 Hz), 3.01 d (1H, CH_2, J = 19 Hz), 3.48 d (1H, CH_2, J = 19 Hz), 7.35 d (2H, C_6H_4, J = 8 Hz), 7.48 d (2H, C_6H_4, J = 8 Hz). ^{13}C NMR spectrum, δ_C, ppm: 27.6 (C^3); 33.5 (C^1); 34.8 (C^2); 38.4 (C^7); 127.9, 129.8, 130.6, 135.1 (C_{arom}); 171.9, 172.8 (CO). Found, %: C 36.58; H 2.13; N 3.28. $C_{12}H_8Br_2ClNO_2$. Calculated, %: C 36.63; H 2.05; N 3.56.

1,1-Dibromo-1-chloro-5-(3-chloro-4-methyl-phenyl)-5-azaspiro[2.4]heptane-4,6-dione (XIXb) was synthesized as described above for compound **XIXa** from 0.40 g (1.4 mmol) of **IVc**. Yield 0.09 g (16%), mp 173–175°C. IR spectrum ($CHCl_3$), ν, cm^{-1}: 1020, 1040, 1090, 1170, 1380 s, 1490, 1720 v.s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.15 d (1H, CH_2, J = 8 Hz), 2.38 s (3H, CH_3), 2.68 d (1H, CH_2, J = 8 Hz), 3.03 d (1H, CH_2, J = 19 Hz), 3.50 d (1H, CH_2, J = 19 Hz), 7.18–7.43 m (3H, C_6H_3). Found, %: C 38.28; H 2.34; N 3.18. $C_{13}H_{10}Br_2ClNO_2$. Calculated, %: C 38.32; H 2.47; N 3.44.

1,1-Dibromo-1-chloro-5-(4-fluorophenyl)-5-aza-spiro[2.4]heptane-4,6-dione (XIXc) was synthesized as described above for compound **XIXa** from 0.40 g (1.6 mmol) of **IVf**. Yield 0.074 g (19%), mp 187–188°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.17 d (1H, CH_2, J = 8 Hz), 2.70 d (1H, CH_2, J = 8 Hz), 3.05 d (1H, CH_2,

J = 19 Hz), 3.48 d (1H, CH_2, J = 19 Hz), 7.16–7.39 m (4H, C_6H_4). Found, %: C 38.14; H 2.23; N 3.57. $C_{12}H_8Br_2FNO_2$. Calculated, %: C 38.23; H 2.14; N 3.72.

Reaction of compounds IVa, IVg, and IVj with *N*-iodosuccinimide. A mixture of compound **IVa**, **IVg**, or **IVj** and 1.5 equiv of *N*-iodosuccinimide in glacial acetic acid was heated for 2 h at 70°C. The solvent was distilled off under reduced pressure, the residue was dissolved in a diethyl ether–ethyl acetate mixture, and the solution was washed with a solution of sodium sulfite. The organic phase was dried over $MgSO_4$ and evaporated, and the residue was subjected to column chromatography on silica gel using hexane–ethyl acetate (3 : 1, by volume) as eluent.

1-Iodo-5-phenyl-5-azaspiro[2.4]heptane-4,6-dione was obtained from 0.23 g (1 mmol) of compound **IVa** and 0.32 g (1.5 mmol) of *N*-iodosuccinimide. The product was isolated as a mixture of *syn* and *anti* isomers **XXa** and **XXIa**.

Isomer **XXa**. Yield 0.13 g (39%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (1H, CH_2, J = 6 Hz), 2.41 d.d (1H, CH_2, J = 6, 3 Hz), 2.93 d (1H, CH_2, J = 18 Hz), 3.16 d (1H, CH_2, J = 18 Hz), 3.37 d.d (1H, CH, J = 6, 3 Hz), 7.32–7.41 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: –4.4 (C^1); 26.4 (C^2); 26.5 (C^3); 39.1 (C^7); 126.7, 129.1, 129.6, 132.4 (C_{arom}); 174.6, 176.3 (CO). Found, %: C 43.98; H 3.23; N 4.11. $C_{12}H_{10}INO_2$. Calculated, %: C 44.06; H 3.08; N 4.28.

Isomer **XXIa**. Yield 0.052 g (16%), yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.79–1.88 m (2H, CH_2), 2.93 s (2H, CH_2), 3.03 t (1H, CH, J = 7 Hz), 7.34–7.47 m (5H, C_6H_5). ^{13}C NMR spectrum, δ_C, ppm: –8.8 (C^1); 24.8 (C^2); 25.2 (C^3); 37.4 (C^7); 126.8, 129.1, 129.5, 132.4 (C_{arom}); 174.0, 174.6 (CO). Found, %: C 44.15; H 3.12; N 4.33. $C_{12}H_{10}INO_2$. Calculated, %: C 44.06; H 3.08; N 4.28.

1-Iodo-5-(3,4-di-methylphenyl)-5-azaspiro-[2.4]heptane-4,6-dione was obtained from 0.21 g (0.9 mmol) of compound **IVg** and 0.30 g (1.3 mmol) of *N*-iodosuccinimide. The product was isolated as a mixture of *syn* and *anti* isomers **XXb** and **XXIb**.

Isomer **XXb**. Yield 0.11 g (35%), light yellow oily substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.41 t (1H, CH_2, J = 6 Hz), 2.30 s (6H, CH_3), 2.38 d.d (1H, CH_2, J = 6, 3 Hz), 2.92 d (1H, CH_2, J = 18 Hz), 3.14 d (1H, CH_2, J = 18 Hz), 3.38 d.d (1H, CH, J = 6, 3 Hz), 7.01–7.30 m (3H, C_6H_3). ^{13}C NMR spectrum, δ_C, ppm: –4.3 (C^1); 19.9 (CH_3); 20.3 (CH_3); 24.7 (C^2); 25.2 (C^3); 37.4 (C^7); 124.2, 127.8, 129.9, 130.7, 138.0, 138.2 (C_{arom}); 174.9, 176.5 (CO). Found, %: C 47.28; H 3.85; N 3.73. $C_{14}H_{14}INO_2$. Calculated, %: C 47.34; H 3.97; N 3.94.

Isomer **XXIb**. Yield 0.057 g (18%), mp 133–134°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.85–1.93 m (2H, CH_2), 2.31 s (6H, CH_3), 2.97 s (2H, CH_2), 3.03 t (1H, CH, J = 7 Hz), 7.05–7.28 m (3H, C_6H_3). ^{13}C NMR spectrum, δ_C, ppm: –8.9 (C^1); 20.0 (CH_3); 20.3 (CH_3); 24.7 (C^2); 25.2 (C^3); 37.4 (C^7); 124.2, 127.8, 129.9, 130.7, 138.0, 138.1 (C_{arom}); 174.3, 174.8 (CO). Found, %: C 47.39; H 3.72; N 3.81. $C_{14}H_{14}INO_2$. Calculated, %: C 47.34; H 3.97; N 3.94.

5-(3-Chlorophenyl)-1-iodo-5-azaspiro[2.4]-heptane-4,6-dione (XXc) and 5-(3-chlorophenyl)-1,1-diiodo-5-azaspiro[2.4]heptane-4,6-dione (XXII) were obtained from 0.25 g (0.9 mmol) of compound **IVj** and 0.33 g (1.5 mmol) of *N*-iodosuccinimide.

Compound **XXc**. Yield 0.14 g (42%), light yellow substance. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.44 t (1H, CH_2, J = 6 Hz), 2.39 d.d (1H, CH_2, J = 6, 3 Hz), 2.93 d (1H, CH_2, J = 18 Hz), 3.14 d (1H, CH_2, J = 18 Hz), 3.37 d.d (1H, CH, J = 6, 3 Hz), 7.24–7.39 m (4H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: –4.5 (C^1); 26.4 (C^2); 26.6 (C^3); 39.1 (C^7); 124.9, 127.0, 129.3, 130.5, 133.4, 135.1 (C_{arom}); 174.2, 175.9 (CO). Found, %: C 39.69; H 2.46; N 3.68. $C_{12}H_9ClINO_2$. Calculated, %: C 39.86; H 2.51; N 3.87.

Compound **XXII**. Yield 0.031 g (7%), mp 163–164°C. IR spectrum, ν, cm^{-1}: 1030, 1150, 1380, 1480, 1590, 1720 v.s, 3050. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 d (1H, CH_2, J = 8 Hz), 2.82 d (1H, CH_2, J = 8 Hz), 3.02 d (1H, CH_2, J = 18 Hz), 3.30 d (1H, CH_2, J = 18 Hz), 7.30–7.45 m (4H, C_6H_4). Found, %: C 29.53; H 1.81; N 2.79. $C_{12}H_8ClI_2NO_2$. Calculated, %: C 29.57; H 1.65; N 2.87.

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