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# Regioselectivity in the Addition of 1,3-Dipolarophiles to 6-Aryl-1,5-diazabicyclo[3.1.0]hexanes

**A. P. Molchanov[1], D. I. Sipkin[1], Yu. B. Koptelov[1], J. Kopf[2], and R. R. Kostikov[1]**

[1] *St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia*
[2] *Institut für anorganische Chemie, Martin-Luter-King Platz 6, Hamburg, D-20146 Germany*

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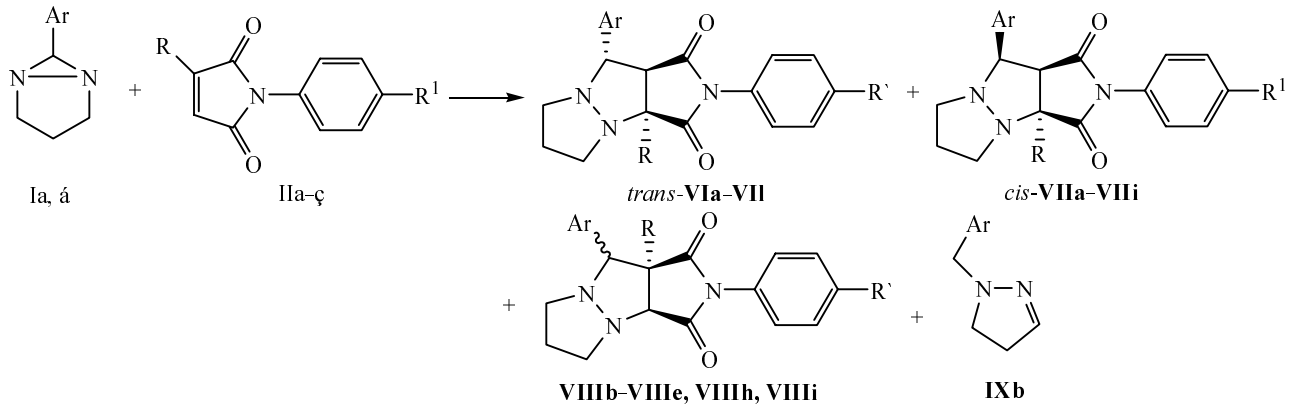
**Abstract**—Thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in the presence of 1,3-dipolarophiles having an unsymmetrically substituted double C=C bond (such as *N*-arylimides derived from 2-aryl-substituted maleic, citraconic, and itaconic acids, ethyl propynoate, aryl isocyanates, and aryl isothiocyanates) leads to formation of the corresponding 1,3-dipolar cycloaddition products. The reaction is regioselective, and in most cases only one regioisomer is obtained. The addition direction depends on the 1,3-dipolarophile structure, i.e., electronic and steric factors determining the most effective orbital interaction upon approach of the reagent to substrate.

In the preceding studies we have found that azomethine imines generated by thermal cleavage of the carbon–nitrogen bond in 6-aryl-1,5-diazabicyclo-[3.1.0]hexanes react with *N*-arylmaleimides to give 1,3-dipolar cycloaddition products, substituted perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-diones as mixtures of *trans* and *cis* isomers [1]. The reactions with *N*-arylmaleimides having a substituent in the *ortho* position of the aromatic ring are characterized by increased stereoselectivity, while the same diazabicyclohexanes react with fumaric acid diesters and fumaronitrile in a stereoselective fashion, yielding products with a *trans,trans* configuration [2].

In the present work we tried to elucidate factors determining the regioselectivity in reactions of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **Ia** and **Ib** with unsaturated compounds having an unsymmetrically substituted double C=C bond, specifically with *N*-arylimides derived from 2-arylmaleic (**IIa**–**IIh**), citraconic (**IIIa**–**IIIg**), and itaconic acids (**IVa** and **IVb**), with compounds possessing a triple carbon–carbon bond (dimethyl acetylene dicarboxylate and ethyl 2-propynoate), and also with aryl isocyanates **Va**–**Vc** and aryl isothiocyanates **Vd–Vf** which have a double C=N bond.

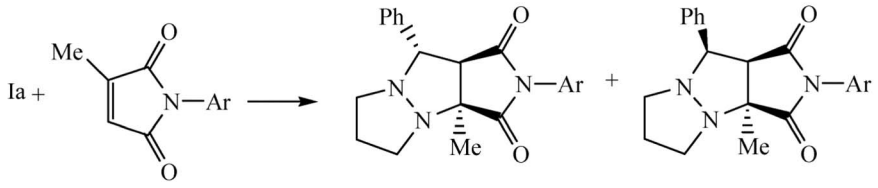
By heating 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **Ia** and **Ib** with *N*-aryl-2-arylmaleimides **IIa**–**IIh** in boiling toluene or *p*-xylene we obtained 20–80% of the corresponding perhydropyrazolo[1,2-*a*]pyrrolo-[3,4-*c*]pyrazole-1,3-diones as mixtures of *trans* (**VIa–VIj**) and *cis* isomers (**VIIa**–**VIIj**) (Scheme 1). In some cases,

**Scheme 1.**




**I**, **IX**, Ar = Ph (**a**), 4-MeOC$_6$H$_4$ (**b**); **II**, R = Ph, R$^1$ = H (**a**), 4-F (**b**), 4-OEt (**c**), 4-Me (**d**), 4-Cl (**e**), 4-MeO (**f**), 3-NO$_2$ (**g**); R = 4-O$_2$NC$_6$H$_4$, R$^1$ = H (**h**); **VI**, **VII**, **VIII**, Ar = R = Ph, R$^1$ = H (**a**), 4-F (**b**), 4-OEt (**c**); Ar = Ph, R = 4-O$_2$NC$_6$H$_4$, R1 = H (**d**), Ar = 4-MeOC$_6$H$_4$, R = Ph, R$^1$ = H (**e**), 4-Me (**f**), 4-Cl (**g**), 4-MeO (**h**), 3-O$_2$N (**i**); Ar = 4-MeOC$_6$H$_4$, R = 4-O$_2$NC$_6$H$_4$, R' = H (**j**).

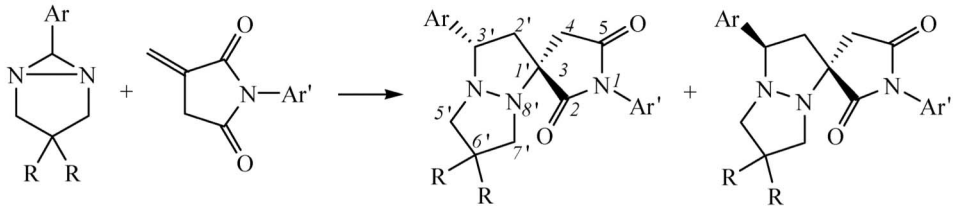
**Scheme 2.**



**IIIa–IIIg** **Xa–Xg** **XIa–XIg**

Ar = Ph (**a**), 4-$MeC_6H_4$ (**b**), 4-$MeOC_6H_4$ (**c**), 4-$EtOC_6H_4$ (**d**), 3-$ClC_6H_4$ (**e**), 3,4-$Cl_2C_6H_4$ (**f**), 3-$O_2NC_6H_4$ (**g**).

**Scheme 3.**



**Ia, Ic** **IVa, IVb** **XIIa–XIId** **XIIIa, XIIId**

**I**, Ar = Ph, R = H (**a**); Ar = 4-$MeOC_6H_4$, R = Me (**c**); **IV**, Ar' = Ph (**a**), 4-$ClC_6H_4$ (**b**); **XII**, **XIII**, Ar = Ar' = Ph, R = H (**a**); Ar = Ph, Ar' = 4-$ClC_6H_4$, R = H (**b**); Ar = 4-$MeOC_6H_4$, Ar' = Ph, R = Me (**c**); Ar = 4-$MeOC_6H_4$, Ar' = 4-$ClC_6H_4$, R = Me (**d**).

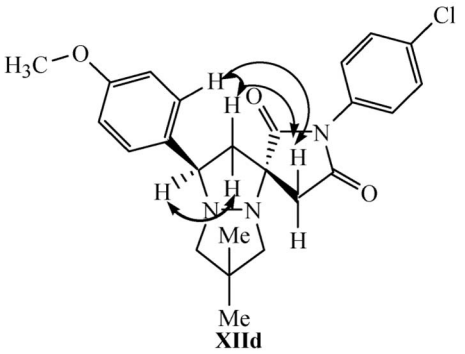
regioisomeric products **VIIIc**, **VIIIe**, and **VIIIg** were isolated. According to the $^1$H NMR data, the ratio of regioisomers (**VI** + **VII**) : **VIII** was 16 : 1 (**b**), 18 : 1 (**c**), 11 : 1 (**d**), 14 : 1 (**e**), 15 : 1 (**h**), and 10.4 : 1 (**i**), and the ratio of stereoisomers **VI** : **VII,** 0.63 (**b**), 0.79 (**c**), 1.2 (**d**), 0.68 (**e**), 0.74 (**h**), and 0.36 (**i**). The isomeric products were separated by column chromatography, and their structure was determined by spectral methods. The configuration of diastereoisomers **VIa**–**VIj** and **VIIa**–**VIIj** was established on the basis of chemical shifts of the 9-H proton and the respective spin–spin coupling constants. The adducts characterized by smaller coupling constants were assigned *trans* configuration (**VI**), while those characterized by greater coupling constants were assumed to have *cis* configuration (**VII**). In the $^1$H NMR spectra of *trans* isomers **VIa**–**VIj** we observed two doublets in the regions δ 3.75–3.84 and 4.47–4.64 ppm ($J$ = 4.4–4.9 Hz), while the corresponding signals from *cis* isomers **VIIa**–**VIIj** appeared at δ 4.09–4.18 and 4.43–4.51 ppm ($J$ = 8.9–10.0 Hz). Regioisomers **VIII** which lack vicinal CH protons showed in the 1H NMR spectra two singlets at δ 4.23–4.32 and 4.80–4.84 ppm. It should be noted that 2-arylmaleimides are less reactive than their unsubstituted analogs; therefore, in some cases the reactions mixtures contained appreciable amounts of the corresponding 1-arylmethyldihydropyrazoles **IXa** and **IXb** which were formed from 6-aryldiazabicyclohexanes **Ia** and **Ib** via concurrent thermal isomerization.

Diazabicyclohexane **Ia** reacted with citraconic acid *N*-arylimides **IIIa**–**IIIg** on heating in toluene. These reactions were regioselective, and the corresponding substituted perhydropyrazolo[1,2-*a*]pyrrolo-[3,4-c]pyrazole-1,3-diones were obtained as mixtures of *trans* (**Xa**–**Xg**) and *cis* (**XIa**–**XIg**) isomers (Scheme 2). According to the $^1$H NMR spectra of the reaction mixtures, the *trans*:*cis* isomer ratio (**X**:**XI**) was equal to 1 (**a**), 2.2 (**b**), 2.1 (**c**), 1.5 (**d**), 3.2 (**e**), and 1.1 (**g**). The diastereoisomers were separated by fractional crystallization, and their relative configurations were determined on the basis of spectral data. In the $^1$H NMR spectra of *trans* isomers **Xa**–**Xg** two characteristic doublets were present at δ 3.36–3.44 and 4.28–4.39 ppm ($J$ = 4.4–5.1 Hz), while the corresponding signals in the spectra of *cis* isomers **XIa**–**XIg** apeared at δ 3.48–3.56 and 4.35–4.46 ppm ($J$ = 8.9–9.8 Hz).

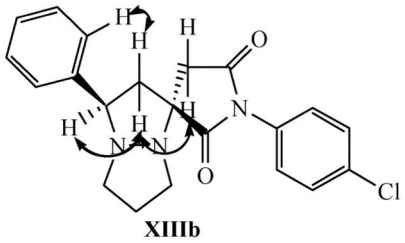
The structure of the products was established on the basis of their elemental compositions and spectral parameters. Compound **XIIb** showed in the 1H NMR spectrum a doublet of doublets at δ 4.18 ppm ($J$ = 7.1, 9.3 Hz), which belongs to the 3'-H proton coupled with nonequivalent protons of the neighboring methylene group ($C^{2'}H_2$); signals from the latter are located at δ 2.18 (d.d, $J$ = 7.1, 13.2 Hz) and 3.35 ppm (d.d, $J$ = 9.3, 13.2 Hz). Signals from methylene protons in the pyrrolidine ring appear at δ 3.00 (d, $J$ = 18.5 Hz) and 3.48 ppm (d, $J$ = 18.5 Hz). The corresponding proton signals of diastereoisomer **XIIIb** were observed in the $^1$H NMR spectrum at δ, ppm: 4.00 t (3'-H, $J$ = 8.4 Hz); 2.72 d.d ($J$ = 8.4, 13.2 Hz) and 2.86 d.d ($J$ = 8.4, 13.2 Hz) ($C^{2'}H_2$), 3.09 d ($CH_2$, pyrrolidine, $J$ = 18.1 Hz), and 3.26 d ($CH_2$, pyrrolidine,

$J$ = 18.1 Hz). The relative configuration of the chiral centers (3*R*,3'*S*) in molecules **XIIa** and **XIIb** was assigned on the basis of the X-ray diffraction data for adduct **XIIa** (see figure); correspondingly, stereoisomers **XIIIa** and **XIIIb** were assigned (3*R*,3'*R*) structure.

The ratios of adducts **XIIa/XIIIa** and **XIIb/XIIIb** are close to 1.5, whereas thermolysis of diazabicyclohexane **Ic** having two methyl groups in position *3* gives rise to only one isomer which was identified as *rel*-(3*R*,3'*S*)-**XIId** on the basis of the $^1$H NMR data. The $^1$H NMR spectrum of **XIId** contained signals at δ, ppm: 4.38 t ($J$ = 8.4 Hz), 2.25 d.d ($J$ = 8.4, 12.8 Hz), and 3.24 d.d ($J$ = 8.4, 12.8 Hz); the observed chemical shifts are fairly similar to those found for compound **XIIb**.

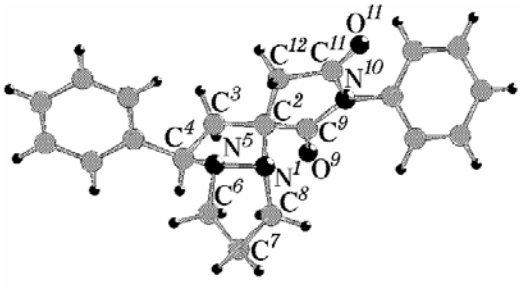



**XIId**




**XIIIb**

The regioselectivity in the addition of *N*-arylimides derived from 2-arylmaleic, citraconic, and itaconic acids to azomethine imines generated from 6-aryldiazabicyclohexanes **Ia**–**Ic** does does not corresponds to that expected under charge or orbital control of the process. The results of MNDO calculations showed that the maximal electron density in imides **II** is localized on the unsubstituted carbon atom at the double bond, and in imides **III** and **IV**, on the quaternary carbon atom. Both double-bonded carbon atoms in imides **II** and **III** are characterized by almost equal coefficients in the lowest unoccupied molecular orbital (LUMO). Therefore, we believe that the regioselectivity in the addition is controlled mainly by steric interactions in the transition state. Scheme 4 illustrates different modes of reactant approach, which are characterized by the least steric interactions in the case of *trans* configuration of intermediate azomethine




Structure of *rel*-(3*R*,3'*S*)-1,3'-diphenylspiro[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole]-2,5-dione (**XIIa**) according to the X-ray diffraction data.

imine. However, although such an approach seems to be the most probable, there are no unambiguous proofs for its configuration. Likewise, the reduced reactivity of maleimides containing substituents at the double bond is likely to result from steric interactions in the transition state.

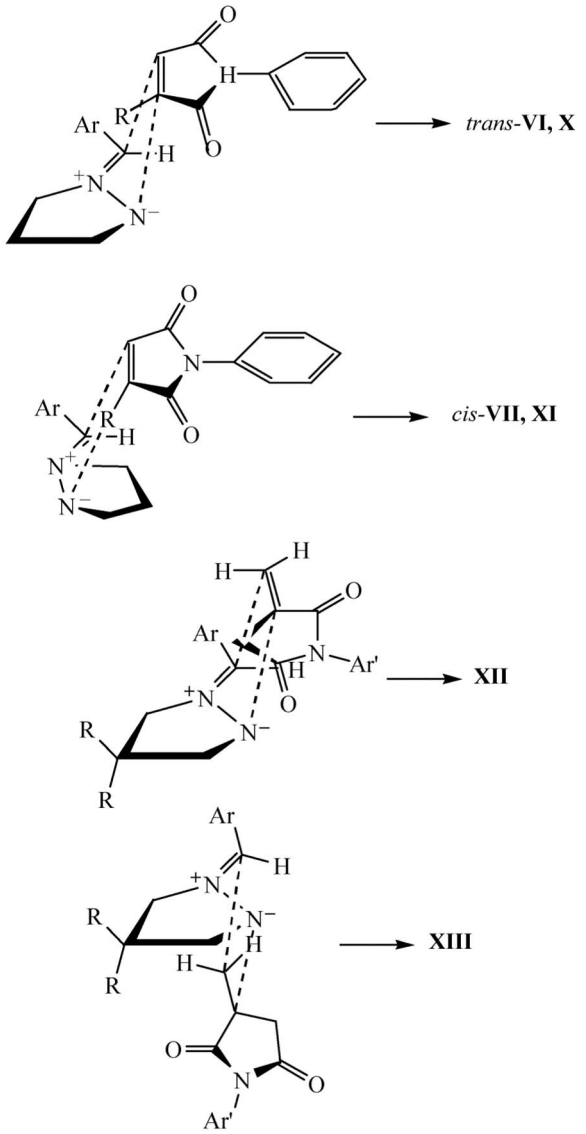
No cycloaddition products were formed when the thermolysis of 6-aryldiazabicyclohexanes was performed in the presence of styrene or cinnamic acid esters, presumably because of insufficient reactivity of these dipolarophiles. Heating of diazabicyclohexane **Ia** in *p*-xylene in the presence of dimethyl acetylenedicarboxylate or of diazabicyclohexane **Ib** in the presence of ethyl 2-propynoate resulted in formation of substituted pyrazolo[1,2-*a*]pyrazolecarboxylates **XIV** and **XV** in 56 and 43% yield, respectively (Scheme 5). The structure of **XIV** and **XV** was established on the basis of analytical and spectral data. The stereoisomeric configuration of **XV** was assigned using $^1$H NMR spectroscopy. In the $^1$H NMR spectrum we observed singlets from the methine proton at δ 5.12 ppm and proton at the double bond at δ 7.12 ppm.

Published data on the regioselectivity of reactions of azomethine imines with propynoates and acrylates are contradictory. Azomethine imine generated *in situ* from 5-phenyl-1,3,4-oxadiazin-2-one and benzaldehyde reacts with methyl acrylate to give product with vicinal aryl and ester groups [3], whereas reactions of methyl propynoate with 5,5-dimethyl-1-(arylmethylene)-3-oxopyrazolidin-1-ium-2-ides generated from 5,5-dimethylpyrazolidin-3-one and aromatic aldehydes lead mainly to formation of mixtures of regioisomeric aducts or sterically less hindered regioisomer (in the case of 2,6-disubstituted benzaldehydes [4]. In the adducts formed by allyl propynoate with azomethine imines having no aryl substituent, e.g., those generated from pyrazolidin-3-ones and formaldehyde, the methylene and ester groups occupy 1,3-positions [5].

As we already reported [6], thermolysis of diazabicyclohexanes **Ia**–**Ih** in the presence of aryl isocyanates **Va**–**Vc** or aryl isothiocyanates **Vd**–**Vf** occurs in a regioselelective fashion to give substituted perhydropyrazolo[1,2-*a*][1,2,4]triazoles **XVIa**–**XVIj** in high yields (Scheme 6). The structure of adducts **XVIa**–**XVIj** was confirmed by their analytical and spectral data.

The regioselectivity in this reaction corresponds to that observed previously for 1-arylmethylene-3-oxo-1-pyrazolidin-1-ium-2-ides [7] and azomethine imines generated from 2-alkyl-3,3-pentamethylene-1-(*p*-tolylsulfonyl)diaziridines [8]: in all cases, 1,2,4-triazole derivatives were obtained.

**Scheme 4.**



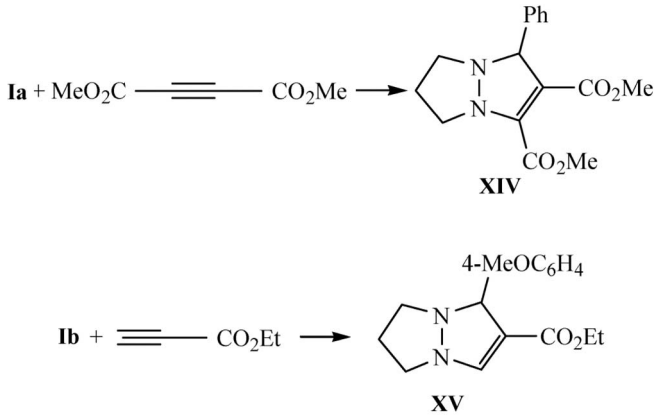

## EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrophotometer from 2% solutions in chloroform. The $^1$H NMR spectra were recorded on a Bruker DPX-300 spectrometer (300 MHz) from 5% solutions in $CDCl_3$.

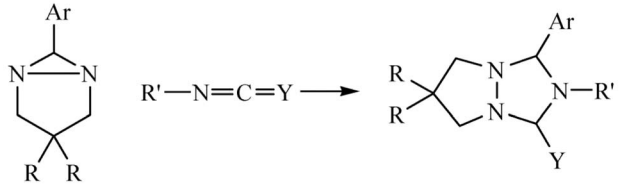
Initial 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **Ia**–**Ih** were synthesized by condensation of 1,3-propanediamine with the corresponding aldehyde, followed by oxidation of the resulting hexahydropyrimidine according to the procedure reported in [1, 9].

**6-(2-Methoxyphenyl)-1,5-diazabicyclo[3.1.0]-hexane (Ih).** A solution of 13.6 g (0.1 mol) of 2-methoxybenzaldehyde in 60 ml of methanol and 30 ml of water was added dropwise with stirring over a period of 3 h to 9.2 ml (0.11 mol) of 1,3-propanediamine, maintaining the temperature not exceeding 45°C (the mixture was cooled with ice water). When the entire amount of the aldehyde was added, the mixture was stirred at room

**Scheme 5.**




**Scheme 6.**




**I**, R = H, Ar = Ph (**a**), Ar = 4-$MeOC_6H_4$ (**b**); R = Me, Ar = 4-$MeOC_6H_4$ (**c**), R = H, Ar = 4-$MeC_6H_4$ (**d**), 4-$ClC_6H_4$ (**e**), 4-$NCC_6H_4$ (**f**), 4-$BrC_6H_4$ (**g**), 2-$MeOC_6H_4$ (**h**); **V**, Y = O, R' = Ph (**a**), 1-naphthyl (**b**), 3,4-$Cl_2C_6H_3$ (**c**); Y = S, R' = Me (**d**), Et (**e**), Ph (**f**); **XVI**, Y = O, R = H, R' = 1-naphthyl, Ar = 4-$MeC_6H_4$ (**a**), 4-$MeOC_6H_4$ (**b**), 4-$ClC_6H_4$ (**c**); R' = Ph, Ar = 4-$NCC_6H_4$ (**d**), 2-$MeOC_6H_4$ (**e**); R' = 3,4-$Cl_2C_6H_3$, Ar = 4-$BrC_6H_4$ (**f**); R = Me, R' = Ph, Ar = 4-$MeOC_6H_4$ (**g**); Y = S, R = H, Ar = Ph, R' = Me (**h**), Et (**i**); Ar = 4-$NCC_6H_4$, R' = Ph (**j**).

temperature (18–20°C). Methanol was distilled off under reduced pressure at a temperature not exceeding 45°C, a 2.5 N alkaline solution of sodium hypochlorite (53 ml, 0.133 mol) was added dropwise to the residue over a period of 20 min under stirring and cooling with ice water, and the mixture was stirred for 1 h at 18–20°C. The organic layer was separated, and the aqueous layer was shaken with benzene. The combined extracts were washed over sodium sulfate, and the solvent was distilled off on a rotary evaporator at a temperature not exceeding 50°C. The residue was recrystallized first from ether containing a small amount of benzene and then from a mixture of benzene, ether, and hexane to obtain 8.4 g (44%) of diazaalkane **Ih**. mp 83–84°C. IR spectrum, ν, $cm^{-1}$: 880, 980, 1040, 1050, 1090, 1120, 1160, 1180, 1260, 1290, 1305, 1340, 1400, 1440, 1465 s, 1495, 1590, 1605, 2840, 2880, 2990 s, 3040. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.88–2.02 m (2H), 3.09–3.23 m (2H), 3.55–3.65 m (2H), 3.62 s (1H), 3.86 s (3H), 6.86 d (1H, 8.0), 6.96 t (1H, 7.3), 7.22–7.28 (1H), 7.36 d (1H, 7.3). Found, %: C 69.32; H 7.27; N 14.89. $C_{11}H_{14}N_2O$. Calculated, %: C 69.45; H 7.42; N 14.73.

**Thermolysis of 1,5-diazabicyclo[3.1.0]hexanes in the presence of dipolarophiles.** A mixture of 1,5-diazabicyclo[3.1.0]hexane and dipolarophile in *p*-xylene was stirred at 135–140°C over a period of 25 min for compound **Ia** or 20 min for **Ib**. The reactions with the other diazabicyclohexanes were carried out in toluene at 110°C (2 h). The solvent was distilled off, and the residue was either recrystallized from appropriate solvent or subjected to column chromatography on silica gel L 100/160 μm (gradient elution with hexane–ethyl acetate, from 6 : 1 do 1 : 1).

**2,3a,9-Triphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIa/VIIa)** was synthesized from 1.54 g (9.6 mmol) of diazabicyclohexane **Ia** and 1.2 g (4.8 mmol) of imide **IIa** in 7 ml of toluene. The product was isolated by column chromatography, followed by recrystallization from ether. Yield 0.19 g (10%) of *trans* isomer **VIa**, mp 148°C, and 0.29 g (15%) of *cis* isomer **VIIa**, mp 173°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIa**: 2.20–2.32 m (2H), 2.74–2.86 m (1H), 3.21–3.38 m (2H), 3.54–3.65 m (1H), 3.83 d (1H, 4.4), 4.60 d (1H, 4.4), 7.30–7.65 (15H); *cis* isomer **VIIa**: 2.23–2.35 m (2H), 2.60–2.71 m (1H), 2.81–2.91 m (1H), 3.16 t.d (1H, 9.4, 4.4), 3.33–3.44 m (1H), 4.18 d (1H, 10.0), 4.50 d (1H, 10.0), 7.07 d (2H, 7.0), 7.30–7.78 (13H). IR spectrum, $cm^{-1}$: *cis* isomer **VIIa**: 1120, 1160, 1240, 1380, 1510, 1600, 1730 s, 2880, 2990, 3040. Found (for isomer mixture **VIa**/**VIIa**), %: C 76.20, 76.19; H 5.65, 5.56; N 9.88, 9.85. $C_{26}H_{23}N_3O_2$. Calculated, %: C 76.26; H 5.66; N 10.26.

**2-(4-Fluorophenyl)-3a,9-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIb/VIIb) and 2-(4-fluorophenyl)-9,9a-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIIb)** were synthesized from 0.96 g (6 mmol) of diazabicyclohexane **Ia** and 0.80 g (3 mmol) of imide **IIb** in 7 ml of toluene. The products were isolated by column chromatography, followed by recrystallization from ether. Yield 0.33 g (26%) of *trans* isomer **VIb**, mp 139°C, and 0.50 g (39%) of *cis* isomer **VIIb**, mp 137°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIb**: 2.22–2.32 m (2H), 2.70–2.81 m (1H), 3.19–3.34 m (2H), 3.49–3.59 m (1H), 3.84 d (1H, 4.9), 4.55 d (1H, 4.9), 7.20–7.43 (10H), 7.51 d (2H, 7.1), 7.62 d (2H, 7.1); *cis* isomer **VIIb**: 2.19–2.30 m (2H), 2.58–2.67 m (1H), 2.83–2.92 m (1H), 3.15 t. d (1H, 9.3, 3.5), 3.33–3.42 m (1H), 4.18 d (1H, 9.7), 4.51 d (1H, 9.7), 7.00–7.09 (4H), 7.33–7.53 (8H), 7.65–7.78 (2H). IR spectrum, ν, $cm^{-1}$: *cis* isomer **VIIa**: 1120, 1160, 1240, 1300, 1380, 1450, 1510, 1730 s, 2870, 2980, 3040. Found (for *trans* isomer **VIb**), %: C 72.86, 72.98; H 5.12, 5.33; N 9.61, 9.76. $C_{26}H_{22}FN_3O_2$. Calculated, %: C 73.05; H 5.19; N 9.83.

Characteristic proton signals of isomer **VIIIb** in the $^1$H NMR spectrum of the reaction mixture, δ, ppm (*J*, Hz): 4.35 s (1H), 4.84 s (1H). Yield of dihydropyrazole **IXb** 0.18 g (19%).

**2-(4-Ethoxyphenyl)-3a,9-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIc/VIIc) and 2-(4-ethoxyphenyl)-9,9a-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIIc)** were obtained from 1.28 g (8 mmol) of diazabicyclohexane **Ia** and 1.17 g (4 mmol) of imide **IIc** in 9 ml of toluene. The products were isolated by column chromatography; *trans* isomer **VIc** was then recrystallized from ether, and *cis* isomer **VIIc** and regioisomer **VIIIc**, from acetone–ether–hexane. Yield 0.66 g (36%) of *trans* isomer **VIc**, mp 182°C, 0.78 g (43%) of *cis* isomer **VIIc**, mp 148°C, and 0.07 g (4%) of isomer **VIIIc**, mp 135°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIc**: 1.46 t (3H, 6.9), 2.18–2.35 m (2H), 2.74–2.84 m (1H), 3.22–3.37 m (2H), 3.54–3.64 m (1H), 3.80 d (1H, 4.4), 4.09 q (2H, 6.9), 4.58 d (1H, 4.4), 7.04 d (2H, 8.8), 7.26–7.44 (8H), 7.52 d (2H, 7.1), 7.62 d (2H, 7.1); *cis* isomer **VIIc**: 1.41 t (3H, 7.0), 2.17–2.35 m (2H), 2.57–2.68 m (1H), 2.81–2.92 m (1H), 3.14 t.d (1H, 9.4, 4.0), 3.32–3.44 m (1H), 3.99 q (2H, 7.0), 4.16 d (1H, 9.8), 4.50 d (1H, 9.8), 6.83 d (2H, 9.0), 6.95 d (2H, 9.0), 7.38–7.75 (10H); isomer **VIIIc**: 1.44 t (3H, 7.0), 2.13–

2.28 m (2H), 2.75–2.87 m (1H), 3.12–3.28 m (2H), 3.47–3.58 m (1H), 4.04 q (2H, 7.0), 4.32 s (1H), 4.80 s (1H), 6.95 d (2H, 8.0), 7.23 d (2H, 8.0), 7.35–7.68 (10H). IR spectrum, ν, $cm^{-1}$: *cis* isomer **VIIc**: 1050, 1120, 1170, 1180, 1260, 1300, 1390, 1450, 1510, 1620, 1730 s, 2880, 2890, 3040; isomer **VIIIc**: 1050, 1120, 1170, 1260, 1310, 1395, 1520, 1620, 1730 s, 2880, 2990, 3040. Found (for *cis* isomer **VIIc**), %: C 74.02, 74.19; H 6.23, 6.15; N 9.48, 9.48. $C_{28}H_{27}N_3O_3$. Calculated, %: C 74.15; H 6.00; N 9.27.

**3a-(4-Nitrophenyl)-2,9-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VId/VIId) and 9a-(4-nitrophenyl)-2,9-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIId)** were synthesized from 0.32 g (2 mmol) of diazabicyclohexane **Ia** and 0.29 g (1 mmol) of imide **IIh** in 6 ml of *p*-xylene. Recrystallization from benzene–hexane and then from acetone–hexane gave 0.11 g (24%) of *trans* isomer **VId**, mp 171°C, and 0.13 g (29%) of *cis* isomer **VIId**, mp 180°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VId**: 2.20–2.40 m (2H), 2.77–2.92 m (1H), 3.25–3.41 m (2H), 3.47–3.57 m (1H), 3.79 d (1H, 4.9), 4.64 d (1H, 4.9), 7.20–7.60 (10H), 7.80 d (2H, 8.5), 8.25 d (2H, 8.5); *cis* isomer **VIId**: 2.21–2.40 m (2H), 2.60–2.72 m (1H), 2.76–2.87 m (1H), 3.13 t.d (1H, 9.1, 4.4), 3.26–3.42 m (1H), 4.12 d (1H, 9.7), 4.47 d (1H, 9.7), 7.09 d (2H, 6.6), 7.30–7.60 (8H), 7.91 d (2H, 8.8), 8.32 d (2H, 8.8). IR spectrum, ν, $cm^{-1}$: *trans* isomer **VId**: 1080, 1120, 1130, 1180, 1240, 1310, 1350 s, 1370, 1500, 1530, 1600, 1730 s, 2860, 2980, 3040. Found (for *cis* isomer **VIId**), %: C 68.57, 68.96; H 4.96, 5.02; N 12.23, 12.38. $C_{26}H_{22}N_4O_4$. Calculated, %: C 68.71; H 4.82; N 12.33.

Characteristic proton signal of isomer **VIIId** in the $^1$H NMR spectrum of the reaction mixture: δ 4.84 ppm (s, 1H).

**9-(4-Methoxyphenyl)-2,3a-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazol-1,3-dione (VIe/VIIe) and 9-(4-methoxyphenyl)-2,9a-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIIe)** were synthesized from 1.9 g (10 mmol) of diazabicyclohexane **Ib** and 1.25 g (5 mmol) of imide **IIa** in 12 ml of toluene. The products were isolated by column chromatography, followed by recrystallization from ether. Yield 0.55 g (25%) of *trans* isomer **VIe**, mp 134°C, 0.61 g (28%) of *cis* isomer **VIIe**, mp 143°C, and 0.11 g (5%) of regioisomer **VIIIe**, mp 141°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIe**: 2.22–2.35 m (2H), 2.73–2.83 m (1H), 3.20–3.32 m (2H), 3.47–3.55 m (1H), 3.81 s (4H), 4.52 d (1H, 4.9), 6.90 d (2H, 8.8), 7.37–7.58 (10H), 7.65 d (2H, 7.1); *cis* isomer **VIIe**: 2.18–2.31 m (2H), 2.62 q (1H, 8.8), 2.80–2.92 m (1H), 3.14 t.d (1H, 9.3, 4.0), 3.31–3.42 m (1H), 3.83 s (3H), 4.15 d (1H, 9.7), 4.47 d (1H, 9.7), 6.95 d (2H, 8.8), 7.08 d (2H, 7.1), 7.30–7.75 (10H); isomer **VIIIe**: 2.15–2.30 m (2H), 2.76–2.85 m (1H), 3.11–3.26 m (2H), 3.49–3.59 m (1H), 3.81 s (3H), 4.27 s (1H), 4.82 s (1H), 6.89 d (2H, 8.0), 7.30–7.50 (10H), 7.62 d (2H, 8.0). IR spectrum, ν, $cm^{-1}$: *trans* isomer **VIe**: 1040, 1115, 1130, 1180, 1260, 1305, 1380, 1465, 1520, 1620, 1725 s, 2840, 2970, 3040; isomer **VIIIe**: 1040, 1115, 1130, 1185, 1260, 1305, 1385, 1520, 1625, 1730 s, 2830, 2890, 2970, 3040. Found (for *trans* isomer **VIe**), %: C 73.82, 73.83; H 5.87, 5.76; N 9.22, 9.22. $C_{27}H_{25}N_3O_3$. Calculated, %: C 73.78; H 5.73; N 9.56.

**9-(4-Methoxyphenyl)-2-(4-methylphenyl)-3a-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]-pyrazole-1,3-dione (VIf/VIIf)** was synthesized from 0.83 g (4.37 mmol) of diazabicyclohexane **Ib** and 0.5 g (1.9 mmol) of imide **IId** in 5 ml of toluene. The product was isolated by column chromatography, followed by recrystallization from ether. Yield 0.07 g (8%) of *trans* isomer **VIf**, mp 112°C, and 0.1 g (12%) of *cis* isomer **VIIf**, mp 138°C. 1H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIf**: 2.15–2.32 m (2H), 2.42 s (3H), 2.71–2.81 m (1H), 3.16–3.35 m (2H), 3.48–3.59 m (1H), 3.77 d (1H, 4.4), 3.81 s (3H), 4.51 d (1H, 4.4), 6.90 d (2H, 8.8), 7.20–7.68 (11H); *cis* isomer **VIIf**: 2.15–2.28 m (2H), 2.33 s (3H), 2.56–2.66 m (1H), 2.79–2.88 m (1H), 3.14 t.d (1H, 9.3, 3.4), 3.30–3.41 m (1H), 3.83 s (3H), 4.12 d (1H, 9.7), 4.45 d (1H, 9.7), 6.90–7.75 (13H). IR spectrum, ν, $cm^{-1}$: *cis* isomer **VIIf**: 1040, 1120, 1180, 1260, 1305, 1380, 1520, 1625, 1730 s, 2870, 2970, 3030. Found, %: for *trans* isomer **VIf**: C 73.90, 74.29; H 6.18, 6.08; N 9.04, 9.09; for *cis* isomer **VIIf**: C 74.14, 74.30; H 6.00, 6.23; N 9.11, 9.10. $C_{28}H_{27}FN_3O_3$. Calculated, %: C 74.15; H 6.00; N 9.27.

**2-(4-Chlorophenyl)-9-(4-methoxyphenyl)-3a-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]-pyrazole-1,3-dione (VIg/VIIg) and 2-(4-chlorophenyl)-9-(4-methoxyphenyl)-9a-phenylperhydro-pyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIIg)** were synthesized from 1.21 g (6.37 mmol) of diazabicyclohexane **Ib** and 0.91 g (3.2 mmol) of imide **IIe** in 9 ml of toluene. The products were isolated by column chromatography, followed by recrystallization from acetone–ether–hexane. Yield 0.3 g (20%) of *trans* isomer **VIg**, mp 139°C, 0.64 g (42%) of *cis* isomer **VIIg**, mp 130°C, and 0.03 g (1.6%) of regioisomer **VIIIg**, mp 110°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIg**: 2.15–2.38 m (2H), 2.66–2.79 m (1H), 3.13–3.30 m (2H), 3.42–3.53 m (1H), 3.81 s (4H),

4.47 d (1H, 4.9), 6.89 d (2H, 8.8), 7.33–7.45 (7H), 7.51 d (2H, 8.8), 7.61 d (2H, 7.1); *cis* isomer **VIIg**: 2.18–2.31 m (2H), 2.54–2.68 m (1H), 2.79–2.92 m (1H), 3.12 t.d (1H, 9.3, 4.0), 3.29–3.43 m (1H), 3.83 s (3H), 4.15 d (1H, 9.9), 4.47 d (1H, 9.9), 6.91 d (2H, 8.8), 7.03 d (2H, 8.8), 7.25–7.75 (9H); isomer **VIIIg**: 2.15–2.28 m (2H), 2.75–2.84 m (1H), 3.11–3.25 m (2H), 3.48–3.56 m (1H), 3.82 s (3H), 4.23 s (1H), 4.81 s (1H), 6.89 d (2H, 8.4), 7.22–7.49 (10H), 7.61 d (2H, 7.1). IR spectrum, ν, $cm^{-1}$: *trans* isomer **VIg**: 1040, 1100, 1130, 1180, 1260, 1305, 1375, 1460, 1495, 1520, 1620, 1730 s, 2840, 2975, 3040. Found (for *trans* isomer **VIg**), %: C 68.74; H 5.14; N 8.72. $C_{27}H_{24}ClN_3O_3$. Calculated, %: C 68.42; H 5.10; N 8.87. Yield of dihydropyrazole **IXb** 0.63 g (52%).

**2,9-Bis(4-methoxyphenyl)-3a-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIh/ VIIh) and 2,9-bis(4-methoxyphenyl)-9a-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIIh)** were synthesized from 1.71 g (9 mmol) of diazabicyclohexane **Ib** and 1.26 g (4.5 mmol) of imide **IIf** in 11 ml of toluene. The products were isolated by column chromatography; *trans* isomer **VIh** was then recrystallized from ether, and *cis* isomer **VIIh,** from acetone–ether–hexane. Yield 0.7 g (33%) of *trans* isomer **VIh**, mp 125°C, and 0.93 g (44%) of *cis* isomer **VIIh**, mp 135°C. 1H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **VIh**: 2.15–2.34 m (2H), 2.72–2.82 m (1H), 3.18–3.31 m (2H), 3.46–3.57 m (1H), 3.75 d (1H, 4.4), 3.80 s (3H), 3.87 s (3H), 4.50 d (1H, 4.4), 6.86 d (2H, 8.8), 7.50 d (2H, 8.8), 7.31–7.45 (7H), 7.57–7.67 (2H); *cis* isomer **VIIh**: 2.17–2.38 m (2H), 2.61 q (1H, 8.8), 2.79–2.90 m (2H), 3.12 t.d (1H, 9.3, 3.5), 3.78 s (3H), 3.83 s (3H), 4.13 d (1H, 9.7), 4.45 d (1H, 9.7), 6.86 d (2H, 9.3), 6.92 d (2H, 8.8), 7.00 d (2H, 8.8), 7.40–7.50 (5H), 7.65–7.75 (2H). IR spectrum, ν, $cm^{-1}$: *cis* isomer **VIIh**: 1040, 1115, 1175, 1260, 1305, 1390, 1450, 1470, 1520, 1620, 1730 s, 2845, 2870, 2940, 2970, 2990, 3040. Found (for *cis* isomer **VIIh**), %: C 71.56, 71.67; H 6.11, 5.74; N 8.69, 8.85. $C_{28}H_{27}N_3O_4$. Calculated, %: C 71.62; H 5.80; N 8.95. Characteristic signal of isomer **VIIIh** in the 1H NMR spectrum of the reaction mixture: δ 4.83 ppm (s, 1H).

**9-(4-Methoxyphenyl)-2-(3-nitrophenyl)-3a-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIi/VIIIi) and 9-(4-methoxy-phenyl)-2-(3-nitrophenyl)-9a-phenylperhydropyrazolo-[1,2-*a*]-pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIIg)** were synthesized from 1.14 g (6 mmol) of diazabicyclohexane **Ib** and 0.88 g (3 mmol) of imide **IIg** in 9 ml of toluene. *cis* Isomer **VIIi** was recrystallized from ether. Yield 0.7 g (48%), mp 172°C. 1H NMR spectrum, δ, ppm (*J*, Hz): 2.14–2.38 m (2H), 2.55–2.69 m (1H), 2.84–2.96 m (1H), 3.14 t.d (1H, 9.3, 3.5), 3.32–3.45 m (1H), 3.87 s (3H), 4.19 d (1H, 9.7), 4.52 d (1H, 9.7), 6.98 d (2H, 8.4), 7.40–7.75 (9H), 7.97 s (1H), 8.13 d (1H, 7.9). IR spectrum, ν, $cm^{-1}$: 1040, 1120, 1175, 1260, 1305, 1350 s, 1380, 1520, 1540, 1620, 1735 s, 2880, 2990, 3040. Found, %: C 66.88, 66.69; H 5.33, 5.16; N 11.30, 11.31. $C_{27}H_{24}N_4O_5$. Calculated, %: C 66.93; H 4.99; N 11.56. Characteristic signals of isomers **VIi** and **VIIIi** in the $^1$H NMR spectrum of the reaction mixture, δ, ppm (*J*, Hz): *trans* isomer **VIi**: 3.10–3.23 m (1H), 3.32–3.45 m (1H), 3.83 s (3H), 4.45 d (1H, 5.1); regioisomer **VIIIi**: 4.32 s (1H), 4.87 s (1H). Yield of dihydropyrazole **IXb** 0.48 g (42%).

**9-(4-Methoxyphenyl)-3a-(4-nitrophenyl)-2-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (VIIj)** was synthesized from 0.38 g (2 mmol) of diazabicyclohexane **Ib** and 0.29 g (1 mmol) of imide **IIh** in 3 ml of toluene. Recrystallization from benzene–hexane gave 0.23 g (47%) of *cis* isomer **VIIj**, mp 183°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.20–2.40 m (2H), 2.58–2.80 m (1H), 2.75–2.85 m (1H), 3.08–3.17 m (1H), 3.27–3.39 m (1H), 3.83 s (3H), 4.10 d (1H, 8.9), 4.43 d (1H, 8.9), 6.94 d (2H, 8.1), 7.11 d (2H, 8.1), 7.31–7.47 (5H), 7.91 d (2H, 8.1), 8.33 d (2H, 8.1). IR spectrum, ν, $cm^{-1}$: 1040, 1120, 1180, 1260, 1300, 1350 s, 1380, 1530, 1620, 1730 s, 2840, 2970, 3020, 3040. Found, %: C 67.10, 66.99; H 5.13, 4.98; N 11.13, 11.47. $C_{27}H_{24}N_4O_5$. Calculated, %: C 66.93; H 4.99; N 11.56.

**3a-Methyl-2,9-diphenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (Xa/XIa)** was synthesized from 0.48 g (3 mmol) of diazabicyclohexane **Ia** and 0.42 g (2.25 mmol) of imide **IIIa** in 5 ml of toluene. The product was recrystallized from a mixture of acetone (3 ml) with ether (1.5 ml) to isolate 0.24 g (31%) of *trans* isomer **Xa**, mp 140°C, and 0.29 g (37%) of *cis* isomer **XIa**, mp 184°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **Xa**: 1.66 s (3H), 2.13–2.27 m (2H), 2.55–2.66 m (1H), 3.12–3.25 m (2H), 3.38 d (1H, 4.6), 3.41–3.53 m (1H), 4.39 d (1H, 4.6), 7.29–7.59 (10H); *cis* isomer **XIa**: 1.73 s (3H), 2.15–2.36 m (2H), 2.74–2.85 m (1H), 2.97 q (1H, 8.8), 3.22–3.34 m (2H), 3.51 d (1H, 9.7), 4.40 d (1H, 9.7), 7.12–7.45 (10H). IR spectrum, ν, $cm^{-1}$: *trans* isomer **Xa**: 1080, 1120, 1140, 1250, 1310, 1370, 1380, 1460, 1510, 1610, 1730 s, 2870, 2980, 3040; *cis* isomer **XIa**: 1120, 1160, 1240, 1290, 1305, 1375, 1390, 1455, 1505, 1610, 1730 s, 2870, 2990, 3040. Found, %: for *trans* isomer **Xa**: C 72.83, 72.76; H 6.16, 6.03; N 12.04, 12.12; for *cis* isomer **XIa**: C 72.86, 72.44; H 6.12, 6.01; N 11.94, 11.98. $C_{21}H_{21}N_3O_2$. Calculated, %: C 72.60; H 6.09; N 12.10.

**3a-Methyl-2-(4-methylphenyl)-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-**

**dione (Xb/XIb)** was synthesized from 0.62 g (3.9 mmol) of diazabicyclohexane **Ia** and 0.6 g (3 mmol) of imide **IIIb** in 7 ml of toluene. Recrystallization from benzene–ether gave 0.55 g (45%) of *trans* isomer **Xb** with mp 143°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.66 s (3H), 2.14–2.25 m (2H), 2.42 s (3H), 2.56–2.67 m (1H), 3.13–3.24 m (2H), 3.36 d (1H, 4.4), 3.40–3.50 m (1H), 4.40 d (1H, 4.4), 7.20 d (2H, 8.1), 7.29–7.44 (5H), 7.58 d (2H, 7.5). IR spectrum, ν, cm$^{-1}$: 915, 1140, 1250, 1370, 1380, 1450, 1520, 1725 s, 2870, 2940, 2980, 3040. Found, %: C 73.30, 73.12; H 6.50, 6.42; N 11.70, 11.60. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63. Characteristic signals of *cis* isomer **XIb** in the $^1$H NMR spectrum of the reaction mixture, δ, ppm (*J*, Hz): 1.72 s (3H), 2.35 s (3H), 2.73–2.84 m (1H), 3.49 d (1H, 9.8), 4.40 d (1H, 9.8).

**2-(4-Methoxyphenyl)-3a-methyl-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (Xc/XIc)** was synthesized from 0.32 g (2 mmol) of diazabicyclohexane **Ia** and 0.33 g (1.5 mmol) of imide **IIIc** in 5 ml of toluene. By fractional crystallization from ether we isolated 0.31 g (55%) of *trans* isomer **Xc**, mp 132°C, and 0.13 g (24%) of *cis* isomer **XIc**, mp 182°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **Xc**: 1.68 s (3H), 2.15–2.25 m (2H), 2.56–2.64 m (1H), 3.12–3.24 m (2H), 3.36 d (1H, 4.9), 3.38–3.49 m (1H), 3.86 s (3H), 4.39 d (1H, 4.9), 7.02 d (2H, 8.1), 7.21–7.40 (5H), 7.58 d (2H, 7.3); *cis* isomer **XIc**: 1.72 s (3H), 2.14–2.37 m (2H), 2.73–2.83 m (1H), 2.92–3.02 m (1H), 3.23–3.24 m (2H), 3.49 d (1H, 8.9), 3.81 s (3H), 4.40 d (1H, 8.9), 6.92 d (2H, 8.1), 7.10 d (2H, 8.1), 7.30–7.47 (5H). IR spectrum, ν, cm$^{-1}$: *cis* isomer **XIc**: 1040, 1120, 1160, 1170, 1180, 1260, 1305, 1390, 1460, 1520, 1620, 1730 s, 2840, 2870, 2940, 2990, 3040. Found (for *cis* isomer **XIc**), %: C 70.11, 69.91; H 6.14, 6.37; N 10.97, 11.04. $C_{22}H_{23}N_3O_3$. Calculated, %: C 70.01; H 6.14; N 11.13.

**2-(4-Ethoxyphenyl)-3a-methyl-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (Xd/XId)** was synthesyzed from 0.62 g (3.9 mmol) of diazabicyclohexane **Ia** and 0.69 g (3 mmol) of imide **IIId** in 7 ml of toluene. Fractional crystallization from acetone–ether gave 0.26 g (22%) *trans* isomer **Xd**, mp 118°C, and 0.66 g (57%) of *cis* isomer **XId**, mp 187°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **Xd**: 1.45 t (3H, 7.1), 1.65 s (3H), 2.12–2.28 m (2H), 2.60 q (1H, 8.8), 3.12–3.25 m (2H), 3.36 d (1H, 4.4), 3.38–3.53 m (1H), 4.08 q (2H, 7.1), 4.39 d (1H, 4.4), 7.00 d (2H, 8.8), 7.22 d (2H, 8.8), 7.30–7.43 d (3H), 7.57 d (2H, 7.5); *cis* isomer **XId**: 1.41 t (3H, 7.1), 1.71 s (3H), 2.18–2.34 m (2H), 2.73–2.84 m (1H), 2.97 q (1H, 8.8), 3.22–3.33 m (2H), 3.48 d (1H, 9.5), 4.01 q (2H, 7.1), 4.39 d (1H, 9.5), 6.90 d (2H, 8.6), 7.08 d (2H, 8.6), 7.30–7.47 (5H). IR spectrum, ν, cm$^{-1}$: *cis* isomer **XId**: 915, 1050, 1120, 1160, 1170, 1245, 1305, 1375, 1390, 1450, 1520, 1620, 1715 s, 2880, 2940, 2990, 3030. Found, %: for *trans* isomer **Xd**: C 70.35, 70.74; H 6.43, 6.53; N 10.81, 10.80; for *cis* isomer **XId**: C 70.58, 70.85; H 6.45, 6.53; N 10.76, 10.73. $C_{23}H_{25}N_3O_3$. Calculated, %: C 70.57; H 6.44; N 10.73.

**2-(3-Chlorophenyl)-3a-methyl-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (Xe/XIe)** was synthesized from 0.62 g (3.9 mmol) of diazabicyclohexane **Ia** and 0.67 g (3 mmol) of imide **IIIe** in 7 ml of toluene. Fractional crystallization of a mixture of *cis* and *trans* isomers from acetone–ether gave 0.52 g (46%) of *trans* isomer **Xe**, mp 164°C, and 0.21 g (18%) of *cis* isomer **XIe**, mp 180°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **Xe**: 1.66 s (3H), 2.15–2.25 m (2H), 2.49–2.62 m (1H), 3.10–3.22 m (2H), 3.28–3.35 m (1H), 3.38 d (1H, 4.4), 4.33 d (1H, 4.4), 7.23–7.62 (9H); *cis* isomer **XIe**: 1.72 s (3H), 2.21–2.35 m (2H), 2.74–2.85 m (1H), 2.92–3.03 m (1H), 3.23–3.33 m (2H), 3.50 d (1H, 9.8), 4.35 d (1H, 9.8), 7.05–7.48 (9H). IR spectrum, ν, cm$^{-1}$: *cis* isomer **XIe**: 1120, 1150, 1240, 1370, 1385, 1455, 1485, 1600, 1735 s, 2870, 2990, 3040. Found (for *cis* isomer **XIe**), %: C 65.90, 65.85; H 5.54, 5.49; N 10.74, 10.92. $C_{21}H_{20}ClN_3O_2$. Calculated, %: C 66.05; H 5.28; N 11.00.

**2-(3,4-Dichlorophenyl)-3a-methyl-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (Xf/XIf)** was synthesized from 0.62 g (3.9 mmol) of diazabicyclohexane **Ia** and 0.77 g (3 mmol) of imide **IIIf** in 7 ml of toluene. Fractional crystallization from acetone–ether–hexane gave 0.35 g (28%) of *trans* isomer **Xf**, mp 152°C, and 0.33 g (27%) of *cis* isomer **XIf**, mp 159°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **Xf**: 1.65 s (3H), 2.16–2.29 m (2H), 2.51 q (1H, 8.8), 3.07–3.17 m (2H), 3.27–3.34 m (1H), 3.38 d (1H, 4.4), 4.28 d (1H, 4.4), 7.26–7.61 (8H); *cis* isomer **XIf**: 1.72 s (3H), 2.20–2.35 m (2H), 2.73–2.84 m (1H), 2.91–3.03 m (1H), 3.27–3.33 m (2H), 3.50 d (1H, 9.5), 4.41 d (1H, 9.5), 7.05–7.15 (1H), 7.30–7.52 (7H). IR spectrum, ν, cm$^{-1}$: *cis* isomer **XIf**: 1040, 1120, 1135, 1155, 1240, 1370, 1385, 1455, 1480, 1730 s, 2870, 2990, 3040. Found, %: for *trans* isomer **Xf**: C 60.65, 60.41; H 4.47, 4.62; N 9.83, 9.80; [dlya tsis-izomera (**XIe**)]: C 60.34, 60.55; H 4.61, 4.62; N 10.04, 10.00. $C_{21}H_{19}Cl_2N_3O_2$. Calculated, %: C 60.59; H 4.60; N 10.09.

**3a-Methyl-2-(3-nitrophenyl)-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (Xg/XIg)** was synthesized from 0.52 g (3.25 mmol) of diazabicyclohexane **Ia** and 0.69 g (2.5 mmol) of imide

**IIIg** in 7 ml of toluene. Recrystallization from acetone–ether gave colorless crystals of *trans* isomer **Xg** with mp 191°C. The mother liquor was evaporated, and the residue was recrystallized from benzene–ether to obtain 0.4 g (41%) of *cis* isomer **XIg** with mp 188°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): *trans* isomer **Xg**: 1.69 s (3H), 2.20–2.30 m (2H), 2.47–2.58 m (1H), 3.07–3.17 m (2H), 3.26–3.35 m (1H), 3.44 d (1H, 5.1), 4.29 d (1H, 5.1), 7.32–7.80 (7H), 8.28–7.31 (2H); *cis* isomer **XIg**: 1.76 s (3H), 2.19–2.38 m (2H), 2.75–2.89 m (1H), 2.93–3.05 m (1H), 3.22–3.37 m (2H), 3.56 d (1H, 9.7), 4.46 d (1H, 9.7), 7.33–7.67 (7H), 8.10 s (1H), 8.18–8.24 (1H). IR spectrum, ν, cm$^{-1}$: *cis* isomer **XIg**: 1020, 1100, 1120, 1140, 1160, 1240, 1315, 1355 s, 1380, 1460, 1490, 1540, 1735 s, 2850, 2880, 2980, 3040. Found, %: for *trans* isomer **Xg**: C 64.44, 64.15; H 5.33, 5.23; N 14.14, 14.34; for *cis* isomer **XIg**: C 64.54, 64.54; H 5.19, 5.29; N 14.18, 14.25. $C_{21}H_{20}N_4O_4$. Calculated, %: C 64.28; H 5.14; N 14.28.

***rel*-(3*R*,3'*S*)-1,3'-Diphenylspiro[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole]-2,5-dione (XIIa) and *rel*-(3*R*,3'*R*)-1,3'-diphenylspiro-[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]-pyrazole]-2,5-dione (XIIIa)** were synthesized from 0.48 g (3 mmol) of diazabicyclohexane **Ia** and 0.56 g (3 mmol) of itaconic acid imide **IVa** in 7 ml of toluene. Recrystallization of the residue from acetone–ether gave 0.18 g (17%) of stereoisomer **XIIa**, mp 167°C, and 0.12 g (12%) of isomer mixture **XIIa**/**XIIIa**. $^1$H NMR spectrum, δ, ppm (*J*, Hz): isomer **XIIa**: 2.05–2.23 m (1H), 2.20 d.d (1H, 13.2, 7.0), 2.29–2.43 m (1H), 2.90–3.03 m (2H), 3.02 d (1H, 18.5), 3.08–3.19 m (1H), 3.19–3.30 m (1H), 3.35 d.d (1H, 13.2, 9.3), 3.48 d (1H, 18.5), 4.20 d.d (1H, 9.3, 7.0), 7.29–7.56 (10H). IR spectrum, ν, cm$^{-1}$: isomer **XIIa**: 1075, 1110, 1130, 1190, 1240, 1380, 1450, 1500, 1595, 1730 s, 2890, 2960, 2980, 3040. Found (for isomer **XIIa**), %: C 72.93, 72.81; H 6.24, 6.27; N 12.32, 12.19. $C_{21}H_{21}N_3O_2$. Calculated, %: C 72.60; H 6.09; N 12.10. Characteristic $^1$H NMR signals of isomer **XIIIa**, δ, ppm (*J*, Hz): 3.28 d (1H, 18.1), 3.95–4.12 m (1H).

***rel*-(3*R*,3'*S*)-1-(4-Chlorophenyl)-3'-phenylspiro[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo-[1,2-*a*]pyrazole]-2,5-dione (XIIb) and *rel*-(3*R*,3'*R*)-1-(4-chlorophenyl)-3'-phenylspiro[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole]-2,5-dione (XIIIb)** were synthesized from 0.64 g (4 mmol) of diazabicyclohexane **Ia** and 0.44 g (2 mmol) of itaconic acid imide **IVb** in 5 ml of toluene. Recrystallization of the residue from acetone gave 0.26 g (34%) of isomer **XIIb**, mp 168°C, and 0.12 g (16%) of isomer **XIIIb**, mp 182°C. 1H NMR spectrum, δ, ppm (*J*, Hz): isomer **XIIb**: 2.06–2.24 m (1H), 2.19 d.d (1H, 13.2, 7.1), 2.29–2.42 m (1H), 2.89–3.01 m (2H), 3.01 d (1H, 18.5), 3.08–3.16 m (1H), 3.17–3.28 m (1H), 3.35 d.d (1H, 13.2, 9.3), 3.48 d (1H, 18.5), 4.18 d.d (1H, 9.3, 7.1), 7.23–7.51 (9H); isomer **XIIIb**: 2.07–2.22 m (1H), 2.23–2.38 m (1H), 2.72 d.d (1H, 13.2, 8.4), 2.75–2.85 m (1H), 2.86 d.d (1H, 13.2, 8.4), 2.96–3.13 m (3H), 3.10 d (1H, 18.1), 3.27 d (1H, 18.1), 4.0 t (1H, 8.4), 7.26–7.40 (5H), 7.47 d (2H, 8.8), 7.61 d (2H, 7.1). $^{13}$C NMR spectrum, $\delta_C$, ppm: isomer **XIIb**: 26.09 ($CH_2$), 45.73 ($CH_2$), 46.84 ($CH_2$), 47.58 ($CH_2$), 50.33 ($CH_2$), 67.76 (CH), 68.88, 127.82, 128.04, 128.07, 129.13, 129.79, 130,69, 134.93, 141.91, 173.95, 176.36; isomer **XIIIb**: 25.40 ($CH_2$), 41.28 ($CH_2$), 46.18 ($CH_2$), 47.90 ($CH_2$), 49.39 ($CH_2$), 66.45 ($CH_2$), 68.37, 128.04, 128.28, 128.81, 129.00, 129.69, 130.68, 134.75, 140.42, 173.35, 177.39. IR spectrum, ν, cm$^{-1}$: isomer **XIIIb**: 1040, 1100, 1180, 1270, 1300, 1380, 1495, 1520, 1620, 1730 s, 2840, 2870, 2960, 3040. Found, %: for isomer **XIIb**: C 65.97, 66.20; H 5.38, 5.25; N 10.93, 10.99; for isomer **XIIIb**: C 66.33, 66.19; H 5.30, 5.24; N 11.07, 11.08. $C_{21}H_{20}ClN_3O_2$. Calculated, %: C 66.05; H 5.28; N 11.00.

***rel*-(3*R*,3'*S*)-3'-(4-Methoxyphenyl)-6',6'-dimethyl-1-phenylspiro[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole]-2,5-dione (XIIc)** was synthesized from 0.33 g (1.5 mmol) of diazabicyclohexane **Ic** and 0.26 g (1.5 mmol) of itaconic acid imide **IVa** in 6 ml of toluene. Recrystallization from a mixture of acetone (3 ml), ether (2 ml), and hexane (2 ml) gave 0.08 g (14%) of isomer **XIIc** with mp 142°C. An additional amount of adduct **XIIc** was isolated from the mother liquor by column chromatography. Overall yield 0.2 g (34%). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.25 s (3H), 1.28 s (3H), 2.25 d.d (1H, 12.8, 8.4), 2.68 d (1H, 8.4), 2.71 d (1H, 10.1), 2.86 d (1H, 10.1), 2.97 d (1H, 18.1), 3.09 d (1H, 8.4), 3.24 d.d (1H, 12.8, 8.4), 3.40 d (1H, 18.1), 3.83 s (3H), 4.38 t (1H, 8.4), 6.91 d (2H, 8.4), 7.29–7.56 (7H). IR spectrum, ν, cm$^{-1}$: 1040, 1120, 1190, 1250, 1300, 1460, 1520, 1620, 1730 s, 2840, 2870, 2960, 3040. Found, %: C 72.93, 72.81; H 6.24, 6.27; N 12.32, 12.19. $C_{24}H_{27}N_3O_3$. Calculated, %: C 72.60; H 6.09; N 12.10.

***rel*-(3*R*,3'*S*)-1-(4-Chlorophenyl)-3'-(4-methoxyphenyl)-6',6'-dimethylspiro[pyrrolidine-3,1'-tetrahydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole]-2,5-dione (XIId)** was synthesized from 0.65 g (3 mmol) of diazabicyclohexane **Ic** and 0.66 g (3 mmol) of itaconic acid imide **IVb** in 7 ml of toluene. Recrystallization from acetone–ether–hexane gave 0.39 g (30%) of stereoisomer **XIId** with mp 168°C. An additional amount of adduct **XIId** was isolated from the mother liquor by column chromatography. Overall yield 0.69 g

(53%). $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.24 s (3H), 1.29 s (3H), 2.23 d.d (1H, 13.1, 8.5), 2.65 d (1H, 8.5), 2.71 d (1H, 10.0), 2.86 d (1H, 10.0), 2.96 d (1H, 18.5), 3.08 d (1H, 8.5), 3.24 d.d (1H, 13.1, 8.5), 3.40 d (1H, 18.5), 3.83 s (3H), 4.37 t (1H, 8.5), 6.91 d (2H, 8.5), 7.30 d (2H, 8.5), 7.34 d (2H, 8.5), 7.48 d (2H, 8.5). IR spectrum, ν, cm$^{-1}$: 1040, 1100, 1180, 1250, 1300, 1380, 1490, 1520, 1620, 1730 s, 2840, 2870, 2960, 3040. Found, %: C 65.72, 65.74; H 6.26, 6.06; N 9.27, 9.55. $C_{24}H_{26}ClN_3O_3$. Calculated, %: C 65.52; H 5.96; N 9.55.

**Dimethyl 5-phenyl-2,3-dihydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole-6,7-dicarboxylate (XIV)** was synthesized from 0.18 g (1.1 mmol) of diazabicyclohexane **Ia** and 0.14 g (1 mmol) of dimethyl acetylenedicarboxylate in 6 ml of *p*-xylene. The product was isolated from the reaction mixture by preparative thin-layer chromatography on silica gel 5/40 μm using hexane–ethyl acetate (3 : 1) as eluent. Yield 0.17 g (56%), mp 80°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.05–2.25 m (2H), 2.85–2.95 m (1H), 3.14-3.25 m (1H), 3.30–3.41 m (1H), 3.45–3.56 m (1H), 3.63 s (3H), 3.95 s (3H), 5.21 s (1H), 7.24–7.48 (5H). IR spectrum, ν, cm$^{-1}$: 1070, 1100, 1140, 1270, 1340, 1440, 1620, 1700 s, 1755 s, 2860, 2960, 3040. Found, %: C 63.77, 63.33; H 6.00, 5.96; N 9.48, 9.29. $C_{16}H_{18}N_2O_4$. Calculated, %: C 63.57; H 6.00; N 9.27.

**Ethyl 5-(4-methoxyphenyl)-2,3-dihydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazole-6-carboxylate (XV).** A mixture of 0.29 g (1.5 mmol) of diazabicyclohexane **Ib** and 0.18 g (1.8 mmol) of ethyl 2-propynoate in 5 ml of *p*-xylene containing a small amount of hydroquinone was stirred for 2 h at 110°C. The product was isolated from the reaction mixture by column chromatography on silica gel 40/60 μm (substrate-to-sorbent ratio 1:50; gradient elution with petroleum ether (bp 40–70°C)–diethyl ether, 3 : 1). Yield 0.2 g (43%), oily substance. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.22 t (3H, 7.1), 2.01–2.21 m (2H), 2.76–2.88 m (1H), 3.08–3.17 m (1H), 3.36–3.53 m (2H), 3.79 s (3H), 4.10 q (2H, 7.1), 5.12 s (1H), 6.85 d (2H, 8.8), 7.12 s (1H), 7.35 d (2H, 8.8). IR spectrum, ν, cm$^{-1}$: 910, 1040, 1080, 1100, 1165, 1180, 1260 s, 1305, 1320, 1380, 1460, 1520, 1610, 1695 s, 2840, 2910, 2940, 2990, 3040. According to the $^1$H NMR data, no other regioisomer was present in the reaction mixture.

**3-(4-Methylphenyl)-2-(1-naphthyl)perhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (XVIa)** was synthesized from 0.44 g (2.5 mmol) of diazabicyclohexane **Id** and 0.42 g (2.5 mmol) of isocyanate **Vc** in 6 ml of toluene. Recrystallization from benzene–hexane gave 0.75 g (87%) of adduct **XVIa** with mp 150°C. 1H NMR spectrum, δ, ppm (*J*, Hz): 2.21–2.42 m (2H), 2.10–2.30 m (1H), 2.28 s (3H), 3.35–3.63 m (2H), 4.06 br.s (1H), 5.82 br.s (1H), 7.05 d (2H, 7.8), 7.07–7.16 m (1H), 7.22 d (2H, 7.8), 7.32–7.40 m (1H), 7.46–7.57 (2H), 7.77 d (1H, 8.1), 7.83–7.91 (2H). IR spectrum, ν, cm$^{-1}$: 1015, 1035, 1075, 1095, 1115, 1155, 1250, 1280, 1295, 1330, 1345, 1380, 1410, 1470, 1595, 1720 s, 2860, 2925, 2980, 3010, 3035. Found, %: C 76.64, 77.03; H 6.03, 6.04; N 12.20, 12.29. $C_{22}H_{21}N_3O$. Calculated, %: C 76.94; H 6.16; N 12.24.

**3-(4-Methoxyphenyl)-2-(1-naphthyl)perhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (XVIb)** was synthesized from 0.67 g (3.5 mmol) of diazabicyclohexane **Ib** and 0.59 g (3.5 mmol) of isocyanate **Vb** in 7 ml of toluene. Recrystallization from benzene–hexane gave 1.13 g (90%) of adduct **XVIb** with mp 149°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.22–2.44 m (2H), 3.06–3.30 m (1H), 3.33–3.62 m (2H), 3.74 s (3H), 3.93–4.18 m (1H), 5.80 br.s (1H), 6.77 d (2H, 8.1), 7.03–7.07 m (1H), 7.26 d (2H, 8.1), 7.32–7.40 m (1H), 7.47–7.58 (2H), 7.77 d (1H, 8.1), 7.83–7.91 (2H). IR spectrum, ν, cm$^{-1}$: 1040, 1070, 1095, 1115, 1150, 1180, 1260, 1290, 1305, 1340, 1375, 1410, 1465, 1520, 1605, 1610, 1720 s, 2840, 2910, 2940, 2970, 3005, 3040. Found, %: C 73.46, 73.60; H 5.57, 5.57; N 11.59, 11.53. $C_{22}H_{21}N_3O_2$. Calculated, %: C 73.59; H 5.89; N 11.69.

**3-(4-Chlorophenyl)-2-(1-naphthyl)perhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (XVIc)** was synthesized from 0.68 g (3.5 mmol) of diazabicyclohexane **Ie** and 0.59 g (3.5 mmol) of isocyanate **Vb** in 7 ml of toluene. Recrystallization from benzene–hexane gave 1.21 g (95%) of compound **XVIc** with mp 126°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.24–2.45 m (2H), 3.10–3.29 m (1H), 3.35–3.63 m (2H), 3.94–4.20 m (1H), 5.83 br.s (1H), 7.02–7.60 (8H), 7.79 d (2H, 8.1), 7.85–7.94 m (1H). IR spectrum, ν, cm$^{-1}$: 1020, 1070, 1095, 1130, 1150, 1235, 1270, 1290, 1345, 1380, 1410, 1465, 1495, 1520, 1540, 1605, 1720 s, 2850, 2915, 2980, 3040. Found, %: C 69.33; H 5.05; N 11.61. $C_{21}H_{18}ClN_3O$. Calculated, %: C 69.32; H 4.99; N 11.55.

**4-(3-Oxo-2-phenylperhydropyrazolo[1,2-*a*]-[1,2,4]triazol-1-yl)benzonitrile (XVId)** was synthesized from 0.24 g (1.3 mmol) of diazabicyclohexane **If** and 0.15 g (1.3 mmol) of isocyanate **Va** in 3 ml of toluene. Recrystalization from ether containing a small amount of acetone gave 0.36 g (92%) of adduct **XVId** with mp 200°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.14–2.30 m (2H), 2.65–2.82 m (1H), 3.14–3.28 m (1H), 3.31–3.45 m (1H), 3.92–4.07 m (1H), 5.89 s (1H), 7.05–7.49 (5H), 7.54 d (2H, 8.4), 7.69 d (2H, 8.4). IR spectrum, ν, cm$^{-1}$: 1040, 1085, 1115, 1150, 1245, 1295, 1330, 1350, 1385 s, 1460, 1505, 1610, 1730 s, 2240, 2855, 2885, 2990, 3040.

Found, %: C 71.02, 71.27; H 5.28, 5.50; N 18.38, 18.29. $C_{18}H_{16}N_4O$. Calculated, %: C 71.04; H 5.30; N 18.41.

**3-(2-Methoxyphenyl)-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (XVIe)** was synthesized from 0.57 g (3 mmol) of diazabicyclohexane **Ih** and 0.36 g (3 mmol) of isocyanate **Va** in 7 ml of toluene. Recrystallization from acetone–ether gave 0.84 g (90%) of adduct **XVIe** with mp 129°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.12–2.25 m (2H), 2.68 q (1H, 9.3), 3.18–3.28 m (1H), 3.36–3.45 m (1H), 3.96 s (3H), 3.97–4.06 m (1H), 6.34 s (1H), 6.90 t (1H, 7.5), 6.98 d (1H, 8.4), 7.02–7.09 m (1H), 7.22–7.35 m (4H), 7.53 d (2H, 7.9). IR spectrum, ν, cm$^{-1}$: 1035, 1055, 1080, 1105, 1110, 1160, 1250, 1280, 1330, 1390 s, 1440, 1465, 1505, 1610, 1720 s, 2845, 2910, 2945, 2980, 3040. Found, %: C 69.32; H 7.27; N 14.89. $C_{18}H_{19}N_3O_2$. Calculated, %: C 69.45; H 7.42; N 14.73.

**3-(4-Bromophenyl)-2-(3,4-dichlorophenyl)perhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (XVIf)** was synthesized from 0.6 g (2.5 mmol) of diazabicyclohexane **Ig** and 0.47 g (2.5 mmol) of isocyanate **Vc** in 6 ml of toluene. Recrystallization from benzene–ether gave 1.01 g (94%) of compound **XVIf** with mp 165°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 2.13–2.27 m (2H), 2.56–2.76 m (1H), 3.14–3.48 m (2H), 3.82–4.08 m (1H), 5.76 s (1H), 7.22–7.30 (3H), 7.34 d (1H, 9.1), 7.53 d (2H, 8.4), 7.75 s (1H). IR spectrum, ν, cm$^{-1}$: 1015, 1035, 1085, 1105, 1140, 1285, 1360, 1380, 1410, 1480 s, 1600, 1730 s, 2850, 2980, 3040. Found, %: C 48.01, 48.21; H 3.26, 3.39; N 9.72, 9.73. $C_{17}H_{14}BrCl_2N_3O$. Calculated, %: C 47.80; H 3.30; N 9.84.

**3-(4-Methoxyphenyl)-6,6-dimethyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (XVIg)** was synthesized from 0.33 g (1.5 mmol) of diazabicyclohexane **Ic** and 0.18 g (1.5 mmol) of isocyanate **Va** in 4 ml of toluene. Recrystallization from acetone–hexane gave 0.39 g (76%) of adduct **XVIg** with mp 170°C. $^1$H NMR spectrum, δ, ppm (*J*, Hz): 1.22 s (3H), 1.26 s (3H), 2.62 br.s (1H), 3.02 br.s (2H), 3.62–3.85 m (1H), 3.79 s (3H), 5.74 br.s (1H), 6.88 d (2H, 8.8), 7.03–7.11 m (1H), 7.03–7.58 (6H). IR spectrum, ν, cm$^{-1}$: 1040, 1075, 1090, 1105, 1120, 1145, 1180, 1260, 1305, 1340, 1380 s, 1460, 1505, 1520, 1600, 1610, 1720 s, 2840, 2875, 2910, 2940, 2965, 3010, 3040. Found, %: C 71.40, 70.94; H 6.81, 6.85; N 12.48, 12.33. $C_{20}H_{23}N_3O_2$. Calculated, %: C 71.19; H 6.87; N 12.45.

**2-Methyl-3-phenylperhydropyrazolo[1,2-*a*]-[1,2,4]triazole-1-thione (XVIh)** was synthesized from 0.48 g (3 mmol) of diazabicyclohexane **Ia** and 0.22 g (3 mmol) of isothiocyanate **Vd** in 5 ml of toluene. Recrystallization from acetone–ether–hexane gave 0.58 g (83%) of compound **XVIh** with mp 115°C. 1H NMR spectrum, δ, ppm (*J*, Hz): 2.10–2.23 m (2H), 2.50–2.64 m (1H), 3.09 s (3H), 3.12–3.24 m (1H), 3.52–3.68 m (1H), 4.22–4.40 m (1H), 5.48 s (1H), 7.30–7.47 (5H). IR spectrum, ν, cm$^{-1}$: 880, 910, 990, 1010, 1050, 1095, 1120, 1170, 1250, 1290, 1305, 1325 s, 1340, 1400, 1460, 1495, 1540, 1605, 2860, 2885, 2915, 2980, 3030. Found, %: C 61.61, 61.73; H 6.67, 6.59; N 18.04, 18.00. $C_{12}H_{15}N_3S$. Calculated, %: C 61.77; H 6.48; N 18.01.

**2-Ethyl-3-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazole-1-thione (XVIi)** was synthesized from 0.48 g (3 mmol) of diazabicyclohexane **Ia** and 0.26 g (3 mmol) of isothiocyanate **Ve** in 5 ml of toluene. Recrystallization from ether containing a small amount of hexane gave 0.66 g (89%) of compound **XVIi** with mp 107°C. 1H NMR spectrum, δ, ppm (*J*, Hz): 1.14 t (3H, 7.1), 2.10–2.24 m (2H), 2.48–2.60 m (1H), 3.13 sext (1H, 7.1), 3.14–3.25 m (1H), 3.43–3.59 m (1H), 4.13 sext (1H, 7.1), 4.29–4.47 m (1H), 5.52 s (1H), 7.30–7.47 (5H). IR spectrum, ν, cm–1: 1015, 1060, 1085, 1120, 1160, 1265 s, 1320, 1340, 1380, 1340, 1455, 1480, 1520, 1600, 2850, 2880, 2940, 2980, 3040. Found, %: C 62.85, 62.96; H 6.80, 6.93; N 17.13, 17.11. $C_{13}H_{17}N_3S$. Calculated, %: C 63.12; H 6.93; N 16.99.

**4-(2-Phenyl-3-thioxoperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-yl)benzonitrile (XVIj)** was synthesized from 0.24 g (1.3 mmol) of diazabicyclohexane **If** and 0.18 g (1.3 mmol) of isothiocyanate **Vf** in 3 ml of toluene. Recrystallization from ether containing a small amount of acetone gave 0.34 g (81%) of compound **XVIj** with mp 160?C. 1H NMR spectrum, δ, ppm (*J*, Hz): 12.23–2.37 m (2H), 2.77–2.90 m (1H), 3.31–3.40 m (1H), 3.49–3.63 m (1H), 4.51–4.64 m (1H), 5.89 s (1H), 7.25–7.42 (5H), 7.45 d (2H, 8.2), 7.63 d (2H, 8.2). IR spectrum, ν, cm–1: 1015, 1055, 1090, 1120, 1260, 1280, 1310, 1315 s, 1405 s, 1460, 1505, 1605, 2240, 2855, 2990, 3040. Found, %: C 67.72, 67.72; H 5.23, 5.26; N 17.56, 17.37. $C_{18}H_{16}N_4S$. Calculated, %: C 67.47; H 5.03; N 17.49.

**X-Ray analysis of compound XIIa.** $C_{21}H_{21}N_3O_2$, *M*347.41; crystal habit 0.3×0.1×0.1 mm; monoclinic crystals, space group $P2_1/c$ (no. 14); unit cell parameters (120°C): *a* = 13.5737 (10), *b* = 7.1974 (5), *c* = 20.6403 (11) A°; b = 120.796(3)°; *V* = 1732.1 (2) A°$^3$; *Z* = 4; $d_{calc}$ = 1.332 g/cm$^{-3}$; m = 0.087 mm$^{-1}$; *F* (000) = 736.0; Mo$K_a$ radiation, l = 0.71073 A, graphite monochromator, $q_{max}$ = 27.45°. Selected bond lengths and bond angles: $N^1$–$C^2$ 1.485(3), $N^1$–$N^5$ 1.467(4), $C^2$–$C^3$ 1.537(3), $C^3$–$C^4$ 1.537(4), $N^5$–$C^4$ 1.497(3), $C^2$–$C^{12}$ 1.531(4), $C^2$–$C^9$ 1.532(4) A; $C^9C^2C^{12}$ 102.86(18), $N^1C^2C^3$ 105.90(16),

$C^3C^2C^{12}C^{11}$ –143.0(2), $C^3C^2C^9N^{10}$ 142.6(2), $N^1C^2C^{12}C^{11}$ 98.4(2), $N^1C^2C^9N^{10}$ –98.6(2). An additional information is available from the Cambridge Crystal Structure Database (CCDC-208216).

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