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Thermally Induced Opening of the Diaziridine Ring in 6-Aryl-2-methyl-1,5-diazabicyclo[3.1.0]hexanes

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Abstract—Thermally induced opening of the diaziridine ring in 6-aryl-2-methyl-1,5-diazabicyclo[3.1.0]-hexanes at the carbon–nitrogen bond is characterized by low regioselectivity; isomerization of unstable intermediate azomethine imines leads to mixtures of the corresponding 1-arylmethyl-5-methyl-4,5-dihydro-1*H*-pyrazoles and 1-arylmethyl-3-methyl-4,5-dihydro-1*H*-pyrazoles at a ratio of ~6:5. Analogous regioselectivity in opening of the three-membered ring is observed in the presence of phenyl isocyanate. In this case, adducts with *cis* arrangement of the aryl and methyl groups are formed as the major products (*cis*/*trans* ratio ~3:1).

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It is known that thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes involves opening of the diaziridine ring at the carbon–nitrogen bond to form unstable intermediate azomethine imines. The latter could either undergo isomerization to the corresponding 1-aryl-4,5-dihydro-1*H*-pyrazoles or give rise to 1,3-dipolar cycloaddition products provided that active 1,3-dipolarophiles are present in the reaction mixture [1–4]. For example, the thermolysis of 6-aryl-1,5-diazabicyclo-[3.1.0]hexanes in the presence of aryl isocyanates or aryl isothiocyanates occurs with high regioselectivity; the resulting adducts [3] are analogous to those obtained from stable azomethine imines having an oxo group in the α-position with respect to the 1,3-dipole fragment [5].

Opening of the three-membered ring in asymmetric diaziridines possessing different substituents on the nitrogen atoms may occur at both carbon–nitrogen bonds with formation of two regioisomeric azomethine imines. Introduction of a substituent into the α-position relative to the nitrogen atom creates some steric hindrances to approach of a 1,3-dipolarophile, which could affect the stereoselectivity of cycloaddition. As 1,3-dipolarophile we used phenyl isocyanate, taking into account that its reactivity is sufficient to trap unstable intermediate azomethine imines [3] and that the formation of only two pairs of regio- and stereoisomers is theoretically possible.

Previously unknown 6-aryl-2-methyl-1,5-diazabicyclo[3.1.0]hexanes **Ia** and **Ib** were synthesized following a conventional procedure, by condensation of 4-methoxy- and 4-bromobenzaldehydes with butane-1,3-diamine and subsequent oxidation of substituted hexahydropyrimidines thus formed with sodium hypochlorite [2]. According to the two-dimensional ^{1}H NMR data (NOESY), compounds **Ia** and **Ib** exist exclusively as *exo*,*exo* isomers in a *boat* conformation. For example, compound **Ia** displayed interaction between proton in the C^3H_2 methylene group (δ 2.06 ppm) and 6-H in the diaziridine ring (δ 3.10 ppm). Figure 1 illustrates the main spatial interactions characterized by cross peaks in the 2D NOESY spectrum of **Ia**.

Thermolysis of unsymmetrically substituted 1,5-diazabicyclohexanes **Ia** and **Ib** in the absence of 1,3-dipolarophiles led to the formation of mixtures of isomeric dihydropyrazoles **IIa**/**IIIa** and **IIb**/**IIIb** at a ratio of ~5:6 (according to the ^{1}H NMR data; Scheme 1). The isomer ratio was determined from the intensities of signals of the methyl groups and benzylic protons; the latter appeared as singlets at δ 4.08 ppm for compounds **IIa** and **IIb** (the corresponding signal of

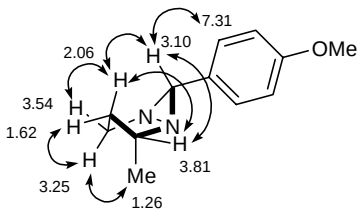
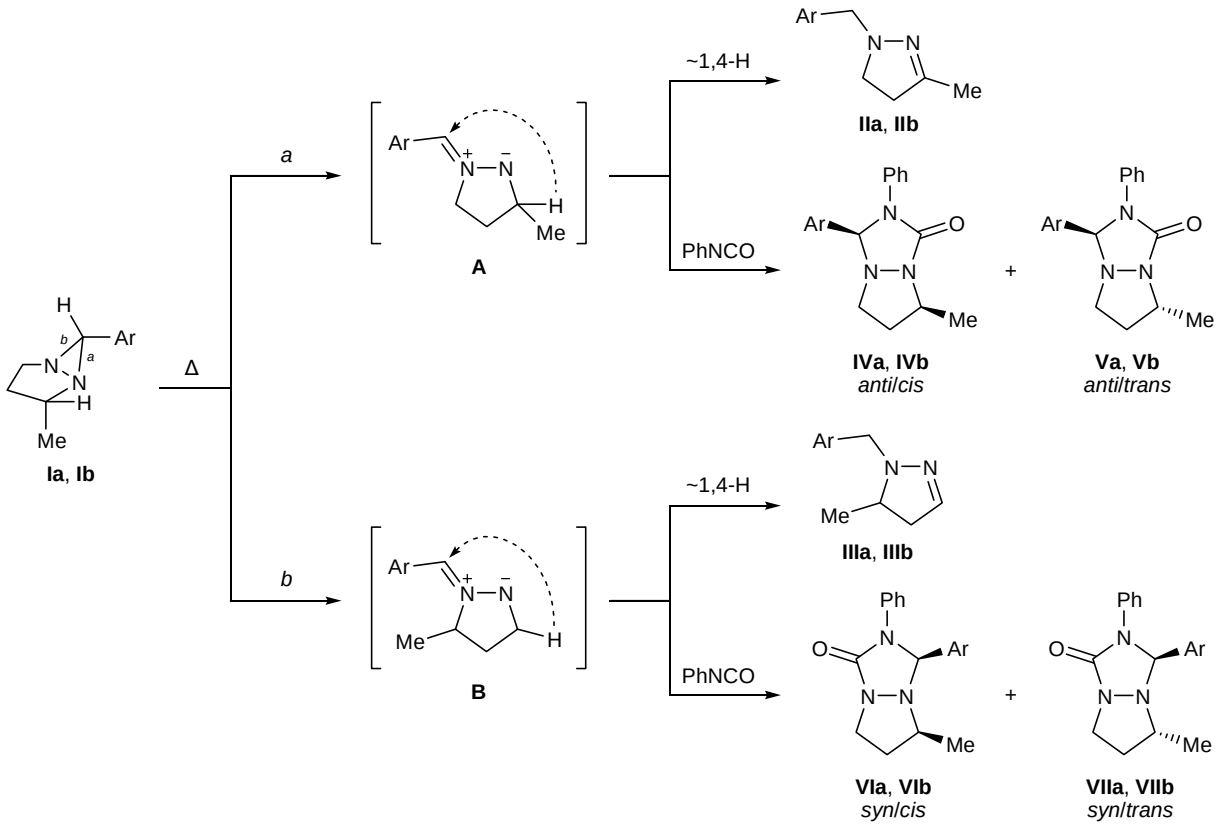


Fig. 1. Main nuclear Overhauser effects in the 2D NOESY spectrum of 1,5-diazabicyclo[3.1.0]hexane **Ia**.

Scheme 1.



Ar = 4-$MeOC_6H_4$ (**a**), 4-BrC_6H_4 (**b**).

1-benzyl-3-methyl-4,5-dihydro-1*H*-pyrazole was located at δ 4.10 ppm [6]) and doublets at δ 4.01 and 4.21 ppm for isomers **IIIa** and **IIIb** (^2J = 13.9 and 14.5 Hz, respectively).

When the thermolysis of diazabicyclohexanes **Ia** and **Ib** was performed in the presence of phenyl isocyanate, we obtained mixtures of all possible regio- and stereoisomers **IV**–**VII**. The ratio of the *anti*- (**IV**, **V**) and *syn*-adducts (**VI**, **VII**) (here, the *anti*- and *syn*-adducts correspond to cleavage of the *a* and *b* bonds in **I**, respectively) was the same as in the reaction without dipolarophile (~5:6), while the ratio of the *cis*- (**IV**, **VI**) and *trans*-adducts (**V**, **VII**) was ~(3–4):1. No other products were detected in the reaction mixtures by ^{1}H NMR spectroscopy.

The relative configuration of compounds **IV**–**VII** was determined on the basis of the 2D NOESY spectra. Figures 2 and 3 show the main spatial interactions in molecules **IVa**, **Vb**, **VIa**, and **VIIb**.

Our results show that opening of the diaziridine ring in unsymmetrically substituted diazabicyclohexanes **Ia** and **Ib** is characterized by relatively poor

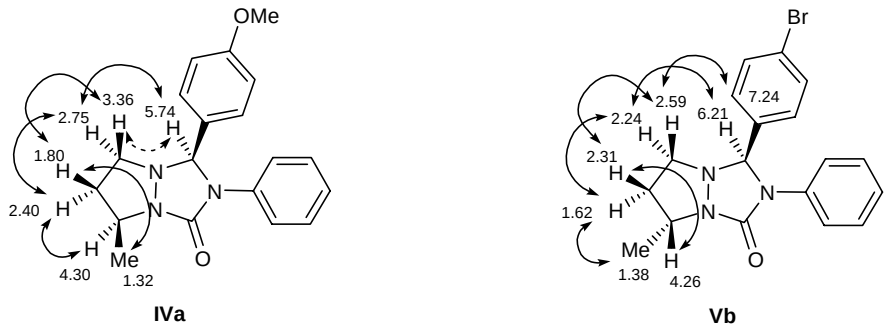


Fig. 2. Main nuclear Overhauser effects in the 2D NOESY spectra of compounds **IVa** and **Vb**.

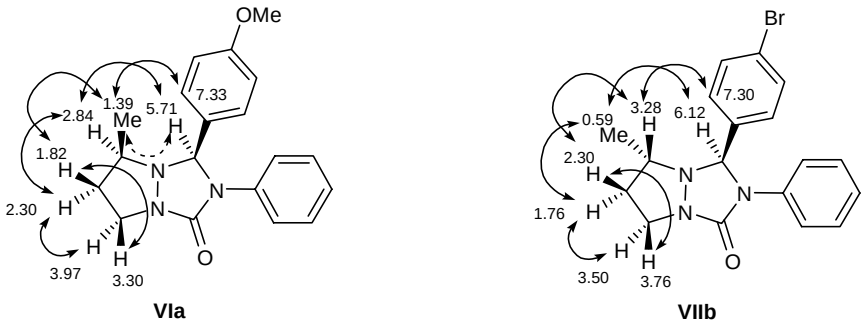
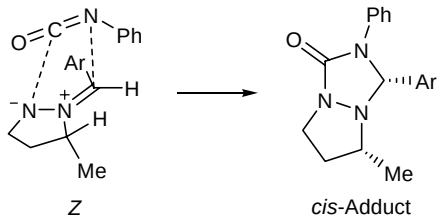


Fig. 3. Main nuclear Overhauser effects in the 2D NOESY spectra of compounds **VIa** and **VIIb**.

regioselectivity. On the one hand, this is not surprising, for introduction of a methyl group into the α-position with respect to the nitrogen atom should weakly affect the relative stability of intermediate azomethine imines **A** and **B**. On the other hand, both in the absence and in the presence of phenyl isocyanate, the carbon–nitrogen bond with no contiguous methyl group was cleaved (path *b*), though cleavage of the other C–N bond (path *a*) seems to be more favorable for steric reasons.

The observed relatively high stereoselectivity of the 1,3-dipolar cycloaddition [stereoisomer ratio (3–4):1] may be rationalized in terms of preferential approach of the dipolarophile (phenyl isocyanate) to intermediate azomethine imine from the side opposite to the methyl group in the trimethylene bridge. Here, it was presumed that, like stable azomethine imines having an oxo group in the α-position [7], unstable azomethine imines derived from 6-aryl-2-methyl-1,5-diazabicyclo-[3.1.0]hexanes **Ia** and **Ib** have *Z* configuration (Scheme 2). Otherwise (*E* configuration), a strong destabilizing spatial interaction should occur between the aryl and methyl groups, whereas the formation of the corresponding *cis*-adduct implies approach of phenyl isocyanate from the side of the methyl group, which seems to be improbable.

Scheme 2.



It is known that the conformation of compounds having a 1,5-diazabicyclo[3.3.0]octane skeleton depends on the substituents in the rings. Although unsubstituted 1,5-diazabicyclo[3.3.0]octane exists mainly as *cis-exo,exo* conformer [8], its substituted analogs could give rise to equilibrium mixtures of different conformers due to inversion of the bridgehead nitrogen atoms. Such inversion often leads to broadening of signals in the ^{1}H NMR spectra at room temperature [9].

Among adducts **IV**–**VII**, only compounds **VIIa** and **VIIb** displayed in the ^{1}H NMR spectra at room temperature strongly broadened singlets from protons in the trimethylene bridge, ArC**H** proton, and protons of the methyl group. When a solution of **VIIb** in $CDCl_3$ was heated to 55°C, the above signals became nar-

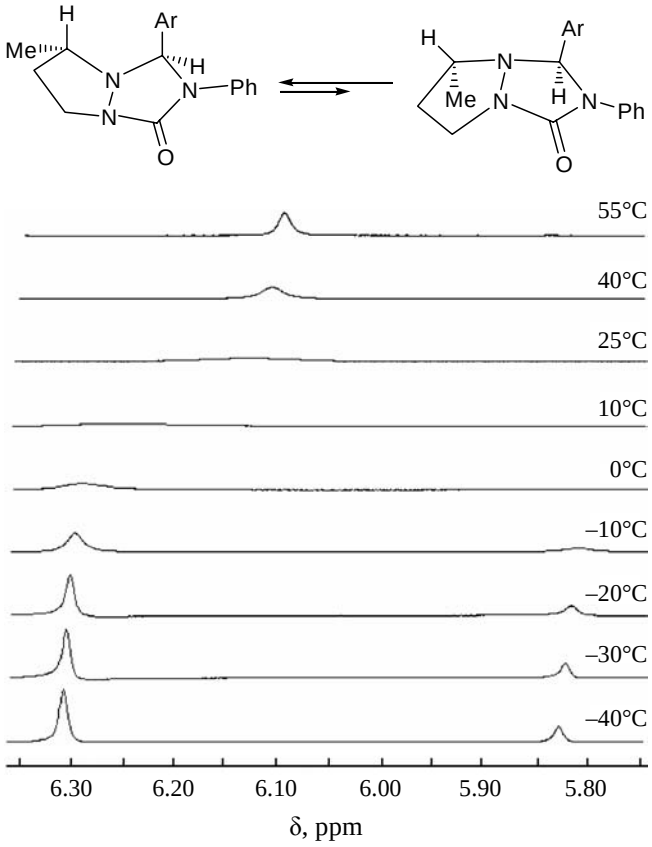


Fig. 4. ^{1}H NMR spectra of adduct **VIIb** ($CDCl_3$) in the region corresponding to resonance of the ArC**H** proton at different temperatures.

rower, and their "fine structure" appeared; in the spectrum recorded at –40°C we observed well resolved signals from both invertomers at a ratio of ~1:3 (Fig. 4). According to the 2D NOESY data, the invertomer with *endo* orientation of the aryl group predominates at –40°C.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from 1–2% solutions in chloroform. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DPX-300 spectrometer at 300.130 and 75.468 MHz, respectively, using $CDCl_3$ as solvent. The chemical shifts were measured relative to the solvent signals ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.16 ppm) [10].

5-Methyl-4,5-dihydro-1*H*-pyrazole. A solution of 75 g (1.07 mol) of crotonaldehyde in 80 ml of ethanol was added over a period of 30 min to 110 g (2.2 mol) of hydrazine hydrate heated to the boiling point. The mixture was heated for 3 h under reflux and cooled, and sodium hydroxide was added in portions until the mixture divided into layers. The organic phase was separated, the aqueous phase was extracted with 50 ml of ethyl acetate, the extract was combined with the organic phase and dried over sodium sulfate. The solvent was distilled off under reduced pressure, and vacuum distillation of the residue gave 33.1 g (37%) of 5-methyl-4,5-dihydro-1*H*-pyrazole with bp 34–37°C (10 mm; published data: bp 50–55°C (20 mm) [11], 40.5–42°C (9 mm) [12].

Butane-1,3-diamine. A 300-ml steel high-pressure reactor was charged with a solution of 33.14 g of 5-methyl-4,5-dihydro-1*H*-pyrazole in 250 ml of ethanol and 4 g of Raney nickel. The mixture was heated at 180°C under a hydrogen pressure of 45–50 atm. After 1 h, the catalyst was filtered off, the solvent was distilled off through a short Vigreaux column, and the residue was distilled under reduced or atmospheric pressure. Yield 18.4 g (53%), bp 137–140°C; published data [13]: bp 138–141°C.

6-(4-Methoxyphenyl)-2-methyl-1,5-diazabicyclo-[3.1.0]hexane (Ia). A mixture of 3 g (34.1 mmol) of butane-1,3-diamine, 20 ml of methanol, and 10 ml of water was cooled with ice water, and a solution of 4.63 g (4.14 ml, 34.1 mmol) *p*-methoxybenzaldehyde in a mixture of 20 ml of methanol and 10 ml of water was added dropwise over a period of 25 min. The cooling bath was removed, and the mixture was stirred for 1 h at room temperature. Most part of methanol was distilled off, the residue was cooled with ice water, and 17 ml of a 2.44 N solution of sodium hypochlorite (0.041 mol) was added dropwise over a period of 20 min. The mixture was stirred for 1 h at room temperature, the organic phase was separated, the aqueous phase was extracted with chloroform (3×20 ml), the extracts were combined with the organic phase and dried over Na_2SO_4, the solvent was distilled off, and the oily residue was purified by column chromatography on silica gel L 100/200 (1:25, by weight) using hexane–ethyl acetate as eluent. Two fractions were collected; the first of these contained *p*-methoxybenzaldehyde, and the second, diazabicyclohexane **Ia**. Yield 0.98 g (14%), oily substance. ^{1}H NMR spectrum, δ, ppm: 1.26 d (3H, J = 6.5 Hz), 1.62 d.d (1H, J = 8.0, 13.1 Hz), 2.06 d.d.d.d (1H, J = 8.0, 8.7, 9.5, 13.1 Hz), 3.10 s (1H, C**H**Ar), 3.25 t.d (1H, J = 8.0, 11.6 Hz), 3.54 d.d (1H, J = 9.5, 11.6 Hz), 3.80 s (3H, OMe), 3.81 q.d.d (1H, C**H**Me, J = 6.5, 8.0, 8.7 Hz), 6.87 d (2H, H_{arom}, J = 8.7 Hz), 7.31 d (2H, H_{arom}, J = 8.7 Hz). Found, %: C 70.71; H 7.86; N 13.59. $C_{12}H_{16}N_2O$. Calculated, %: C 70.56; H 7.90; N 13.71.

6-(4-Bromophenyl)-2-methyl-1,5-diazabicyclo-[3.1.0]hexane (Ib). A solution of 9.3 g (0.05 mol) of 4-bromobenzaldehyde in a mixture of 70 ml of methanol and 10 ml of water was added dropwise over a period of 1 h to 5.3 g (0.06 mol) of butane-1,3-diamine cooled to 0–5°C. The cooling bath was removed, the mixture was stirred for 1 h at room temperature, most part of methanol was distilled off under reduced pressure, the residue was cooled with ice water, and 31.4 ml of a 2.10 N solution of sodium hypochlorite (0.066 mol) was added over a period of 1 h. The mixture was stirred for 1 h at room temperature, the organic phase was separated, the aqueous phase was extracted with benzene (3×40 ml), the extracts were combined with the organic phase and dried over K_2CO_3, the solvent was distilled off under reduced pressure, and the oily residue was purified by column chromatography on silica gel L 160/200 (1:10, by weight) using hexane–ethyl acetate (gradient elution from 16:1 to 8:1). We thus isolated an oily material enriched in compound **Ib**; after treatment with ether, crystals separated and were filtered off. Recrystallization from diethyl ether gave 1.1 g of almost pure compound **Ib**. An additional amount of **Ib**, 2.1 g, was isolated from the mother liquor by column chromatography. After recrystallization from hexane–diethyl ether, the overall yield of **Ib** was 3.1 g (25%), mp 58–60°C. IR spectrum, ν, cm^{-1}: 1025, 1050, 1080, 1110, 1125, 1220, 1235, 1255, 1275, 1300, 1325, 1385, 1430, 1465, 1500, 1605, 1715, 2890, 2940, 2980, 3040. ^{1}H NMR spectrum, δ, ppm: 1.26 d (3H, J = 6.5 Hz), 1.67 d.d (1H, J = 8.1, 13.5 Hz), 2.04 m (1H),

3.10 s (1H, C**H**Ar), 3.25 t.d (1H), 3.55 m (1H), 3.82 m (1H, C**H**Me, J = 6.5, 8.0, 8.7 Hz), 6.87 d (2H, H_{arom}, J = 8.4 Hz), 7.24 d (2H, H_{arom}, J = 8.4 Hz). Found, %: C 52.22; H 5.23; N 11.09. $C_{11}H_{13}BrN_2$. Calculated, %: C 52.19; H 5.18; N 11.07.

Thermolysis of compounds Ia and Ib in the absence of dipolarophiles. A solution of 6-aryl-2-methyl-1,5-diazabicyclo[3.1.0]hexane in *p*-xylene (c = 0.1–1.0 M) was stirred for 20–25 min at a bath temperature of 140°C. After cooling, the solvent was distilled off under reduced pressure. The isomer ratio **II/III** was ~1:(1.1–1.2), regardless of the concentration of initial diazabicyclohexane **Ia** or **Ib** (according to the ^{1}H NMR data).

1-(4-Methoxybenzyl)-3-methyl-4,5-dihydro-1*H*-pyrazole (IIa). ^{1}H NMR spectrum, δ, ppm: 1.98 s (3H, Me), 2.55 t (2H, J = 9.2 Hz), 2.90 t (2H, J = 9.2 Hz), 3.80 s (3H, OMe), 4.08 s (2H), 6.89 d (2H, H_{arom}, J = 9.2 Hz), 7.31 d (2H, H_{arom}, J = 9.2 Hz).

1-(4-Methoxybenzyl)-5-methyl-4,5-dihydro-1*H*-pyrazole (IIIa). ^{1}H NMR spectrum, δ, ppm: 1.24 d (3H, J = 6.2 Hz), 2.31–2.41 m (1H), 2.68–2.80 m (1H), 3.02–3.17 m (1H, C**H**Me), 3.79 s (3H, OMe), 4.01 d (1H, J = 13.9 Hz), 4.21 d (1H, J = 13.9 Hz), 6.71 s (1H, 3-H), 6.89 d (2H, H_{arom}, J = 9.2 Hz), 7.31 d (2H, H_{arom}, J = 9.2 Hz).

1-(4-Bromobenzyl)-3-methyl-4,5-dihydro-1*H*-pyrazole (IIb). ^{1}H NMR spectrum, δ, ppm: 2.00 s (3H, Me), 2.59 t (2H, J = 9.0 Hz), 2.93 t (2H, J = 9.0 Hz), 4.08 s (2H), 7.27 d (2H, H_{arom}, J = 8.0 Hz), 7.47 d (2H, H_{arom}, J = 8.0 Hz).

1-(4-Bromobenzyl)-5-methyl-4,5-dihydro-1*H*-pyrazole (IIIb). ^{1}H NMR spectrum, δ, ppm: 1.27 d (3H, J = 6.6 Hz), 2.30–2.39 m (1H), 2.73–2.82 m (1H), 3.05–3.18 m (1H, C**H**Me), 4.01 d (1H, J = 14.5 Hz), 4.21 d (1H, J = 14.5 Hz), 6.75 s (1H, 3-H), 7.27 d (2H, H_{arom}, J = 8.0 Hz), 7.47 d (2H, H_{arom}, J = 8.0 Hz).

Thermolysis of compounds Ia and Ib in the presence of phenyl isocyanate. An equivalent amount of phenyl isocyanate was added to a solution of 2–3 mmol of compound **Ia** or **Ib** in 2–3 ml of *p*-xylene. The mixture was stirred for 25 min at a bath temperature of 140°C and cooled, the solvent was distilled off under reduced pressure, and the products were isolated by fractional crystallization or column chromatography (silica gel L 35/70, weight ratio 1:125; eluent hexane–ethyl acetate, 10:1); the progress of chromatographic separation was monitored by TLC on Silufol UV-254 plates (triple elution with hexane–ethyl acetate, 5:1; development with iodine vapor).

From 573 mg (2.8 mmol) of compound **Ia** and 332 mg (2.8 mmol) of phenyl isocyanate we isolated by recrystallization from acetone 54 mg (6%) of compound **IVa**; addition of diethyl ether to the mother liquor gave 32 mg (3.5%) of **VIa**. Also, 128 mg (14%) of a mixture of **IVa** and **VIa** at a ratio of ~1.7:1 (^{1}H NMR data) was isolated. The overall yield of isomers **IVa** and **VIa** isolated by crystallization was 214 mg (23.6%). Compounds **Va** and **VIIa** were not isolated as individual substances. According to the ^{1}H NMR spectrum of the reaction mixture, the ratio **VIIa/VIa/Va/IVa** was ~0.07:1.0:0.26:0.61.

***rel*-(3*R*,7*R*)-3-(4-Methoxyphenyl)-7-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (IVa).** mp 178–180°C. ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, J = 6.5 Hz), 1.74–1.87 m (1H), 2.34–2.46 m (1H), 2.69–2.81 m (1H), 3.36 d.d (1H, $J \approx$ 8.0, 8.0 Hz), 3.79 s (3H, OMe), 4.23–4.37 m (1H, C**H**Me), 5.74 s (1H), 6.85–6.92 m (2H, H_{arom}), 7.04–7.09 m (1H, H_{arom}), 7.26–7.37 m (4H, H_{arom}), 7.48–7.54 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.2 (CH_3), 33.7 (CH_2), 52.6 (CH), 54.0 (CH_2), 54.9 (OCH_3), 78.1 (CH), 113.9 ($2CH_{arom}$), 119.1 (CH_{arom}), 123.4 ($2CH_{arom}$), 127.7 (CH_{arom}), 128.6 ($2CH_{arom}$), 129.7 ($2C_{arom}$), 137.9 (C_{arom}), 159.6 (C=O), 161.0 (C_{arom}). Found, %: C 70.11; H 6.58; N 12.70. $C_{19}H_{21}N_3O_2$. Calculated, %: C 70.57; H 6.55; N 12.99.

***rel*-(3*R*,5*S*)-3-(4-Methoxyphenyl)-5-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (VIa).** mp 154–156°C. ^{1}H NMR spectrum, δ, ppm: 1.39 d (3H, $J \approx$ 6.5 Hz), 1.73–1.89 m (1H), 2.21–2.39 m (1H), 2.76–2.91 m (1H, C**H**Me), 3.24–3.36 m (1H), 3.90–4.03 m (1H), 3.79 s (3H, OMe), 5.71 s (1H), 6.88–6.92 m (2H, H_{arom}), 7.03–7.11 m (1H, H_{arom}), 7.25–7.36 m (4H, H_{arom}), 7.50–7.55 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 16.6 (CH_3), 33.4 (CH_2), 43.8 (CH_2), 55.0 (OCH_3), 58.2 (CH), 76.1 (CH), 114.2 ($2CH_{arom}$), 118.4 ($2CH_{arom}$), 123.3 (CH_{arom}), 127.2 (CH_{arom}), 128.6 ($2CH_{arom}$), 129.4 ($2CH_{arom}$), 138.0 (C_{arom}), 159.7 (C=O), 161.1 (C_{arom}). Found, %: C 70.68; H 6.60; N 12.81. $C_{19}H_{21}N_3O_2$. Calculated, %: C 70.57; H 6.55; N 12.99.

***rel*-(3*R*,7*S*)-3-(4-Methoxyphenyl)-7-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (Va).** ^{1}H NMR spectrum (some signals in the spectrum of isomer mixture), δ, ppm: 1.41 d (3H, J = 6.5 Hz), 1.61–1.74 m (1H), 2.54–2.66 m (1H), 4.20–4.33 m (1H, C**H**Me), 6.25 s (1H).

***rel*-(3*R*,5*R*)-3-(4-Methoxyphenyl)-5-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (VIIa).** ^{1}H NMR spectrum (some signals in the

spectrum of isomer mixture), δ, ppm: 0.55 br.s (3H), 6.32 br.s (1H).

Chromatographic separation of the product mixture obtained from 500 mg (~2 mmol) of compound **Ib** and 235 mg (2 mmol) of phenyl isocyanate gave 150 mg (20.4%) of **IVb**, 40 mg (5.4%) of **Vb**, 109 mg (14.8%) of **VIb**, and 80 mg (10.9%) of **VIIb**; in addition, 114 mg (15.5%) of isomer mixtures was isolated. The overall preparative yield of all isomers was 493 mg (67.1%). According to the ^{1}H NMR spectrum of the reaction mixture, the ratio **VIIb**/**VIb**/**Vb**/**IVb** was ~0.4:1.1:0.3:1.0.

***rel*-(3*R*,7*R*)-3-(4-Bromophenyl)-7-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (IVb).** mp 177–178°C. IR spectrum, ν, cm^{-1}: 1025, 1060, 1085, 1110, 1115, 1160, 1260, 1300, 1330, 1365, 1385, 1415, 1460, 1510, 1610, 1720 (C=O), 2850, 2885, 2940, 2990, 3040. ^{1}H NMR spectrum, δ, ppm: 1.32 d (3H, *J* = 6.75 Hz), 1.70–1.87 m (1H), 2.36–2.46 m (1H), 2.71–2.80 m (1H), 3.34–3.39 m (1H), 4.24–4.35 m (1H, C**H**Me), 5.75 s (1H), 7.06–7.11 m (1H, H_{arom}), 7.28–7.32 m (4H, H_{arom}), 7.45–7.51 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 22.6, 34.2, 53.1, 54.5, 78.2, 119.5, 123.0, 124.2, 128.6, 129.3, 132.1, 137.0, 138.0, 161.2. Found, %: C 58.12; H 4.94; N 11.15. $C_{18}H_{18}BrN_3O$. Calculated, %: C 58.08; H 4.87; N 11.29.

***rel*-(3*R*,7*S*)-3-(4-Bromophenyl)-7-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (Vb).** mp 101–102°C. IR spectrum, ν, cm^{-1}: 1025, 1085, 1125, 1140, 1170, 1260, 1290, 1310, 1320, 1380, 1420, 1460, 1515, 1610, 1720 (C=O), 2865, 2880, 2940, 2988, 3040. ^{1}H NMR spectrum, δ, ppm: 1.41 d (3H, *J* = 6.5 Hz), 1.61–1.74 m (1H), 2.19–2.38 m (2H), 2.54–2.66 m (1H), 4.20–4.33 m (1H, C**H**Me), 6.21 s (1H), 6.85–6.92 m (2H, H_{arom}), 7.06–7.14 m (1H, H_{arom}), 7.19–7.33 m (6H, H_{arom}), 7.48 d (2H, H_{arom}). Found, %: C 58.41; H 5.19; N 10.95. $C_{18}H_{18}BrN_3O$. Calculated, %: C 58.08; H 4.87; N 11.29.

***rel*-(3*R*,5*S*)-3-(4-Bromophenyl)-5-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (VIb).** mp 126–128°C. IR spectrum, ν, cm^{-1}: 1025, 1085, 1100, 1115, 1120, 1145, 1160, 1250, 1285, 1300, 1315, 1335, 1350, 1390, 1415, 1460, 1510, 1610, 1720 (C=O), 2860, 2885, 2940, 2980, 3025, 3040. ^{1}H NMR spectrum, δ, ppm: 1.39 d (3H, *J* = 6.75 Hz), 1.74–1.87 m (1H), 2.27–2.37 m (1H), 2.79–2.91 m (1H, C**H**Me), 3.25–3.33 m (1H), 3.92–4.01 m (1H), 5.70 s (1H), 7.07–7.12 m (H_{arom}), 7.26–7.34 m (4H, H_{arom}), 7.48–7.53 m (4H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 17.1, 33.8, 44.3, 58.8, 76.2, 118.8, 123.1, 124.1, 128.3, 129.3, 132.1, 136.8, 138.1, 161.4. Found, %: C 58.35; H 4.88; N 11.26. $C_{18}H_{18}BrN_3O$. Calculated, %: C 58.08; H 4.87; N 11.29.

***rel*-(3*R*,5*R*)-3-(4-Bromophenyl)-5-methyl-2-phenylperhydropyrazolo[1,2-*a*][1,2,4]triazol-1-one (VIIb).** mp 176°C. IR spectrum, ν, cm^{-1}: 1025, 1080, 1115, 1135, 1150, 1160, 1265, 1290, 1305, 1390, 1420, 1460, 1510, 1610, 1720 (C=O), 2885, 2915, 2940, 2980, 3020, 3040, 3070. ^{1}H NMR spectrum (55°C), δ, ppm: 0.60 d (3H, *J* = ~5.9 Hz), 1.69–1.80 m (1H), 2.25–2.37 m (1H), 3.21–3.33 m (1H, C**H**Me), 3.45–3.58 m (1H), 3.61–3.75 m (1H), 6.12 s (1H), 7.02–7.10 m (1H, H_{arom}), 7.21–7.31 m (6H, H_{arom}), 7.45–7.51 m (2H, H_{arom}). Found, %: C 58.03; H 4.89; N 11.22. $C_{18}H_{18}BrN_3O$. Calculated, %: C 58.08; H 4.87; N 11.29.

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