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

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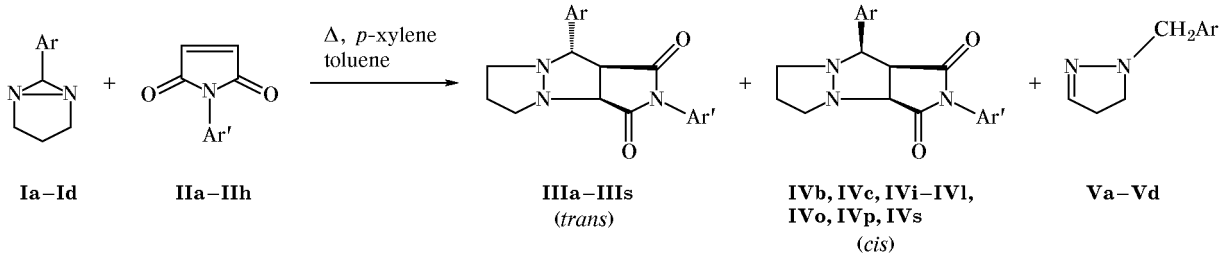
Abstract—Thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in the presence of *N*-arylmaleimides having a substituent in the *ortho* position of the aromatic ring leads to predominant formation of the corresponding *trans*-9-arylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-diones. 6-Aryl-1,5-diazabicyclo[3.1.0]hexanes react with fumaric acid derivatives in a stereoselective fashion, affording perhydropyrazolo[1,2-*a*]pyrazoles with a *trans*,*trans* configuration.

We previously showed that thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes involves cleavage of the nitrogen–carbon bond with formation of azomethinimine which is then converted into dihydropyrazole [1] or trapped by active dipolarophiles, e.g., *N*-arylmaleimides [2]. In the present work we tried to elucidate factors determining stereoselectivity of the cycloaddition. For this purpose, we examined the reaction of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **Ia**–**Id** with *ortho*-substituted *N*-arylmaleimides **IIa**–**IIh**, fumaric acid esters, and fumaronitrile. According to the X-ray diffraction data, crystalline 6-phenyl- (**Ia**, Fig. 1) and 6-(4-methoxyphenyl)-1,5-diazabicyclo-[3.1.0]hexanes (**Ib**), as well as previously reported 6-(4-chlorophenyl)-1,5-diazabicyclo[3.1.0]hexane (**Ic**) [3], exist as *exo* isomers in which the six-membered ring has a *boat* conformation and the benzene ring is located in the bisector plane of the diaziridine ring.

By heating of *exo*-6-aryl-1,5-diazabicyclo[3.1.0]-hexanes **Ia**–**Id** with *N*-arylmaleimides **IIa**–**IIh** we obtained the corresponding perhydropyrazolo[1,2-*a*]-pyrrolo[3,4-*c*]pyrazole-1,3-diones as mixtures of *trans* (**IIIa**–**IIIs**) and *cis* isomers (**IVb**, **IVc**, **IVi**–**IVl**, **IVo**, **IVp**, **IVs**) (Scheme 1). Their structure was established on the basis of their spectral parameters and elemental analyses.

While studying the reaction of diazabicyclohexanes with *para*-substituted *N*-arylmaleimides we showed that the ratio of *trans* and *cis* isomers in the products depends on the nature of substituents in the aryl ring of both diazabicyclohexane and maleimide [2]. The results of the present study indicate that introduction

Scheme 1.



I, **V**, Ar = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-ClC_6H_4 (**c**), 4-MeC_6H_4 (**d**); **II**, Ar′ = 2,4,6-$Me_3C_6H_2$ (**a**), 2,5-$Me_2C_6H_3$ (**b**), 2,6-$Cl_2C_6H_3$ (**c**), 2,4-$Cl_2C_6H_3$ (**d**), 1-naphthyl (**e**), 2,4-$Me_2C_6H_3$ (**f**), 2-BrC_6H_4 (**g**), 2-ClC_6H_4 (**h**); **III**, **IV**, Ar = Ph, Ar′ = 2,4,6-$Me_3C_6H_2$ (**a**), 2,5-$Me_2C_6H_3$ (**b**), 2,6-$Cl_2C_6H_3$ (**c**), 2,4-$Cl_2C_6H_3$ (**d**), 1-naphthyl (**e**), 2,4-$Me_2C_6H_3$ (**f**), 2-BrC_6H_4 (**g**); Ar = 4-$MeOC_6H_4$, Ar′ = 2,4,6-$Me_3C_6H_2$ (**h**), 2,6-$Cl_2C_6H_3$ (**i**), 2,4-$Cl_2C_6H_3$ (**j**), 1-naphthyl (**k**), 2-BrC_6H_4 (**n**), 2-ClC_6H_4 (**m**); Ar = 4-ClC_6H_4, Ar′ = 2,4,6-$Me_3C_6H_2$ (**n**), 2,6-$Cl_2C_6H_3$ (**o**), 2,4-$Cl_2C_6H_3$ (**p**), 1-naphthyl (**q**), 2-BrC_6H_4 (**r**); Ar = 4-MeC_6H_4, Ar′ = 2,6-$Cl_2C_6H_3$ (**s**).

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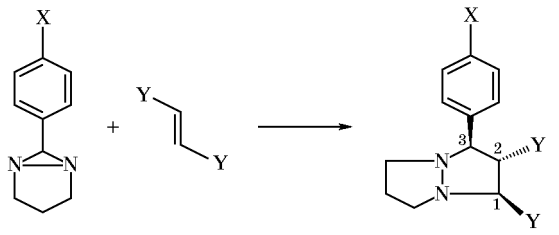
of substituents into the *ortho* position of the aromatic ring of *N*-arylmaleimide considerably increases the fraction of the corresponding *trans* isomer **III**. The isomer ratios **III**:**IV** are as follows: 5:1 (**b**), 7:1 (**c**), 11:1 (**i**), 6:1 (**j**), 12:1 (**k**), 7:1 (**l**), 13:1 (**o**), 5:1 (**p**), and 15:1 (**s**). In the other cases, no *cis* isomer **IV** was detected.

It should be noted that the reaction of diazabicyclohexanes with *ortho*-substituted maleimides gives two rotamers of each *trans*- (**III**) and *cis*-adduct (**IV**) due to restricted rotation of the aryl group in the pyrrolidine ring; the rotamers can be distinguished by the ^{1}H NMR spectra [4]. These results support the previous assumption that dipolarophile approaches intermediate *trans*-azomethinimine (formed via thermally allowed conrotatory opening of nonplanar 6-aryl-1,5-diazabicyclohexane) preferentially from the *exo* side, giving rise to *trans* isomer **III**. The *trans*/*cis* isomer ratio does not change on temperature variation from 110 to 140°C.

The reaction of diazabicyclohexanes **Ia**–**If** with fumaric acid derivatives **VIa**–**VIc** at 110–140°C gave substituted perhydropyrazolo[1,2-*a*]pyrazoles **VIIa**–**VIIh** (Scheme 2). Their structure was derived from their spectral parameters and elemental composition. The ^{1}H NMR spectrum of **VIIb** contained two doublets from aromatic protons at δ 7.41 (2H, J = 8.5 Hz) and 6.94 ppm (2H, J = 8.5 Hz), a doublet from the 1-H proton at δ 4.35 ppm (J = 4.2 Hz), a doublet from 3-H at δ 3.97 ppm (J = 7.5 Hz), a singlet from the methoxy group at δ 3.84 ppm, a doublet of doublets from 2-H at δ 3.52 ppm (J = 7.5 and 4.2 Hz), and multiplet signals from protons of the trimethylene group in the regions δ 2.60–3.27 ppm (NC**H**$_2$) and 2.20–2.81 ppm (NCH$_2$C**H**$_2$). Magnetic nonequivalence of the methylene protons results from their pseudoaxial or pseudoequatorial orientation.

Scheme 2.



Ia–If **VIa–VIc** **VIIa–VIIh**

I, X = H (**a**), MeO (**b**), Cl (**c**), Me (**d**), CN (**e**), Br (**f**); **VI**, Y = CN (**a**), CO_2Ph (**b**), CO_2Me (**c**); **VII**, Y = CN, X = H (**a**), MeO (**b**), Me (**c**), CN (**d**), Cl (**e**), Br (**f**); X = H, Y = CO_2Ph (**g**), CO_2Me (**h**).

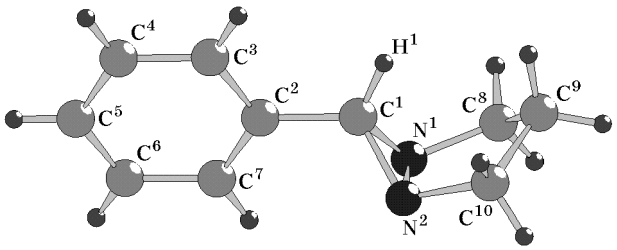
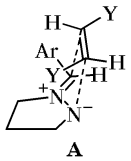


Fig. 1. Structure of 6-phenyl-1,5-diazabicyclohexane (**Ia**) according to the X-ray diffraction data.

The relative configuration of the substituents in positions *2* and *3* was established by analysis of the two-dimensional ^{1}H NMR spectrum of compound **VIIb**, as well as by NOE experiments. In the 2D spectrum of **VIIb** (Fig. 2), *ortho*-protons of the methoxyphenyl group in position *3* give cross peaks with protons in positions *3* and *2*. This is possible only when the methoxyphenyl and cyano groups are arranged *trans*. The lack of nuclear Overhauser effect on successive irradiation of each of the three protons (1-H, 2-H, and 3-H) also supports the *trans*,*trans* configuration of the adducts.

Thus we presume that the reaction with fumaric acid derivatives involves formation of a transition state like **A**:



A

In this case, steric interactions between the electron-acceptor group in fumaric acid derivative and aryl group of azomethinimine are stronger than interaction with the trimethylene bridge, so that the *trans*,*trans*-adduct is obtained.

EXPERIMENTAL

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

Initial 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **Ia**–**Id** were prepared by condensation of the corresponding aromatic aldehyde with 1,3-diaminopropane, followed by oxidation of intermediate hexahydropyrimidine according to the procedure reported in [2].

4-(1,5-Diazabicyclo[3.1.0]hex-6-yl)benzonitrile (Ie). A solution of 6.6 g (0.05 mol) of 4-cyanobenz-

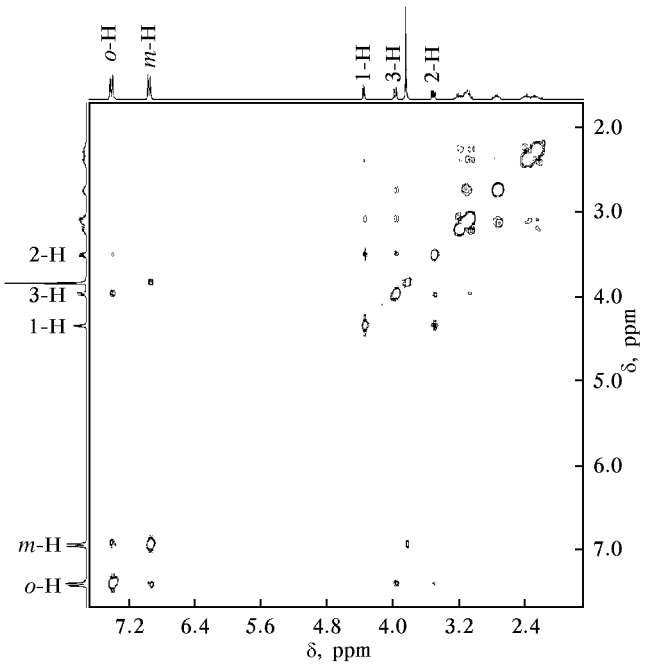


Fig. 2. Two-dimensional ^{1}H NMR spectrum of *rel*-(1*R*,2*R*,3*S*)-3-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]-pyrazole-1,2-dicarbonitrile (**VIIb**).

aldehyde in a mixture of 70 ml of methanol and 35 ml of water was added dropwise under stirring and cooling with ice water to 8.3 ml (0.1 mol) of 1,3-diaminopropane, maintaining the temperature below 45°C. When the addition was complete, the mixture was stirred for 3.5 h at 20°C, methanol was distilled under reduced pressure at a temperature not exceeding 45°C, 74 ml (0.17 mol) of a 2.3 N solution of sodium hypochlorite 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 20°C. The organic phase was separated, and the aqueous phase was extracted with benzene. The extracts were combined with the organic phase and dried over sodium sulfate, and the solvent was distilled off on a rotary evaporator at a temperature not exceeding 50°C. The product was isolated by column chromatography on silica gel (L 100/200; substrate-to-sorbent weight ratio 1:16; eluent diethyl ether), followed by recrystallization from diethyl ether. Yield 3.94 g (43%), mp 102–103°C. IR spectrum, ν, cm^{-1}: 880, 960, 975 s, 1025, 1110, 1190, 1260, 1290, 1310, 1340, 1380, 1430, 1455, 1470, 1510, 1610, 2240 s, 2885, 2955, 2990 s, 3030 s. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.85–2.03 m (2H), 3.05–3.22 m (3H), 3.58–3.65 m (2H), 7.37 d (2H, 8.5), 7.52 d (2H, 8.5). ^{13}C NMR spectrum, δ_C, ppm: 21.36, 52.16, 55.42, 111.90, 118.62, 128.01, 131.83, 142.49. Found, %: C 71.39; H 5.95; N 22.81. $C_{11}H_{11}N_3$. Calculated, %: C 71.33; H 5.99; N 22.69.

6-(4-Bromophenyl)-1,5-diazabicyclo[3.1.0]-hexane (If). A solution of 18.5 g (0.1 mol) of 4-bromobenzaldehyde in a mixture of 140 ml of methanol and 20 ml of water was added over a period of 3 h under stirring and cooling with ice water to 10 ml (0.12 mol) of 1,3-diaminopropane, maintaining the temperature below 45°C. The mixture was stirred for 1 h at 20°C, methanol was distilled off under reduced pressure at a temperature not exceeding 45°C, 50 ml (0.125 mol) of a 2.5 N solution of sodium hypochlorite 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 20°C. The organic phase was separated, and the aqueous phase was extracted with benzene. The extracts were combined with the organic phase and dried over sodium sulfate, and the solvent was distilled off on a rotary evaporator at a temperature not exceeding 50°C. Recrystallization of the residue from ether containing small amounts of benzene and hexane gave 16.7 g (70%) of diazabicyclohexane **If** as colorless crystals with mp 99–101°C. IR spectrum, ν, cm^{-1}: 880, 965, 980, 1020, 1075, 1095, 1190, 1255, 1300, 1340, 1380, 1430, 1455, 1490, 1605, 1640, 2885, 2990 s, 3040 s. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.82–2.03 m (2H), 3.09 s (1H), 3.12–3.23 m (2H), 3.52–3.66 m (2H), 7.23 d (2H, 7.9), 7.47 d (2H, 7.9). Found, %: C 50.19, 50.12; H 4.41, 4.60; N 11.82, 11.68. $C_{10}H_{11}BrN_2$. Calculated, %: C 50.23; H 4.64; N 11.72.

Thermolysis of 1,5-diazabicyclo[3.1.0]hexanes in the presence of dipolarophiles. A mixture of 1,5-diazabicyclo[3.1.0]hexane **Ia**–**If** and the corresponding dipolarophile in *p*-xylene was stirred for 20 min (**Ib**, **Id**), 25 min (**Ia**), or 30 min (**Ic**) at 135–140°C (or in toluene, for 2 h at 110°C). The solvent was distilled off, and the residue was either recrystallized from appropriate solvent or purified by chromatography. The products were colorless crystalline substances.

***rel*-(3a*S*,9*S*,9a*R*)-2-Mesityl-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIa)** was synthesized from 0.64 g (4 mmol) of diazabicyclohexane **Ia** and 0.86 g (4 mmol) of imide **IIa** in 8 ml of *p*-xylene. Recrystallization from acetone–diethyl ether–petroleum ether (bp 40–70°C) gave 0.6 g (40%) of *trans* isomer **IIIa**. mp 174–175°C. IR spectrum, ν, cm^{-1}: 1040, 1240, 1310, 1340, 1380, 1455, 1490, 1620, 1730 s, 1795, 2860, 2930, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.09 s (3H), 2.17 s (3H), 2.19–2.30 m (2H), 2.32 s (3H), 2.44–2.56 m (1H), 2.62–2.73 m (1H), 3.20–3.22 m (1H), 3.38–

3.50 m (1H), 3.97–4.12 m (2H), 4.73 br.s (1H), 6.98 s (2H), 7.32–7.67 (5H). Found, %: C 73.50, 73.38; H 6.60, 6.78; N 10.98, 10.90. $C_{23}H_{25}N_3O_2$. Calculated, %: C 73.57; H 6.71; N 11.19. When the reaction was carried out in toluene, the yield of compound **IIIa** was 89%.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,5-Dimethylphenyl)-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIb) and *rel*-(3a*S*,9*R*,9a*R*)-2-(2,5-dimethylphenyl)-9-phenylperhydropyrazolo[1,2-a]-pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVb)** were synthesized from 0.4 g (2.5 mmol) of compound **Ia** and 0.5 g (2.5 mmol) of imide **IIb** in 12 ml of *p*-xylene. Recrystallization from diethyl ether containing a small amount of acetone gave 0.55 g (61%) of *trans* isomer **IIIb**. mp 161–162°C. IR spectrum, ν, cm^{-1}: 1240, 1370, 1715 s, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.12 s and 2.20 s (3H), 2.22–2.30 m (2H), 2.35 s (3H), 2.44–2.75 m (2H), 3.15–3.34 m (1H), 3.37–3.53 m (1H), 3.93–4.09 m (2H), 4.73 br.s (1H), 6.92 s and 6.98 s (1H), 7.14–7.65 (7H). Found, %: C 73.27, 72.96; H 6.53, 6.64; N 11.72, 11.69. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63. Characteristic ^{1}H signals of *cis* isomer **IVb**, δ, ppm (*J*, Hz): 4.37 d (1H, 8), 6.73 s and 6.77 s (1H). When the reaction was carried out in toluene, the yield of **IIIb** was 83%.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,6-Dichlorophenyl)-9-phenylperhydropyrazolo[1,2-*a*]pirrolo[3,4-*c*]pyrazole-1,3-dione (IIIc) and *rel*-(3a*S*,9*R*,9a*R*)-2-(2,6-dichlorophenyl)-9-phenylperhydropyrazolo[1,2-*a*]-pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVc)** were obtained from 0.32 g (2 mmol) of compound **Ia** and 0.48 g (2 mmol) of imide **IIc** in 6 ml of *p*-xylene. Recrystallization from a mixture of 28 ml of acetone and 2 ml of diethyl ether gave 0.61 g (76%) of *trans* isomer **IIIc**. mp 198–199°C. IR spectrum, ν, cm^{-1}: 1240, 1370, 1445, 1465, 1730 s, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.13–2.32 m (2H), 2.45–2.60 m (1H), 2.70–2.82 m (1H), 3.25–3.39 m (1H), 3.43–3.56 m (1H), 4.15–4.19 m (2H), 4.88 br.s (1H), 7.32–7.50 (6H), 7.64 d (2H, 7.5). Found, %: C 59.94, 59.82; H 4.42, 4.45; N 10.48, 10.50. $C_{20}H_{17}Cl_2N_3O_2$. Calculated, %: C 59.71; H 4.26; N 10.45. Characteristic ^{1}H signals of *cis* isomer **IVc**, δ, ppm (*J*, Hz): 3.99 d.d (1H, 9, 8), 4.40 d (1H, 9), 4.50 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,4-Dichlorophenyl)-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIId)** was synthesized from 0.40 g (2.5 mmol) of compound **Ia** and 0.61 g (2.5 mmol) of imide **IId** in 6 ml of toluene. Recrystallization from acetone–ether–hexane gave 0.79 g (79%) of *trans* isomer **IIId**. mp 169–170°C. IR spectrum, ν, cm^{-1}: 1065, 1105, 1150, 1185, 1240, 1375, 1390, 1480, 1610, 1735 s, 2850, 2890, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.16–2.35 m (2H), 2.44–2.80 m (2H), 3.19–3.35 m (1H), 3.39–3.54 m (1H), 4.02–4.16 m (2H), 4.73 br.s and 4.82 br.s (1H), 7.17–7.64 (8H). Found, %: C 59.46, 59.66; H 4.48, 4.42; N 10.68, 10.49. $C_{20}H_{17}Cl_2N_3O_2$. Calculated, %: C 59.71; H 4.26; N 10.45.

***rel*-(3a*S*,9*S*,9a*R*)-2-(1-Naphthyl)-9-phenylperhydropyrazolo[1,2-*a*]pirrolo[3,4-*c*]pyrazole-1,3-dione (IIIe)** was synthesized from 0.40 g (2.5 mmol) of compound **Ia** and 0.61 g (2.5 mmol) of imide **IIe** in 6 ml of toluene. Recrystallization from acetone–diethyl ether gave 0.8 g (84%) of *trans* isomer **IIIe**. mp 178–179°C. IR spectrum, ν, cm^{-1}: 1190, 1220, 1240, 1345, 1370, 1405, 1730 s, 2860, 2880, 2980, 3040, 3060. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.18–2.35 m (2H), 2.42–2.81 m (2H), 3.22–3.38 m (1H), 3.42–3.56 m (1H), 4.00–4.22 m (2H), 4.83 br.s and 4.95 br.s (1H), 7.33–8.20 (12H). Found, %: C 75.33; H 5.57; N 11.27. $C_{24}H_{21}N_3O_2$. Calculated, %: C 75.18; H 5.52; N 10.96.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,4-Dimethylphenyl)-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIf)** was synthesized from 0.32 g (2 mmol) of compound **Ia** and 0.40 g (2 mmol) of imide **IIf** in 4 ml of toluene. Recrystallization from a minimal amount of acetone with addition of diethyl ether gave 0.52 g (72%) of *trans* isomer **IIIf**. mp 165–166°C. IR spectrum, ν, cm^{-1}: 1195, 1240, 1380, 1510, 1610, 1730 s, 2860, 2890, 2930, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.10 s and 2.20 s (3H), 2.19–2.34 m (2H), 2.37 s (3H), 2.45–2.74 m (2H), 3.19–3.33 m (1H), 3.37–3.52 m (1H), 3.93–4.09 m (2H), 4.70 br.s (1H), 6.95–7.65 (8H). Found, %: C 72.83, 72.91; H 6.56, 6.49; N 11.61, 11.62. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2-Bromophenyl)-9-phenylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIg)** was synthesized from 0.48 g (3 mmol) of compound **Ia** and 0.76 g (3 mmol) of imide **IIg** in 12 ml of *p*-xylene. Recrystallization from a small amount of acetone with addition of diethyl ether gave 0.6 g (49%) of *trans* isomer **IIIg**. mp 154–155°C. IR spectrum, ν, cm^{-1}: 1040, 1060, 1120, 1190, 1240, 1310, 1340, 1380, 1450, 1480, 1600, 1665, 1740 s, 2850, 2890, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.14–2.34 m (2H), 2.42–2.82 m (2H), 3.22–3.37 m (1H), 3.41–3.55 m (1H), 4.02–4.15 m (2H), 4.71 br.s and 4.92 br.s (1H), 7.22–7.76 (9H). Found, %: C 58.19, 57.97; H 4.51, 4.61; N 9.85, 10.03.

$C_{20}H_{18}BrN_3O_2$. Calculated, %: C 58.26; H 4.40; N 10.19.

***rel*-(3a*S*,9*S*,9a*R*)-2-Mesityl-9-(4-methoxyphenyl)-perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIh)** was synthesized from 0.57 g (3 mmol) of compound **Ib** and 0.65 g (3 mmol) of imide **IIa** in 7 ml of toluene. Recrystallization from benzene–ether gave 0.88 g (72%) of *trans* isomer **IIIh**. mp 134–135°C. IR spectrum, ν, cm^{-1}: 1040, 1195, 1260, 1310, 1380, 1470, 1490, 1615, 1715 s, 2840, 2960, 2970, 3030. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.09 s (3H), 2.17 s (3H), 2.19–2.30 m (2H), 2.32 s (3H), 2.44–2.56 m (1H), 2.62–2.73 m (1H), 3.20–3.22 m (1H), 3.38–3.50 m (1H), 3.97–4.12 m (2H), 4.73 br.s (1H), 6.98 s (2H), 7.32–7.67 (5H). Found, %: C 70.99, 70.77; H 6.55, 6.65; N 10.27, 10.09. $C_{24}H_{27}N_3O_3$. Calculated, %: C 71.09; H 6.71; N 10.36.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,6-Dichlorophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo-[3,4-*c*]pyrazole-1,3-dione (IIIi) and *rel*-(3a*S*,9*R*,9a*R*)-2-(2,6-dichlorophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVi)** were obtained from 0.48 g (2.5 mmol) of compound **Ib** and 0.61 g (2.5 mmol) of imide **IIc** in 6 ml of toluene. Recrystallization from acetone with addition of a small amount of ether gave 0.94 g (87%) of *trans* isomer **IIIi**. mp 196–197°C. IR spectrum, ν, cm^{-1}: 1040, 1110, 1185, 1240, 1260, 1300, 1370, 1440, 1460, 1520, 1620, 1740 s, 2840, 2970, 3040. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.15–2.31 m (2H), 2.44–2.57 m (1H), 2.68–2.77 m (1H), 3.25–3.36 m (1H), 3.43–3.54 m (1H), 3.83 s (3H), 4.07–4.17 m (2H), 4.85 br.s (1H), 6.95 d (2H, 8.4), 7.3–7.40 m (1H), 7.45 d (2H, 7.5), 7.55 d (2H, 8.4). Found, %: C 58.57, 58.42; H 4.55, 4.61; N 9.65, 9.64. $C_{21}H_{19}Cl_2N_3O_3$. Calculated, %: C 58.34; H 4.43; N 9.72. Characteristic ^1H signals of *cis* isomer **IVi**, δ, ppm (*J*, Hz): 3.78 s (3H), 3.94 d.d (1H, 8, 8), 4.35 d (1H, 8), 4.48 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,4-Dichlorophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo-[3,4-*c*]pyrazole-1,3-dione (IIIj) and *rel*-(3a*S*,9*R*,9a*R*)-2-(2,4-dichlorophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVj)** were obtained from 0.38 g (2 mmol) of compound **Ib** and 0.48 g (2 mmol) of imide **IId** in 12 ml of *p*-xylene. Recrystallization from acetone containing a small amount of hexane gave 0.49 g (56%) of *trans* isomer **IIIj**. mp 145–146°C. IR spectrum, ν, cm^{-1}: 1040, 1060, 1110, 1150, 1180, 1250, 1310, 1380, 1390, 1460, 1480, 1520, 1620, 1740 s, 2840, 2920, 2960, 3040. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.12–2.29 m (2H), 2.41–2.55 m (1H), 2.56–2.75 m (1H), 3.20–3.32 m (1H), 3.37–3.50 (1H), 3.84 s (3H), 3.98–4.12 m (2H), 4.67 br.s and 4.76 br.s (1H), 6.85–7.62 (7H). Found, %: C 58.57, 58.45; H 4.53, 4.58; N 9.55, 9.71. $C_{21}H_{19}Cl_2N_3O_3$. Calculated, %: C 58.34; H 4.43; N 9.72. Characteristic ^1H signals of *cis* isomer **IVj**, δ, ppm (*J*, Hz): 3.85 s (3H), 4.36 d (1H, 9), 4.48 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-9-(4-methoxyphenyl)-2-(1-naphthyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIk) and *rel*-(3a*S*,9*R*,9a*R*)-9-(4-methoxyphenyl)-2-(1-naphtyl)perhydropyrazolo-[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVk)** were obtained from 0.38 g (2 mmol) of compound **Ib** and 0.45 g (2 mmol) of imide **IIe** in 5 ml of toluene. Recrystallization from a mixture of 3 ml of acetone and 3 ml of ether gave 0.71 g (90%) of *trans* isomer **IIIk**. mp 188°C. IR spectrum, ν, cm^{-1}: 1040, 1190, 1230, 1260, 1305, 1345, 1370, 1405, 1465, 1520, 1620, 1720 s, 2840, 2910, 2970, 2980, 3040. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.15–2.38 m (2H), 2.46–2.57 m (1H), 2.60–2.79 m (1H), 3.21–3.39 m (1H), 3.42–3.55 m (1H), 3.84 s (3H), 4.01–4.20 m (2H), 4.75 br.s and 4.89 br.s (1H), 6.95 d (2H, 8.4), 7.34–8.01 (9H). Found, %: C 72.98, 72.80; H 5.69, 5.75; N 10.28, 10.26. $C_{25}H_{23}N_3O_3$. Calculated, %: C 72.62; H 5.65; N 10.16. Characteristic ^1H signals of *cis* isomer **IVk**, δ, ppm (*J*, Hz): 3.79 s (3H), 4.57 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-2-(2-Bromophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]-pyrazole-1,3-dione (IIIl) and *rel*-(3a*S*,9*R*,9a*R*)-2-(2-bromophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVl)** were obtained from 0.48 g (2.5 mmol) of compound **Ib** and 0.63 g (2.5 mmol) of imide **IIg** in 6 ml of toluene. Recrystallization from a benzene–ether mixture gave 0.6 g (72%) of *trans* isomer **IIIl**. mp 160–161°C. IR spectrum, ν, cm^{-1}: 1020, 1050, 1180, 1230, 1260, 1380, 1480, 1520, 1560, 1580, 1620, 1630, 1720 s, 1730 s, 2850, 2940, 2970, 3040. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.15–2.32 m (2H), 2.41–2.77 m (2H), 3.21–3.35 m (1H), 3.38–3.53 m (1H), 3.83 s (3H), 3.96–4.13 m (2H), 4.71 br.s and 4.87 br.s (1H), 6.95 d (2H, 8.4), 7.21–7.56 (5H), 7.72 d (2H, 8.4). Found, %: C 56.70, 57.17; H 4.75, 4.75; N 9.47, 9.30. $C_{21}H_{20}BrN_3O_3$. Calculated, %: C 57.02; H 4.56; N 9.50. Characteristic ^1H signals of *cis* isomer **IVl**, δ, ppm (*J*, Hz): 3.79 s (3H), 4.35 d (1H, 10), 4.50 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-2-(2-Chlorophenyl)-9-(4-methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]-pyrazole-1,3-dione (IIIm)** was synthesized from 0.48 g (2.5 mmol) of compound **Ib** and 0.52 g

(2.5 mmol) of imide **IIh** in 6 ml of toluene. Recrystallization from benzene–hexane gave 0.77 g (77%) of *trans* isomer **IIIm**. mp 150–151°C. IR spectrum, ν, cm^{-1}: 1040, 1070, 1090, 1240, 1260, 1310, 1340, 1380, 1450, 1460, 1480, 1520, 1560, 1580, 1620, 1730 s, 2860, 2940, 2970, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.15–2.35 m (2H), 2.45–2.77 m (2H), 3.21–3.34 m (1H), 3.39–3.52 m (1H), 3.83 s (3H), 3.95–4.11 m (2H), 4.71 br.s and 4.79 br.s (1H), 6.94 d (2H, 8.4), 7.23–7.58 (6H). Found, %: C 63.50, 63.53; H 5.27, 5.30; N 10.57, 10.64. $C_{21}H_{20}ClN_3O_3$. Calculated, %: C 63.40; H 5.07; N 10.56.

***rel*-(3a*S*,9*S*,9a*R*)-9-(4-Chlorophenyl)-2-mesitylperhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIn)** was synthesized from 0.49 g (2.5 mmol) of compound **Ic** and 0.54 g (2.5 mmol) of imide **IIa** in 6 ml of toluene. Recrystallization from benzene–diethyl ether gave 0.94 g (92%) of *trans* isomer **IIIn**. mp 157–158°C. IR spectrum, ν, cm^{-1}: 1040, 1070, 1090, 1240, 1260, 1310, 1340, 1380, 1450, 1460, 1480, 1520, 1560, 1580, 1620, 1730 s, 2860, 2940, 2970, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.08 s (3H), 2.17 s (3H), 2.20–2.31 m (2H), 2.32 s (3H), 2.42–2.55 m (1H), 2.60–2.70 m (1H), 3.16–3.30 m (1H), 3.35–3.45 m (1H), 3.93–4.05 m (2H), 4.65 br.s (1H), 6.97 s (2H), 7.38 d (2H, 7.5), 7.58 (2H, 7.5). Found, %: C 67.14, 66.98; H 5.84, 6.05; N 9.94, 10.04. $C_{23}H_{24}ClN_3O_2$. Calculated, %: C 67.39; H 5.90; N 10.25.

***rel*-(3a*S*,9*S*,9a*R*)-9-(4-Chlorophenyl)-2-(2,6-dichlorophenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIo) and *rel*-(3a*S*,9*R*,9a*R*)-9-(4-chlorophenyl)-2-(2,6-dichlorophenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVo)** were obtained from 0.49 g (2.5 mmol) of compound **Ic** and 0.61 g (2.5 mmol) of imide **IIc** in 6 ml of toluene. Recrystallization from benzene with addition of a small amount of diethyl ether gave 0.9 g (82%) of *trans* isomer **IIIo**. mp 178–179°C. IR spectrum, ν, cm^{-1}: 1020, 1100, 1190, 1240, 1340, 1370, 1450, 1470, 1500, 1575, 1730 s, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.18–2.29 m (2H), 2.44–2.58 m (1H), 2.68–2.78 m (1H), 3.23–3.35 m (1H), 3.43–3.54 m (1H), 4.01–4.16 m (2H), 4.88 br.s (1H), 7.35–7.49 (5H), 7.58 d (2H, 8.4). Found, %: C 55.02, 55.01; H 3.89, 3.95; N 9.65, 9.79. $C_{20}H_{16}Cl_3N_3O_2$. Calculated, %: C 55.00; H 3.69; N 9.62. Characteristic ^{1}H signals of *cis* isomer **IVo**, δ, ppm (*J*, Hz): 3.98 d.d (1H, 9, 8), 4.38 d (1H, 9), 4.48 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-9-(4-chlorophenyl)-2-(2,4-dichlorophenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIp) and *rel*-(3a*S*,9*R*,9a*R*)-9-(4-chlorophenyl)-2-(2,4-dichlorophenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVp)** were obtained from 0.39 g (2 mmol) of compound **Ic** and 0.48 g (2 mmol) of imide **IId** in 4 ml of toluene. Recrystallization from benzene–hexane gave 0.5 g (57%) of *trans* isomer **IIIp**. mp 157–158°C. IR spectrum, ν, cm^{-1}: 890, 1020, 1070, 1100, 1110, 1150, 1190, 1230, 1340, 1380, 1395, 1490, 1590, 1730 s, 2855, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.18–2.35 m (2H), 2.45–2.75 m (2H), 3.16–3.32 m (1H), 3.37–3.54 m (1H), 3.90–4.09 m (2H), 4.63 br.s and 4.70 br.s (1H), 7.16–7.59 (7H). Found, %: C 55.01, 54.74; H 3.96, 3.82; N 9.47, 9.40. $C_{20}H_{16}Cl_3N_3O_2$. Calculated, %: C 55.00; H 3.69; N 9.62. Characteristic ^{1}H signals of *cis* isomer **IVp**, δ, ppm (*J*, Hz): 4.38 d (1H, 9), 4.48 d (1H, 8).

***rel*-(3a*S*,9*S*,9a*R*)-9-(4-Chlorophenyl)-2-(1-naphthyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIq)** was synthesized from 0.58 g (3 mmol) of compound **Ic** and 0.67 g (3 mmol) of imide **IIe** in 7 ml of toluene. Recrystallization from benzene–diethyl ether gave 1.18 g (94%) of *trans* isomer **IIIq**. mp 190–191°C. IR spectrum, ν, cm^{-1}: 1020, 1095, 1190, 1240, 1350, 1370, 1405, 1490, 1610, 1730 s, 2850, 2980, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22–2.38 m (2H), 2.45–2.80 m (2H), 3.22–3.35 m (1H), 3.44–3.55 m (1H), 4.01–4.21 m (2H), 4.70 br.s and 4.81 br.s (1H), 7.34–8.02 (11H). Found, %: C 68.92, 68.68; H 4.84, 4.81; N 10.06, 9.82. $C_{24}H_{20}ClN_3O_2$. Calculated, %: C 68.98; H 4.82; N 10.06.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2-Bromophenyl)-9-(4-chlorophenyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIr)** was synthesized from 0.49 g (2.5 mmol) of compound **Ic** and 0.63 g (2.5 mmol) of imide **IIg** in 6 ml of toluene. Recrystallization from acetone–hexane gave 0.84 g (75%) of *trans* isomer **IIIr**. mp 148–149°C. IR spectrum, ν, cm^{-1}: 1020, 1060, 1100, 1195, 1240, 1380, 1450, 1480, 1595, 1630, 1735 s, 2850, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.16–2.38 m (2H), 2.43–2.79 m (2H), 3.16–3.33 m (1H), 3.40–3.53 m (1H), 3.91–4.10 m (2H), 4.65 br.s and 4.81 br.s (1H), 7.25–7.60 (7H), 7.73 d (1H, 7.9). Found, %: C 53.71, 53.65; H 4.00, 4.02; N 9.28, 9.12. $C_{20}H_{17}BrClN_3O_2$. Calculated, %: C 53.77; H 3.84; N 9.41.

***rel*-(3a*S*,9*S*,9a*R*)-2-(2,6-Dichlorophenyl)-9-(4-tolyl)perhydropyrazolo[1,2-*a*]pyrrolo[3,4-*c*]pyrazole-1,3-dione (IIIs) and *rel*-(3a*S*,9*R*,9a*R*)-2-(2,6-dichlorophenyl)-9-(4-tolyl)perhydropyrazolo[1,2-*a*]-pyrrolo[3,4-*c*]pyrazole-1,3-dione (IVs)** were obtained from 0.52 g (3 mmol) of compound **Id** and 0.73 g

(3 mmol) of imide **IIc** in 7 ml of toluene. Recrystallization from benzene with addition of a small amount of diethyl ether gave 1.03 g (82%) of *trans* isomer **IIIs**. mp 197–198°C (decomp.). IR spectrum, ν, cm^{-1}: 1115, 1190, 1240, 1340, 1370, 1445, 1470, 1575, 1730 s, 2860, 2900, 2930, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.13–2.25 m (2H), 2.39 s (3H), 2.45–2.55 m (1H), 2.68–2.77 m (1H), 3.24–3.38 m (1H), 3.40–3.53 m (1H), 4.05–4.40 m (2H), 4.87 br.s (1H), 7.20 d (2H, 7.9), 7.30–7.40 (1H), 7.45 d (2H, 8.8), 7.52 d (2H, 7.9). Found, %: C 60.81; H 4.84; N 10.11. $C_{21}H_{19}Cl_2N_3O_2$. Calculated, %: C 60.59; H 4.60; N 10.09. Characteristic ^{1}H signals of *cis* isomer **IVs**, δ, ppm (*J*, Hz): 2.32 s (3H), 3.95 d.d (1H, 9, 8), 4.35 d (1H, 9), 4.47 d (1H, 8).

***rel*-(1*R*,2*R*,3*S*)-3-Phenylperhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarbonitrile (VIIa)** was synthesized from 0.4 g (2.5 mmol) of compound **Ia** and 0.2 g (2.5 mmol) of fumaronitrile (**VIa**) in 8 ml of *p*-xylene. The product was isolated by flash chromatography using gradient elution with hexane, hexane–ether (1 : 1), and ether. Yield 0.3 g (50%), undistillable oily substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25–2.50 m (2H), 2.77 t.d (1H, 9.8, 5.0), 3.05–3.28 m (3H), 3.53 d.d (1H, 7.5, 4.0), 4.03 d (1H, 7.5), 4.36 d (1H,4.0), 7.36–7.55 m (5H).

***rel*-(1*R*,2*R*,3*S*)-3-(4-Methoxyphenyl)perhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarbonitrile (VIIb)** was synthesized from 0.38 g (2 mmol) of compound **Ib** and 0.16 g (2 mmol) of fumaronitrile (**VIa**) in 8 ml of *p*-xylene. Recrystallization from 2-propanol–ether–hexane gave 0.4 g (75%) of dinitrile **VIIb**. mp 100–101°C. IR spectrum, ν, cm^{-1}: 910, 950, 980, 1040 s, 1110, 1150, 1180, 1260 s, 1305, 1360, 1370, 1440, 1460, 1520, 1585, 1620, 2260, 2840, 2870, 2890, 2920, 2940, 2970, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.20–2.48 m (2H), 2.75 t.d (1H, 9.9, 5.2), 3.04–3.21 m (3H), 3.52 d. d (1H, 7.5, 4.2), 3.84 s (3H), 3.97 d (1H, 7.5), 4.35 d (1H, 4.2), 6.94 d (2H, 8.6), 7.41 d (2H, 8.6). Found, %: C 67.18, 67.45; H 5.95, 5.91; N 20.62, 20.86. $C_{15}H_{16}N_4O$. Calculated, %: C 67.15; H 6.01; N 20.88.

***rel*-(1*R*,2*R*,3*S*)-3-(4-Tolyl)perhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarbonitrile (VIIc)** was synthesized from 0.52 g (3 mmol) of compound **Id** and 0.23 g (3 mmol) of fumaronitrile (**VIa**) in 12 ml of *p*-xylene. Recrystallization from acetone–hexane gave 0.41 g (54%) of dinitrile **VIIc**. mp 144–145°C. IR spectrum, ν, cm^{-1}: 870, 910, 950, 975, 1030 s, 1050, 1110 s, 1150, 1250, 1290, 1310, 1350, 1360, 1465, 1520, 2255, 2870, 2930, 2990 s, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22–2.48 m (2H), 2.39 s (3H), 2.75 t. d (1H, 10.2, 5.5), 3.04–3.27 m (3H), 3.54 d.d (1H, 8.2, 4.1), 3.99 d (1H, 8.2), 4.35 d (1H, 4.1), 7.23 d (2H, 7.7), 7.37 d (2H, 7.7). Found, %: C 71.55, 71.61; H 6.24, 6.34; N 22.14, 22.42. $C_{15}H_{16}N_4$. Calculated, %: C 74.40; H 6.34; N 22.20. When the reaction was carried out in toluene, the yield of product **VIIc** was 62%.

***rel*-(1*R*,2*R*,3*S*)-3-(4-Cyanophenyl)perhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarbonitrile (VIId)** was obtained from 0.24 g (1.3 mmol) of compound **Ie** and 0.1 g (1.3 mmol) of fumaronitrile (**VIa**) in 3 ml of toluene. Recrystallization from acetone–ether–hexane gave 0.22 g (64%) of dinitrile **VIId**. mp 144–145°C. IR spectrum, ν, cm^{-1}: 910, 950, 975, 1025, 1110, 1150, 1250, 1280, 1300, 1360, 1420, 1460, 1510, 1620, 2240 s, 2865, 2975, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.27–2.51 m (2H), 2.75 t.d (1H, 9.7, 6.2), 3.10–3.29 m (3H), 3.51 d.d (1H, 7.1, 4.4), 4.13 d (1H, 7.1), 4.37 d (1H, 4.4), 7.64 d (2H, 8.4), 8.24 d (2H, 8.4). Found, %: C 68.27; H 5.06; N 26.90. C15H13N5. Calculated, %: C 68.42; H 4.98; N 26.60.

***rel*-(1*R*,2*R*,3*S*)-3-(4-Chlorophenyl)perhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarbonitrile (VIIe)** was obtained from 0.58 g (3 mmol) of compound **Ic** and 0.23 g (3 mmol) of fumaronitrile (**VIa**) in 7 ml of toluene. Recrystallization from acetone–ether gave 0.6 g (74%) of dinitrile **VIIe**. mp 153–155°C. IR spectrum, ν, cm^{-1}: 910, 950, 1020, 1090 s, 1150, 1295, 1320, 1350, 1490 s, 1610, 2255, 2865, 2990, 3030. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25–2.48 m (2H), 2.74 t.d (1H, 9.8, 5.6), 3.05–3.27 m (3H), 3.50 d.d (1H, 7.7, 4.2), 4.03 d (1H, 7.7), 4.35 d (1H, 4.2), 7.35–7.48 (4H). Found, %: C 61.89, 61.46; H 4.83, 4.73; N 20.38, 20.68. $C_{14}H_{13}ClN_4$. Calculated, %: C 61.65; H 4.80; N 20.54.

***rel*-(1*R*,2*R*,3*S*)-3-(4-Bromophenyl)perhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarbonitrile (VIIf)** was obtained from 0.91 g (3.8 mmol) of compound **If** and 0.3 g (3.8 mmol) of fumaronitrile **VIa** in 7 ml of toluene. Recrystallization from acetone–ether–hexane gave 0.83 g (69%) of dinitrile **VIIf**. mp 155–157°C (decomp.). IR spectrum, ν, cm^{-1}: 910, 950, 1020, 1090 s, 1150, 1295, 1320, 1350, 1490 s, 1610, 2255, 2865, 2990, 3030. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.25–2.48 m (2H), 2.74 t.d (1H, 9.8, 6.0), 3.05–3.28 m (3H), 3.50 d.d (1H, 7.7, 4.2), 4.01 d (1H, 7.7), 4.35 d (1H, 4.2), 7.38 d (2H, 8.0), 7.56 d (2H, 8.0). Found, %: C 53.05, 52.92; H 4.05, 4.03; N 17.66, 17.28. $C_{14}H_{13}BrN_4$. Calculated, %: C 53.01; H 4.13; N 17.66.

Diphenyl *rel*-(1*R*,2*R*,3*S*)-3-phenylperhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarboxylate (VIIg) was synthesized from 0.53 g (3.3 mmol) of compound **Ia**

and 0.8 g (3 mmol) of diphenyl fumarate (**VIb**) in 12 ml of *p*-xylene. Recrystallization from diethyl ether gave 0.8 g (62%) of diester **VIIg**. mp 100–101°C. IR spectrum, ν, cm^{-1}: 960, 1080, 1110, 1170 s, 1240 s, 1500, 1600, 1760 s, 2890, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.08–2.23 m (1H), 2.31–2.45 m (1H), 2.93–3.04 (1H), 3.18–3.35 m (2H), 3.50 t.d (1H, 9.5, 4.6), 4.18 d.d (1H, 8.2, 5.6), 4.32 d (1H, 8.2), 4.57 d (1H, 5.6), 7.06 d (2H, 8.2), 7.20–7.48 (11H), 7.59 d (2H, 7.2). Found, %: C 72.88, 73.19; H 5.63, 5.55; N 6.61, 6.70. $C_{26}H_{24}N_2O_4$. Calculated, %: C 72.88; H 5.65; N 6.54.

Dimethyl *rel*-(1*R*,2*R*,3*S*)-3-phenylperhydropyrazolo[1,2-*a*]pyrazole-1,2-dicarboxylate (VIIh) was obtained from 0.58 g (3.6 mmol) of 6-phenyl-1,5-diazabicyclo[3.1.0]hexane (**Ia**) and 0.5 g (3.5 mmol) of dimethyl fumarate (**VIc**). The product was isolated by preparative thin-layer chromatography on silica gel (5/40 μm) using diethyl ether as eluent. Yield 0.53 g (50%), undistillable oily substance. IR spectrum, ν, cm^{-1}: 1020, 1085, 1110, 1130, 1240, 1330, 1360, 1380, 1440, 1460, 1600, 1750 s, 2860, 2890, 2960, 2990, 3040. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.00–2.13 m (1H), 2.22–2.39 m (1H), 2.82–2.93 (1H), 3.08–3.18 m (2H), 3.35 t.d (1H, 9.6, 4.4), 3.69 s (3H), 3.83 s (3H), 3.87 d.d (1H, 8.4, 5.1), 4.10 d (1H, 8.4), 4.19 d (1H,5.1), 7.24–7.48 (5H).

X-Ray analysis. *6-Phenyl-1,5-diazabicyclo[3.1.0]-hexane (**Ia**).* $C_{10}H_{12}N_2$; *M* 160.22; rhombic crystals, space group $Pna2_1$ (no. 33); unit cell parameters at 20°C: *a* = 8.845(1), *b* = 8.798(1), *c* = 11.327(1) Å; *V* = 881.45(16) $Å^3$; *Z* = 4; d_{calc} = 1.207 g/cm^3; μ = 0.57 mm^{-1}; *F*(000) = 344.0; CuK_α iradiation, λ = 1.54178 Å, graphite monochromator; θ_{max} = 76.58°. Some bond lengths and angles: C^1-N^1 1.452 (0.003), C^1-N^2 1.459 (0.003), N^1-N^2 1.494 (0.003), N^2-C^{10} 1.486 (0.004), N^1-C^8 1.470 (0.004), C^1-H^1 0.980, C^1-C^2 1.481 (0.003) Å; $N^1C^1N^2$ 61.73 (0.17), $C^1N^2N^1$ 58.91 (0.16), $N^2N^1C^1$ 59.36 (0.17); $C^1N^1N^2C^{10}$ –105.68 (0.25), $N^1C^8C^9C^{10}$ 26.10 (0.33)°. The overall set of crystallographic parameters of compound **Ia** was included into the Cambridge Crystal Structure Database (CCDC-179633).

*6-(4-Methoxyphenyl)-1,5-diazabicyclo[3.1.0]hexane (**Ib**).* $C_{11}H_{14}N_2O$; *M* 190.25; crystal habit 0.8 × 0.6 × 0.5 mm; rhombic crystals, space group *Pbca* (no. 61); unit cell parameters at 20°C: *a* = 8.450(1), *b* = 9.236(1), *c* = 26.103(1) Å; *V* = 2037.19(34) $Å^3$; *Z* = 8; d_{calc} = 1.240 g/cm^3; μ = 0.65 mm^{-1}; *F*(000) = 816.0; CuK_α irradiation, λ = 1.54178 Å, graphite monochromator, θ_{max} = 76.41°. Some bond lengths and angles: C^1-N^1 1.447 (0.002), C^1-N^2 1.456 (0.002), N^1-N^2 1.505 (0.002), N^2-C^{10} 1.483 (0.002), N^1-C^8 1.477 (0.002), C^1-H^1 0.980, C^1-C^2 1.485 (0.002) Å; $N^1C^1N^2$ 62.48 (0.08), $C^1N^2N^1$ 58.46 (0.07), $N^2N^1C^1$ 59.05 (0.07); $C^1N^1N^2C^{10}$ –105.81 (0.12), $N^1C^8C^9C^{10}$ 26.49 (0.15)°. The overall set of crystallographic parameters of compound **Ib** was included into the Cambridge Crystal Structure Database (CCDC-179634).

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