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Stable Azomethine Imines Having a 3,4-Dihydroisoquinoline Fragment and Their Cycloaddition to *N*-Arylmaleimides

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Abstract—Aroylation of 5,6,8,8a,13,14,16,16a-octahydro[1,2,4,5]tetrazino[6,1-*a*:3,4-*a*′]diisoquinoline or 1,3,4,8b-tetrahydro[1,2]diazireno[3,1-*a*]isoquinoline, as well as reactions of 2-(2-bromoethyl)benzaldehyde with aroylhydrazines followed by treatment with triethylamine, led to the formation of stable azomethine imines, aroyl(3,4-dihydroisoquinolinium-2-yl)azanides. 1,3-Dipolar cycloaddition of the latter to *N*-mesitylmaleimide was stereoselective: the ratio of the *trans*- and *cis*-adducts was ~(3–7):1, the former prevailing. The reactions with *N*-arylmaleimides having no *ortho*-substituents in the aryl group gave the corresponding *cis*-adducts as the major products [*trans*/*cis* ratio ~1:(2.5–10)].

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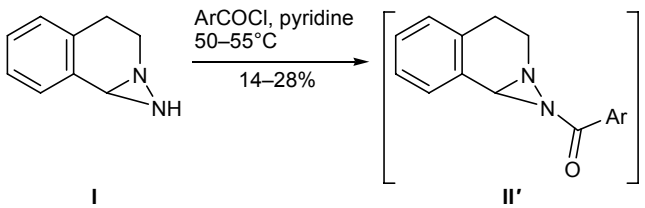
Azomethine imines in which both nitrogen atoms or one nitrogen and one carbon atoms are incorporated into a polycyclic system are convenient synthons for building up various heteropolycyclic, fused, and spirocyclic systems often exhibiting biological activity [1]. A conventional method for generation of such azomethine imines is based on opening of the diaziridine fragment at the carbon–nitrogen bond in fused bicyclic systems. This process may be accompanied by reversible dimerization [2], isomerizations, and various rearrangements [3, 4]. The presence of an electron-withdrawing substituent in the α-position with respect to the nitrogen atom in bicyclic diaziridine, e.g., of an oxo group in 6-aryl-1,5-diazabicyclo[3.1.0]hexan-2-ones, facilitates opening of the diaziridine ring due to stabilization of the resulting azomethine imines, so that it occurs even at room temperature [5]. Ortega et al. [6] reported that aroylation of 1,3,4,8b-tetrahydro[1,2]diazireno[3,1-*a*]isoquinoline (**I**) afforded stable *N*-aroyldiaziridines **II′** (Scheme 1). The authors assigned the signal at δ 9.67–9.77 ppm in the ^{1}H NMR spectra of the products to the CH proton in the diaziridine ring.

Scheme 1.



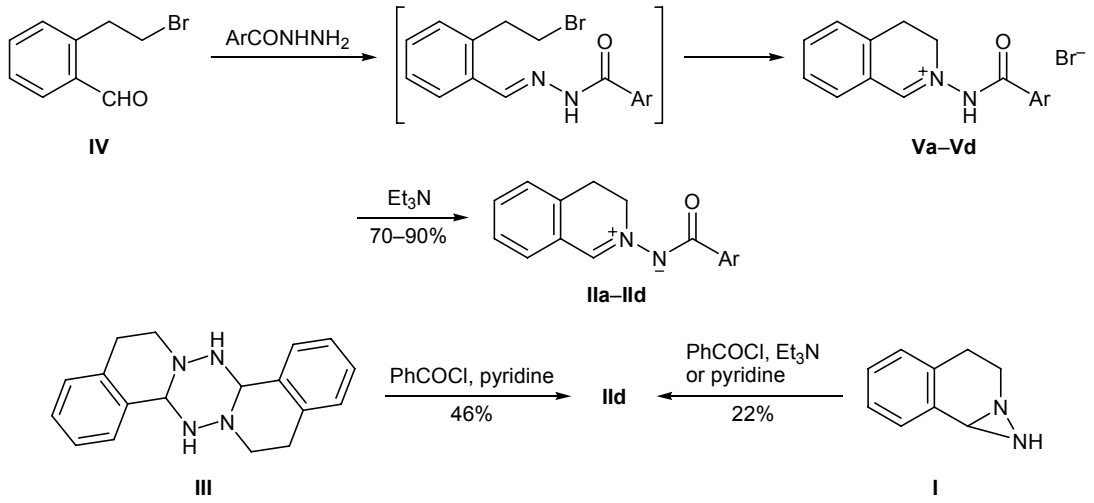
I **II′**

However, such chemical shift is quite untypical of bicyclic diaziridines. For example, the 8b-H proton in initial compound **I** resonates at δ 4.06 ppm [7], and in 1-methyl- and 1,3,3-trimethyl-1,3,4,8b-tetrahydro[1,2]diazireno[3,1-*a*]isoquinolines, at δ 3.36 ppm [8].

We presumed that the authors [6] isolated stable azomethine imines **II** rather than diaziridines **II′**. We reproduced the procedure reported in [6] and also synthesized compounds **IIa**–**IId** in two ways: by benzoylation of hexahydrotetrazinodiisoquinoline **III** and by reaction of substituted benzoic acid hydrazides with 2-(2-bromoethyl)benzaldehyde (**IV**) in boiling ethanol, followed by treatment of intermediate salts **V** with triethylamine (Scheme 2). In both cases, the products were identical in physical properties to the compounds prepared as described in [6]. Azomethine imine **IId** was reported previously [9], and its preparation from aldehyde **IV** has been described recently [10]. We failed to detect signals of probable intermediates **II′** in the ^{1}H NMR spectra of the reaction mixtures when the aroylation of diaziridine **I** was carried out in chloroform-*d* at –20°C in the presence of triethylamine or pyridine. Thus our results allow us to contend that aroylation of **I** yields only the corresponding stable azomethine imines **IIa**–**IId**.

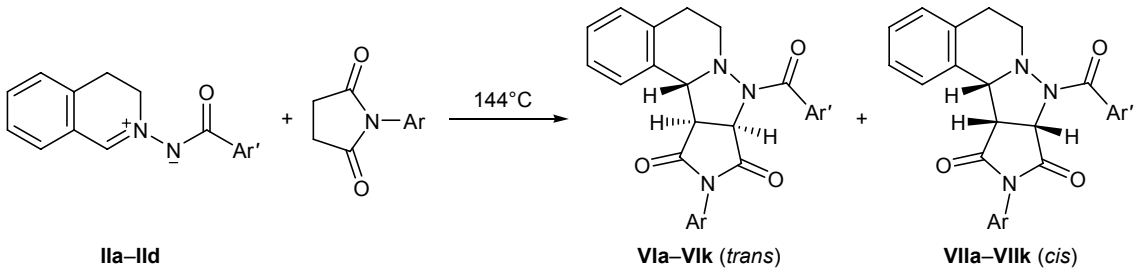
The ^{1}H NMR spectrum ($CDCl_3$) of azomethine imine salt **Va** contained signals from methyl protons at δ 2.37 ppm (3H, s), methylene protons at δ 3.46 (2H, t, J = 8.0 Hz) and 4.53 ppm (2H, t, J = 8.0 Hz), aromatic

Scheme 2.



Ar = 4-MeC_6H_4 (**a**), 4-$MeOC_6H_4$ (**b**), 4-$O_2NC_6H_4$ (**c**), Ph (**d**).

Scheme 3.



II, Ar′ = 4-MeC_6H_4 (**a**), 4-$MeOC_6H_4$ (**b**), 4-$O_2NC_6H_4$ (**c**), Ph (**d**); **VI**, **VII**, Ar = 2,4,6-$Me_3C_6H_2$, Ar′ = Ph (**a**), 4-MeC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**), 4-$O_2NC_6H_4$ (**d**); Ar = Ph, Ar′ = Ph (**e**), 4-MeC_6H_4 (**f**), 4-$MeOC_6H_4$ (**g**), 4-$O_2NC_6H_4$ (**h**); Ar = 4-BrC_6H_4, Ar′ = Ph (**i**), 4-MeC_6H_4 (**j**), 4-$MeOC_6H_4$ (**k**).

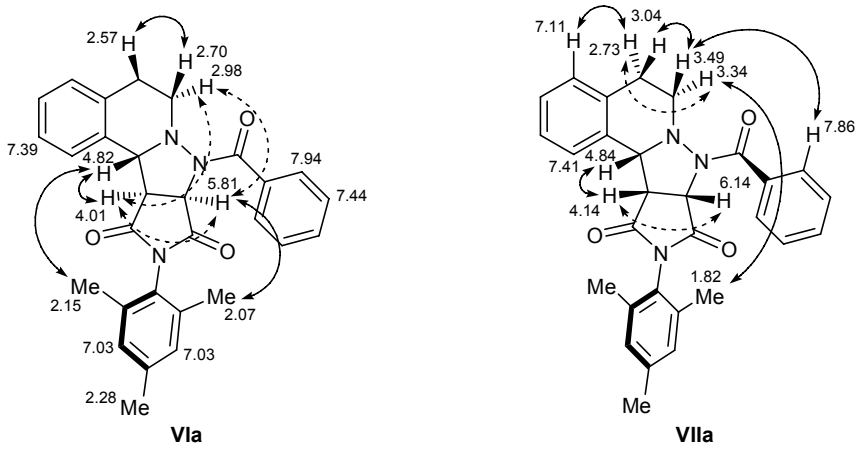
protons in the region δ 7.24–8.07 ppm (8H), 1-H at δ 9.37 ppm (1H, s), and NH proton at δ 13.49 ppm (1H). Azomethine imines **IIa**–**IId** characteristically displayed in the ^{1}H NMR spectra ($CDCl_3$) the following signals, δ, ppm: 3.23–3.26 t (2H, J = 7.6 Hz) and 4.25–4.29 t (2H, J = 7.6 Hz) (3-H, 4-H), 6.84–8.15 m (8H or 9H for **IIa**–**IIc** and **IId**, respectively), and 9.59–9.75 m (HC=N); the position of the latter signal depended on the water content in the sample or solvent.

Ratios of *trans* (**VIa**–**VIk**) and *cis* adducts (**VIIa**–**VIIk**) formed by 1,3-polar cycloaddition of azomethine imines **IIa**–**IId** to *N*-arylmaleimides

Ar	Ar′			
	Ph	4-$MeOC_6H_4$	4-MeC_6H_4	4-$O_2NC_6H_4$
2,4,6-$Me_3C_6H_2$	75:25	72:28	73:27	88:12
Ph	10:90	10:90	10:90	29:71
4-BrC_6H_4	11:89	8:92	8:92	–

In continuation of our studies on the chemical behavior of azomethine imines having a 3,4-dihydroisoquinoline fragment [8, 11], we examined reactions of compounds **IIa**–**IId** with *N*-arylmaleimides. The reactions were carried out by heating the reactants in boiling *o*-xylene (144°C) over a period of 2 h (TLC). After removal of the solvent, the mixtures were analyzed by ^{1}H NMR spectroscopy. The ratios of the resulting *trans*- and *cis*-adducts **VIa**–**VIk** and **VIIa**–**VIIk** were determined with an accuracy of ~5% (Scheme 3, see table).

The reactions of aroyl(3,4-dihydroisoquinolinium-2-yl)azanides **IIa**–**IId** with *N*-mesitylmaleimide resulted in the formation of mixtures of *trans*- and *cis*-adducts **VIa**–**VId** and **VIIa**–**VIId**, the former prevailing. According to our previous data, the cycloaddition of di-*ortho*-substituted *N*-arylmaleimides to (3,4-dihydroisoquinolinium-2-yl)methylazanides [8] and aryl(3,4-dihydroisoquinolinium-2-yl)azanides [11] afford-



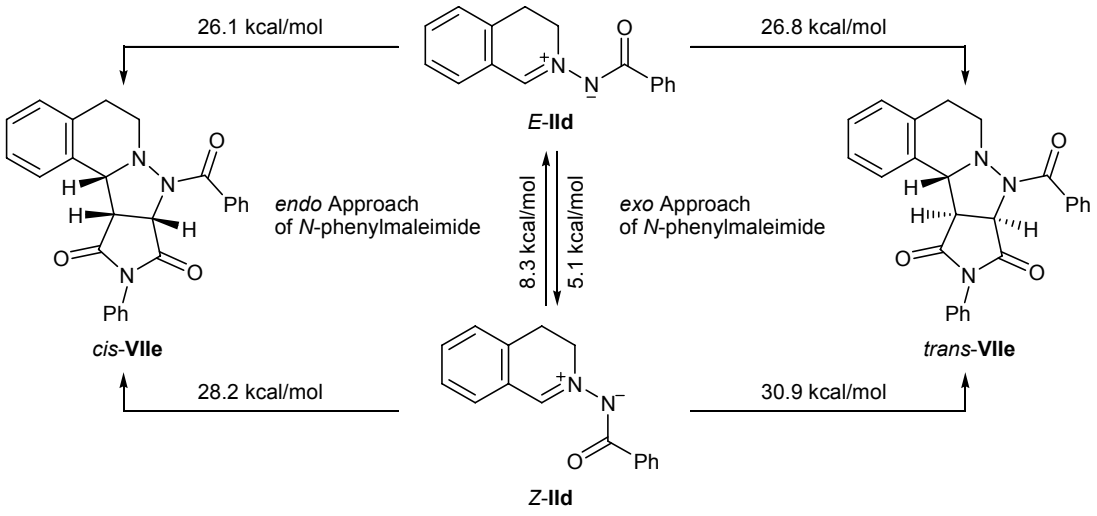
Principal nuclear Overhauser effects in the 2D NOESY ^{1}H NMR spectra of stereoisomeric compounds **VIa** (DMSO-d_6) and **VIIa** ($CDCl_3$).

ed exclusively the corresponding *trans* isomers. In going from benzoyl derivative **IId** to 4-methylbenzoyl and 4-methoxybenzoyl analogs **IIa** and **IIb**, the diastereoselectivity [*trans*/*cis* ratio (72–75):(25–28)] almost did not change, whereas the fraction of *trans*-adduct **VId** in the reaction with azomethine imine **IIc** having a strong electron-withdrawing nitro group increased from 72–75 to 88%.

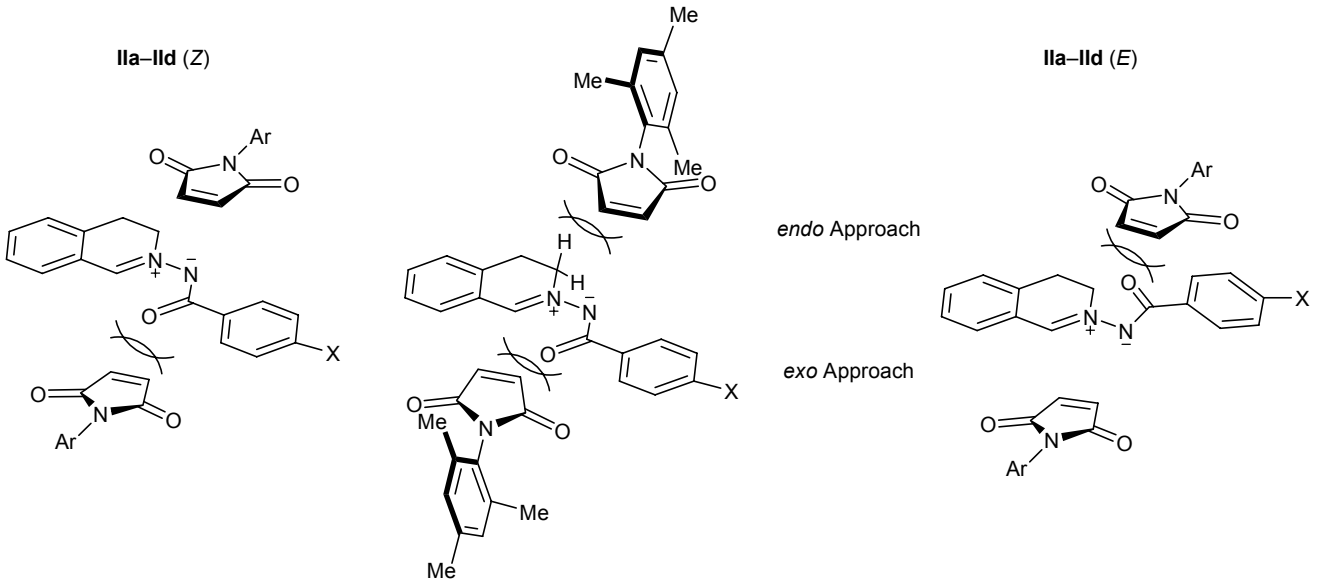
When *N*-arylmaleimides having no *ortho*-substituents were used as dipolarophiles, the corresponding *cis*-adducts predominated in the reactions mixtures [according to the ^{1}H NMR data, the *cis*/*trans* ratio for azomethine imines **IIa**, **IIb**, and **IId** was ~(89–92):(8–11)]. In the cycloadditions with (3,4-dihydroisoquinolinium-2-yl)methylazanides and aryl(3,4-dihydroisoquinolinium-2-yl)azanides, *trans*-adducts were always formed as the major products [8, 11]. In the reaction with nitro-substituted compound **IIc**, the fraction of *trans* isomer **VId** increased from ~10 to 29%.

The structure of adducts **VI** and **VII** was determined on the basis of the 2D NOESY ^{1}H NMR spectra of compounds **VIa** and **VIIa**. Figure shows the chemical shifts of selected protons and principal nuclear Overhauser effects (spatial interactions) in molecules **VIa** and **VIIa**. Here, the most important coupling is that between protons in the *ortho*-methyl group (δ 2.15 ppm) and 11b-H resonating at δ 4.82 ppm. The presence of the corresponding cross peak in the NOESY spectrum of **VIa** allowed us to unambiguously assign *trans* configuration of 11a-H and 11b-H in molecule **VIa**. The signal assignments made for adducts **VIa** and **VIIa** were used to determine configuration of the other cycloaddition products, compounds **VIb**–**VIk** and **VIIb**–**VIIk**.

Scheme 4.



Scheme 5.



Quantum-chemical calculations in terms of the density functional theory [DFT, 6-31(*d*) basis set, B3LYP functional; Gaussian-03 [12]) showed that the *Z* isomer of azomethine imine **IId** is more energetically favorable (~98%). The *endo* approach of *N*-phenylmaleimide to *Z*-**IId** is more probable than the *exo* approach by a factor of ~25. In the cycloaddition to *E*-**IId**, the *endo* approach of *N*-phenylmaleimide is more probable than the *exo* approach by a factor of ~2 (Scheme 4). These findings led us to presume that the cycloaddition involves mainly the *Z* isomer of azomethine imine **IId**.

Analysis of possible dipolarophile approaches to azomethine imines **IIa**–**IId** revealed that *exo* approach of *N*-mesitylmaleimide to the *Z* isomers of **II** should be hindered due to strong steric interaction between the aroyl carbonyl group in **II** and mesityl group in maleimide. *endo* Approach of *N*-mesitylmaleimide should also be hindered due to steric interaction between the $C^3H_2C^4H_2$ ethylene fragment in **II** and *o*-methyl group in the imide. Presumably, preferential formation of *trans* adducts in the reactions with sterically crowded *N*-mesitylmaleimide is determined by participation of less stable but more reactive *E* isomer of **II** and *exo* approach of the dipolarophile. In the cycloadditions to *N*-arylmaleimides having no substituents in the *ortho* positions of the benzene ring, the *endo* approach to predominating *Z* isomer of **II** is less sterically hindered than the *exo* approach; therefore, the major products are the corresponding *cis* adducts.

Summarizing the data on cycloaddition reactions of azomethine imines having a 3,4-dihydroisoquinoline fragment, we can conclude that, unlike *N*-methyl- [8] and *N*-aryl-substituted azomethine imines [11] for which steric effect of the 3,4-dihydroisoquinoline fragment was determining in 1,3-dipolar cycloaddition to di-*ortho*-substituted *N*-arylmaleimides, the formation of appreciable amounts of *cis* adducts in going to *N*-aroyl-substituted azomethine imines indicates increased contribution of their *Z* isomers and determining effect of the *N*-aroyl group on the cycloaddition process.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer from 1–2% solutions in chloroform. The NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300.130 (^{1}H) and 75.468 MHz (^{13}C). The chemical shifts were measured relative to the residual proton and carbon signals of deuterated solvents ($CHCl_3$, δ 7.26 ppm; $CDCl_3$, δ_C 77.16 ppm; DMSO-d_5, δ 2.50 ppm; DMSO-d_6; δ_C 39.52 ppm) [13]. The elemental compositions were determined on a Hewlett–Packard 185-B CHN analyzer. *N*-Arylmaleimides were synthesized according to the procedure described in [14]. 2-(2-Bromoethyl)benzaldehyde (**IV**) was prepared by bromination of isochroman [15] which was synthesized in turn by chloroformylation of β-phenylethyl alcohol [16].

1,3,4,8b-Tetrahydro[1,2]diazireno[3,1-*a*]isoquinoline (I) was synthesized from 9.3 g (71 mmol) of 3,4-dihydroisoquinoline as described in [7]. Yield 2.8 g (28%), mp 97–98°C; published data [7]: mp 97–99°C.

^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.30 d (1H, NH, J = 6.9 Hz), 2.41 d.d.d (1H, CH_2, J = 1.2, 4.2, 15.3 Hz), 2.72 d.d.d (1H, CH_2, J = 4.2, 12.6, 13.1 Hz), 2.95 d.d.d (1H, CH_2, J = 6.1, 12.6, 15.3 Hz), 3.58 d.d.d (1H, CH_2, J = 1.2, 6.1, 13.1 Hz), 4.06 d (1H, NCHN, J = 6.9 Hz), 7.05–7.12 (1H, H_{arom}), 7.21–7.33 (2H, H_{arom}), 7.39–7.46 (1H, H_{arom}). The ^{13}C NMR spectrum was consistent with that given in [6].

5,6,8,8a,13,14,16,16a-Octahydro[1,2,4,5]tetrazino[6,1-*a*:3,4-*a′*]diisoquinoline (III) was synthesized from 4.2 g (0.02 mol) of 2-(2-bromoethyl)benzaldehyde (**IV**) as described in [16]. Yield 1.6 g (54%), mp 242°C (decomp.); published data [16]: mp 247–252°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 3.22 t (4H, CH_2, J = 7.7 Hz), 3.67 t (4H, CH_2, J = 7.7 Hz), 5.51 s (2H, CH), 7.10–7.34 (8H, H_{arom}, NH), 7.45 d (2H, H_{arom}, J = 7.1 Hz).

Benzoyl(3,4-dihydroisoquinolinium-2-yl)azanide (IId) [10]**.** *a*. A mixture of 1.00 g (6.8 mmol) of compound **I** and 1.25 ml (9.0 mmol) of triethylamine in 5 ml of methylene chloride was cooled to –20°C, and a solution of 1.06 g (7.5 mmol) of benzoyl chloride in 5 ml of methylene chloride was added dropwise at such a rate that the temperature did not exceed –15°C. The mixture was then shaken with water (3×5 ml), the organic phase was separated and dried over sodium sulfate, the solvent was distilled off, and the residue was recrystallized from anhydrous tetrahydrofuran with addition of hexane. Yield 374 mg (22%), bright yellow powder which bleached on exposure to air due to formation of hydrate, mp 137–138°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.26 t (2H, CH_2, J = 7.6 Hz), 4.29 t (2H, CH_2, J = 7.6 Hz), 7.28–7.54 m (7H, H_{arom}), 8.10 m (2H, H_{arom}), 9.63 s (1H, C=N$^+$). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.9 (CH_2), 54.9 (CH_2), 126.9 (C_{arom}), 127.8 (CH_{arom}), 128.1 (4C, CH_{arom}), 128.2 (CH_{arom}), 129.9 (CH_{arom}), 130.5 (CH_{arom}), 133.5 (CH_{arom}), 133.9 (C_{arom}), 137.2 (C_{arom}), 148.9 (CH=N$^+$), 170.9 (C=O).

b. A suspension of 500 mg (1.7 mmol) of compound **III** in 80 ml of pyridine was heated to 80°C, and 0.5 ml of benzoyl chloride was added dropwise over a period of 30 min. The mixture was kept until it became homogeneous and poured into water. The white powder was filtered off and recrystallized from anhydrous tetrahydrofuran with addition of hexane. Yield 394 mg (46%).

Azomethine imines IIa–IId (*general procedure*). A solution of 10 mmol of the corresponding substituted benzoic acid hydrazide in ethanol was heated to 70°C, 10 mmol of 2-(2-bromoethyl)benzaldehyde (**IV**) was added, and the mixture was heated to the boiling point and was kept boiling for 1 h. Triethylamine, 30 mmol, was carefully added, and the mixture was kept for 15 min more, cooled, and poured into cold water. The precipitate was filtered off, dried under reduced pressure at 60–70°C, and recrystallized from THF with addition of hexane.

(3,4-Dihydroisoquinolinium-2-yl)(4-methylbenzoyl)azanide (IIa). Yield 1.9 g (72%), mp 160–162°C; published data [6]: mp 155–156°C.

(3,4-Dihydroisoquinolinium-2-yl)(4-methoxybenzoyl)azanide (IIb). Yield 2.2 g (79%), mp 156–157°C; published data [6]: mp 164–165°C.

(3,4-Dihydroisoquinolinium-2-yl)(4-nitrobenzoyl)azanide (IIc). Yield 2.4 g (81%), mp 175–176°C; published data [6]: mp 178–179°C.

Benzoyl(3,4-dihydroisoquinolinium-2-yl)azanide (IId). Yield 1.9–2.2 g (76–88%).

2-(4-Methylbenzoylamino)-3,4-dihydroisoquinolinium bromide (Vd). After addition of aldehyde **IV**, a sample was withdrawn from the reaction mixture, dissolved in chloroform-*d*, and analyzed by NMR. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.37 s (3H, Me), 3.46 t (2H, CH_2, J = 8.0 Hz), 4.53 t (2H, CH_2, J = 8.0 Hz), 7.24 d (2H$_{arom}$, J = 8.1 Hz), 7.43 d (1H$_{arom}$, J = 7.6 Hz), 7.51 m (1H, H_{arom}), 7.78 m (1H, H_{arom}), 7.90 d (1H, H_{arom}, J = 7.6 Hz), 8.07 d (2H, H_{arom}, J = 8.1 Hz), 9.37 s (1H, C=N$^+$), 13.49 s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.8 (CH_3), 26.3 (CH_2), 53.9 (CH_2), 123.8 (C_{arom}), 126.2 (C_{arom}), 128.7 (CH_{arom}), 128.8 (2C, CH_{arom}), 129.0 (CH_{arom}), 129.7 (2C, CH_{arom}), 134.9 (CH_{arom}), 136.4 (C_{arom}), 139.2 (CH_{arom}), 144.8 (C_{arom}), 165.0 (C=O), 166.2 (CH=N$^+$).

Reaction of azomethine imines IIa–IId with *N*-arylmaleimides (*general procedure*). A suspension of 1 mmol of azomethine imine **IIa–IId** (dried just before use) and 1 mmol of the corresponding *N*-arylmaleimide in 2 ml of *o*-xylene was heated for 2 h at 140–145°C (oil bath) under stirring. The solvent was distilled off under reduced pressure, and the residue was analyzed by ^{1}H NMR. Solid residues (stereoisomer mixtures **VIa**/**VIIa**, **VId**/**VIId**, **VIe**/**VIIe**, **VIf**/**VIIf**, **VIg**/**VIIg**, and **VIk**/**VIIk**) were recrystallized from chloroform–methanol to isolate major products **VId**, **VIIe**, **VIIf**, **VIIg**, and **VIIk**. Mixtures **VIb**/**VIIb**, **VIc**/**VIIc**, **VIh**/**VIIh**, **VIi**/**VIIi**, and **VIj**/**VIIj** were not separated. The spectral parameters of minor products and components of unseparated

mixtures were determined from the spectra of the corresponding mixtures.

***rel*-(8a*R*,11a*S*,11b*R*)-8-Benzoyl-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]pyrazolo-[5,1-*a*]isoquinoline-9,11-dione (VIa) and *rel*-(8a*R*,11a*S*,11b*S*)-8-benzoyl-10-(2,4,6-trimethylphenyl) perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]-isoquinoline-9,11-dione (VIIa)** were obtained from azomethine imine **IId** and *N*-mesitylmaleimide. Yield of mixture **VIa**/**VIIa** 417 mg (90%). The stereoisomer mixture was separated by column chromatography on silica gel (Silicagel L, 35–70 μm; substrate–sorbent weight ratio 1:200; eluent hexane–ethyl acetate, 2:1); the separation process was monitored by TLC (Silufol UV-254; hexane–ethyl acetate, 1:1; development with iodine vapor). According to the ^{1}H NMR data, the ratio of isomers **VIa** and **VIIa** in the reaction mixture was ~75:25.

Compound **VIa**. Yield 46 mg (10%), mp 250–251°C (decomp.). IR spectrum, ν, cm^{-1}: 3040, 3015, 2965, 2925, 2865, 1800, 1720 v.s, 1655, 1600, 1490, 1455, 1380 s, 1325, 1305, 1260, 1180 s, 1120, 1040, 1020. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.11 s (3H, Me), 2.22 s (3H, Me), 2.32 s (3H, Me), 2.58–2.73 m (1H, CH_2), 2.78–2.98 m (3H, CH_2), 3.84 d.d (1H, CH, *J* = 8.5, 8.6 Hz), 4.84 d (1H, CH, *J* = 8.5 Hz), 5.76 d (1H, CH, *J* = 8.6 Hz), 6.94–7.01 m (2H, H_{arom}), 7.05–7.14 m (1H, H_{arom}), 7.20–7.32 m (2H, H_{arom}), 7.34–7.44 m (2H, H_{arom}), 7.45–7.54 m (1H, H_{arom}), 7.55–7.63 m (1H, H_{arom}), 8.08 d (2H, H_{arom}, *J* = 7.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 17.9 (CH_3), 18.1 (CH_3), 21.2 (CH_3), 29.0 (CH_2), 49.0 (CH_2), 51.4 (CH), 60.7 (CH), 66.2 (CH), 127.0 (C_{arom}), 127.1 (CH_{arom}), 128.0 (2C, CH_{arom}), 128.1 (CH_{arom}), 128.3 (CH_{arom}), 128.4 (CH_{arom}), 129.6 (CH_{arom}), 129.7 (3C, CH_{arom}), 132.1 (CH_{arom}), 132.3 (C_{arom}), 132.5 (C_{arom}), 133.5 (C_{arom}), 135.2 (C_{arom}), 135.7 (C_{arom}), 139.8 (C_{arom}), 168.9 (C=O), 170.4 (C=O), 173.6 (C=O). Found, %: C 74.64; H 5.79; N 8.74. $C_{29}H_{27}N_3O_3$. Calculated, %: C 74.82; H 5.85; N 9.03.

Compound **VIIa**. Yield 44 mg (9%), ratio **VIIa**:**VIa** ≈ 91:9, mp 244–245°C (decomp.). IR spectrum, ν, cm^{-1}: 3040, 3015, 2965, 2925, 2860, 1800, 1720 v.s, 1655, 1600, 1490, 1455, 1380 s, 1325, 1305, 1280, 1260, 1215, 1190 s, 1130, 1040. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.82 s (3H, Me), 2.01 s (3H, Me), 2.24 s (3H, Me), 2.73 d.d.d (1H, CH_2, *J* = 2.2, 3.3, 16.3 Hz), 3.04 m (1H, CH_2, *J* = 5.2, 16.3 Hz), 3.34 m (1H, CH_2, *J* = 3.3, 10.5 Hz), 3.49 d.d.d (1H, CH_2, *J* = 2.2, 5.2, 10.5 Hz), 4.14 d.d (1H, CH, *J* = 9.0, 9.2 Hz), 4.84 d (1H, CH, *J* = 9.2 Hz), 6.14 d (1H, CH, *J* = 9.0 Hz), 6.80 s (1H, H_{arom}), 6.90 s (1H, H_{arom}), 7.11 d (1H, H_{arom}, *J* = 7.3 Hz), 7.15–7.29 m (2H, H_{arom}), 7.35–7.51 m (4H, H_{arom}), 7.81–7.88 m (2H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 18.1 (CH_3), 18.2 (CH_3), 21.1 (CH_3), 29.3 (CH_2), 49.9 (CH_2), 50.8 (CH), 59.7 (CH), 65.6 (CH), 127.0 (C_{arom}), 127.1 (CH_{arom}), 128.0 (2C, CH_{arom}), 128.1 (CH_{arom}), 128.3 (CH_{arom}), 128.4 (CH_{arom}), 129.6 (CH_{arom}), 129.7 (3C, CH_{arom}), 132.1 (CH_{arom}), 132.3 (C_{arom}), 132.5 (C_{arom}), 133.5 (C_{arom}), 135.2 (C_{arom}), 135.7 (C_{arom}), 139.8 (C_{arom}), 168.9 (C=O), 170.4 (C=O), 173.6 (C=O). Found, %: C 74.67; H 5.84; N 8.94. $C_{29}H_{27}N_3O_3$. Calculated, %: C 74.82; H 5.85; N 9.03.

***rel*-(8a*R*,11a*S*,11b*R*)-8-(4-Methylbenzoyl)-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]-pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIb) and *rel*-(8a*R*,11a*S*,11b*S*)-8-(4-methylbenzoyl)-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIb)** were obtained from azomethine imine **IIa** and *N*-mesitylmaleimide. According to the ^{1}H NMR data, the stereoisomer ratio **VIb**:**VIIb** in the reaction mixture was ~73:27.

Compound **VIb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.11 s (3H, Me), 2.21 s (3H, Me), 2.31 s (3H, Me), 2.40 s (3H, Me), 2.64–2.73 m (1H, CH_2), 2.84–2.98 m (3H, CH_2), 3.83 d.d (1H, CH, *J* = 8.5, 8.6 Hz), 4.84 d (1H, CH, *J* = 8.6 Hz), 5.76 d (1H, CH, *J* = 8.5 Hz), 6.94–7.00 m (2H, H_{arom}), 7.07–7.12 m (1H, H_{arom}), 7.15–7.29 m (4H, H_{arom}), 7.55–7.60 m (1H, H_{arom}), 8.00 d (2H, H_{arom}, *J* = 8.1 Hz).

Compound **VIIb**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.80 s (3H, Me), 2.01 s (3H, Me), 2.24 s (3H, Me), 2.39 s (3H, Me), 2.71 m (1H, CH_2, *J* = 16.1 Hz), 3.02 m (1H, CH_2), 3.32 m (1H, CH_2), 3.49 m (1H, CH_2), 4.09 d.d (1H, CH, *J* = 9.0, 9.2 Hz), 4.80 d (1H, CH, *J* = 9.2 Hz), 6.14 d (1H, CH, *J* = 9.0 Hz), 6.80 s (1H, H_{arom}), 6.90 s (1H, H_{arom}), 7.11 m (1H, H_{arom}), 7.17–7.29 m (5H, H_{arom}), 7.78 d (2H, H_{arom}, *J* = 8.1 Hz).

***rel*-(8a*R*,11a*S*,11b*R*)-8-(4-Methoxybenzoyl)-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]-pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIc) and *rel*-(8a*R*,11a*S*,11b*S*)-8-(4-methoxybenzoyl)-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]-pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIc)** were obtained from azomethine imine **IIb** and *N*-mesitylmaleimide. According to the ^{1}H NMR data, the stereoisomer ratio **VIc**:**VIIc** in the reaction mixture was ~72:28.

Compound **VIc**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.11 s (3H, Me), 2.20 s (3H, Me), 2.31 s (3H, Me), 2.63–2.73 m (1H, CH_2), 2.84–2.99 m (3H, CH_2), 3.82 d.d (1H, CH, J = 8.5, 8.6 Hz), 3.86 s (3H, OMe), 4.83 d (1H, CH, J = 8.7 Hz), 5.76 d (1H, CH, J = 8.6 Hz), 6.89 d (2H, H_{arom}, J = 8.8 Hz), 6.95–6.99 m (2H, H_{arom}), 7.07–7.12 m (1H, H_{arom}), 7.15–7.29 m (2H, H_{arom}), 7.57–7.61 m (1H, H_{arom}), 8.14 d (2H, H_{arom}, J = 8.8 Hz).

Compound **VIIc**. Some signals in the ^{1}H NMR spectrum of mixture **VIc**/**VIIc** ($CDCl_3$), δ, ppm: 1.79 s (3H, Me), 2.01 s (3H, Me), 2.23 s (3H, Me), 2.74 m (1H, CH_2, J = 16.1 Hz), 3.02 m (1H, CH_2), 3.33 m (1H, CH_2), 3.50 m (1H, CH_2), 3.85 s (3H, OMe), 4.08 d.d (1H, CH, J = 9.1, 9.3 Hz), 4.82 d (1H, CH, J = 9.3 Hz), 6.14 d (1H, CH, J = 9.1 Hz), 6.80 s (1H, H_{arom}), 7.94 d (2H, H_{arom}, J = 8.8 Hz).

***rel*-(8a*R*,11a*S*,11b*R*)-8-(4-Nitrobenzoyl)-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]-pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VId) and *rel*-(8a*R*,11a*S*,11b*S*)-8-(4-nitrobenzoyl)-10-(2,4,6-trimethylphenyl)perhydropyrrolo[3′,4′:3,4]pyrazolo-[5,1-*a*]isoquinoline-9,11-dione (VIId)** were obtained from azomethine imine **IIc** and *N*-mesitylmaleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VId** and **VIId** in the reaction mixture was ~88:12.

Compound **VId**. Yield 298 mg (61%), mp 266–268°C. IR spectrum, ν, cm^{-1}: 3040, 2925, 2860, 1800, 1720 v.s, 1655, 1600, 1525, 1490, 1415, 1380 s, 1345 s, 1320, 1305, 1280, 1180 s, 1120, 1040, 1020. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.08 s (3H, Me), 2.18 s (3H, Me), 2.29 s (3H, Me), 2.58–2.77 m (3H, CH_2), 3.03 m (1H, CH_2), 4.06 d.d (1H, CH, J = 7.8, 8.9 Hz), 4.87 d (1H, CH, J = 8.9 Hz), 5.84 d (1H, CH, J = 7.8 Hz), 7.03 s (2H, H_{arom}), 7.15 m (1H, H_{arom}), 7.26 m (2H, H_{arom}), 7.37 m (1H, H_{arom}), 8.18 d (2H, H_{arom}, J = 8.1 Hz), 8.29 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 17.4 (CH_3), 17.7 (CH_3), 20.6 (CH_3), 28.2 (CH_2), 48.8 (CH_2), 51.6 (CH), 60.9 (CH), 64.5 (CH), 123.1 (2C, CH_{arom}), 126.4 (CH_{arom}), 127.2 (C_{arom}), 127.7 (2C, CH_{arom}), 128.3 (CH_{arom}), 128.9 (CH_{arom}), 129.1 (CH_{arom}), 130.4 (2C, CH_{arom}), 132.4 (C_{arom}), 132.5 (C_{arom}), 135.4 (C_{arom}), 135.7 (C_{arom}), 138.8 (C_{arom}), 140.0 (C_{arom}), 149.0 (C_{arom}), 165.7 (C=O), 170.7 (C=O), 173.3 (C=O). Found, %: C 68.27; H 5.16; N 10.69. $C_{29}H_{26}N_4O_5$. Calculated, %: C 68.22; H 5.13; N 10.97.

Compound **VIId**. Some signals in the ^{1}H NMR spectrum of mixture **VId**/**VIId** (DMSO-d_6), δ, ppm: 1.97 s (3H, Me), 2.00 s (3H, Me), 2.20 s (3H, Me), 4.47 d.d (1H, CH, J = 8.9, 9.3 Hz), 4.93 d (1H, CH, J = 9.3 Hz), 6.04 d (1H, CH, J = 8.9 Hz), 6.88 s (1H, H_{arom}), 6.95 s (1H, H_{arom}), 7.95 d (2H, H_{arom}, J = 8.6 Hz).

***rel*-(8a*R*,11a*S*,11b*R*)-8-Benzoyl-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIe) and *rel*-(8a*R*,11a*S*,11b*S*)-8-benzoyl-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo-[5,1-*a*]isoquinoline-9,11-dione (VIIe)** were obtained from azomethine imine **IId** and *N*-phenylmaleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIe** and **VIIe** in the reaction mixture was ~10:90.

Compound **VIe**. Some signals in the ^{1}H NMR spectrum of mixture **VIe**/**VIIe** (DMSO-d_6), δ, ppm: 3.89 d.d (1H, CH, J = 8.5, 9.1 Hz), 5.08 d (1H, CH, J = 9.1 Hz), 5.73 d (1H, CH, J = 8.5 Hz).

Compound **VIIe**. Yield 300 mg (71%), mp 252–253°C. IR spectrum, ν, cm^{-1}: 3060, 3010, 2860, 1800, 1720 v.s, 1660, 1600, 1500, 1450, 1380 s, 1330, 1280, 1180 s, 1125, 1040, 1020. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.72 m (1H, CH_2), 2.87–3.07 m (2H, CH_2), 3.44 m (1H, CH_2), 4.09 d.d (1H, CH, J = 8.6, 8.9 Hz), 4.76 d (1H, CH, J = 8.9 Hz), 6.07 d (1H, CH, J = 8.6 Hz), 7.07–7.51 m (12H, H_{arom}), 7.84 d (2H, H_{arom}, J = 7.1 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 29.8 (CH_2), 50.4 (CH_2), 51.2 (CH), 61.1 (CH), 65.4 (CH), 126.6 (CH_{arom}), 127.3 (2C, CH_{arom}), 128.0 (CH_{arom}), 128.8 (2C, CH_{arom}), 129.0 (3C, CH_{arom}), 129.6 (CH_{arom}), 130.1 (3C, CH_{arom}), 131.1 (C_{arom}), 131.7 (CH_{arom}), 133.0 (C_{arom}), 133.8 (C_{arom}), 135.5 (C_{arom}), 172.6 (C=O), 174.8 (C=O), 175.1 (C=O). Found, %: C 73.53; H 5.03; N 9.71. $C_{26}H_{21}N_3O_3$. Calculated, %: C 73.74; H 5.00; N 9.92.

***rel*-(8a*R*,11a*S*,11b*R*)-8-(4-Methylbenzoyl)-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIf) and *rel*-(8a*R*,11a*S*,11b*S*)-8-(4-methylbenzoyl)-10-phenylperhydropyrrolo-[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIf)** were obtained from azomethine imine **IIa** and *N*-phenylmaleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIf** and **VIIf** in the reaction mixture was ~10:90.

Compound **VIf**. Some signals in the ^{1}H NMR spectrum of mixture **VIf**/**VIIf** (DMSO-d_6), δ, ppm: 3.89 d.d (1H, CH, J = 8.5, 9.0 Hz), 5.08 d (1H, CH, J = 9.0 Hz), 5.72 d (1H, CH, J = 8.5 Hz).

Compound **VIIf**. Yield 253 mg (58%), mp 272–273°C. IR spectrum, ν, cm^{-1}: 3060, 3010, 2970, 2925,

2860, 1800, 1720 v.s, 1650, 1610, 1500, 1460, 1410, 1380 s, 1330, 1305, 1290, 1260, 1180 s, 1120, 1060, 1010. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.33 s (3H, Me), 2.63–2.89 m (3H, CH_2), 3.47 m (1H, CH_2), 4.31 d.d (1H, CH, J = 8.9, 9.3 Hz), 4.70 d (1H, CH, J = 9.0 Hz), 5.92 d (1H, CH, J = 8.6 Hz), 7.09–7.21 m (5H, H_{arom}), 7.24 d (2H, H_{arom}, J = 7.8 Hz), 7.37–7.43 m (2H, H_{arom}), 7.46 d (2H, H_{arom}, J = 7.8 Hz), 7.64 d (2H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.0 (CH_3), 28.8 (CH_2), 49.4 (CH_2), 50.1 (CH), 60.1 (CH), 64.5 (CH), 125.6 (CH_{arom}), 126.3 (2C, CH_{arom}), 127.0 (CH_{arom}), 128.0 (CH_{arom}), 128.3 (2C, CH_{arom}), 128.4 (2C, CH_{arom}), 128.5 (CH_{arom}), 129.1 (3C, CH_{arom}), 130.1 (C_{arom}), 131.4 (C_{arom}), 132.0 (C_{arom}), 132.8 (C_{arom}), 140.7 (C_{arom}), 171.4 (C=O), 173.9 (C=O), 174.2 (C=O). Found, %: C 74.02; H 5.33; N 9.50. $C_{27}H_{23}N_3O_3$. Calculated, %: C 74.12; H 5.30; N 9.60.

***rel*-(8a*R*,11a*S*,11b*R*)-8-(4-Methoxybenzoyl)-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIg) and *rel*-(8a*R*,11a*S*,11b*S*)-8-(4-methoxybenzoyl)-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIg)** were obtained from azomethine imine **IIb** and *N*-phenylmaleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIg** and **VIIg** in the reaction mixture was ~10:90.

Compound **VIg**. Some signals in the ^{1}H NMR spectrum of mixture **VIg**/**VIIg** ($CDCl_3$), δ, ppm: 4.13 d.d (1H, CH, J = 8.5, 8.7 Hz), 4.79 d (1H, CH, J = 8.5 Hz), 5.72 d (1H, CH, J = 8.7 Hz), 8.17 (2H, H_{arom}, J = 8.9 Hz).

Compound **VIIg**. Yield 285 mg (63%), mp 212–213°C. IR spectrum, ν, cm^{-1}: 3080, 3040, 3010, 2970, 2940, 2900, 2860, 2845, 1800, 1720 v.s, 1640, 1605 s, 1500, 1460, 1425, 1380 s, 1340, 1310, 1260, 1180 s, 1130, 1060, 1040, 1010. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.75 m (1H, CH_2), 2.94 m (1H, CH_2), 3.08 m (1H, CH_2), 3.50 m (1H, CH_2), 3.83 s (3H, OMe), 4.06 d.d (1H, CH, J = 8.7, 8.9 Hz), 4.75 d (1H, CH, J = 8.9 Hz), 6.09 d (1H, CH, J = 8.7 Hz), 6.89 d (2H, H_{arom}, J = 8.8 Hz), 7.08–7.42 m (9H, H_{arom}), 7.93 d (2H, H_{arom}, J = 8.8 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.6 (CH_2), 50.1 (CH_2), 50.2 (CH), 55.4 (OCH_3), 59.7 (CH), 65.8 (CH), 113.2 (2C, CH_{arom}), 125.6 (C_{arom}), 125.7 (2C, CH_{arom}), 126.3 (CH_{arom}), 127.9 (CH_{arom}), 128.6 (CH_{arom}), 128.7 (CH_{arom}), 129.0 (CH_{arom}), 129.2 (2C, CH_{arom}), 129.4 (C_{arom}), 131.5 (2C, CH_{arom}), 131.6 (C_{arom}), 133.0 (C_{arom}), 162.1 (C_{arom}), 170.6 (C=O), 173.2 (C=O), 173.7 (C=O). Found, %: C 71.46; H 5.10; N 9.15. $C_{27}H_{23}N_3O_4$. Calculated, %: C 71.51; H 5.11; N 9.27.

***rel*-(8a*R*,11a*S*,11b*R*)-8-(4-Nitrobenzoyl)-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIh) and *rel*-(8a*R*,11a*S*,11b*S*)-8-(4-nitrobenzoyl)-10-phenylperhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIh)** were obtained from azomethine imine **IIc** and *N*-phenylmaleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIh** and **VIIh** in the reaction mixture was ~29:71.

Compound **VIh**. Some signals in the ^{1}H NMR spectrum of mixture **VIh**/**VIIh** (DMSO-d_6), δ, ppm: 3.90 m (1H, CH, J = 8.3 Hz), 4.80 m (1H, CH), 5.71 d (1H, CH, J = 8.3 Hz).

Compound **VIIh**. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.60–2.84 m (3H, CH_2), 3.26 m (1H, CH_2), 4.24 d.d (1H, CH, J = 8.5, 8.7 Hz), 4.78 d (1H, CH, J = 8.7 Hz), 5.88 d (1H, CH, J = 8.5 Hz), 6.97–7.20 m (5H, H_{arom}), 7.26–7.39 m (3H, H_{arom}), 7.40–7.48 m (1H, H_{arom}), 7.86 d (2H, H_{arom}, J = 8.6 Hz), 8.16 d (2H, H_{arom}, J = 8.7 Hz).

***rel*-(8a*R*,11a*S*,11b*R*)-8-Benzoyl-10-(4-bromophenyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIi) and *rel*-(8a*R*,11a*S*,11b*S*)-8-benzoyl-10-(4-bromophenyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIi)** were obtained from azomethine imine **IId** and *N*-(4-bromophenyl)maleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIi** and **VIIi** in the reaction mixture was ~11:89.

Compound **VIi**. Some signals in the ^{1}H NMR spectrum of mixture **VIi**/**VIIi** (DMSO-d_6), δ, ppm: 3.82 m (1H, CH, J = 8.8 Hz), 4.79 m (1H, CH), 5.70 d (1H, CH, J = 8.8 Hz), 8.09 d (2H, H_{arom}, J = 7.2 Hz).

Compound **VIIi**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.71 m (1H, CH_2), 2.83–3.07 m (2H, CH_2), 3.44 m (1H, CH_2), 4.08 d.d (1H, CH, J = 8.6, 8.8 Hz), 4.76 d (1H, CH, J = 8.8 Hz), 6.06 d (1H, CH, J = 8.6 Hz), 7.02–7.13 m (3H, H_{arom}), 7.18–7.31 m (2H, H_{arom}), 7.32–7.43 m (3H, H_{arom}), 7.46 m (1H, H_{arom}), 7.53 d (2H, H_{arom}, J = 8.6 Hz), 7.82 d (2H, H_{arom}, J = 7.6 Hz).

***rel*-(8a*R*,11a*S*,11b*R*)-10-(4-Bromophenyl)-8-(4-methylbenzoyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIj) and *rel*-(8a*R*,11a*S*,11b*S*)-10-(4-bromophenyl)-8-(4-methylbenzoyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIj)** were obtained from azomethine imine **IIa** and *N*-(4-bromophenyl)male-

imide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIj** and **VIIj** in the reaction mixture was ~8:92.

Compound **VIj**. Some signals in the ^{1}H NMR spectrum of mixture **VIj**/**VIIj** (DMSO-d_6), δ, ppm: 3.81 m (1H, CH_2, J = 8.4 Hz), 4.78 m (1H, CH_2), 5.69 d (1H, CH_2, J = 8.4 Hz), 8.01 d (2H, H_{arom}, J = 7.8 Hz).

Compound **VIIj**. Yield 316 mg (61%), mp 255–256°C. IR spectrum, ν, cm^{-1}: 3040, 3010, 2970, 2930, 2860, 1800, 1720 v.s, 1650, 1605, 1495, 1380 s, 1325, 1305, 1285, 1260, 1180 s, 1130, 1080, 1020. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 (3H, Me), 2.72 m (1H, CH_2), 2.85 m (1H, CH_2), 3.03 m (1H, CH_2), 3.46 m (1H, CH_2), 4.07 d.d (1H, CH, J = 8.7, 9.0 Hz), 4.74 d (1H, CH, J = 9.0 Hz), 6.09 d (1H, CH, J = 8.7 Hz), 7.01–7.14 m (3H, H_{arom}), 7.16–7.39 m (5H, H_{arom}), 7.52 d (2H, H_{arom}, J = 8.5 Hz), 7.76 d (2H, H_{arom}, J = 8.1 Hz). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 21.0 (CH_3), 28.8 (CH_2), 49.5 (CH_2), 50.2 (CH), 60.1 (CH), 64.5 (CH), 121.5 (C_{arom}), 125.6 (CH_{arom}), 127.0 (CH_{arom}), 128.1 (CH_{arom}), 128.3 (2C, CH_{arom}), 128.4 (4C, CH_{arom}), 129.0 (CH_{arom}), 130.1 (C_{arom}), 131.2 (C_{arom}), 131.3 (C_{arom}), 132.1 (2C, CH_{arom}), 132.8 (C_{arom}), 140.7 (C_{arom}), 171.4 (C=O), 173.6 (C=O), 174.0 (C=O). Found, %: C 62.71; H 4.24; N 8.01. $C_{27}H_{22}BrN_3O_3$. Calculated, %: C 62.80; H 4.29; N 8.14.

***rel*-(8a*R*,11a*S*,11b*R*)-10-(4-Bromophenyl)-8-(4-methoxybenzoyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIk) and *rel*-(8a*R*,11a*S*,11b*S*)-10-(4-bromophenyl)-8-(4-methoxybenzoyl)perhydropyrrolo[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-9,11-dione (VIIk)** were obtained from azomethine imine **IIb** and *N*-(4-bromophenyl)maleimide. According to the ^{1}H NMR data, the ratio of stereoisomers **VIk** and **VIIk** in the reaction mixture was ~8:92.

Compound **VIk**. Some signals in the ^{1}H NMR spectrum of mixture **VIk**/**VIIk** (DMSO-d_6), δ, ppm: 3.80 m (1H, CH_2, J = 8.8 Hz), 4.78 m (1H, CH_2), 5.70 d (1H, CH_2, J = 8.5 Hz), 8.14 d (2H, H_{arom}, J = 7.8 Hz).

Compound **VIIk**. Yield 390 mg (73%), mp 207–208°C. IR spectrum, ν, cm^{-1}: 3010, 2970, 2935, 2850, 1800, 1720 v.s, 1650, 1605, 1510, 1495, 1375 s, 1330, 1305, 1260, 1180 s, 1130, 1080, 1040, 1020. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.74 m (1H, CH_2), 2.86 m (1H, CH_2), 3.08 m (1H, CH_2), 3.46 m (1H, CH_2), 3.84 (3H, OMe), 4.06 d.d (1H, CH, J = 8.7, 8.9 Hz), 4.76 d (1H, CH, J = 8.9 Hz), 6.10 d (1H, CH, J = 8.7 Hz), 6.89 d (2H, H_{arom}, J = 8.7 Hz), 7.05 d (2H, H_{arom}, J = 8.5 Hz), 7.11 d (1H, H_{arom}, J = 6.5 Hz), 7.18–7.40 m (3H, H_{arom}), 7.52 d (2H, H_{arom}, J = 8.5 Hz), 7.92 d (2H, H_{arom}, J = 8.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 29.5 (CH_2), 50.2 (CH_2), 50.3 (CH), 55.5 (OCH_3), 59.7 (CH), 65.9 (CH), 113.2 (2C, CH_{arom}), 122.6 (C_{arom}), 125.4 (C_{arom}), 126.3 (CH_{arom}), 127.3 (2C, CH_{arom}), 128.0 (CH_{arom}), 128.6 (CH_{arom}), 128.9 (CH_{arom}), 129.3 (C_{arom}), 130.6 (C_{arom}), 131.5 (2C, CH_{arom}), 132.4 (2C, CH_{arom}), 133.0 (C_{arom}), 162.2 (C_{arom}), 170.5 (C=O), 172.9 (C=O), 173.4 (C=O). Found, %: C 60.88; H 4.22; N 7.63. $C_{27}H_{22}BrN_3O_4$. Calculated, %: C 60.91; H 4.17; N 7.89.

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