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Thermolysis of 6-Aryl-1,5-diazabicyclo[3.1.0]hexanes in the Presence of *N*-Arylmaleimides

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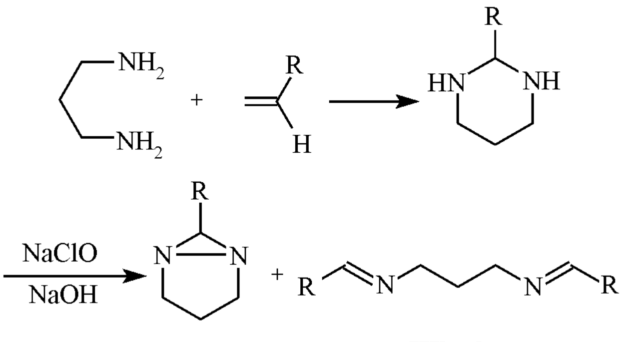
Abstract—Heating of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes in the presence of N-arylmaleimides gives rise to 2,9-diarylperhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-diones. It is presumed that thermal cleavage of the C–N bond in the diaziridine fragment of the 6-aryl-1,5-diazabicyclo[3.1.0]hexanes results in formation of labile azomethinimines that react with *N*-arylmaleimides to afford the products of 1,3-dipolar cycloaddition. The rate of accumulation thereof depends only on the character of substituents in the aromatic ring of the 1,5-diazabicyclo[3.1.0]hexanes and is independent of maleimide. The thermal isomerization of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes without 1,3-dipolarophiles yields the corresponding 2-pyrazolines.

Reactions of *N,N*-dialkyl-substituted diaziridines proceed with the cleavage of the diaziridine ring at N–N or C–N bonds. Monocyclic 1,2-disubstituted diaziridines that exist mainly as trans-isomers react with activated olefins to afford addition products by cleavage of the N–N bond [1, 2]. However the presence at the diaziridine carbon of two stabilizing substituents, i.e. in 3,3-dialkyl-1,2-disubstituted diaziridines results in opening of the C–N bond [3]. In the transformations of bicyclic diaziridines where the nitrogen atoms are connected by a trimethylene bridge also prevail those with the cleavage of the C–N bond: Thus formed azomethinimine undergoes further stabilization through rearrangement [4], proton transfer [5] or elimination of various moieties [6]. The azomethinimine formation is especially favored by the presence of an electron-withdrawing group at nitrogen atom, e.g. in 1,5-diazabicyclo-[3.1.0]hexan-2-ones [7, 8]. We showed formerly that the thermolysis of 1,5-diazabicyclo[3.1.0]hexane and its 6-methyl and 6-phenyl-substituted analogs [10] resulted in the corresponding 1-alkyl(aryl)-2-pyrazolines, and in the presence of *N*-arylmaleimides the products of 1,3-dipolar cycloaddition were obtained: cis and trans-isomers of 2-arylperhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione [10].

We report here on the study of the effect produced by substituents in position 6 of 1,5-diazabicyclo-[3.1.0]hexanes **Ia**–**e** and in *N*-arylmaleimides **IIa**–**e** on the direction and rate of the reaction. Compounds **Ia**–**e** were obtained by condensation of an aromatic aldehyde with 1,3-diaminopropane followed by oxidation with sodium hypochlorite [11].



Ia-e **IIIb–d**

R = Ph (**a**), 4-MeOC_6H_4 (**b**), 4-MeC_6H_4 (**c**), 4-ClC_6H_4 (**d**), 3-$NO_2C_6H_4$ (**e**).

1,5-Diazabicyclo[3.1.0]hexanes **Ia, b** were described before [10], compounds **Ic**–**e** were obtained for the first time; their structure and composition was confirmed by spectral data (Table 1) and elemental analyses. In the ^{1}H NMR spectra of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes appears a singlet from the methine proton of the diaziridine ring in the δ 3.00–3.4 ppm region and also two multiplets corresponding to the axial and equatorial protons of the CH_2–N groups at 2.8–4.0 ppm. The preparative yield of diazabicyclohexanes **Ia**–**d** amounted to 43–33%, that of diazabicyclohexane **Ie** to 20%.

Alongside 6-aryl-1,5-diazabicyclo[3.1.0]hexanes **Ib**–**d** in the reaction under consideration arise *N,N'*-bis(arylmethylene)-1,3-diaminopropanes **IIIb**–**d**. The presence in the reaction mixtures of compounds **IIIb**–**d** was revealed by ^{1}H NMR: in the spectra were

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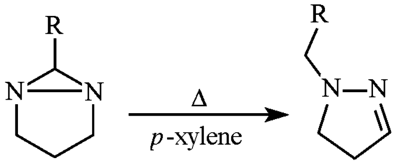
observed a singlet at 8.28–8.30 ppm, signals of the aromatic protons in 7.20–7.70 ppm region, triplet at 3.66–3.70 ppm, and quintet at 2.00–2.13 ppm with intensity ratio 1 : 4 : 2 : 1. The spectral characteristics of *N,N*'-bis(4-chlorophenylmethylene)-1,3-diaminopropane (**IIId**) were identical to those of the compound obtained under the other conditions [12]. The ^{1}H NMR spectra of the reaction mixtures show that 1,5-diazabicyclo[3.1.0]hexanes **Ib–d** and *N,N*'-bis(arylmethylene)-1,3-diaminopropane **IIIb–d** form in the course of process in approximately equal amounts. However the latter compounds were not isolated in pure form because they easily hydrolyzed to the corresponding aldehydes during the separation of the reaction mixture by chromatography on silica gel.

The heating of compounds **Ic–e** in *p*-xylene at 135–140°C for 20–35 min afforded 1-arylmethyl-2-pyrazolines **IVa–c** isolated in 69–75% yield [10]. The conversion into 2-pyrazolines is due to cleavage of the C–N bond in the diaziridine fragment and subsequent stabilization of the intermediate through proton transfer.



Ib–e **IVa–c**

R = 4-MeC_6H_4 (**a**), 4-ClC_6H_4 (**b**), 3-$NO_2C_6H_4$ (**c**).

The structure of the first synthesized 2-pyrazolines **IVa–c** was proved by spectral data. A characteristic feature of the ^{1}H NMR spectra of the N-substituted 2-pyrazolines is the singlet from a proton of the N=CH group that appears in δ 6.80–6.95 ppm region, and also a singlet belonging to the benzyl protons at δ 4.18–4.26 ppm.

The kinetics of thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes (**Ia–d**) at 110°C was studied by means of liquid chromatography. The values found for the rate constants of thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes (**Ia–e**) are listed in the Experimental.

We established that the thermal transformation of 6-phenyl-1,5-diazabicyclo[3.1.0]hexane (**Ia**) is a first order reaction and its rate is independent of the presence of *N*-phenylmaleimide in the reaction mixture: the rate constant is $k_{av}(4.2 \pm 0.1) \times 10^{-4} s^{-1}$ (in the absence of the dipolarophile) and $k_{av}(4.2 \pm 0.6) \times 10^{-4}$ s^{-1} (in the presence of the dipolarophile).

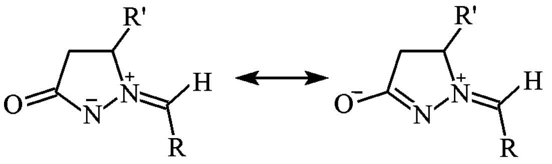
The mechanism of reaction between 1,2-disubstituted diaziridines with compounds containing activated double bonds (e.g., with ketenes or aryl and aroyl isocyanates) assumed in [1] included a primary nucleophilic attack of the nitrogen from diaziridine on the carbon atom with the least electron density (carbonyl carbon in the above examples). However the first order of the thermal transformation of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes and unchanged value of the rate constant at addition of *N*-arylmaleimide suggest that 6-aryl-1,5-diazabicyclo[3.1.0]hexanes (**Ia–e**) do not directly react with the dipolarophile.

The data obtained show that the electron-donor substituents in the aromatic ring accelerate the thermolysis, and the electron-withdrawing substituents retard it. Therewith the best correlation exists with the Hammett's σ-constants:

$$\log k_R/k_H = -(0.36 \pm 0.03)\sigma + (0.025 \pm 0.009)$$

$$n\ 5,\ r\ 0.990.$$

In [7] was demonstrated that the rate of opening at heating of the diaziridine fragment in the 1,5-diazabicyclo[3.1.0]hexan-2-ones correlates with the σ^+-constants with the ρ value around –2. We believe that the change in the correlation type and the reduced sensitivity to the substituents in the 1,5-diazabicyclo-[3.1.0]hexanes is caused by the presence in the 1,5-diazabicyclo[3.1.0]hexan-2-ones of the oxo group that increases the positive charge on the ylide moiety by conjugation effect and thus increases its electrophilicity. In agreement with this reasoning in [7] was observed the dependence of the process rate on the medium polarity (for instance, in acetonitrile the rate was by an order of magnitude greater than in nonpolar solvents).



In the 6-aryl-1,5-diazabicyclo[3.1.0]hexanes the rupture of the C–N bond of the diaziridine fragment causes less pronounced change in the charge distribution than in the 1,5-diazabicyclo[3.1.0]hexan-2-ones and therefore the influence of substituent in the former is smaller.

Table 1. IR and ^{1}H NMR spectra of compounds synthesized

Compd. no.	IR spectrum, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
Ic	880, 960, 980, 1025, 1095, 1110, 1260, 1290, 1310, 1340, 1385, 1455, 1470, 1520, 1620, 2880, 2990 s, 3030 s	1.90 m (2H), 2.30 s (3H), 2.97 m (2H), 3.22 s (1H), 3.51 m (2H), 7.11 d (2H, 7.9), 7.24 d (2H, 7.9)
Id	870, 969, 980, 1020, 1095, 1250, 1300, 1340, 1380, 1430, 1450, 1495, 1600, 2880, 2990 s, 3030 s	1.92 m (2H), 2.98 m (2H), 3.33 s (1H), 3.54 m (2H), 7.35 m (4H)
Ie	920, 940, 965, 980, 1080, 1090, 1110, 1260, 1280, 1295, 1320, 1355 s, 1460, 1490, 1540, 1590, 2885, 2960, 2990 s, 3035 s	1.94 m (2H), 3.18 m (2H), 3.24 s (1H), 3.64 m (2H), 7.52 t (1H, 7.9), 7.70 d (1H, 7.9), 8.18 d (1H, 7.9), 8.25 s (1H)
IVa	850, 880, 940, 1000, 1030, 1050, 1110, 1160, 1260, 1290, 1310, 1360, 1380, 1440, 1460, 1520, 1580, 1600, 1620, 2830, 2930, 2990, 3030 s	2.36 s (3H), 2.65 m (2H), 2.93 m (2H), 4.17 s (2H), 6.83 s (1H), 7.17 d (2H, 7.7), 7.29 d (2H, 7.7)
IVb	850, 880, 920, 960, 990, 1160, 1250, 1290, 1350, 1410, 1440, 1500, 1600, 1630, 2840, 2930, 3030 s	2.66 m (2H), 2.94 m (2H), 4.17 s (2H), 6.84 s (1H), 7.33 m (4H)
IVc	850, 880, 900, 940, 1000, 1060, 1100, 1170, 1250, 1290, 1320, 1350 s, 1440, 1485, 1540, 1585, 1600, 1720, 1780, 2840, 2930, 3035	2.70 m (2H), 3.01 m (2H), 4.26 s (2H), 6.88 s (1H), 7.53 m (1H), 7.76 d (1H, 7.4), 8.15 d (1H, 8.2), 8.29 s (1H)
Va	1240, 1380, 1500, 1600, 1730 s, 1790, 2860, 2990, 3040	2.25 m (2H), 2.66 m (2H), 3.27 m (1H), 3.45 m (1H), 4.00 m (2H), 4.70 ¼.s (1H), 7.30–7.65 (10H)
Vb	[a]1040, 1240, 1260, 1300, 1390, 1460, 1520, 1610, 1730 s, 1790, 2845, 2970, 3040	2.23 m (2H), 2.65 m (2H), 3.27 m (1H), 3.46 m (1H), 3.84 s 7.60 d (2H, 7.5)
Vf	[a]1040, 1110, 1240, 1260, 1310, 1380, 1470, 1520, 1620, 1730 s, 1790, 2840, 2980, 3040	2.25 m (2H), 2.60 m (2H), 3.26 m (1H), 3.45 m (1H), 3.83 s (3H), 3.98 m (2H), 4.67 br.s (1H), 6.87–7.52 (9H)
Vg	1040, 1110, 1260 s, 1305, 1390, 1440, 1470, 1520, 1610, 1730 s, 1790, 2845, 2910, 2940, 2970, 3040	2.22 m (2H), 2.60 m (2H), 3.27 m (1H), 3.44 m (1H), 3.84 s (6H), 3.96 m (2H), 4.66 br.s (1H), 6.94 d (2H, 8.4), 7.00 d (2H, 8.8), 7.25 d (2H, 8.8), 7.51 d (2H, 8.4)
Vk	[a]1010, 1040, 1100, 1240, 1385, 1500, 1600, 1610, 1730 s, 1790, 2860, 2990, 3040	2.23 m (2H), 2.35 s (3H), 2.64 m (2H), 3.28 m (1H), 3.47 m (1H), 3.99 m (2H), 4.68 br.s (1H), 15–7.50 (9H)
Vl	[a]1040, 1110, 1240, 1260, 1300, 1390, 1470, 1520, 1680, 1730 s, 2845, 2970, 3040	2.22 m (2H), 2.38 s (3H), 2.65 m (2H), 3.27 m (1H), 3.46 m (1H), 3.84 s (3H), 3.98 m (2H), 4.66 br.s (1H), 6.92–7.50 (8H)
Vm	1100, 1240, 1380, 1520, 1730 s, 1800, 2860, 2890, 2930, 2990, 3040	2.25 m (2H), 2.33 s (3H), 2.40 s (3H), 2.63 m (2H), 3.27 m (1H), 3.46 m (1H), 3.99 m (2H), 4.67 br.s (1H), 7.02–7.50 (8H)
Vn	1020, 1080, 1190, 1240, 1380, 1495, 1525, 1730 s, 2860, 2990, 3040	2.25 m (2H), 2.38 s (3H), 2.63 m (2H), 3.25 m (1H), 3.45 m (1H), 3.98 m (2H), 4.64 br.s (1H), 7.17–7.27 (4H), 7.47 d (2H, 7.9), 7.62 d (2H, 8.4)
Vo	[a]1100, 1240, 1350, 1385, 1540, 1730 s, 2860, 2990, 3050	2.25 m (2H), 2.39 s (3H), 2.61 m (2H), 3.28 m (1H), 3.47 m (1H), 4.03 m (2H), 4.47 br.s (1H), 7.09–8.37 (8H)
Vp	[a]1040, 1240, 1380, 1500, 1600, 1730 s, 1790, 2860, 2990, 3040	2.26 m (2H), 2.65 m (2H), 3.26 m (1H), 3.47 m (1H), 3.93 m (2H), 4.60 br.s (1H), 7.05–7.56 (9H)
Vq	[a]1040, 1100, 1240, 1260, 1300, 1390, 1500, 1520, 1610, 1730 s, 2840, 2970, 3040	2.24 m (2H), 2.62 m (2H), 3.25 m (1H), 3.46 m (1H), 3.84 s (3H), 3.93 m (2H), 4.58 br.s (1H), 6.91–7.55 (8H)
Vr	[a]1020, 1100, 1240, 1380, 1500, 1520, 1730 s, 2860, 2990, 3040	2.25 m (2H), 2.40 s (3H), 2.62 m (2H), 3.25 m (1H), 3.47 m (1H), 3.92 m (2H), 4.59 br.s (1H), 7.01–7.56 (8H)
Vs	[a]1040, 1080, 1100, 1130, 1240, 1380, 1500, 1730 s, 2860, 2990, 3040	2.25 m (2H), 2.62 m (2H), 3.22 m (1H), 3.46 m (1H), 3.94 m (2H), 4.57 br.s (1H), 7.10–7.65 (8H)
Vt	1100, 1180, 1240, 1300, 1350,	2.26 m (2H), 2.60 br.s (2H), 3.21 br.s (1H), 3.44 m (1H),

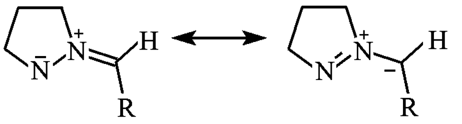
Table 1. (Contd.)

Compd. no.	IR spectrum, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
	1370, 1500, 1530, 1600, 1735 s, 1800, 2860, 2890, 3040	3.97 m (2H), 4.58 br.s (1H), 7.41 d (2H, 8.4), 7.54 d (2H, 8.4), 7.64 d (2H, 9.1), 8.37 d (2H, 9.1)
Vu	[a]1010, 1030, 1240, 1350, 1385, 1510, 1540, 1610, 1730 s, 2870, 2990, 3045	2.25 m (2H), 2.65 m (2H), 3.28 m (1H), 3.49 m (1H), 3.98 m (2H), 4.60 br.s (1H), 7.15–8.47 (9H)
Vv	[a]1040, 1110, 1240, 1260, 1300, 1350, 1390, 1470, 1540, 1610, 1730 s, 2860, 2970, 3040	2.25 m (2H), 2.60 m (2H), 3.19 m (1H), 3.48 m (1H), 3.82 s (3H), 3.99 m (2H), 4.60 br.s (1H), 6.86–8.47 (8H)
Vw	[a]1100, 1240, 1350, 1385, 1540, 1730 s, 2860, 2990, 3050	2.25 m (2H), 2.39 s (3H), 2.60 m (1H), 2.73 m (1H), 3.18 m (1H), 3.48 m (1H), 3.97 m (2H), 4.61 br.s (1H), 7.01–8.47 (8H)
Vx	[a]1080, 1240, 1350, 1380, 1495, 1540, 1730 s, 2860, 2990, 3040	2.30 m (2H), 2.57 m (1H), 2.69 m (1H), 3.16 m (1H), 3.48 m (1H), 3.98 m (2H), 4.57 br.s (1H), 7.04–8.45 (8H)
Vy	1110, 1180, 1240, 1310, 1350 s, 1370,1510, 1540, 1610, 1740 s, 2860, 2990, 3045	2.35 m (2H), 2.59 m (1H), 2.72 br.s (1H), 3.18 m (1H), 3.49 t.d (1H, 9.8, 5.6), 4.00 m (2H), 4.59 br.s (1H), 7.64 m (3H), 7.95 d (1H, 7.7), 8.24 d (1H, 7.7), 8.38 d (2H, 9.1), 8.49 s (1H)
VIa		2.25 m (2H), 2.94 m (2H), 3.27 m (1H), 3.45 m (1H), 3.9 d.d (1H, 9.3, 7.5), 4.38 d (1H, 9.3), 4.40 d (1H, 7.5), 7.15–7.53 (10H)
VIb		2.23 m (2H), 2.94 m (2H), 3.27 m (1H), 3.46 m (1H), 3.80 s (3H), 3.86 d.d (1H, 9.4, 7.5), 4.32 d (1H, 9.4), 4.38 d (1H, 7.5), 6.90–7.50 (9H)
VIf		2.25 m (2H), 2.91 m (2H), 3.26 m (1H), 3.45 m (1H), 3.80 s (4H), 4.32 d (1H, 9.3), 4.39 d (1H, 7.5), 6.87–7.52 (9H)
VIg		2.25 m (2H), 2.90 m (2H), 3.27 m (1H), 3.43 m (1H), 3.80 s (7H), 4.33 d (1H, 9.3), 4.39 d (1H, 7.5), 6.85–7.35 (8H)
VIk		2.23 m (2H), 2.33 s (3H), 2.93 m (2H), 3.28 m (1H), 3.47 m (1H), 3.87 d.d (1H, 9.3, 7.5), 4.34 d (1H, 9.3), 4.41 d (1H, 7.5), 7.15–7.50 (9H)
VIl		2.22 m (2H), 2.34 s (3H), 2.92 m (2H), 3.27 m (1H), 3.46 m (1H), 3.81 s (3H), 3.85 m (1H), 4.33 d (1H, 9.3), 4.39 d (1H, 7.5), 6.92–7.50 (8H)
VIm		2.25 m (2H), 2.33 s (3H), 2.40 s (3H), 2.92 m (2H), 3.27 m (1H), 3.46 m (1H), 3.86 m (1H), 4.34 d (1H, 9.7), 4.40 d (1H, 7.5), 7.02–7.50 (8H)
VIn	1020, 1080, 1110, 1130, 1190, 1240, 1380, 1495, 1525, 1730 s, 12860, 2990, 3040	2.25 m (2H), 2.35 s (3H), 2.93 m (2H), 3.28 m (1H), 3.49 t.d (1H, 9.3, 3.5), 3.87 d.d (1H, 9.4, 7.5), 4.35 d (1H, 9.4), 4.41 d (1H, 7.5), 7.09 d (2H, 8.2), 7.17 d (2H, 8.2), 7.32 d (2H, 8.4), 7.55 d (2H, 8.4)
VIo		2.25 m (2H), 2.36 s (3H), 2.95 m (2H), 3.29 m (1H), 3.52 t.d (1H, 9.3, 3.5), 3.92 d.d (1H, 9.3, 7.8), 4.39 (1H, 9.3), 4.46 d (1H, 7.8), 7.18 d (2H, 7.9), 7.30 d (2H, 7.9), 7.45 d (2H, 8.8), 8.29 d (2H, 8.8)
VIp		2.26 m (2H), 2.84 m (1H), 2.97 m (1H), 3.26 m (1H), 3.47 m (1H), 3.89 d.d (1H, 9.2, 7.7), 4.36 d (1H, 9.2), 4.40 d (1H, 7.7), 7.05–7.56 (9H)

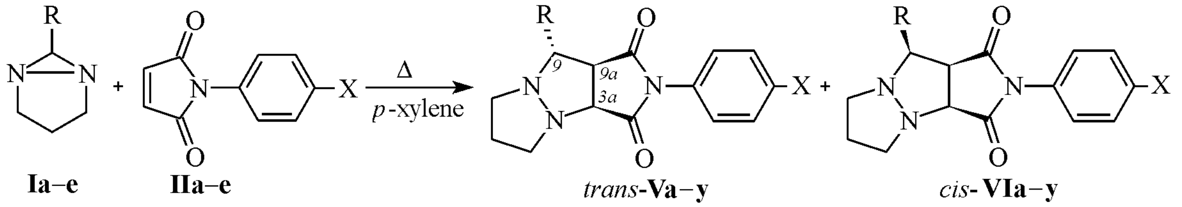
Table 1. (Contd.)

Compd. no.	IR spectrum, cm^{-1}	^{1}H NMR spectrum, δ, ppm (*J*, Hz)
VIq		2.24 m (2H), 2.83 m (1H), 2.96 m (1H), 3.25 m (1H), 3.46 m (1H), 3.81 s (3H), 3.88 d.d (1H, 9.7, 7.7), 4.34 d (1H, 9.7), 4.38 d (1H, 7.7), 6.91–7.55 (8H)
VIr		2.25 m (2H), 2.36 (3H), 2.84 m (1H), 2.96 m (1H), 3.25 m (1H), 3.47 m (1H), 3.88 m (1H), 4.35 d (1H, 9.7), 4.39 d (1H, 7.2), 7.01–7.56 (8H)
VIs		2.25 m (2H), 2.84 m (2H), 3.22 m (1H), 3.46 m (1H), 3.87 d.d (1H, 9.7, 7.7), 4.36 d (1H, 9.7), 4.40 d (1H, 7.7), 7.10–7.65 (8H)
VIt		2.30 m (2H), 2.95 m (2H), 3.25 m (1H), 3.48 m (1H), 3.94 d.d (1H, 9.2, 7.7), 4.40 d (1H, 9.2), 4.46 d (1H, 7.7), 7.31–8.40 (8H)
VIu		2.25 m (2H), 2.82 m (1H), 2.99 m (1H), 3.30 m (1H), 3.49 m (1H), 3.90 d.d (1H, 9.1, 7.7), 4.43 d (1H, 7.7), 4.47 d (1H, 9.1), 7.15–8.47 (9H)
VIv		2.25 m (2H), 2.60 m (1H), 2.82 m (1H), 3.30 m (1H), 3.48 m (1H), 3.77 s (3H), 3.91 d.d (1H, 9.2, 7.3), 4.41 d (1H, 7.3), 4.46 d (1H, 9.2), 6.86–8.47 (8H)
VIw		2.27 m (5H), 2.60 m (1H), 2.82 m (1H), 3.30 m (1H), 3.48 m (1H), 3.89 d.d (1H, 9.5, 7.7), 4.42 d (1H, 7.7), 4.46 d (1H, 9.5), 7.01–8.35 (8H)
VIx		2.30 m (2H), 2.85 m (2H), 3.31 m (1H), 3.48 m (1H), 3.90 m (1H), 4.45 m (2H), 7.04–8.45 (8H)
VIy		2.35 m (2H), 2.86 m (1H), 3.04 m (1H), 3.33 m (1H), 3.51 m (1H), 4.03 d.d (1H, 9.1, 7.7), 4.52 d (1H, 7.7), 4.54 d (1H, 9.1), 7.43–8.34 (8H)

[a] IR spectrum of a mixture of *trans*-/*cis*-isomers (**V/VI**).



The heating of diazobicyclohexanes **Ia–e** in the presence of *N*-arylmaleimides **IIa–e** in *p*-xylene yielded the corresponding perhydropyrazolo[1,2-a]-pyrrolo[3,4-c]pyrazole-1,3-diones as a mixture of *trans*-isomers **Va–y** and *cis*-isomers **VIa–y**. Compounds **V/VIc, d, e, h, i, j** were described before [10]. The structure and composition of the newly prepared compounds **Va–y** and **VIa–y** were established from the IR and ^{1}H NMR spectra, and from elemental analysis (Table 1 and Experimental).



II, X = H (**a**), OMe (**b**), Me (**c**), Br (**d**), NO_2 (**e**); **V, VI**: R = Ph, X=H (**a**), OMe (**b**), Me (**c**), Br (**d**), NO_2 (**e**); R = 4-$MeOC_6H_4$, X = H (**f**), OMe (**g**), Me (**h**), Br (**i**), NO_2 (**j**); R = 4-MeC_6H_4, X = H (**k**), OMe (**l**), Me (**m**), Br (**n**), NO_2 (**o**); R = 4-ClC_6H_4, X = H (**p**), OMe (**q**), Me (**r**), Br (**s**), NO_2 (**t**); R = 3-$NO_2C_6H_4$, X = H (**u**), OMe (**v**), Me (**w**), Br (**x**), NO_2 (**y**).

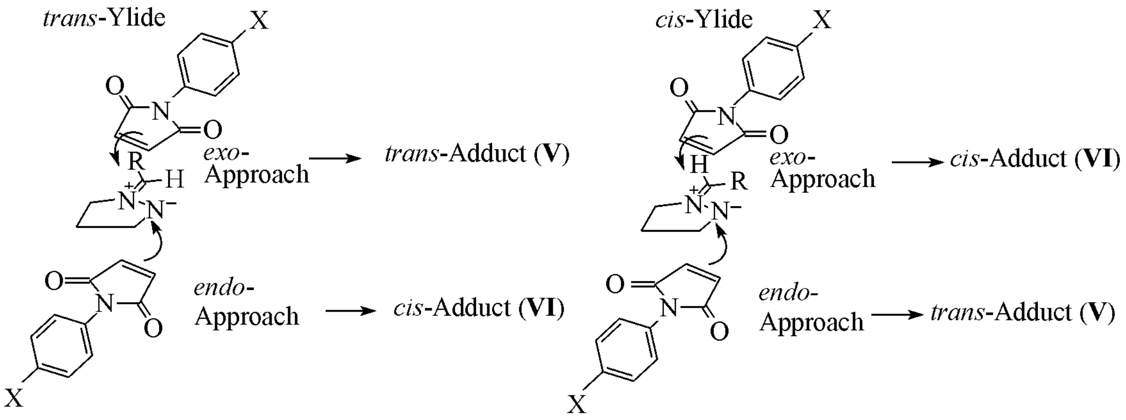
Table 2. Ratio of *trans*/*cis*-isomers (**V**/**VI**) in reaction products of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes with *N*-arylmaleimides

Compd. no.	**Ia**	**Ib**	**Ic**	**Id**	**Ie**
IIa	2.7	1.8	1.9	2.3	2.1
IIb	3.2	1.4	1.7	1.8	2.1
IIc	3.0	2.1	2.5	3.0	2.8
IId	2.1	1.7	1.9	1.8	1.6
IIe	1.5	1.3	1.6	1.7	1.5

Thus in the ^{1}H NMR spectrum of the mixture of isomers **Vn/VIn** the methine protons signals are observed in δ 3.8–4.7 ppm region. Therewith the proton signals of the trans-isomer (one-proton singlet at δ 4.64 ppm and poorly resolved two-proton multiplet at δ 3.98 ppm) are broadened due to fast interconversion of invertomers of the trans-adduct [10]. The signals from the cis-isomer are a doublet of doublets belonging to methine proton in *9a* position at δ 3.87 ppm (*J* 9.4, 7.5 Hz), and two doublets of the methine protons in positions *9* and *3a* at δ 4.35 ppm (*J* 9.4 Hz) and 4.41 ppm (*J* 7.5Hz) respectively. The doublet with the larger coupling constant was assigned to the proton in *9* position for this signal shifts downfield on introduction of a nitro group into the aromatic ring located in *9* position.

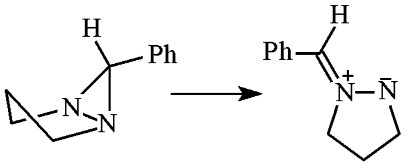
The ^{1}H NMR spectra of the reaction mixtures obtained at boiling diazabicyclohexanes **Ia**–**e** with maleimides **IIa**–**e** in *p*-xylene contained mainly the signals of isomeric adducts and of trace amounts of the corresponding 2-pyrazolines. At it, when the reaction was carried out at equimolar amounts of the initial compounds, no signals of 2-pyrazolines appeared in the spectra. The ratio of *trans*- and *cis*-isomers formed (**V/VI**) (Table 2) was determined from the integral intensity of the broadened methine proton signal of *trans*-isomer **V** and of two downfield signals of methine protons belonging to *cis*-isomer **VI**. In some cases this ratio was evaluated also from the proton signals of methyl or methoxy groups or from that of aromatic protons (determination error ~20%).

It was shown that the heating of the individual *trans*- and *cis*-isomers **V** and **VI** under the reaction condition did not lead to their interconversion. Thus the ratio of *trans*- (**V**) and *cis*- (**VI**) isomers formed is due to the isomerism of the intermediate ylide **VII** and to the direction of the maleimide approach. The formation of the isomer adducts in dependence on the configuration of the intermediate azomethinimine may be described by the following scheme:

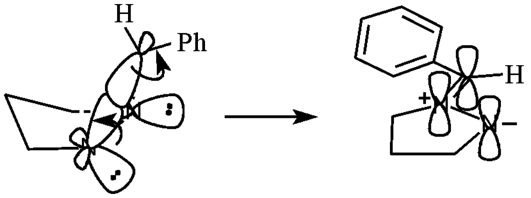


Since the molecule of 1,5-diazabicyclo[3.1.0]-hexane is nonplanar, its 6-substituted derivatives can exist as two spatial isomers, 6-*exo*- and 6-*endo*-substituted. However analogously to cyclohexanes the 1,3-spatial interaction in the 1,5-diazabicyclo-[3.1.0]hexanes results in existence of exclusively *exo*-isomers, e.g., in 6-alkyl-substituted compounds [13] or in 6-aryl-1,5-diazabicyclo[3.1.0]hexan-2-ones [14]. We believe that 6-aryl-1,5-diazabicyclo[3.1.0]hexanes also are present as exclusively *exo*-isomers.

The calculation of 6-*exo*-phenyl-1,5-diazabicyclo-[3.1.0]hexane by MNDO method shows that although the formation enthalpies of *cis*- and *trans*-azomethines have close values ($\Delta\Delta H_f <$ 0.5 kcal mol^{-1}) the use as reaction coordinate of the increase in the C–N bond length results in a *trans*-oriented azomethine:



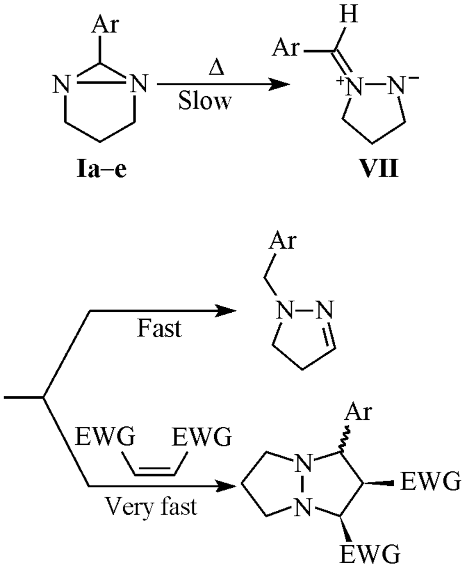
On the other hand, the heterolytic opening of the C–N bond and ylide structure formation both in diaziridines and aziridines involves four electrons, therefore thermally permissible by symmetry is the conrotatory process. The analysis of the conrotatory opening of the diaziridine ring shows that in this case in the nonplanar molecule of 6-*exo*-phenyl-1,5-diazabicyclo[3.1.0]hexane the counter-clockwise rotation of the phenyl ring providing formation of the *trans*-azomethinimine should occur with the least energy consumption since the opportunities to orbitals rotation in the bicyclic structure are strongly limited by degrees of freedom. Besides the orbital of nitrogen “bearing” the electron pair makes a minimal turn to take its position in the arising ylide, and the “exempt” orbital of carbon immediately interacts with a lone electron pair of another nitrogen.



Therefore we believe that the principal part in formation of a definite isomer plays the approach of the dipolarophile to the intermediate trans-azomethinimine. It may be expected that the bulky substituents in the *2* position of the aromatic ring in the maleimide would sterically hinder the formation of cis-isomer **V** with the corresponding increase in the fraction of *trans*-isomer **VI**.

Besides the isomer ratio is affected by activity of the dipole and dipolarophile. As seen from Table 2, the electron-withdrawing substituents in the aromatic ring of maleimides in general reduce the process selectivity.

Thus the limiting stage in thermolysis of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes (**Ia–e**) is the opening of the C–N bond in the diaziridine fragment; therewith in the transition state on the nitrogen arises a partial negative, and on the carbon partial positive charge. Consequently the process is accelerated by electron-donor substituents in the aromatic ring. Next the arising *trans*-azomethinimine **VII** is rapidly stabilized by formation of *N*-substituted 2-pyrazolines or reacts with 1,3-dipolarophile to yield a cycloaddition product.



EXPERIMENTAL

IR spectra were recorded on spectrophotometer UR-20 from 2% solutions of compounds in chloroform. ^{1}H NMR spectra were registered on Bruker DPX-300 instrument (300 MHz) from solutions in $CDCl_3$ or $(CD_3)_2CO$. UV spectra were measured in dichloroethane solutions on Specord UV-Vis spectrometer. HPLC analysis were carried out on HPP-5001 instrument; detector by refraction index RIDK-102, column Separon SGx CN 5μ 33000 Tp/m, 150 mm long, eluent tetrahydrofuran–hexane, 1 : 1, flow rate 0.2 ml min^{-1}, sample volume 3 μl.

Kinetic study of 6-aryl-1,5-diazabicyclo[3.1.0]-hexanes (Ia–e) thermolysis. Solutions of compounds **Ia–e** in *p*-xylene were heated at 110°C, the samples taken were fast cooled and analyzed. The rate constants were calculated from the decrease in the concentration of the initial compound determined with the help of an internal standard. The rate constant of the reaction was calculated by the least-mean-squares procedure along the equation

$$\ln[A] = \ln[A_0] - kt ,$$

where t is time (s), $[A]$ is the fraction of the initial compound at the time moment t, $[A_0]$ is the fraction of the initial compound at the starting moment $t = 0$.

The [*A*] value was measured by liquid chromatography. In the calculations was used the ratio of the peak height of the corresponding 1,5-diazabicyclo-[3.1.0]hexane to the peak height of an internal standard. Alkanes $C_{19}H_{40}$ or $C_{21}H_{44}$ served as internal standards. The measurements were carried out on solutions of 0.25 g of 6-aryl-1,5-diazabicyclo-[3.1.0]hexane **Ia–e** in 11 ml of *p*-xylene at 110±1°C. Time of sampling: 0, 10, 20, 30, 45, 60 and 90 min. Below are given compd. no., $k \times 10^4$ s^{-1}, conversion in 90 min: **Ia**, 4.2±0.2, 87; **Ib**, 5.5±0.2, 93; **Ic**, 5.4±0.1, 90; **Id**, 3.7±0.1, 81; **Ie**, 2.5±0.1, 70.

General procedure for preparation of 1,5-diazabicyclo[3.1.0]hexanes Ia–c. To 1,3-diaminopropane taken in 9–20% excess at cooling with ice water was added dropwise while stirring the appropriate aldehyde maintaining the reaction temperature below 45°C. On completion of addition the mixture was stirred for 1–2 h at 18–20°C. Then was added dropwise alkaline solution of sodium hypochlorite keeping the temperature in the same limits, and again the stirring was carried on for 1 h at 18–20°C. The organic layer was separated, the water layer was extracted with benzene. The combined organic solution was dried with sodium sulfate, and benzene was distilled off on a rotary evaporator at the temperature not exceeding 50°C. The residue was recrystallized from an appropriate solvent to obtain colorless crystals.

6-Phenyl-1,5-diazabicyclo[3.1.0]hexane (Ia) was prepared from 10 ml (0.12 mol) of 1,3-diaminopropane and 11.2 ml (0.11 mol) of benzaldehyde with subsequent addition of 95.6 ml (0.11 mol) of 1.15 N solution of sodium hypochlorite. Yield 6.5 g (37%), mp 93–94°C [10] (from benzene with a little hexane added).

6-(4-Methoxyphenyl)-1,5-diazabicyclo[3.1.0]-hexane (Ib) was prepared from 5 ml (0.06 mol) of 1,3-diaminopropane (20% excess and 6 ml (0.05 mol) of anisaldehyde with subsequent addition of 43.5 ml (0.05 mol) of 1.15 N solution of sodium hypochlorite. Yield 3.8 g (40%), mp 98–99°C [10] (from benzene with a little hexane added).

6-(4-Tolyl)-1,5-diazabicyclo[3.1.0]hexane (Ic) was prepared from 2.5 ml (0.03 mol) of 1,3-diaminopropane (20% excess) and 3 ml (0.025 mol) of 4-methylbenzaldehyde with subsequent addition of 22 ml (0.025 mol) of 1.15 N solution of sodium hypochlorite. Yield 1.85 g (42%), mp 89–90°C [10] (from acetone–hexane, 2:1). Found, %: C 75.25, 75.43; H 7.97, 8.26; N 16.38, 16.43. $C_{11}H_{14}N_2$. Calculated, %: C 75.82; H 8.10; N 16.08.

General procedure for preparation of 1,5-diazabicyclo[3.1.0]hexanes Id, e. To 1,3-diaminopropane taken in 2.4-fold excess at heating on a water bath (40–45°C) was added dropwise at stirring a solution of an appropriate aldehyde in anhydrous benzene or ether. After completion of addition the reaction mixture was stirred for 1 h more, then the solvent was distilled off on a rotary evaporator, and to the residue at cooling with ice water was added dropwise equimolar to diaminopropane amount of alkaline sodium hypochlorite solution. Then the reaction mixture was stirred for 1 h at 18–20°C. The organic layer was separated, the water layer was extracted with benzene. Combined organic solutions were dried with sodium sulfate, and benzene was distilled off on the rotary evaporator maintaining the temperature below 55°C. The reaction product was isolated from the residue by flash chromatography on silica gel L 5/40 μ, eluent tetrahydrofuran–hexane, 1:1. On evaporating the eluent the product was recrystallized from acetone with a little hexane added.

6-(4-Chlorophenyl)-1,5-diazabicyclo[3.1.0]-hexane (Id) was prepared from 5 ml (0.06 mol) of 1,3-diaminopropane and 3.78 g (0.025 mol) of 4-chlorobenzaldehyde with subsequent addition of 27 ml (0.06 mol) of 2.2 N solution of sodium hypochlorite. Yield 1.6 g (33%), mp 104–105°C (decomp.). Found, %: C 61.67, 62.09; H 5.58, 5.72; N 14.36, 14.35. $C_{10}H_{11}ClN_2$. Calculated, %: C 61.70; H 5.70; N 14.39.

6-(3-Nitrophenyl)-1,5-diazabicyclo[3.1.0]hexane (Id) was prepared from 5 ml (0.06 mol) of 1,3-diaminopropane and 3.78 g (0.025 mol) of 3-nitrobenzaldehyde with subsequent addition of 27 ml (0.06 mol) of 2.2 N solution of sodium hypochlorite. On recrystallization yellow crystals were obtained, yield 1.05 g (20%), mp 105°C (decomp.). Found, %: C 58.72, 58.86; H 5.33, 5.54; N 20.63, 20.67. $C_{10}H_{11}N_3O_2$. Calculated, %: C 58.53; H 5.40; N 40.48.

***N,N*'-Bis-(4-chlorophenylmethylene)-1,3-diaminopropane (IIId).** To 2.8 g (0.02 mol) of 4-chlorobenzaldehyde in 20 ml of anhydrous benzene was added dropwise at stirring 0.83 ml (0.01 mol) of 1,3-diaminopropane. Then the mixture was stirred at 55–60°C for 2 h. Benzene was evaporated, and colorless crystals of compound **IIId** were obtained, mp 65–67°C (from ethanol) [11].

1-(4-Arylmethyl)-2-pyrazolines (IVa–c). 6-Aryl-1,5-diazabicyclo[3.1.0]hexanes (Ic–e) were heated in 5 ml of *p*-xylene for 140°C for 20, 30, and 35 min. Compound obtained (**IVa, IVb**) was distilled in a vacuum or separated from the reaction mixture by preparative TLC (compound **IVc**) on silica gel 5/40 μ, eluent ether.

1-(4-Tolyl)-2-pyrazoline (IVa) was obtained from 0.5 g (2.87 mmol) of diazaalkane **Ic**. Oily liquid, bp 79–80°C (0.2 mm Hg). Yield 345 mg (69%).

1-(4-Chlorophenylmethyl)-2-pyrazoline (IVb) was obtained from 0.5 g (2.57 mmol) of diazaalkane **Id**. Oily liquid, bp 90–95°C (0.2 mm Hg). Yield 356 mg (71%).

1-(3-Nitrophenylmethyl)-2-pyrazoline (IVc) was obtained from 0.4 g (1.95 mmol) of diazaalkane **Id**. Oily liquid. Yield 300 mg (75%).

General procedure for thermolysis of 1,5-diazabicyclo[3.1.0]hexanes in the presence of *N*-phenylmaleimides. A mixture of 1,5-diazabicyclo[3.1.0]-hexane (in 10% excess) and of dipolarophile in 6 ml of *p*-xylene was stirred for 20 min (compounds **Ib, c**), 25 min (compound **Ia**), 30 min (compound **Id**) or 35 min (compound **Ie**) at 135–140°C. The solvent was distilled off, the residue was recrystallized from an appropriate solvent or separated by chromatography. The reaction products are colorless crystalline compounds.

2-Aryl-9-arylperhydropyrazolo[1,2-a]pyrrolo-[3,4-c]pyrazole-1,3-diones (Vc–e, h–j, VIc–e, h–j) by physical and spectral characteristics corresponded to the previously obtained compounds [10] and were isolated in overall preparative yields 73, 68, 53, 75, 75, and 85% respectively.

2,9-Diphenylperhydropyrazolo[1,2-a]pyrrolo-[3,4-c]pyrazole-1,3-dione (Va, VIa) was obtained from 0.264 g (1.65 mmol) of diazaalkane **Ia** and 0.259 g (1.5 mmol) of imide **IIa**. On fractional crystallization from acetone with a little ether we obtained 0.11 g (22%) of *trans*-isomer **Va**, mp 180–182°C, and a mixture of *trans*- and *cis*-isomers **Va, VIa**, yield 0.245 g (49%). Overall yield 0.355 g (71%). Found, % (for *trans*-isomer): C 71.89, 72.15; H 5.73, 5.97; N 12.74, 13.00. $C_{20}H_{19}N_3O_2$. Calculated, %: C 72.05; H 5.74; N 12.60.

2-(4-Methoxyphenyl)-9-phenylperhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vb, VIb) was obtained from 0.264 g (1.65 mmol) of diazaalkane **Ia** and 0.264 g (1.5 mmol) of imide **IIb**. On fractional crystallization from acetone with a little ether we obtained 0.22 g (40%) of trans-isomer **Vb**, mp 186–187°C, and a mixture of *trans*- and *cis*-isomers **Vb, VIb**, yield 0.151 g (28%). Overall yield 0.371 g (68%). Found, % (for *trans*-isomer): C 69.53, 69.78; H 5.81, 5.75; N 11.55, 12.29. $C_{21}H_{21}N_3O_3$. Calculated, %: C 69.41; H 5.82; N 11.56.

9-(4-Methoxyphenyl)-2-phenylperhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vf, VIf) was obtained from 0.209 g (1.1 mmol) of diazaalkane **Ib** and 0.173 g (1 mmol) of imide **IIa**. On recrystallization from acetone with a little ether we obtained a mixture of *trans*- and *cis*-isomers **Vf, VIf**, yield 0.2 g (53%). Found, %: C 70.56, 70.18; H 6.02, 5.89; N 11.92, 11.80. $C_{21}H_{21}N_2O_3$. Calculated, %: C 69.41; H 5.82; N 11.56.

2,9-Bis-(4-methoxyphenylperhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vg, VIg) was obtained from 0.209 g (1.1 mmol) of diazaalkane **Ib** and 0.203 g (1 mmol) of imide **IIb**. On fractional crystallization from acetone with a little ether we obtained 0.05 g (13%) of trans-isomer **Vg**, mp 209–210°C, and a mixture of colorless crystals of *trans*- and *cis*-isomers **Vg, VIg**, yield 0.228 g. Overall yield 0.278 g (71%). Found, % (for *trans*-isomer): C 67.55, 67.13; H 5.97, 5.91; N 10.84, 10.81. $C_{22}H_{23}N_3O_4$. Calculated, %: C 67.16; H 5.89; N 10.68.

9-(4-Tolyl)-2-phenylperhydropyrazolo[1,2-a]-pyrrolo[3,4-c]pyrazole-1,3-dione (Vk, VIk) was obtained from 0.191 g (1.1 mmol) of diazaalkane **Ic** and 0.173 g (1 mmol) of imide **IIa**. On recrystallization from ether–acetone mixture, 3:1, we obtained a mixture of trans- and cis-isomers **Vk, VIk**, yield 0.208 g (60%). Found, %: C 72.44, 72.92; H 6.11, 6.14; N 12.08, 11.98. $C_{21}H_{21}N_3O_2$. Calculated, %: C 72.60; H 6.09; N 12.10.

9-(4-Tolyl)-2-(4-methoxyphenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vl, VIl) was obtained from 0.191 g (1.1 mmol) of diazaalkane Ic and 0.203 g (1 mmol) of imide **IIb**. On recrystallization from acetone with a little hexane we obtained a mixture of *trans*- and *cis*-isomers **Vl, VIl**, yield 0.3 g (80%). Found, %: C 69.72, 69.89; H 6.32, 6.06; N 10.92, 11.16. $C_{22}H_{23}N_3O_3$. Calculated, %: C 70.01; H 6.14; N 11.13.

2,9-Bis-(4-tolylperhydropyrazolo[1,2-a]pyrrolo-[3,4-c]pyrazole-1,3-dione (Vm, VIm) was obtained from 0.191 g (1.1 mmol) of diazaalkane **Ic** and 0.187 g (1 mmol) of imide **IIc**. On fractional crystallization from acetone with a little hexane we obtained 0.05 g (14%) of *trans*-isomer **Vm**, mp 190–191°C, and a mixture of *trans*- and *cis*-isomers **Vm, VIm**, yield 0.25 g (69%). Overall yield 0.3 g (83%). Found, % (for *trans*-isomer): C 73.34, 72.94; H 6.62, 6.26;

N 11.60, 11.68. $C_{22}H_{23}N_3O_2$. Calculated, %: C 73.11; H 6.41; N 11.63.

2-(4-Bromophenyl)-9-(4-tolyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vn, VIn) was obtained from 0.383 g (2.2 mmol) of diazaalkane **Ic** and 0.504 g (2 mmol) of imide **IId**. The reaction products were separated by column chromatography on silica gel L 40/100, substance–to–sorbent ratio 1:50, gradient elution with hexane and hexane-THF mixture, 1:1. *trans*-Isomer (**V°**), mp 163–164°C, yield 0.318 g (37%). *cis*-Isomer (**VI°**), mp 208–211°C, yield 0.116 g (14%). Overall yield 0.434 g (51%). Found, % (for *trans*-isomer): C 58.94, 59.11; H 4.74, 4.65; N 9.87, 9.75. $C_{21}H_{20}BrN_3O_2$. Calculated, %: C 59.17; H 4.73; N 9.86. Found, % (for *cis*-isomer): C 59.44, 59.44; H 4.83, 4.83; N 9.69, 9.77. $C_{21}H_{20}BrN_3O_2$. Calculated, %: C 59.17; H 4.73; N 9.86.

9-(4-Tolyl)-2-(4-nitrophenyl)perhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vo, VIo) was obtained from 0.191 g (1.1 mmol) of diazaalkane **Ic** and 0.218 g (1 mmol) of imide **IIe**. On recrystallization from acetone with a little ether we obtained a mixture of *trans*- and *cis*-isomers **Vo**, **VIo**, yield 0.255 g (65%). Found, %: C 64.47, 64.60; H 5.25, 5.45; N 14.39, 14.29. $C_{21}H_{20}N_4O_4$. Calculated, %: C 64.28; H 5.14; N 14.28.

2-Phenyl-9-(4-chlorophenyl)perhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vp, VIp) was obtained from 0.21 g (1.1 mmol) of diazaalkane **Id** and 0.17 g (1 mmol) of imide **IIa**. On recrystallization from acetone with a little ether we obtained a mixture of *trans*- and *cis*-isomers **Vp**, **VIp**, yield 0.27 g (73%). Found, %: C 65.21, 65.65; H 4.73, 4.95; N 11.52, 11.25. $C_{20}H_{18}ClN_3O_2$. Calculated, %: C 65.31; H 4.93; N 11.42.

2-(4-Methoxyphenyl)-9-(4-chlorophenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vq, VIq) was obtained from 0.21 g (1.1 mmol) of diazaalkane **Id** and 0.2 g (1 mmol) of imide IIb. On recrystallization from acetone with a little ether we obtained a mixture of *trans*- and *cis*-isomers **Vq, VIq**, yield 0.27 g (68%). Found, %: C 63.30, 63.60; H 4.96, 4.95; N 10.63, 10.45. $C_{21}H_{20}ClN_3O_3$. Calculated, %: C 63.40; H 5.07; N 10.56.

2-(4-Tolyl)-9-(4-chlorophenyl)perhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vr, VIr) was obtained from 0.21 g (1.1 mmol) of diazaalkane **Id** and 0.19 g (1 mmol) of imide **IIc**. On recrystallization from acetone with a little ether we obtained a mixture of *trans*- and *cis*-isomers **Vr, VIr**, yield 0.25 g (65%). Found, %: C 66.05, 65.96; H 5.24, 5.17; N 11.15, 10.85. $C_{21}H_{20}ClN_3O_2$. Calculated, %: C 66.05; H 5.28; N 11.00.

2-(4-Bromophenyl)-9-(4-chlorophenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vs, VIs) was obtained from 0.21 g (1.1 mmol) of diazaalkane **Id** and 0.25 g (1 mmol) of imide **IId**. On recrystallization from acetone with a little ether we obtained a mixture of *trans*- and *cis*-isomers **Vs, VIs**, yield 0.3 g (67%). Found, %: C 53.79, 53.76; H 3.93, 3.74; N 9.40, 9.35. $C_{20}H_{17}BrClN_3O_2$. Calculated, %: C 53.77; H 3.84; N 9.41.

2-(4-Nitrophenyl)-9-(4-chlorophenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vt, VIt) was obtained from 0.21 g (1.1 mmol) of diazaalkane **Id** and 0.22 g (1 mmol) of imide **IIe**. On recrystallization from acetone with a little ether we obtained 0.06 g (15%) of *trans*-isomer **Vt**, mp 190–191°C, and 0.28 g (68%) of a mixture of *trans*- and *cis*-isomers **Vt, VIt**. Overall yield 0.34 g (83%). Found, % (for *trans*-isomer): C 58.17, 58.28; H 4.35, 4.30; N 13.42, 13.45. $C_{20}H_{17}ClN_4O_4$. Calculated, %: C 58.19; H 4.15; N 13.57.

9-(3-Nitrophenyl)-2-phenylperhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vu, VIu) was obtained from 0.226 g (1.1 mmol) of diazaalkane **Ie** and 0.173 g (1 mmol) of imide **IIa**. On recrystallization from acetone–ether mixture, 1:2, we obtained a mixture of *trans*- and *cis*-isomers **Vu, VIu**, yield 0.265 g (70%). Found, %: C 63.57, 63.31; H 5.00, 4.90; N 14.77, 14.71. $C_{20}H_{18}N_4O_4$. Calculated, %: C 63.49; H 4.79; N 14.81.

2-(4-Methoxyphenyl)-9-(3-nitrophenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vv, VIv) was obtained from 0.226 g (1.1 mmol) of diazaalkane **Ie** and 0.203 g (1 mmol) of imide **IIb**. On recrystallization from 2-propanol with a little acetone we obtained a mixture of *trans*- and *cis*-isomers **Vv, VIv**, yield 0.257 g (63%). Found, %: C 61.66, 61.76; H 5.00, 5.04; N 13.64, 13.66. $C_{21}H_{20}N_4O_5$. Calculated, %: C 61.76; H 4.94; N 13.72.

2-(4-Tolyl)-9-(3-nitrophenyl)perhydropyrazolo-[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vw, VIw) was obtained from 0.226 g (1.1 mmol) of diazaalkane **Ie** and 0.187 g (1 mmol) of imide **IIc**. On recrystallization from 2-propanol–acetone mixture, 2:1, we obtained a mixture of *trans*- and *cis*-isomers **Vw, VIw**, yield 0.29 g (74%). Found, %: C 64.22, 64.43; H 5.19, 5.33; N 14.16, 14.13. $C_{21}H_{20}N_4O_4$. Calculated, %: C 64.28; H 5.14; N 14.28.

2-(4-Bromophenyl)-9-(3-nitrophenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vx, VIx) was obtained from 0.226 g (1.1 mmol) of diazaalkane **Ie** and 0.252 g (1 mmol) of imide **IId**. On recrystallization from 2-propanol with a little acetone we obtained a mixture of *trans*- and *cis*-isomers **Vx, VIx**, yield 0.35 g (77%). Found, %: C 52.67, 52.63; H 3.90, 3.83; N 11.91, 11.95. $C_{20}H_{17}BrN_4O_4$. Calculated, %: C 52.53; H 3.75; N 12.25.

2-(4-Nitrophenyl)-9-(3-nitrophenyl)perhydropyrazolo[1,2-a]pyrrolo[3,4-c]pyrazole-1,3-dione (Vy, VIy) was obtained from 0.226 g (1.1 mmol) of diazaalkane **Ie** and 0.218 g (1 mmol) of imide **IIe**. On fractional crystallization from 2-propanol–acetone mixture, 2:1, we obtained 0.04 g (9%) of *trans*-iso0 mer **Vy**, mp 173–174°C, and a mixture of *trans*- and *cis*-isomers **Vy, VIy**, yield 0.31 g (73%). Overall yield 0.35 g (83%). Found, % (for *trans*-isomer): C 56.38, 56.82; H 4.13, 4.11; N 16.52, 16.68. $C_{20}H_{17}N_5O_6$. Calculated, %: C 56.74; H 4.05; N 16.54.

Characteristics of UV spectra of compounds Ia, IIa, and their mixtures. The UV spectrum of diazabicyclohexane **Ia** contained bands with λ_{max} at 259 nm (ε 508.2 l mol^{-1} cm^{-1}), 265 nm (ε 472.1 l mol^{-1} cm^{-1}), and 271 nm (ε 314.8 l mol^{-1} cm^{-1}). UV spectrum of *N*-phenylmaleimide **IIa** contained bands with λ_{max} at 318 nm (ε 457.8 l mol^{-1} cm^{-1}) and 266 nm (ε 490.0 l mol^{-1} cm^{-1}).

UV spectra of compounds **Ia** and **IIa** with concentrations (a) 3.08×10^{-3} mol l^{-1} and 2.48×10^{-3} mol l^{-1} or (b) 6.29×10^{-3} mol l^{-1} and 4.93×10^{-3} mol l^{-1} respectively comprise a superimposed individual spectra of compounds **Ia** and **IIa** both immediately after mixing the solutions and in several days of standing at room temperature. No changes were found in the spectrum of (b) solution after 4 days of standing at room temperature.

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