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Oxidative Addition of *N*-Aminophthalimide to Conjugated and Nonconjugated Alkylazoalkanes

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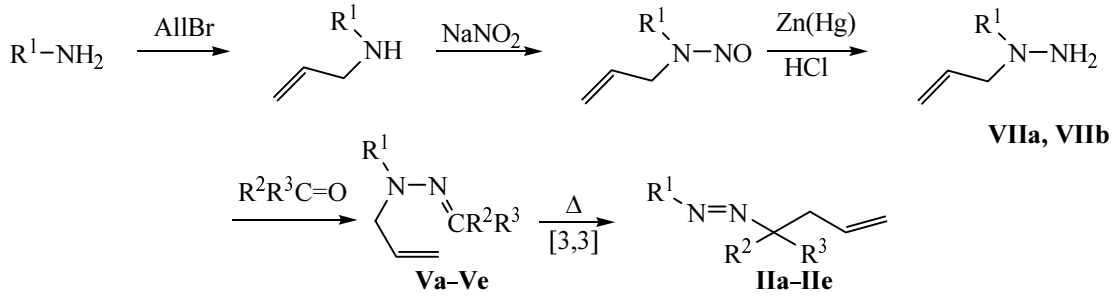
Abstract—A series of γ,δ-unsaturated azo compounds was prepared by thermal isomerization of allylalkylhydrazones obtained from the simplest carbonyl compounds. The oxidation of *N*-aminophthalimide with lead tetraacetate in the presence of these unsaturated compounds gave rise to mixtures of adducts at the azo group, regioisomers of phthalimidoazimines. The oxidative addition of *N*-aminophthalimide to 1-isopropylazocycloalkenes afforded bicyclic C-isopropylazo-*N*-phthalimidoaziridines, but the same reaction with 2-alkylazopropenes did not result in any adducts with these conjugated azocompounds.

We recently demonstrated that oxidation of *N*-aminophthalimide (**I**) with lead tetraacetate in the presence of conjugated phenylazoalkenes and also of cyclic azoalkene, 3,3,5-trimethyl-3*H*-pyrazole, furnished a wide range of compounds: C-azoaziridines, phthalimidoazimines, 2*H*-1,2,3-triazole derivatives etc. [1, 2]. However our first attempts to bring 2-alkylazopropenes into this reaction were unsuccessful, although with γ,δ-unsaturated azo compounds we obtained the corresponding unsaturated phthalimidoazimines [3]. Therefore we believe that a closer look at the oxidative addition of *N*-aminophthalimide to a series of conjugated and nonconjugated alkylazaalkenes is called for. We selected for the study 4-alkylazo-1-alkenes **IIa–IIe** in whose structure the mutual influence of the C=C and N=N bonds was negligible, and also 2-alkylazo-propenes **IIIa, IIIb** and 1-iso-propylazocycloalkenes **IVa, IVb** with a conjugated bond system C=C–N=N.

To the preparation of homoallyl azo compounds **IIa–IIe** we applied the [3,3]-sigmatropic rearrangement of alkylallylhydrazones [4]. Initial hydrazones **Va–Ve** were obtained from primary amines, allyl bromide, and carbonyl compounds along the common procedure.

The rearrangement of alkylallylhydrazones **Va–Ve** into γ,δ-unsaturated azo compounds **IIa–IIe** was performed by heating the initial hydrazones in sealed ampules at 170–185°C for 20–35 h. In keeping with [4] the rearrangement rate decreased at the growing number of substituents in the carbonyl moiety. In the course of formaldehyde allylmethylhydrazone (**Va**) isomerization the reaction



VI,VII, R^1 = Me (**a**), *i*-Pr (b); **II,V**, R^1 = Me, $R^2 = R^3$ = H (**a**), Me (**b**); R^1 = *i*-Pr, R^2 = H, R^3 = H (**c**), Me (**d**), $R^2 = R^3$ = Me (**e**).

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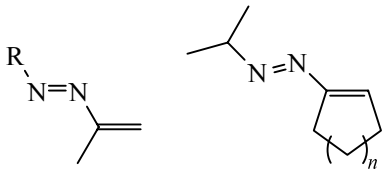
mixture often suffered tarring, and then the yield of azoalkene **IIa** sharply decreased. In the other cases the yield of the azo compound depended mainly on the length of heating time; therewith the clean and relatively fast isomerization of allylisopropylhydrazones of formaldehyde (**Vc**) and acetaldehyde (**Vd**) (20–30 h, 180°C) yielded virtually individual azo compounds **IIc, IId** (>95% according to GLC data). However at the isomerization under the same conditions of acetone allylisopropylhydrazone (**Ve**) after ~25 h of heating the sealed ampules twice exploded apparently due to decomposition of the reaction product. In further experiments in the course of this hydrazone isomerization we cautiously opened the ampule after every 10–14 h of heating, flushed it with inert gas, and sealed again. In this way we succeeded to prepare also azo compound **IIe**.

As a result of theses syntheses were isolated and characterized for the first time nitrosamines **VIa, VIb** {allylmethylnitrosamine (**VIa**) had been formerly used without purification for preparation of the respective hydrazine [4]}, 1-allyl-1-isopropylhydrazine (**VIIb**), hydrazones **Vc–Ve**, and three isopropylazoalkenes **IIc–IIe**. Their structure follows from the synthesis method and is confirmed by the sum of physicochemical and spectral characteristics. The mass spectra of hydrazones **Vc–Ve** we synthesized were presented and discussed in [5].

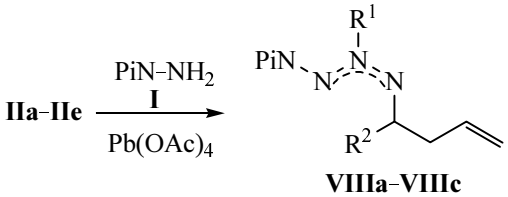
In the ^{1}H NMR spectra of azo compounds **IIc–IIe** a single set of signals from substituents was present. It means that these compounds are formed as a single spatial isomer and apparently they belong to the (*E*) series (cf. [4]). In the ^{1}H NMR spectra of nitrosamines **VIa, VIb** two sets of signals are observed due to the partially double character of the N–N bond resulting in appearance of the corresponding *syn*- and *anti*-isomers. It is presumable that in both cases the isomer prevails where the oxygen is nearer to the less bulky substituent (Me in **VIa**, All in **VIb**). Then the comparison of the chemical shift values for the respective pairs of signals shows that the N=O group exerts shielding effect on the protons of the *syn*-located substituent.

Conjugated alkylazoalkenes **III** and **IV** were prepared from the corresponding alkylhydrazines and α-chloroketones by procedure [6] slightly modified for 1- isopropylazocycloalkenes **IV**. By the example of compound **IVb** synthesis we found that cooling to –20...–15°C at the moment of reagents mixing and isolation of the reaction product by column chromatography provided better yield of the unsaturated azo compound. As a result 1-isopropylazocyclohexene (**IVb**) was obtained in dichloromethane at the use of potassium carbonate as dehydrating agent in an almost quantitative yield, but the yield of the less stable 1-isopropylazocyclopentene (**IVa**) under these conditions attained only 25%. We succeeded in raising the yield of azo compound **IVa** twofold by using as solvent ethyl ether and as dehydrating agent the neutral sodium sulfate. 1-Isopropyl-azo-cycloalkenes **IVa, IVb** prepared by us for the first time are greenish viscous fluids with a sweetish odor that decompose at room temperature. Their structure expected for the given method of synthesis was confirmed by the ^{1}H and ^{13}C NMR spectra.

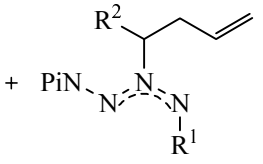


IIIa, IIIb **IVa, IVb**

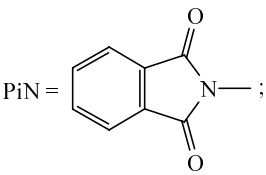
The oxidative addition of *N*-aminophthalimide (**I**) to γ,δ-unsaturated azo compounds **IIa–IIe** was carried out by bringing lead tetraacetate in a dispersion of imide **I** and potassium carbonate in a solution of the azo compound in CH_2Cl_2. From the reaction mixtures obtained with substrates **IIa, IIc, IId** we succeeded to isolated by column chromatography substances characterized by similar values of R_f (0.35–0.50 in a system benzene–ethyl acetate, 7:1, SiO_2) which were yellow oily substances slowly crystallizing on standing. The sum of their characteristics shows that in these cases in 15–50% yields were obtained mixtures containing regioisomers resulting from oxidative addition of the *N*-aminophthalimide to the



VIIIa–VIIIc



IXa–IXc



; **VIII, IX**, R^1 = Me, R^2 = H (**a**); R^1 = *i*-Pr, R^2 = H (**b**), Me (**c**).

azo group, (1*Z*,2*E*)-1-alkenyl-2-alkyl- (**VIIIa–VIIIc**) and (1*Z*,2*E*)-2-alkenyl-1-alkyl-3-phthalimidoazimines (**IXa–IXc**).

The elemental analyses really show that these compounds are adduct of imide **I** with homoallyl azo compounds, 1:1. In their ^{1}H NMR spectra apart from the downfield signal of the phthalimide fragment in the region 4.9–6.2 ppm appears a characteristic multiplet of olefin protons from the allyl group whose presence is additionally confirmed by the signal of its methylene protons (~2.6 ppm) and the corresponding signals in the ^{13}C NMR spectrum of azimines **VIIIa+ IXa** mixture. Inasmuch as the allyl group in the compounds is retained, the reaction obviously proceeds at the N=N bond affording phthalimidoazimines **VIII+ IX**.This assumption is confirmed by signals of protons contiguous to nitrogens characteristic of azimines in the region 3.5–4.9 ppm.

The position of substituents in the azimine fragment was deduced from the ^{1}H NMR spectra. As already mentioned [7, 8], the signals of the α-protons of alkyl groups attached to the central nitrogen of the azimine system, on the one hand, and those at the N*1* atom, on the other hand, are present in essentially different regions of the spectrum, and the position of these signals is virtually insensitive to the geometry of the molecule or to the kind of the substituent at the neighboring nitrogen atom. The comparison of chemical shifts corresponding to these protons in adducts **VIII + IX** with the chemical shifts of the relevant protons for 1,2-dialkyl-3-phthalimidoazimines described in the literature [7, 8] suggests that the main reaction products **VIIIa, VIIIc, IXb** contain the smaller substituent at the central nitrogen of the azimine system, and in the minor products this substituent is attached to the terminal nitrogen atom.

Each of the regioisomeric phthalimidoazimines formed as a single stereoisomer. Therewith the chemical shifts of alkyl protons virtually coincide with the corresponding values in the spectra of already described (1*Z*,2*E*)-1,2-dialkyl-3-phthalimidoazimines [7, 8]. At the same time the change in the geometry of the molecule is usually reflected in significant shift of the signals in the ^{1}H NMR spectra [7, 8]. This fact permits attribution of adducts **VIII + IX** to the same series of stereoisomers as the main products of the oxidative addition of imide **I** to the (*E*)-azoalkanes, namely, to (1*Z*,2*E*)-azimines.

In the ^{1}H NMR spectra of reaction mixtures obtained with substrates **IIa, IIc, IId** no significant additional signals were observed as compared to the spectra of azimines **VIII + IX**. This fact evidences the lack of adducts across the C=C bond, the corresponding phthalimidoaziridines. Actually, to the phthalimidoaziridine structure should correspond not only the presence in the ^{1}H NMR spectra of characteristic multiplets of the aziridine protons in the region 2.5–4.5 ppm, but also a significant upfield shift of the methylene protons of the previous allyl fragment (from ~2.6 to 1.5–1.8 ppm). Inasmuch as no signals appear in this region of the ^{1}H NMR spectra of the reaction mixtures, we can conclude that even if the phthalimido-aziridines form their amounts are insufficient to be detected by ^{1}H NMR spectroscopy, TLC, and to be isolated preparatively. It may be rationalized by reminding that the oxidative addition of *N*-aminoheterocycles to a nonconjugated terminal C=C bond of 1-alkenes usually occurs to an insignificant extent (cf. [9]).

From the reaction mixtures obtained with compounds **IIb, IIe** having a tertiary substituent at the azo group we failed to isolate both phthalimidoazimines and phthalimidoaziridines. In these cases we obtained as the main product phthalimide arising due to oxidation of aminoimide **I** in the absence of any reactive [10]. The similar chromatographic behavior of all phthalimidoazimines obtained from azoalkenes **IIa, IIc, IId** suggests that the corresponding adducts with azo compounds **IIb, IIe** either do not form at all or are unstable under the isolation conditions.

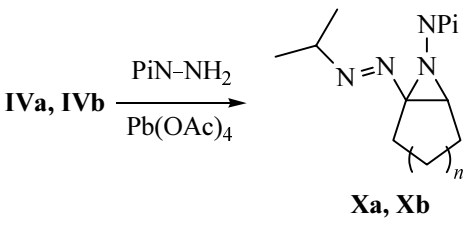
Thus the oxidative addition of aminoimide **I** to γ,δ-unsaturated azo compounds **II** occurs only at the azo group affording the corresponding phthalimidoazimines **VIII + IX**. No wonder that the reaction follows the rules which we have established for the series of (*E*)-azoalkanes [7, 11]: The reaction proceeds stereospecifically, with retention of azo group configuration, and regioselectively, affording predominantly adducts containing the smaller substituent at the central nitrogen of the azoimine system. The decisive role belongs here apparently to the steric effect of the substituents. With their growing bulk the yield decreases, and the presence of a tertiary substituent at the N=N bond prevents the adduct formation (Cf. [7, 11]). The specific effect of the alkenyl substituent is manifested only in formation in some experiments with substrates **IIb–IId** of unidentified products of pronounced oligomeric character.

The reactions with conjugated azoalkenes **IIIa, IIIb** were performed by the same procedure as with substrates **II**. On completion of the reaction the precipitate of inorganic salts was filtered off and washed with dichloromethane. The filtrate was green-yellow, and its color was considerably different from the bright yellow one of the initial azo compound. On storage of this solution

at 5°C for 24 h no precipitate separated, and the characteristic color remained. In the cases of both initial compounds the evaporation of the filtrate obtained from the reaction mixture we isolated only two products: phthalimide (70–75%) and a colorless powdery substance that decomposed at ~150°C, was virtually insoluble in the common organic solvents, and reacted with DMSO and DMF with heat and gas evolution. The yield of the latter compound was 12–14% of the weight of the residue after evaportion of the filtrate.

The large amount of phthalimide in reaction products evidences the low reactivity of azoalkenes **IIIa, IIIb**. It is in agreement with the result of the GLC analysis of the reaction mixture obtained from 2-isopropylazopropene **IIIb**: According to these data ~70% of the azo compound remains in the reaction mixture also when all $Pb(OAc)_4$ is added. However it is necessary to state that neither at oxidation of hydrazide **I** in the absence of any substrates [10] nor in the many described examples of its oxidative addition to olefins, dienes, enynes, styrenes, azo compound etc. [11, 12] has been observed a formation of compound like the insoluble substance we have obtained. Hence it is presumable that the conjugated azoalkene still takes part in the reaction giving rise to an unstable compound that at evaporation of its green-yellow solution in CH_2Cl_2 suffers decomposition and/or oligomerization.

In the IR spectrum of the insoluble substances that we obtained in both reactions appeared strong absorption bands corresponding to the stretching vibrations of the C=O bonds at ~1750 cm^{-1}, and also vibration bands of the aromatic ring. Therefore most probably the phthaloyl fragment is retained in these molecules. The elemental analyses of these products may be attributed (although with a large error) to a formula $(C_8H_4N_2O_2)_n$. Then at n = 1 this empirical formula might correspond to the structure of phthalazine-1,4-dione, and at n = 2 to bisphthaloyltetrazene.



Xa, Xb

n = 1 (**a**), 2 (**b**).

However the properties of the known bisphthaloyltetrazene [10] are quite different from those of the products we obtained, and the phthalazinedione-1,4 is stable only in solution [13]. Therefore in the empirical formula of the compound $(C_8H_4N_2O_2)_n$ $n \geq 3$. At the same time it should be mentioned that in [13] was described the oxidation of 2,3-dihydrophthalazine-1,4-dione with $Pb(OAc)_4$ giving bright-green solution of phthalazine-1,4-dione which reacted with 1,3-dienes by Diels–Alder type process. On storage of this solution an amorphous colorless precipitate separated that contained 16% of nitrogen, was insoluble in water and common organic solvents, and decomposed at heating to 190–200°C. Clement [13] believed that this compound originated from phthalazinedione polymerization.

Notwithstanding a certain likeness of the properties of the latter compound and our products we should take into account, firstly, that the oxidation of aminophthalimide **I** does not yield the phthalazine-1,4-dione, and secondly, that in the absence of the conjugated azoalkenes we do not obtain these products. Thus the question of the character of insoluble compound obtained remains open.

Finally we may state that under the given reaction conditions and workup procedure we failed to isolate any products of aminoimide **I** oxidative addition to α,β-unsaturated azo compounds **IIIa, IIIb**, and they apparently were also lacking in the dry residue after evaporation of the reaction mixture. In contrast, aminoimide **I** oxidative addition to very similar 1-isopropylazocycloalkenes **IVa, IVb** resulted in bicyclic 1 isopropylazoaziridines **Xa, Xb**, yet in a low yield.

In the similar way this reaction occurs with 1-phenylazocyclohexane, and the properties of adducts **Xa**, **Xb** are like the characteristics of the 1-phenylazo-7-phthalimido-7-azabicyclo-[4.1.0]heptane we have described before [1, 2]. In the ^1H NMR spectra of azoaziridines **Xa**, **Xb** appears a characteristic doublet of the aziridine proton at ~4 ppm, in the ^{13}C NMR spectrum the two carbon atoms of the three-membered ring are observed at ~70–80 (C^1) and 50 ppm. A known characteristic feature of N-aminoaziridine derivative is the high barrier to aziridine nitrogen inversion [14]. Inasmuch as in the ^1H and ^{13}C NMR spectra of both bicyclic aziridines **Xa**, **Xb** as also in the spectra of 1 phenyl-azo-7-phthalimido-7-azabicyclo[4.1.0]heptane [1, 2] only a single set of signals is clearly observed they evidently to over 90% exist in the form of the more stable invertomer with the *syn*-position of the aziridine proton and the heterocyclic fragment.

The formation of azoaziridines **Xa**, **Xb** may be either due to the difference in the reactivity of the trisubstituted bond >C=CH– in compounds **IVa, IVb** and of the 1,1

disubstituted bond >C=CH_2 in azoalkenes **IIIa, IIIb** or simply to the greater stability of these products under conditions of the reaction and workup; however, the reasons thereof are unclear. It is also interesting that the oxidative addition of aminoimide **I** to both 1-isopropylazocycloalkenes **IVa, IVb** afforded azoaziridines whereas the only product of this reaction with 1-phenylazocyclopentene was 2-phenyl-2,4,5,6-tetrahydrocyclopenta-[*d*][1,2,3]triazole [1, 2]. This fact once more shows the high sensitivity of the reaction under study to relatively small changes in the structure of the initial azoalkene.

EXPERIMENTAL

^{1}H NMR spectra of compounds **II, III, V–IX** were registered on spectrometers Varian EM-360 (60 MHz) and HA-100D-15 (100 MHz) from 5–25% solutions in $CDCl_3$ or CCl_4 using HMDS or TMS as internal reference. ^{1}H and ^{13}C NMR spectra of compounds **IV** and **X** were recorded on spectrometer Varian Gemini-2000 (200 MHz) from solutions in $CDCl_3$, internal reference TMS or the solvent signals. Mass spectra of liquids were obtained on a GC-MS LKB-2091 instrument, ionizing electrons energy 70 and 12 eV, mass spectra of solid samples were measured on Hewlett-Packard HP-5985A installation at direct admission of the sample into the ion source, ionizing electrons energy 70 eV. IR spectra were taken on UR-10 spectrometer from samples prepared as pellets with KBr or as mulls in mineral oil.

GLC analysis was carried out on a chromatograph LKhM-8MD, detector katharometer, column 2300 × 3 mm, stationary phase 5% SE-30 on Inerton-Super 0.16–0.20, carrier gas helium, flow rate 25–30 ml/min.

Elemental analyses were performed on a CHN-analyzer Hewlett-Packard HP-185B. The preparative separation of reaction mixtures was done by column chromatography on silica gel 40–100 μm. The composition of reaction mixtures obtained by fractions separation, and the purity of products isolated were tested by TLC on Silufol UV-254 plates.

Refraction indices of liquids were measured on Abbe refractometer IFR-22 with an accuracy to 2×10^{-4} and on Pulfrich refractometer of IRF-23m type with an accuracy to 2×10^{-5}. Densities were measured with the use of Byron pycnometers of 1–10 ml volume accurate to 5×10^{-4}–5×10^{-5} g/cm^3.

Conjugated alkylazopropenes **III** were synthesized by procedure [6]. *N*-Aminophthalimide **I** was obtained as described in [15].

Allylisopropylamine. To 118 g (2 mol) of isopropylamine was slowly added while cooling with ice–salt mixture 121 g (1 mol) of allyl bromide. The separated precipitate was filtered off, the filtrate was subjected to distillation on a column (12 plates) collecting the fraction of bp 95–98°C (AllNHPr-*i*). The precipitate was treated with 50% KOH solution while distilling off the volatile products up to bp 100°C, the distillate was dried over KOH and subjected to column distillation over alkali collecting the fractions of bp 30–33°C (isopropylamine) and 96–97°C (AllNHPr-*i*). The overall yield of allylisopropylamine was 23.6 g (24%), n_D^{20} 1.4158 (publ.: bp 96–97°C, n_D^{25} 1.4140 [16]).

Alkylallylnitrosamines VIa, VIb. To a solution of 105 ml of concn. hydrochloric acid (d 1.19 g/cm^3) in 200 ml of water while cooling with ice–salt mixture was slowly added dropwise at stirring 1 mol of alkylallylamine and then by small portions 105 g (1.5 mol) of $NaNO_2$. The reaction mixture was heated for 30 min at stirring on a boiling water bath, and afterwards the upper layer was separated, dried with $MgSO_4$, and distilled in a vacuum.

Allylmethylnitrosamine (VIa). Yield 82%, bp 79°C (30 mm Hg), d_4^{20} 0.9767, n_D^{20} 1.4640, MR_D 28.29, calc. 28.00. A mixture of *syn-anti*-isomers in a ratio ~3:8. ^{1}H NMR spectrum (60 MHz), δ, ppm: 2.90 s and 3.70 s (intensity ratio ~8:3, overall intensity 3H, CH_3), 4.15 d (J 5 Hz) and 4.74 d (J 5 Hz) (intensity ratio ~3:8, overall intensity 2H, CH_2), 5.06–5.50 m (2H, =CH_2), 5.64–6.33 m (1H, =CH). Mass spectrum, *m/z* (I_{rel}, %): 101 (2), 100 (33) [M]$^+$, 99 (2), 84 (6), 83 (100), 73 (4), 70 (4), 69 (6), 68 (18), 59 (13), 57 (10), 56 (4), 55 (10), 54 (7), 45 (1), 44 (14), 43 (41), 42 (81), 41 (6), 40 (5), 39 (30), 38 (3), 37 (2), 32 (5), 31 (6), 30 (25).

Allylisopropylnitrosamine (VIb). Yield 80%, bp 91–92°C (20 mm Hg), d_4^{20} 0.9435, n_D^{20} 1.4590, MR_D 37.12, calc. 37.30. A mixture of *syn-anti*-isomers in a ratio ~1:10. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.13 d (J 6.5 Hz) and 1.45 d (J 6.5 Hz) (intensity ratio ~1:10, overall intensity 6H, $2CH_3$), 4.08 d (CH_2 of main isomer, J 5 Hz), ~4.7 sept (>CH of main isomer, J 6.5 Hz) on the background of 4.40–5.03 m (CH_2 and >CH of minor isomer, overall intensity 3H), 5.03–6.29 m (3H, CH=CH_2). Mass spectrum, *m/z* (I_{rel}, %): 129 (4) 128 (37) [M]$^+$, 113 (2), 112 (2), 111 (19), 98 (8), 97 (1), 96 (2), 87 (5), 86 (11), 84 (1), 83 (12), 82(20), 71 (3), 70 (5), 69 (37), 68 (15), 59 (2), 58 (8), 57 (4), 56 (40), 55 (16), 54 (7), 44 (5), 43 (95), 42 (28), 41 (100), 40 (9), 39 (28), 38 (2), 32 (5), 30 (10); (12 eV): 129 (8), 128 (100) [M]$^+$,

113 (2), 112 (35), 111 (48), 99 (14), 98 (45), 87 (86), 86 (19), 70 (28), 69 (62), 68 (17), 59 (21), 57 (15), 56 (5), 43 (18), 42 (3), 41 (5), 40 (3); *m** 96.2 (128 > 111).

1-Alkyl-1-allylhydrazines VIIa, VIIb (by procedure [17]). Into a thick-walled tough vessel of 3 liter capacity equipped with a powerful stirrer was charged 200 ml of water, 78 g (1.2 mol) of zinc, 10 ml of mercury, and 30 ml of concn. HCl. At starting the stirrer zinc was covered with an amalgam, the vessel was cooled with water-ice mixture, and 400 ml of water and 250 ml of concn. HCl was added. At cooling and vigorous stirring to the mixture within 1 h was added dropwise 0.6 mol of nitrosamine **VIa, VIb**. The stirring was continued till the end of heat liberation (~2.5 h), the solution was poured into a flask of 2 liter capacity, a solution of 130 g of NaOH in 130 ml of water was added, and the mixture was subjected to steam distillation. The process was carried out till the n_D^{20} of the distillate coming into the receiver became smaller that 1.3360 (300–400 ml of total distillate). The distillate was saturated with KOH (~350 g), the organic layer was separated, dried over KOH, and hydrazines **VIIa, VIIb** were distilled in a nitrogen flow.

Allylisopropylhydrazine (VIIb). Yield 40%, bp 70–72°C (76 mm Hg), d_4^{20} 0.8351, n_D^{20} 1.4448, MR_D 36.38, calc. 36.82. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.00 d (6H, $2CH_3$, *J* 6.5 Hz), ~2.7 sept (CH, *J* 6.5 Hz) on the background of a wide signal 2.47–3.03 (NH_2, CH_2, overall intensity 5H), 4.97–5.50 m (2H, $=CH_2$), 5.67–6.43 m (1H, =CH). Mass spectrum, *m/z* (I_{rel}, %): 115 (4), 114 (48) $[M]^+$, 113 (11), 100 (7), 99 (100), 87 (2), 84 (1), 74 (1), 73 (25), 72 (2), 71 (4), 70 (1), 69 (2), 68 (2), 67 (3), 59 (2), 58 (5), 57 (12), 56 (53), 55 (7), 54 (7), 45 (18), 44 (15), 43 (23), 42 (13), 41 (57), 40 (3), 39 (16), 38 (1), 31 (5), 30 (9), 29 (9), 28 (25); *m** 86 (114 > 99), 46.8 (114 > 73); (12 eV): 115 (12), 114 (100) $[M]^+$, 100 (5), 99 (71), 87 (1), 74 (1), 73 (25), 56 (2), 43 (2), 41 (1).

Formaldehyde alkylallylhydrazones Va, Vc. To 0.3 mol of 1-alkyl-1-allyl-hydrazine **VIIa, VIIb** was slowly added at stirring while cooling with ice 29 ml (0.3 mol) of 34% formaldehyde water solution. Then at cooling 20 g of KOH was added, the organic layer was separated, dried over potassium carbonate, and distilled in a vacuum.

Formaldehyde allylisopropylhydrazone (Vc). Yield 72%, bp 78°C (105 mm Hg), d_4^{20} 0.8402, n_D^{20} 1.4565, MR_D 40.84, calc. 40.41. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.11 d (6H, $2CH_3$, *J* 6.5 Hz), ~3.5 sept (CH, *J* 6.5 Hz) on the background of a signal at 3.30–3.80 m (CH_2, overall intensity 3H), 4.90–5.33 m (2H, $=CH_2$), 5.52–6.20 m (3H, =CH and $N=CH_2$).

Acetaldehyde allylisopropylhydrazone (Vd). To 17 g (0.15 mol) of 1-allyl-1-isopropylhydrazine (**VIIb**) was added at stirring while cooling with ice-water mixture 9 g (0.2 mol) of acetaldehyde. The reaction mixture was heated at 40°C for 1h, the organic layer was separated, dried over potassium carbonate, and distilled in a vacuum. Yield 15.4 g (73%), bp 65°C (74 mm Hg), d_4^{20} 0.8376, n_D^{20} 1.4552, MR_D 45.42, calc. 45.06. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.10 d (6H, $2CH_3$, *J* 6.5 Hz), 1.83 d (3H, CH_3, *J* 5.2 Hz), ~3.5 sept (CH, *J* 6.5 Hz) on the background of a signal 3.13–3.87 m (CH_2, overall intensity 3H), 4.99–5.50 m (2H, $=CH_2$), 5.60–6.30 m (1H, =CH), 6.70 q (1H, N=CH, *J* 5.2 Hz).

Acetone alkylallylhydrazones Vb, Ve. To a cooled with ice water mixture of 12 g (0.2 mol) of acetone, 0.8 g of calcium chloride, and 10 ml of anhydrous ether was slowly added at intermittent shaking 0.1 mol of hydrazine **VIIa, VIIb**, then the mixture was heated for 1 h at 35–45°C. On cooling the water formed was separated, the reaction product was dried over potassium carbonate and distilled in a vacuum.

Acetone allylisopropylhydrazone (Ve). Yield 55%, bp 72°C (37 mm Hg), d_4^{20} 0.8216, n_D^{20} 1.4447, MR_D 49.77, calc. 49.71. ^{1}H NMR spectrum (60 MHz), δ, ppm: 0.95 d (6H, $2CH_3$, *J* 6.5 Hz), 1.88 s (6H, $2CH_3$), 2.87 sept (1H, CH, *J* 6.5 Hz), 3.17 d (2H, CH_2, *J* 6.5 Hz), 4.82–5.23 m (2H, $=CH_2$), 5.43–6.10 m (1H, =CH).

Isomerization of alkylallylhydrazones V into γ,δ-unsaturated azo compounds II [4]. Into an ampule of 10 ml capacity made of molybdenum glass was charged 4–6 ml of hydrazone **V**. Through the fluid nitrogen or argon was bubbled for 10–15 min, then the ampule was sealed and heated on an oil bath at 170–185°C for 20–35 h. On cooling the ampule was opened and the product was distilled.

4-Methylazo-1-butene (IIa). In most runs in 20 h at 170–175°C the reaction mixture suffered tarring. Its distillation afforded 15–25% of target reaction product **IIa** (bp 90–98°C, n_D^{20} 1.4200–1.4330) with an admixture of up to 25% of the initial hydrazone and a fraction of sufficiently pure formaldehyde allyl-methylhydrazone (**Va**) (bp 118–120°C, n_D^{20} 1.4598). The recovery of the latter (30–40%) varied depending on the heating period. The repeated isomerization of the recovered hydrazone occurred as a rule without tarring and afforded sufficiently pure azo compound **IIa** in a 20–30% yield, bp 89–92°C, n_D^{20} 1.4196×1.4210 (publ.: bp 87–90°C, n_D^{20} 1.4185 [4]).

4-Methyl-4-methylazo-1-pentene (IIb) was obtained by heating compound **Vb** for 30 h at 185°C in a 88% yield (contained 12% of initial hydrazone **Vb**), bp 118–120°C, n_D^{20} 1.4298 (publ.: bp 113–115°C, n_D^{20} 1.4270 [4]).

4-Isopropylazo-1-butene (IIc) was obtained by heating hydrazone **Vc** for 20 h at 180–185°C. Yield 80%, bp 127–128°C, d_4^{20} 0.7891, n_D^{20} 1.4208, MR_D 40.54, calc. 40.08. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.23 d (6H, $2CH_3$, *J* 6.5 Hz), 2.50 q (2H, CH_2, *J* 7 Hz), 3.64 sept (1H, CH, *J* 6.5 Hz), 3.83 t (2H, CH_2N, *J* 7 Hz), 4.84–5.30 m (2H, $=CH_2$), 5.50–6.24 m (1H, =CH). Mass spectrum, *m/z* (I_{rel}, %): 127 (3), 126 (25) $[M]^+$, 111 (4), 85 (2), 84 (2), 83 (6), 70 (3), 69 (4), 57 (3), 56 (25), 55 (94), 54 (5), 53 (7), 51 (1), 44 (4), 43 (100), 42 (8), 41 (43), 40 (4), 39 (21), 38 (13), 32 (9), 30 (1); (12 эВ): 127 (9), 126 (96) $[M]^+$, 112 (1), 111 (15), 85 (3), 84 (6), 83 (21), 70 (9), 69 (11), 57 (9), 56 (63), 55 (100), 54 (7), 44 (14), 43 (58), 42 (3).

4-Isopropylazo-1-pentene (IId) was obtained by heating hydrazone **Vd** for 30 h at 180°C. Yield 60%, bp 140–142°C, d_4^{20} 0.7862, n_D^{20} 1.4214, MR_D 45.18, calc. 44.73. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.16 d (9H, $3CH_3$, *J* 6.5 Hz), 2.15–2.51 m (2H, CH_2), 3.13–3.50 m (2H, 2CHN), 4.69–5.15 m (2H, $=CH_2$), 5.28–6.01 m (1H, =CH). Mass spectrum, *m/z* (I_{rel}, %): 141 (1), 140 (8) $[M]^+$, 125 (1), 99 (1), 97 (1), 84 (1), 83 (1), 71 (3), 70 (9), 69 (53), 68 (4), 67 (3), 57 (3), 56 (5), 55 (2), 54 (1), 53 (4), 44 (2), 43 (40), 42 (9), 41 (100), 40 (3), 39 (12); (12 eV): 141 (2), 140 (18) $[M]^+$, 125 (1), 98 (1), 97 (1), 84 (4), 83 (2), 71 (12), 70 (32), 69 (100), 57 (4), 56 (13), 43 (27), 41 (8).

4-Isopropylazo-4-methyl-1-pentene (IIe) was obtained in a 45% yield. Admixture of hydrazone **Ve** about 10%, bp 155–158°C, d_D^{20} 0.7987, n_D^{20} 1.4303, MR_D 49.92, calc. 49.38. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.09 C (6H, $2CH_3$), 1.25 d (6H, $2CH_3$, *J* 6.5 Hz), 2.10 d (2H, CH_2, *J* 7 Hz), 3.53 sept (1H, CHN, *J* 6.5 Hz), 4.82–5.25 m (2H, $=CH_2$), 5.39–6.09 m (1H, =CH).

1-Isopropylazocyclopentene (IVa). To a cooled to –20°C dispersion of 3.55 g of sodium sulfate in a mixture of 25 ml of ethyl ether and 2.37 g (20 mmol) of 2-chlorocyclopentanone was added dropwise at vigorous stirring a solution of 2.96 g (40 mmol) of isopropyl-hydrazine in 10 ml of ethyl ether. The reaction mixture was additionally stirred for 30 min at –20°C and then it was allowed to slowly warm up to room temperature. The yellowish solution was passed through a 4 cm bed of silica gel on a glass frit filter and the silica gel was washed with ethyl ether. The solvent was distilled off in a vacuum, the oily residue was subjected to chromatography on a column charged with 30 g of silica gel (eluent petroleum–ethyl ether, 5:1). Yield of 1 isopropyl-azocyclopentene (**IVa**) 1.35 g (49%), yellowish fluid of sharp odor, quickly decomposing at room temperature. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 d (6H, $2CH_3$, *J* 6.6 Hz), 1.97 quint (2H, H^4, *J* 7.8 Hz), 2.40–2.56 m (4H, $H^{3,5}$), 3.68 sept (1H, CH, *J* ~6.5 Hz), 6.60 t.t (1H, H^2, ^3J 2.8, ^4J 1.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.7 ($2CH_3$), 22.0 (C^4), 27.7 (C^3), 41.2 (C^5), 67.8 (CH), 138.2 (C^2), 159.2 (C^1).

1-Isopropylazocyclohexene (IVb). To a cooled to –10°C dispersion of 2.07 g of potassium carbonate in a mixture of 1.33 g (10 mmol) of 2-chlorcyclohexanone and 25 ml of dichloromethane was added dropwise at vigorous stirring a solution of 1.48 g (20 mmol) of isopropylhydrazine in 15 ml of dichloromethane. The reaction mixture was additionally stirred for 30 min at cooling and then it was allowed to warm up to room temperature. The greenish solution was passed through a 4 cm bed of silica gel on a glass frit filter, and the silica gel was washed with dichloromethane. The solvent was distilled off in a vacuum, the oily residue was subjected to chromatography on a column charged with 25 g of silica gel (eluent petroleum ether–ethyl ether, 5:1). Yield of compound **IVb** 1.44 g (95%), greenish fluid with a pleasant sweetish odor, R_f 0.28 (hexane–ethyl ether, 9:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.26 d (6H, $2CH_3$, *J* 6.6 Hz), 1.70 m (4H, $H^{4,5}$), 2.19 m (2H) and 2.65 m (2H, $H^{3,6}$), 3.68 sept (1H, CH, *J* 6.6 Hz), 6.60 t (1H, H^2, *J* ~5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.7 ($2CH_3$), 22.0, 22.3, 22.5 ($C^{3,4,5}$), 25.7 (C^6), 67.3 (CH), 137.6 (C^2), 153.7 (C^1).

Oxidative addition of *N*-aminophthalimide (I) to azoalkenes II and III. To a cooled to –20°C dispersion of 1.62 g (10 mmol) of aminoimide **I** and 4 g (30 mmol) of fine powder of potassium carbonate in a solution of 10 mmol of azo compound in 50 ml of dichloromethane was added within 30 min a solution of 4.43 g (10 mmol) of $Pb(OAc)_4$ in a minimum volume of dichloromethane (~50 ml). The reaction mixture was stirred for 1 h and then the cold reaction mixture was filtered through 10 g of silica gel (40–100 μm). The precipitate was washed with cold dichloromethane till colorless filtrate (~50 ml). The solution obtained was evaporated in a vacuum to dryness.

In reactions with γ,δ-unsaturated azo compounds **IIa–IIe** the residue after solvent evaporation was subjected to chromatography on a column charged with 25–30 g

of silica gel (40–100 μm) eluting with a mixture benzene–ethyl acetate, 7:1, and collecting the fractions of R_f 0.5–0.3 (yellow) and 0.25–0.15 (colorless). On evaporating the solvent in a vacuum we obtained from the first fraction a yellow oily substance that slowly crystallized on standing (sometimes within 2–3 days). According to the ^{1}H NMR spectra this fraction usually contained a mixture of two regioisomeric phthalimidoazimines. From the second fraction in all cases was isolated only phthalimide.

From 0.38 g (3.9 mmol) of 4-methylazo-1-butene (**IIa**) and 0.63 g (3.8 mmol) of imide **I** after oxidation with 1.8 g (4.7 mmol) of $Pb(OAc)_4$ with added 1.5 g of potassium carbonate we obtained 0.965 g of dry residue of the reaction mixture. As a result of its separation on a column charged with 10 g of silica gel we isolated 205 mg (38%) of phthalimide of R_f 0.21–0.25 and 512 mg (49%) of a ~1.5:1 mixture of **1-(buten-3-yl)-2-methyl-3-phthalimidoazimine (VIIIa)** and **2-(buten-3-yl)-1-methyl-3-phthalimidoazimine (IXa)** of R_f 0.42–0.54, mp 79–81.5°C. ^{1}H NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 2.60 m (2H, CH_2C=), 3.47 s (N^1CH_3), 3.67 t (N^1CH_2, *J* 7 Hz), 3.91 s (N^2CH_3), 4.15 t (N^2CH_2, *J* 7 Hz), overall intensity of the latter four signals equals to 5H, intensity ratio in the pairs of singlets at 3.91 and 3.47 ppm and triplets at 3.67 and 4.15 ppm ~1.5:1; 4.90–5.30 m (2H, $=CH_2$), 5.45–6.08 m (1H, =CH), 7.70–7.94 m (4H, PiN). ^{13}C NMR spectrum (Varian CFT-20 instrument, 20 MHz, $CDCl_3$), δ, ppm: 32.3 ($\underline{C}H_2C$=, both isomers), 42.8 (N^1CH_3), 49.9 (N^2CH_3), 54.7 (N^1CH_2), 60.7 (N^2CH_2), 116.1 and 118.1 ($=CH_2$), 123.7 and 124.5 (PiN, $C^{3,6}$), 130.8 and 132.9 (PiN, $C^{1,2}$), 133.9 and 134.6 (PiN, $C^{4,5}$), 135.2 and 136.4 (=CH), 166.0 and 166.4 (C=O). IR spectrum, ν, cm^{-1}: 3090 v.w, 3039 v.w, 3018 v.w, 2940 v.w, 2880 v.w 1783 m, narrow, 1725 v.s, broad; 1650 w, 1613 w, 1498 s, 1450 m. Found, %: C 60.2; H 5.2; N 20.6. $C_{13}H_{14}N_4O_2$. Calculated, %: C 60.5; H 5.5; N 21.7.

In the experiment with 5 mmol of 4-methylazo-4-methyl-1-pentene (**IIb**) (the azo compound contained an impurity of the initial hydrazone) we failed to obtain adducts with the azo compound. The chromatographic separation of the reaction mixture yielded phthalimide (~70%) and 80 mg of unidentified substance of R_f 0.60–0.48 (benzene–ethyl acetate, 7:1) with the following ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.10 s (6H), 1.45 s (3H), 2.01 s (2H), 2.30–2.38 distorted d (?) (2H, *J* ~7 Hz), 4.90–6.30 m (3H), 7.80–8.00 m (3H).

From 1.29 g (10 mmol) of 4-isopropylazo-1-butene (**IIc**) we obtained 1.23 g of yellow oily substance of R_f 0.35–0.47 (benzene–ethyl acetate, 7:1). The reaction product partially crystallized at storage, the crystalline compound was separated and washed with a little ether. The weight of crystals was 319 mg. ^{1}H NMR spectrum (60 MHz), δ, ppm: 1.10–1.53 m (5H), 2.10–2.51 m (4H), 2.66–2.83 m (2H), 7.74–8.00 m (5H) (the intensity values of signals were approximated to the nearest integer). Found, %: C 68.7; H 5.8; N 11.7. $(C_7H_7NO)_n$. Calculated, %: C 69.4; H 5.8; N 11.6. On evaporating the filtrate 560 mg of yellow oily substance was isolated that gradually solidified at cooling furnishing a low-melting (mp 45–47.5°C) compound composed of a mixture of **(buten-3-yl)isopropyl-3-phthalimidoazimines (VIIIb)** and **(IXb)** in a ratio ~1:2.5. The product obtained was reprecipitated from 2 ml of ether by adding 1 ml of pentene to isolate 120 mg of fine crystals of mp 45–47°C. Yield of the pure azimine mixture in two runs was 22 and 28%. ^{1}H NMR spectrum (100 MHz), δ, ppm: 1.30 d (*J* 6.5 Hz), 1.38 d (*J* 6.5 Hz) (intensity ratio ~2.5:1, overall intensity 6H, $2CH_3$), 2.60 m (2H, CH_2), 3.68 t (N^1CH_2, *J* 7 Hz) and 4.08 t (N^2CH_2, *J* 7 Hz) (intensity ratio ~1:2.5, the downfield triplet is the stronger one; overall intensity 2H), 4.34 sept (N^1CH, *J* 6.5 Hz) and 4.74 sept (N^2CH, *J* 6.5 Hz, overall intensity 1H), 4.90–5.32 m (2H, $=CH_2$), 5.51–6.15 m (1H, =CH), 7.71–7.95 m (4H, PiN). Found, %: C 62.4; H 6.2; N 19.4. $C_{15}H_{18}N_4O_2$. Calculated, %: C 62.9; H 6.3; N 19.6.

In reaction of 1.52 g (10.8 mmol) of 4-isopropylazo-1-pentene (**IId**) with 1.59 g (9.8 mmol) of aminoimide **I** according to TLC data at least two products were obtained characterized by close values of R_f (0.50 and 0.45 in the system benzene–ethyl acetate, 7:1). We succeeded in their separation, although with great losses. The product of R_f 0.50 was a mixture of similar amounts of azimine regioisomers **VIIIc** and **IXc,** the former compound, **(1*Z*,2*E*)-2-isopropyl-1-(1-methyl-buten-3-yl)-3-phthalimidoazimine (VIIIc),** slightly prevailing**.** ^{1}H NMR spectrum (100 MHz), δ, ppm: 1.24–1.45 m (9H, $3CH_3$), 2.20–2.80 m (2H, CH_2C), 4.28–4.92 m (2H, $CHN^{2,3}$), 4.96–5.30 m (2H, $=CH_2$), 5.40–6.18 m (1H, =CH), 7.68–7.96 m (4H, PiN). Found, %: C 63.2; H 6.5; N 17.9. $C_{16}H_{20}N_4O_2$. Calculated, %: C 64.0; H 6.7; N 18.6. Compound of R_f 0.45 had the ^{1}H NMR spectrum identical to that of the substance of the assumed empirical formula $(C_7H_7NO)_n$ isolated in the experiment involving 4-isopropylazo-1-butene (**IIc**), mp 92–98°C (decomp.).

In the experiment with 15 mmol of 4-isopropylazo-4-methyl-1-pentene (**IIe**) we failed to isolate any adducts with the azoalkene, and only 56% of phthalimide was obtained.

Reaction with conjugated azoalkenes IIIa, IIIb. Along the general procedure from 1.67 g (10.3 mmol) of aminoimide **I** and 0.89 g (10.6 mmol) of 2 methylazo-1-propene (**IIIa**) we obtained 1.72 g of dry residue containing according to TLC data (benzene–ethyl acetate, 7:1) two substances characterized by R_f 0.38 and 0.21. A portion of this residue (0.23 g) was extracted with 15 ml of chloroform (5×3 ml). From the extract after evaporation and recrystallization from ethanol we obtained 0.175 g (76%) of phthalimide (R_f 0.21, mp 228–233°C, no melting point depression in the mixture with an authentic sample). The residue insoluble in $CHCl_3$ (32 mg, 14%) was a colorless powdery substance that completely decomposed at heating to ~150°C, reacted with dimethyl sullfoxide and dimethylformamide with self-heating and gas evolution, and was not notably soluble in any of the common organic solvents. IR spectrum, ν, cm^{-1}: 3308 v.w, 3269 w, 3110 v.w, 3070 v.w, 2927 v.w, 2863 v.w, 1793 m, 1750 and 1730 v.s, 1613 w, 1475 m. Found, %: C 58.2; H 3.1; N 16.6. $(C_8H_4N_2O_2)_n$. Calculated, %: C 60.0; H 2.52; N 17.5.

The oxidation of 1.60 g (9.9 mmol) of aminoimide **I** in the presence of 1.18 g (10.3 mmol) of 2 isopropylazo-1-propene (**IIIb**) gave similar results. GLC analysis of the reaction mixture by the method of internal reference (isooctane) showed that after addition of the total amount of $Pb(OAc)_4$ the mixture contained ~70% of initial azo compound **IIIb**. The dry residue after evaporation of the reaction mixture contained according to TLC data (benzene–ethyl acetate, 7:1) two substances characterized by R_f 0.44 and 0.20. Applying the procedure described above from the residue were isolated phthalimide (71%) and 13% (by weight) of insoluble residue possessing the same characteristics as the unidentified product from the previous run. IR spectrum, ν, cm^{-1}: 3103 v.w, 3070 v.w, 3040 v.w, 2930 v.w, 2860 v.w, 1795 m, 1745 v.s, 1615 w, 1473 m. Found, % : C 57.5; H 2.7; N 16.4. $(C_8H_4N_2O_2)_n$. Calculated, %: C 60.0; H 2.52; N 17.5.

Oxidative addition of *N*-aminophthalimide (I) to 1-isopropylazocycloalkenes IV. To a dispersion of 4.83 g (35 mmol) of potassium carbonate in 50 ml of anhydrous dichloromethane containing 5 mmol of azo compound was added within 30 min while stirring at cooling to –20×–30°C in small portions by turns 810 mg (5 mmol) of aminoimide **I** and 2.60 g (5 mmol) of lead tetraacetate containing 15% of acetic acid. The reaction mixture was stirred for 20 min at the same temperature and then it was allowed to warm to 12–16°C, was filtered through a silica gel bed 1.5–2 cm thick. Washing with dichloromethane was continued till colorless filtrate. The solvent was distilled off under reduced pressure of a water-jet pump, and the residue was subjected to further workup.

Reaction with 1-isopropylazo-1-cyclopentene (IVa). The oily residue (846 mg) was ground with 50 ml of pentane, the precipitate was filtered off (phthalimide, 324 mg). The filtrate was evaporated, the residue was applied on 30 g of silica gel, gradual elution with pentane–ether, from 5:1 to 1:1. We obtained 7 mg of the initial azo compound and 158 mg (11%) of **1 isopropylazo-6-phthalimido-6-azabicyclo-[3.1.0]hexane (Xa)**. Yellowish oily substance, R_f 0.59 (ethyl ether). ^{1}H NMR spectrum, δ, ppm: 1.11 d (*J* 6.3 Hz) and 1.13 d (*J* 5.6 Hz) (6H, $2CH_3$), 1.57–1.78 m (2H, H^3), 1.90–2.04 m (1H), 2.10–2.18 m (1H), 2.27–2.40 m (2H), 3.60 sept (1H, *i*-Pr, CH, *J* 6.5 Hz), 4.19 d (1H, H^5, *J* 2.8 Hz), 7.61–7.73 m (4H, PiN). ^{13}C NMR spectrum, δ, ppm: 19.86 (C^3), 19.90 and 19.98 ($2CH_3$), 26.3 and 27.3 ($C^{2,4}$), 54.9 (C^5), 68.1 (*i*-Pr, CH), 81.0 (C^1), 122.7 (PiN, $C^{3,6}$), 130.6 (PiN, $C^{1,2}$), 133.7 (PiN, $C^{4,5}$), 165.0 (C=O).

The last fractions contained 88 mg of phthalimide [overall amount 412 mg (56%)].

Reaction with 1-isopropylazo-1-cyclohexene (IVb). The oily residue (1.01 g) was subjected to chromatography on a column packed with 55 g of silica gel, gradual elution with pentane–ether, from 9:1 to 5:1. We obtained 130 mg (17%) of the initial azo compound and 498 mg (32, 38% taking into consideration the unreacted azo compound) of **1-isopropyl-azo-7-phthalimido-7-azabicyclo[4.1.0]heptane (Xb)**. Greenish glassy crystalline compound, mp 92–95°C. ^{1}H NMR spectrum, δ, ppm: 1.10 d and 1.11 d (6H, $2CH_3$, *J* 6.6 Hz), 1.29–1.39 m and 1.46–1.62 m (4H, $H^{3,4}$), 2.01–2.09 m (2H), 2.38 m (1H), 2.65 m (1H), 3.59 sept (1H, *i*- Pr, CH, *J* 6.6 Hz), 3.71 d (1H, H^6, *J* 4.6 Hz), 7.61–7.72 m (4H, PiN). ^{13}C NMR spectrum, δ, ppm: 19.9 and 20.0 ($2CH_3$), 20.2 ($C^{3,4}$), 23.2 and 23.3 ($C^{2,5}$), 49.1 (C^6), 67.7 (*i*-Pr, CH), 71.2 (C^1), 122.5 (PiN, $C^{3,6}$), 130.7 (PiN, $C^{1,2}$), 133.5 (PiN, $C^{4,5}$), 164.9 (PiN, C=O). Found, %: C 65.39; H 6.36; N 17.85. $C_{17}H_{20}N_4O_2$. Calculated, %: C 65.37; H 6.45; N 17.94.

The last fractions contained 119 mg (16%) of phthalimide.

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