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Oxidative Addition of *N*-Aminophthalimide to Alkenyl-4,5-dihydropyrazoles and Alkenylpyrazoles. Synthesis of Aziridinylpyrazoles

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Abstract—Oxidation of *N*-aminophthalimide with lead tetraacetate in the presence of 1,5-diaryl-3-[(*E*)-2-arylethenyl]-1*H*-pyrazoles, as well as of 1,3-diphenyl-5-[(*E*)-2-phenylethenyl]-1*H*-pyrazole, gives adducts at the exocyclic C=C bond, the corresponding phthalimidoaziridinylpyrazoles. From 1,5-diphenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-1*H*-pyrazole, only product of addition at both exocyclic C=C bonds was obtained. In the reaction with 1-phenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-5-[(*E*)-2-phenylethenyl]-1*H*-pyrazole, the adduct at the styryl C=C bond was isolated. Analogous 4,5-dihydropyrazoles, 1,5-diphenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-4,5-dihydro-1*H*-pyrazole and 1-phenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-5-[(*E*)-2-phenylethenyl]-4,5-dihydro-1*H*-pyrazole, turned out to be inert in oxidative addition of *N*-aminophthalimide.

Oxidation of many N-amino-substituted nitrogen-containing heterocycles, primarily of *N*-aminophthalimide (NAPhth) and various 3-aminoquinazolinones, in the presence of compounds having a C=C bond underlies a general procedure for the synthesis of *N*-aminoaziridine derivatives (oxidative aminoaziridination) [1–4]. Oxidative addition of *N*-aminophthalimide to various azo compounds occurs under analogous conditions and smoothly affords adducts at lone electron pair of one of the nitrogen atoms, phthalimido azo imides [5]. Formerly, it was presumed that both these reactions involve intermediate formation of the corresponding aminonitrenes. However, in 1987, Atkinson showed that, at least under usual conditions of oxidative aminoaziridination (e.g., in the oxidation of 3-aminoquinazolinones and *N*-aminophthalimide with lead tetraacetate), aziridines are formed through a different intermediate, *N*-acetoxyhydrazine, without participation of aminonitrenes [3, 4].

Taking into account that oxidative addition of *N*-acetoxyhydrazine (or aminonitrene) to olefins occurs at the π-bond and that the attack in reactions with azo compounds is directed at lone electron pair of the nitrogen atom, the question arises as to what reaction path is operative with a C=N bond. No such reactions with Schiff bases have been reported so far. The only exception is the publication by Kumar [6] who reported that oxidation of *N*-aminophthalimide with lead tetraacetate in the presence of aryl isocyanates leads to the corresponding 1-aryl-2-phthalimidodiaziridinones in good yields. However, we showed that the product obtained in such a way from phenyl isocyanate is not 1-phenyl-2-phthalimidodiaziridinone but *N*-phenyl-1,3-dioxo-1,3-dihydroisoindole-2-carboxamide [7]. It is likely to be formed via conventional nucleophilic addition to phenyl isocyanate of phthalimide resulting from oxidation of *N*-aminophthalimide. Our numerous attempts to effect oxidative addition of *N*-aminophthalimide to various compounds containing isolated, conjugated, or cumulated C=N bonds were still unsuccessful [7]. Moreover, some our experiments on oxidative addition of *N*-aminophthalimide to several compounds possessing a C=C–C=N fragment showed that neither C=N nor usually highly reactive conjugated C=C bond was involved [7].

On the other hand, Batori *et al*. [8] reported on the successful oxidative addition of an *N*-aminoheterocycle with a fairly complex structure at the exocyclic double C=C bond in 2-vinylpyridine, which can formally be regarded as a part of a C=C–C=N system [8]. We presumed that incorporation of C=N bond into an aromatic heterocycle is essential and tried to elucidate the role of this factor using as models two types of structurally related alkenyl-substituted aromatic and nonaromatic heterocyclic compounds with endocyclic C=N bond. For this purpose, we examined

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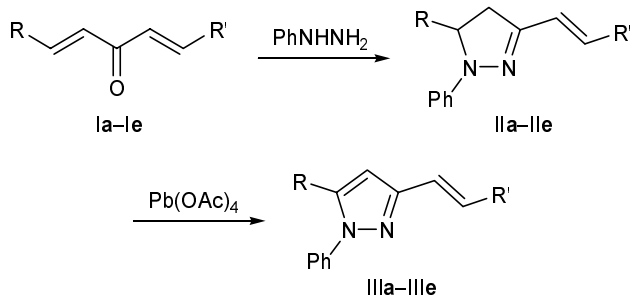
oxidative addition of *N*-aminophthalimide to alkenyl-substituted *N*-phenyl-4,5-dihydropyrazoles **II** and *N*-phenylpyrazoles **III**. Initial styryl-4,5-dihydropyrazoles **IIa**–**IIe** were synthesized from phenylhydrazine and the corresponding unsaturated ketones **Ia**–**Ie** according to the known procedures [9–12]. Dihydropyrazoles **IIa**–**IIe** were then oxidized to pyrazoles **IIIa**–**IIIe** with lead tetraacetate in methylene chloride at room temperature according to [13] (Scheme 1).

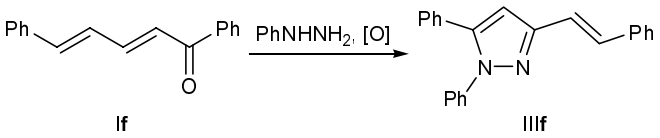
Scheme 1.



R = R' = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**); R' = PhCH=CH, R = Ph (**d**), PhCH=CH (**e**).

No expected dihydropyrazole was isolated in the reaction of phenylhydrazine with 1,5-diphenyl-2,4-pentadien-1-one (**If**) (cf. [11, 14]). Presumably, it undergoes fast oxidation with atmospheric oxygen, and the product is pyrazole **IIIf** (yield 31%, Scheme 2). 1,5-Bis(4-nitrophenyl)-1,4-pentadien-3-one failed to react with phenylhydrazine in acetic acid, and the initial compounds were recovered from the reaction mixture.

Scheme 2.

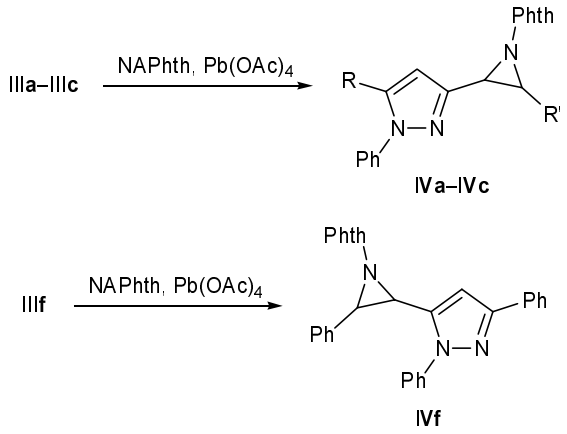


Previously reported alkenyldihydropyrazoles **IIa**–**IIe** and alkenylpyrazoles **IIIa**–**IIIc** and **IIIf** were characterized, at best, by melting points. Therefore, the structure of all these compounds was confirmed by the ^1H NMR spectra, and of pyrazoles **IIIa**–**IIIf**, by the ^{13}C NMR spectra. In particular, *trans* configuration of all exocyclic C=C bonds in molecules **IIa**–**IIe** and **IIIa**–**IIIf** follows from the corresponding vicinal proton coupling constants (^3J = 15–17 Hz). Some signals from the olefinic protons in **IIa**–**IId** are overlapped by the aromatic multiplet. However, in the ^1H NMR spectrum of dihydropyrazole **IIe** these signals appeared separately, and we were able to assign them using ^1H–^1H COSY and NOESY techniques.

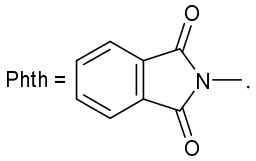
Dihydropyrazoles **IIa**–**IIe** characteristically showed in the ^1H NMR spectra three doublets of doublets in a moderate field: from 5-H at δ 5.2–5.3 ppm (a multiplet at δ 4.9 ppm for 5-styryl-substituted compound **IIe**) and from two diastereotopic protons on C^4 at δ 3.4–3.8 and 2.95–3.05 ppm. Among the two latter, the downfield signal is most likely to belong to the proton in the *cis*-position with respect to the 5-substituent. This follows from an appreciable shift of that signal upon replacement of the 5-aryl group in **IIa**–**IId** by styryl (i.e., in going to dihydropyrazole **IIe**), as well as from the coupling constant with 5-H (~12 Hz) which is very large for five-membered rings. The observed coupling constant $^3J_{4,5}$ indicates pseudoaxial orientation of both protons and an *envelope* conformation of the five-membered ring with pseudoequatorial orientation of the bulky substituent on C^5. It should be noted that the geminal coupling constant for 4-H (^2J = 16.6–16.9 Hz) also considerably exceeds its usual value (12–14 Hz). The singlet from the only proton in the heteroring of pyrazoles **IIIa**–**IIIf** appears in the ^1H NMR spectra at δ 6.7–7.0 ppm, and the C^4 nucleus characteristically gives a signal in a weakly populated region of the ^{13}C NMR spectrum, at δ_C 100–105 ppm.

Oxidative addition of *N*-aminophthalimide to alkenylpyrazoles **IIIa**–**IIIf** was carried out by adding in succession small portions of lead tetraacetate and *N*-aminophthalimide to a solution of pyrazole in methylene chloride on cooling. The structure of the isolated products (compounds **IVa**–**IVf**, Scheme 3) was confirmed by elemental analyses and ^1H and ^{13}C NMR and mass spectra. By reactions with 5-styrylpyrazoles **IIIa**–**IIIc** and **IIIf** we obtained 52–77% of addition products at the exocyclic C=C bonds, compounds **IVa**–**IVc** and **IVf**, which are the first representatives of the aziridinylpyrazole series. *N*-Aminoaziridine derivatives are characterized by slow (on the NMR time scale) inversion of the endocyclic nitrogen atom [15]. As a result, the ^1H NMR spectra of **IVa**–**IVc** and **IVf** in the δ region from 3.9 to 5.3 ppm contained four doublets corresponding to protons in the aziridine ring of both invertomers. The observed vicinal coupling constants (^3J = 5.4–6.2 Hz) are typical of *trans* arrangement of the aziridine ring protons. This is not surprising, for the configuration of double bond is known to be always conserved in oxidative aminoaziridination [1–4]. The invertomer ratio varies from ~3 : 1 to ~6 : 1, and in almost all cases signals from protons of the major invertomer appear in a stronger

Scheme 3.



R = R' = Ph (**a**), 4-ClC_6H_4 (**b**), 4-$MeOC_6H_4$ (**c**);



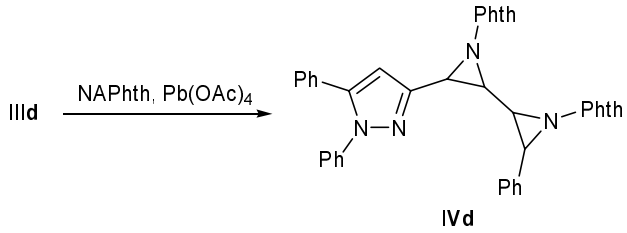
field relative to the corresponding signals of the minor invertomer. Unfortunately, the available data did not allow us to assign the configuration of these invertomers to *syn* or *anti* series (cf. [15]).

The ^{13}C NMR spectra of aziridinylpyrazoles **IVa**–**IVc** and **IVf** clearly displayed signals from the carbonyl carbon atoms in the phthalimide fragment (δ_C 165–166 ppm), carbon atoms in the aziridine ring (δ_C 45–51 ppm), and C^4 in the pyrazole ring (δ_C 104–110 ppm). The latter signal is displaced downfield by 4–5 ppm, as compared to the initial styrylpyrazoles. The other carbon signals appear in the regions typical of aromatic and olefinic carbon atoms (δ_C 113–152 ppm). In the mass spectra of **IVa**–**IVc** and **IVf** we observed the corresponding molecular ion peaks and strong fragment ion peaks with *m*/*z* 146 and/or 147 which are very characteristic of phthalimidoaziridines; they originate from elimination of the phthalimide fragment from the molecular ion.

Although isomeric pyrazoles **IIIa** and **IIIf** differ essentially in the character of conjugation between the styryl substituent and the heteroring, in both cases the corresponding aziridinylpyrazoles **IVa** and **IVf** are formed. The yield of compound **IVf** is slightly lower, presumably due to steric shielding of the exocyclic C=C bond in initial pyrazole **IIIf** by the neighboring phenyl group.

The reaction with pyrazole **IIId** having a diene fragment, performed under standard phthalimidoaziridination conditions, was accompanied by strong tarring. We succeeded in isolating only 4% of the product (compound **IVd**). Surprisingly, it was formed as a result of addition of two molecules of *N*-aminophthalimide at both exocyclic C=C bonds of the substrate (Scheme 4).

Scheme 4.



The structure of bis-adduct **IVd** follows from its elemental composition and NMR spectra. The ^1H NMR spectrum of **IVd** contains three sets of aziridine proton signals at a ratio of ~6:6:1 (δ 3–5 ppm); their overall intensity corresponds to four rather than two protons. All coupling constants for the doublet signals range from 5.0 to 6.5 Hz, indicating *trans* configuration of protons in the aziridine rings. This means that the presence of several forms is not the result of distortion of stereoselectivity in the addition. On the one hand, the reaction could give rise to two diastereoisomeric bis-adducts via addition from the same or different sides of the formal plane of the diene moiety; on the other hand, slow inversion of the aziridine nitrogen atoms implies formation of four invertomers for each of the above diastereoisomers. However, we cannot still determine the steric structure of the isomeric species.

The upfield region of the ^{13}C NMR spectrum of **IVd** (δ_C 43–50 ppm) contained eight signals from the aziridine carbon atoms in the two major stereoisomers, and in the downfield region (δ_C 164–166 ppm) we observed signals from the imide carbonyl carbon atoms, two of which overlapped each other. Signals from C^4 in the pyrazole ring (δ_C ~110 ppm) appeared separately from the aromatic carbon signals. No molecular ion peak (*m*/*z* 668) was present in the mass spectrum of bis-adduct **IVd**, while the heaviest ions with *m*/*z* 522 [*M* – 146] and 521 [*M* – 147] corresponded to loss of the phthalimide residue, which is typical of phthalimidoaziridines.

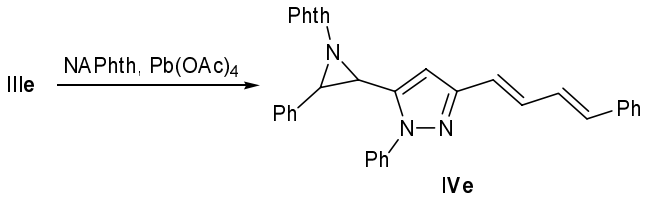
Thus the structure of bis-adduct **IVd** unambiguously follows from the spectral data. Its formation is quite unusual, for oxidative addition of *N*-aminophthalimide simultaneously at both double bonds of a diene system was not reported previously. The only close analogy may be the behavior of the cumulated

diene system in methyl 2-methyl-2,3-butadienoate which gave rise only to the corresponding bis-adduct in 14% yield [16].

The isolation of only bis-adduct **IVd** may be interpreted in terms of low stability of initially formed vinylaziridine (or vinylaziridines?) which readily undergoes tarring during the reaction and isolation procedure. In order to trap the above intermediate more successfully we used stoichiometric amounts of the reactants, i.e., 2 equiv of NAPhth and $Pb(OAc)_4$ with respect to initial pyrazole **IIId**. We thus succeeded in raising the yield of bis-adduct **IVd** to 25%.

Taking into account that the substitution pattern in pyrazole **IIIe** is related to both compound **IIId** and **IIIf**, we anticipated the oxidative addition of *N*-aminophthalimide to occur at both styryl and conjugated diene fragment. In this case, up to 3 equiv of the aziridinating agent could add. However, the reaction under standard conditions using 1 equiv of the aziridinating agent afforded 24% of monoadduct **IVe** as the only isolated product (Scheme 5).

Scheme 5.



The mass spectrum of compound **IVe** contained a strong peak from the molecular ion with *m*/*z* 534. In the ^{1}H NMR spectrum of **IVe** we observed characteristic doublet signals in the region δ 3.8–5.1 ppm from protons in the aziridine ring of two invertomers at a ratio of ~6:1. As in the above cases, the coupling constant ^3J = 5.6 Hz indicated *trans* configuration of substituents in the aziridine ring, and the lack of additional splitting unambiguously determined the site of addition. The downfield region of the spectrum, apart from signals from protons in the aromatic and phthalimide fragments, contained a singlet from 4-H in the pyrazole ring and (unlike the other isolated aziridine derivatives), an unresolved signal from four olefinic protons in the region δ 6.55–7.05 ppm. The ^{13}C NMR spectrum of the product displayed two signals from carbon atoms in the aziridine ring of the major invertomer, carbonyl carbon signal at δ_C 165.6 ppm, signal from C^4 in the pyrazole ring at δ_C 103.2 ppm, and a number of signals from aromatic and olefinic carbon atoms at δ_C 122–139 ppm.

Insofar as the yield of monoadduct **IVe** in the reaction with pyrazole **IIIe** was much lower than the yield of analogous compound **IVf** from pyrazole **IIIf**, we believe that oxidative addition of *N*-aminophthalimide largely occurs at the diene moiety to produce unstable vinylaziridines. By analogy with compound **IIId** we made an attempt to detect them by raising the amount of the aziridinating agents. In fact, in the ^{1}H NMR spectra of the reaction mixtures obtained with 2–3 equiv of NAPhth and $Pb(OAc)_4$ we observed signals from both monoadduct **IVe** and other possible products (δ 3–5.5 ppm). However, we failed to isolate these products as individual substances by recrystallization or preparative chromatography.

The first attempt to effect oxidative addition of *N*-aminophthalimide to styryldihydropyrazole **IIa** was made by Kumar [6] and was unsuccessful. Therefore, in the present work we used dihydropyrazoles **IId** and **IIe** with different conjugated bond systems. The reactions were carried out according to the same procedure as with pyrazoles **IIIa**–**IIIf**. However, we failed to isolate the corresponding phthalimidoaziridines. In both cases, a large amount of the initial compounds was recovered and phthalimide was formed. The latter is a usual product in reactions with weakly reactive substrates [17]. This result may be expected for dihydropyrazole **IId**, but it was quite surprising for compound **IIe** whose molecule includes both Ph–C=C–C=C–C=N bond sequence and an isolated styryl fragment. Styrene and its derivatives are known to smoothly react with *N*-aminophthalimide (for example, the yield of the corresponding aziridine from *trans*-β-methylstyrene is 34% [18]; see also [1–4]), while the effect of the C=N bond on the remote styryl substituent could seemingly be neglected.

To conclude, we can state that oxidative addition of *N*-aminophthalimide to unsaturated compounds containing a C=N bond is successful only when that bond is a part of an aromatic system. Presumably, in other cases intially formed aminonitrenoid (or aminonitrene) attacks just the C=N bond (most probably, at the lone electron pair on the nitrogen atom) to produce an intermediate incapable of forming adducts at C=C bonds.

EXPERIMENTAL

The elemental compositions were determined on a Hewlett–Packard HP-185B C,H,N-analyzer. The ^{1}H and ^{13}C NMR spectra ((300 and 75.4 MHz, respectively) were recorded on a Bruker DPX-300 spectrometer from solutions in $CDCl_3$; the chemical shifts were

measured relative to the solvent signals (δ 7.26 ppm, δ_C 77.0 ppm). Signals in the ^{13}C NMR spectra were assigned using DEPT sequence. The mass spectra (electron impact, 70 eV) were run on an MKh-1321 instrument. The progress of reactions and the purity of products were monitored by thin-layer chromatography on Silufol UV-254 plates.

N-Aminophthalimide was synthesized by the procedure described in [19]. 1,5-Diaryl-1,4-pentadien-3-ones **Ia**–**Ic** and tetraenone **Ie** were prepared as described in [20], and 1,7-diphenyl-1,4,6-heptatrien-3-one (**Id**) and 1,5-diphenyl-2,4-pentadien-1-one (**If**) were obtained according to [21] and [14], respectively.

1,5-Diaryl-3-[(*E*)-2-arylethenyl]-4,5-dihydro-1*H*-pyrazoles IIa–IIc and 1,5-diphenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-4,5-dihydro-1*H*-pyrazole (IId) (*general procedure*****).** An equimolar amount of phenylhydrazine was added to a 0.4 M solution of the corresponding unsaturated ketone in glacial acetic acid. The mixture was heated for 5 min under reflux and left overnight. The precipitate was filtered off, washed with alcohol, and dried in air.

1,5-Diphenyl-3-[(*E*)-2-phenylethenyl]-4,5-dihydro-1*H*-pyrazole (IIa). Yield 69%, mp 156°C; published data [13]: mp 152–153°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.05 d.d (1H, 4-H, *J* = 7.1, 16.7), 3.75 d.d (1H, 4-H, *J* = 12.4, 16.7), 5.28 d.d (1H, 5-H, *J* = 7.1, 12.4), 6.56 d (1H, =CH, *J* = 16.3), 6.80–7.46 m (16H, H_{arom}, =CH).

5-(4-Chlorophenyl)-3-[(*E*)-2-(4-chlorophenyl)-ethenyl]-1-phenyl-4,5-dihydro-1*H*-pyrazole (IIb). Yield 72%, mp 210–212°C; published data [10]: mp 212°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.99 d.d (1H, 4-H, *J* = 6.6, 16.8), 3.75 d.d (1H, 4-H, *J* = 12.3, 16.8), 5.27 d.d (1H, 5-H, *J* = 6.6, 12.3), 6.50 d (1H, =CH, *J* = 16.3), 6.80–7.40 m (14H, H_{arom}, =CH).

5-(4-Methoxyphenyl)-3-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1-phenyl-4,5-dihydro-1*H*-pyrazole (IIc). Yield 45%, mp 159–163°C; published data [10]: mp 159°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.00 d.d (1H, 4-H, *J* = 6.6, 16.9), 3.69 d.d (1H, 4-H, *J* = 12.3, 16.9), 3.80 s (3H, OCH_3), 3.84 s (3H, OCH_3), 5.20 d.d (1H, 5-H, *J* = 6.6, 12.3), 6.52 d (1H, =CH, *J* = 16.3), 6.76–7.52 m (14H, H_{arom}, =CH).

1,5-Diphenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-4,5-dihydro-1*H*-pyrazole (IId). Yield 31%, mp 106–108°C; published data [12]: mp 107°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.98 d.d (1H, 4-H, *J* = 6.5, 16.7), 3.68 d.d (1H, 4-H, *J* = 12.4, 16.7), 5.26 d.d (1H, 5-H, *J* = 6.5, 12.4), 6.42 d.d (1H, =CH, *J* = 10.5, 15.2), 6.60 d (1H, =CH, *J* = 15.6), 6.76–7.47 m (17H, H_{arom}, =CH).

1-Phenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-5-[(*E*)-2-phenylethenyl]-4,5-dihydro-1*H*-pyrazole (IIe). Phenylhydrazine, 2.6 ml (2.8 g, 26 mmol), was added to a solution of 7.5 g (26 mmol) of 1,9-diphenyl-1,3,6,8-nonatetraen-5-one (**Ie**) in 20 ml of glacial acetic acid. The mixture was heated for 15 min on a boiling water bath, diluted with 30 ml of ethanol, and heated for an additional 30 min. It was then cooled, and the precipitate was filtered off, washed with ethanol, and dried in air. Yield 19%, mp 141–143°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.95 d.d (1H, 4-H, *J* = 6.5, 16.6), 3.68 d.d (1H, 4-H, *J* = 11.6, 16.6), 4.91 m (1H, 5-H), 6.26 d.d (1H, *J* = 7.4, 15.9), 6.48 d.d (1H, *J* = 10.6, 15.6), 6.65 d (1H, *J* = 15.9), 6.68 d (1H, *J* = 15.6), 6.78 d (1H, *J* = 15.6), 6.97 d.d (1H, *J* = 10.6, 15.6); 6.85 t (1H) and 7.10–7.53 m (14H) (H_{arom}); assignment according to the COSY and NOESY data, δ, ppm: 6.26 d.d and 6.65 d (1-H and 2-H in 2-C_6H_5); 6.78 d (1-H), 6.48 d.d (2-H), 6.97 d.d (3-H), 6.68 d (4-H) (C_6H_5CH=CH–CH=CH). Dihydropyrazole **IIe** was noted in patent [22].

Oxidation of alkenyldihydropyrazoles IIa–IIe to alkenylpyrazoles IIIa–IIIe (*general procedure*****).** A solution of dihydropyrazole **IIa**–**IIe** in methylene chloride was treated with 1.5 equiv of lead tetraacetate at room temperature. After 30 min, the mixture was filtered through a layer of silica gel, and the sorbent was washed with methylene chloride until colorless filtrate. The filtrate was combined with the washings and evaporated, the residue was crystallized by treatment with diethyl ether, and the crystals were filtered off, washed with diethyl ether, and recrystallized from alcohol.

1,5-Diphenyl-3-[(*E*)-2-phenylethenyl]-1*H*-pyrazole (IIIa). Yield 89%, mp 133°C; published data [13]: mp 141°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 6.75 s (1H, 4-H), 7.21 d (1H, =CH, *J* = 16.7), 7.24 d (1H, =CH, *J* = 16.7); 7.25–7.55 m (13H) and 7.54 d (2H, *J* = 7.7) (H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 104.99 (C^4), 120.42 (=CH), 125.11, 126.50, 127.38 (C^p), 127.72 (C^p), 128.32 (C^p), 128.45, 128.67, 128.70, 128.90, 130.41 (C^i), 130.67 (=CH), 137.08 (C^i), 139.97 (C^i), 144.16 (C^5), 151.16 (C^3).

5-(4-Chlorophenyl)-3-[(*E*)-2-(4-chlorophenyl)-ethenyl]-1-phenyl-1*H*-pyrazole (IIIb). Yield 69%, mp 140–142°C; published data: mp 145–146 [13], 140–141°C [14]. ^1H NMR spectrum, δ, ppm (*J*, Hz):

6.72 s (1H, 4-H), 7.16 s (2H, HC=CH), 7.18 d (2H, J = 8.1), 7.27–7.38 m (9H) and 7.45 d (2H, J = 8.1) (H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 105.17 (C^4), 120.82 (=CH), 125.12, 127.64, 127.72 (C^p), 128.74 (C^i), 128.78, 128.87, 129.07, 129.47 (=CH), 129.89, 133.36 (C^i), 134.49 (C^i), 135.50 (C^i), 139.66 (C^i), 143.01 (C^5), 150.91 (C^3).

5-(4-Methoxyphenyl)-3-[(*E*)-2-(4-methoxyphenyl)ethenyl]-1-phenyl-1*H*-pyrazole (IIIc). Yield 85%, mp 166–168°C. ^1H NMR spectrum, δ, ppm (J, Hz): 3.81 s (3H, OCH_3), 3.83 s (3H, OCH_3), 6.66 s (1H, 4-H); 6.84 d (2H, J = 8.5), 6.92 d (2H, J = 8.5), 7.12 d (2H, H_{arom}, J = 8.5), 7.18 d (2H, H_{arom}, J = 9.2), 7.27–7.36 m (3H, H_{arom}), 7.47 d (2H, H_{arom}, J = 8.5), 7.33 s (2H, HC=CH). ^{13}C NMR spectrum, δ_C, ppm: 104.23 (C^4), 113.89, 114.34, 118.38 (=CH), 122.84 (C^i), 125.11, 127.21 (C^p), 127.71, 128.85, 129.94 (C^i), 129.98, 130.19 (=CH), 140.10 (C^i), 143.94 (C^5), 151.35 (C^3), 159.37 (C–O), 159.58 (C–O).

1,5-Diphenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-1*H*-pyrazole (IIId). Yield 70%, mp 128–130°C. ^1H NMR spectrum, δ, ppm (J, Hz): 6.68 s (1H, 4-H), 6.67–7.36 m (17H) and 7.45 d (2H, J = 7.3) (H_{arom}, =CH). ^{13}C NMR spectrum, δ_C, ppm: 105.13 (C^4), 124.25 (=CH), 125.12, 126.43, 127.38 (C^p), 127.59 (C^p), 128.31 (C^p), 130.41 (C^i), 137.24 (C^i), 139.95 (C^i), 144.13 (C^5), 151.13 (C^3).

1-Phenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-5-[(*E*)-2-phenylethenyl]-1*H*-pyrazole (IIIe). Yield 71%, oily substance. ^1H NMR spectrum, δ, ppm (J, Hz): 6.83 s (1H, 4-H), 6.67–7.53 m (18H, H_{arom}, =CH), 7.12 d (1H, =CH, J = 16.7). ^{13}C NMR spectrum, δ_C, ppm: 101.19 (C^4), 115.50 (=CH), 124.21 (=CH), 125.35, 126.44, 126.65, 127.59 (C^p), 127.95 (C^p), 128.33 (C^p), 128.62, 128.76, 129.01 (=CH), 129.23, 131.25 (=CH), 131.29 (=CH), 133.12 (=CH), 136.37 (C^i), 137.25 (C^i), 139.40 (C^i), 142.25 (C^5), 151.13 (C^3).

1,3-Diphenyl-5-[(*E*)-2-phenylethenyl]-1*H*-pyrazole (IIIf). Phenylhydrazine, 2.12 ml (2.3 g, 21.4 mmol), was added to a solution of 5 g (21.4 mmol) of 1,5-diphenyl-2,4-pentadien-1-one (**If**) in 30 ml of glacial acetic acid, and the mixture was heated for 12 h on a boiling water bath. The solvent was distilled off, 15 ml of alcohol was added to the residue, and the precipitate was filtered off, washed with alcohol, and recrystallized from alcohol. Yield 2.14 g (31%), mp 142–144°C. ^1H NMR spectrum, δ, ppm (J, Hz): 6.95 d (1H, =CH, J = 16.4), 7.00 s (1H, 4-H), 7.16 d (1H, =CH, J = 16.4), 7.27–7.61 m (13H) and 7.92 d (2H, J = 7.2) (H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 101.14 (C^4), 115.67 (=CH), 125.53, 125.53 (C^p), 125.78 (C^p), 126.64, 127.96, 128.30 (C^p), 128.60, 128.75, 129.23, 132.09 (=CH), 133.01 (C^i), 136.43 (C^i), 139.58 (C^i), 142.51 (C^5), 151.98 (C^3).

Oxidative addition of *N*-aminophthalimide to arylethenyl-1*H*-pyrazoles III (*general procedure*). *N*-Aminophthalimide, 1.62 g (10 mmol), and lead tetraacetate, 4.43 g (10 mmol), were added in small portions (one by one) over a period of 15 min to a suspension of 10 mmol of pyrazole **III** and 6.9 g (50 mmol) of potassium carbonate in 80 ml of methylene chloride under stirring and cooling to –12°C. The mixture was stirred for 30 min and filtered through a layer of silica gel, and the inorganic salts were washed with methylene chloride until colorless filtrate. The filtrate was evaporated, and diethyl ether (in the reactions with pyrazoles **IIIa**–**IIIc**, **IIIe**, and **IIIf**) or a 1:1 (by volume) diethyl ether–hexane mixture (in the reaction with **IIId**) was added to the residue. The crystalline product was filtered off, washed with diethyl ether, and recrystallized from ethanol (**IVa**–**IVc**, **IVf**) or butanol (**IVd**, **IVe**).

1,5-Diphenyl-3-(3-phenyl-1-phthalimidoaziridin-2-yl)-1*H*-pyrazole (IVa). Yield 74%, mp 182–184°C. A mixture of two invertomers at a ratio of ~4:1 (according to the NMR data). ^1H NMR spectrum, δ, ppm (J, Hz): major invertomer: 4.29 d (J = 5.5), 5.16 d (J = 5.5), 6.83 s (aziridine protons and 4-H); minor invertomer: 4.51 d (J = 6), 5.32 d (J = 6), 7.01 s (aziridine protons and 4-H) (total of 3H); both invertomers: 6.95 d (J = 7.1), 7.24–7.65 m, 7.79 d (J = 7.1) (total of 15H, H_{arom}), 7.83–7.95 m (4H, C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 47.65 and 48.74 (C_{azir}); 109.45 (C^4), 124.80 (C^b), 126.62, 127.18, 127.37 (C^p), 128.02 (C^p), 128.08 (C^p), 128.32, 128.50, 129.93 (C^i), 130.45 (C^a), 133.67 (C^c), 139.46 (C^i), 139.58 (C^i); 143.68 and 145.11 (C^3, C^5); 165.11 (C=O). Mass spectrum, m/z (I_{rel}, %): 482 (11) $[M]^+$, 465 (10), 464 (18), 335 (40) [M – PhthNH], 233 (16), 180 (35), 147 (40) [PhthNH], 105 (30), 104 (68), 103 (30), 91 (20), 77 (100), 76 (63), 64 (10), 52 (28), 51 (33). Found, %: C 77.04; H 4.84; N 11.61. $C_{31}H_{22}N_4O_2$. Calculated, %: C 77.18; H 4.56; N 11.62.

5-(4-Chlorophenyl)-3-[3-(4-chlorophenyl)-1-phthalimidoaziridin-2-yl]-1-phenyl-1*H*-pyrazole (IVb). Yield 77%, mp 202–204°C. A mixture of two invertomers at a ratio of 77:23 (according to the NMR data). ^1H NMR spectrum, δ, ppm (J, Hz): major invertomer: 4.21 d (J = 5.4), 5.11 d (J = 5.4), 6.83 s (aziridine protons and 4-H); minor invertomer: 4.47 d

(J = 5.8), 5.23 d (J = 5.8), 7.00 s (aziridine protons and 4-H) (total of 3H); both invertomers: 6.92 d (J = 7.3), 7.16–7.6 m, 7.20 d (J = 8), 7.71 d (J = 8) (H_{arom}, total of 13H); 7.83–7.94 m (4H, *o*-C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 47.54 and 48.08 (C_{azir}); 109.61 (C^4), 124.81 (C^b), 127.69 (C^p); 128.56, 128.69, 128.80, 129.82 (C^o, C^m); 128.25, 134.48, 134.98, 139.28, 142.57, 144.96, 148.83 (C^i, C^p, C^3, C^5); 130.34 (C^a), 133.77 (C^c), 165.03 (C=O). Mass spectrum, m/z (I_{rel}, %): 552 (18) [M + 2], 550 (27) $[M]^+$, 416 (38), 415 (42), 413 (100), 412 (54), 405 (46), 403 (63) [M – PhthNH], 272 (23), 270 (71), 147 (88) [PhthNH], 130 (48), 104 (77), 77 (67), 76 (69), 50 (31). Found, %: C 67.28; H 3.66; N 10.22. $C_{31}H_{20}Cl_2N_4O_2$. Calculated, %: C 67.51; H 3.63; N 10.16.

5-(4-Methoxyphenyl)-3-[3-(4-methoxyphenyl)-1-phthalimidoaziridin-2-yl]-1-phenyl-1*H*-pyrazole (IVc). Yield 77%, mp 165–167°C. A mixture of two invertomers at a ratio of 73:27 (according to the NMR data). ^1H NMR spectrum, δ, ppm (J, Hz): major invertomer: 3.97 s, 4.03 s, 4.26 d (J = 5.8), 5.09 d (J = 5.8), 6.75 s (MeO, aziridine protons, 4-H); minor invertomer: 3.93 s, 4.00 s, 4.26 d (J = 6.2), 5.05 d (J = 6.2), 6.85 s MeO, aziridine protons, 4-H) (total of 9H); both invertomers: 6.92–7.40 m, 7.50–7.56 m, 7.67 d (J = 8.7), 7.71 d (J = 8.7) (H_{arom}, total of 13H); 7.81–7.95 m (4H, *o*-C_6H_4). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 47.46 and 48.53 (C_{azir}); 55.20 and 55.31 (MeO); 108.88 (C^4); 113.77, 113.98, 124.81, 128.46, 128.60, 129.94 (C^o, C^m); 122.69 (C^b), 127.25 (C^p); 125.39, 127.69, 139.73, 143.50, 145.16, 159.51 (C^i, C^p, C^3, C^5); 130.86 (C^a), 133.62 (C^c), 165.12 (C=O). Mass spectrum, m/z (I_{rel}, %): 552 (18) [M + 2], 550 (27) $[M]^+$, 416 (38), 415 (42), 413 (100), 412 (54), 405 (46), 403 (63) [M – PhthNH], 272 (23), 270 (71), 147 (88) [PhthNH], 130 (48), 104 (77), 77 (67), 76 (69), 50 (31). Found, %: C 72.98; H 5.03; N 10.00. $C_{33}H_{26}N_4O_4$. Calculated, %: C 73.06; H 4.80; N 10.33.

Reaction of *N*-aminophthalimide with 1,5-diphenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-1*H*-pyrazole (IIId). *a*. Following the general procedure, from 2.12 g (6.1 mmol) of pyrazole **IIId**, 4.2 g (31 mmol) of potassium carbonate, 987 mg (6.1 mmol) of *N*-aminophthalimide, and 2.7 g (6.1 mmol) of lead tetraacetate in 30 ml of methylene chloride we obtained 0.18 g (4%) of bis-adduct **IVd**.

1,5-Diphenyl-3-[3-(3-phenyl-1-phthalimidoaziridin-2-yl)-1-phthalimidoaziridin-2-yl]-1*H*-pyrazole (IVd). mp 228–230°C. A mixture of three stereoisomers at a ratio of 46:46:8 (according to the NMR data). ^1H NMR spectrum, δ, ppm (J, Hz): two major isomers: 3.05 d.d (J = 5.1, 6.5), 4.04 d (J = 5.8), 4.08–4.17 m, 4.29 d (J = 5.1), 4.48 m, 4.75 d (J = 5.4) (aziridine protons); minor isomer: 3.58 t (J = 5.0), 3.97 d (J = 5.4), 4.51 t (J = 5.4), 4.80 d (J = 5.4) (total of 4H); all isomers: 6.67 s (1H, 4-H); 6.51 d (J = 7.7), 6.74 d (J = 6.9), 6.95–7.53 m (H_{arom}, total of 15H; 7.55–7.79 m (8H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: two major isomers: 43.60, 43.87, 43.99, 44.94, 46.53, 47.82, 49.79, 49.92 (C_{azir}); 109.83, 110.24 (C^4); 122.71 (2C), 124.49, 124.77 (C^b); 127.34, 128.10, 128.25, 128.30, 128.37, 128.46, 128.55, 128.63, 129.58 (C^o, C^m); 127.05, 127.30, 127.99, 128.68 (C^p); 129.98, 130.16, 130.65, 130.70 (C^a); 133.54, 133.66 (2C), 133.82 (C^c); 136.10, 139.41, 139.61, 143.43, 143.61, 144.10, 144.59 (C^i, C^3, C^5); 164.97, 165.06, 165.63 (4C) (C=O). Mass spectrum, m/z (I_{rel}, %): 522 (15) [M – 146], 521 (38) [M – PhthNH], 519 (26), 518 (21), 378 (33), 374 (21), 373 (18), 272 (15), 237 (18), 236 (100), 180 (36), 147 (59) [PhthNH], 130 (35), 105 (21), 104 (85), 103 (26), 77 (74), 76 (74), 51 (18), 50 (31). Found, %: C 73.49; H 4.23; N 12.34. $C_{41}H_{28}N_6O_4$. Calculated, %: C 73.65; H 4.19; N 12.58.

b. From 2.03 g (5.8 mmol) of pyrazole **IIId**, 8.03 g (58 mmol) of potassium carbonate, 1.89 g (11.7 mmol) of *N*-aminophthalimide, and 5.16 g (11.7 mmol) of lead tetraacetate in 30 ml of methylene chloride we obtained 0.99 g (25%) of compound **IVd**. The product was identical in the NMR spectra to a sample prepared as described in *a*.

Reaction of *N*-aminophthalimide with 1-phenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-5-[(*E*)-2-phenylethenyl]-1*H*-pyrazole (IIIe). *a*. Following the general procedure, from 209 mg (0.56 mmol) of pyrazole **IIIe**, 386 mg (2.8 mmol) of potassium carbonate, 91 mg (0.56 mmol) of *N*-aminophthalimide, and 248 mg (0.56 mmol) of lead tetraacetate in 20 ml of methylene chloride we obtained 71 mg (24%) of compound **IVe**.

1-Phenyl-3-[(1*E*,3*E*)-4-phenyl-1,3-butadienyl]-5-(3-phenyl-1-phthalimidoaziridin-2-yl)-1*H*-pyrazole (IVe). mp 189–191°C. A mixture of two invertomers at a ratio of 85:15 (according to the NMR data). ^1H NMR spectrum, δ, ppm (J, Hz): major invertomer: 3.84 d (J = 5.6), 4.70 d (J = 5.6) (aziridine protons); minor invertomer; 3.94 d (J = 5.6), 5.04 d (J = 5.6) (aziridine protons) (total of 2H); both invertomers: 6.23 s (1H, 4-H), 6.55–7.05 m (4H, CH=CH), 7.20–7.65 m (15H, H_{arom}), 7.55–7.85 m (4H, C_6H_4). ^{13}C NMR spectrum,

δ_C, ppm: 45.02, 50.56 (C_{azir}); 103.24 (C^4), 123.26 (C^b), 125.75, 127.02, 127.67 (C^p), 128.36 (C^p), 128.44 (C^p), 128.62, 128.65, 129.00 (C^i), 130.45 (C^a), 134.28 (C^c); 135.41, 135.68, 137.07, 139.07 (C^i, C^3, C^5); 165.61 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 535 (29) [*M* + 1], 534 (76) $[M]^+$, 458 (29), 457 (76), 388 (24), 387 (62) [*M* – PhthNH], 386 (20), 311 (26), 310 (100), 283 (29), 236 (47), 207 (26), 206 (20), 172 (32), 147 (71) [PhthNH], 130 (26), 128 (26), 104 (71), 103 (28), 91 (28), 77 (56), 76 (71), 50 (38). Found, %: C 78.64; H 4.88; N 10.40. $C_{35}H_{26}N_4O_2$. Calculated, %: C 78.65; H 4.87; N 10.49.

b. The reaction was carried out with 311 mg (0.83 mmol) of pyrazole **IIIe** in 20 ml of methylene chloride, 1.15 g (8.3 mmol) of potassium carbonate, 269 mg (1.66 mmol) of *N*-aminophthalimide, and 737 mg (1.66 mmol) of lead tetraacetate. According to the ^{1}H NMR data, the reaction mixture contained adduct **IVe** and unidentified products which gave rise to signals in the region δ 3–4 ppm, typical of aziridine protons. We failed to isolate these products from the reaction mixture by recrystallization or preparative chromatography. Presumably, the mixture contained unstable bis- and tris-adducts.

1,3-Diphenyl-5-(3-phenyl-1-phthalimidoaziridin-2-yl)-1*H*-pyrazole (IVf). Yield 24%, mp 215–216°C. A mixture of two invertomers at a ratio of 85:15 (according to the NMR data). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): major invertomer: 3.87 d (*J* = 5.8), 4.74 d (*J* = 5.8), 6.38 s (aziridine protons, 4-H); minor invertomer: 3.96 d (*J* = 5.7), 5.07 d (*J* = 5.7), 6.92 s (aziridine protons, 4-H) (total of 3H); both invertomers: 7.25–7.75 m (17H, H_{arom}); 7.91 d (*J* = 7.3, minor invertomer) and 8.06 d (*J* = 7.3, major invertomer) (1H each, *o*-H in 3-Ph). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 45.16, 50.57 (C_{azir}); 103.98 (C^4), 122.65 (C^b), 125.68, 125.88, 127.02, 128.00 (C^p), 128.35 (C^p), 128.42 (C^p), 128.53, 128.64, 129.37, 130.00 (C^a), 134.24 (C^c); 132.60, 135.44, 135.92, 139.22, 151.30 (C^i, C^3, C^5); 165.62 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 482 (24) $[M]^+$, 379 (24), 378 (54), 335 (43) [*M* – PhthNH], 246 (40), 237 (24), 236 (96), 232 (33), 231 (100), 147 (28) [PhthNH], 130 (28), 104 (39), 77 (54), 76 (35). Found, %: C 77.04; H 4.63; N 11.52. $C_{31}H_{22}N_4O_2$. Calculated, %: C 77.18; H 4.56; N 11.62.

Attempted oxidative addition of *N*-aminophthalimide to 4,5-dihydropyrazoles IId and IIe. *N*-Aminophthalimide, 86 mg (0.53 mmol), and lead tetraacetate, 236 mg (0.53 mmol), were added in small portions (one by one) over a period of 15 min to a suspension of 0.53 mmol of dihydropyrazole **IId** or **IIe** and 366 mg (0.53 mmol) of potassium carbonate in 20 ml of methylene chloride under stirring and cooling to –12°C. The mixture was stirred for 30 min and filtered through a layer of silica gel, and the inorganic salts and the sorbent were washed with methylene chloride until colorless washings. The filtrate was evaporated, the residue was treated with diethyl ether, and the crystals were filtered off and washed with diethyl ether. In both cases, the product was identified as phthalimide. Removal of the solvent from the ether solution, followed by crystallization of the residue with hexane, gave initial dihydropyrazoles **IId** and **IIe**. No possible adducts were detected in the reaction mixtures by ^{1}H NMR spectroscopy and thin-layer chromatography.

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