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Dedicated to Full Member of the Russian Academy of Sciences G.A. Tolstikov on his 80th anniversary

Thermal Transformations of Alk-1-enyl-*N*-phthalimidoaziridines

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Abstract—Thermolysis of alk-1-enyl-*N*-phthalimidoaziridines leads to products of 1,5-electrocyclization of intermediate azomethine ylides with participation of C=C bonds. If acyl or alkoxycarbonyl substituent is present in the aziridine ring, the C=O bond is also involved. Thermolysis of the title compounds in the presence of *N*-phenylmaleimide or dimethyl acetylenedicarboxylate under analogous conditions gives products of 1,3-dipolar cycloaddition of azomethine ylides to the double or triple bond of the dipolarophile.

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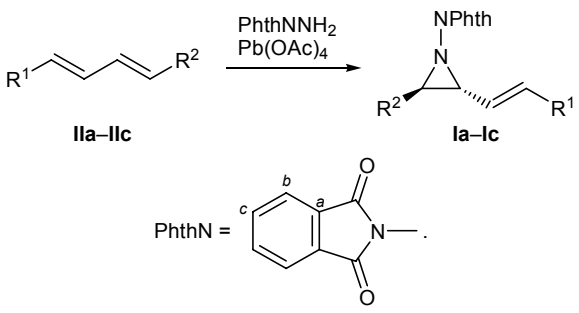
Thermally or photochemically induced cleavage of C–C bond in a strained aziridine ring generates so-called azomethine ylides (1,3-dipoles) [1] whose further transformations may follow several pathways. From the synthetic viewpoint, the most interesting is 1,3-dipolar cycloaddition of azomethine ylides at multiple bonds of dipolarophiles, which leads to the formation of various nitrogen-containing heterocycles [1, 2]. Furthermore, azomethine ylides conjugated to C=O, C=N, and C=C bonds are capable of undergoing intramolecular 1,5-electrocyclization to form other five-membered nitrogen-containing heterocycles [3–8].

Analogous transformations of *N*-aminoaziridine derivatives provide synthetic routes to difficultly accessible *N*-amino heterocycles. For example, we recently demonstrated the possibility for thermal generation of azomethine ylides from 2,3-disubstituted *N*-phthalimidoaziridines and their participation in subsequent 1,3-dipolar cycloadditions [9–11]. On the other hand, 2-acyl-*N*-phthalimidoaziridines on heating are readily converted into oxazoles, which may be regarded as the result of 1,5-electrocyclization of intermediate azomethine ylides accompanied by elimination of phthalimide and aromatization [6–8].

The goal of the present work was to find out whether 1,5-electrocyclization of alk-1-enyl azomethine ylides generated by thermolysis of the corresponding *N*-phthalimidoaziridine derivatives is possible and estimate prospects in their use in 1,3-dipolar cycloaddition reactions. As substrates we selected vinylaziridines **Ia**–**If**, some of which contain substituents with a C=O bond, taking into account that the latter can also be involved in 1,5-electrocyclization of intermediate azomethine ylides. *N*-Phenylmaleimide (PMI) and dimethyl acetylenedicarboxylate (DMAD) were taken as dipolarophiles.

Aziridines **Ia**–**Ie** were synthesized from the corresponding 1,3-dienes **IIa**–**IId** according to the optimized standard procedure for oxidative addition of *N*-aminophthalimide to unsaturated compounds [12] (Scheme 1). As a rule, mixtures of mono- and bis-adducts were obtained, from which pure monoaziridines were isolated.

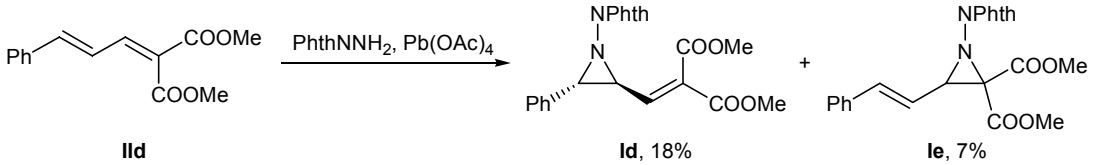
Scheme 1.



I, **II**, $R^1 = R^2 =$ Ph (**a**); $R^1 =$ Ph, $R^2 =$ PhC(O) (**b**); $R^1 =$ Me, $R^2 =$ MeOC(O) (**c**).

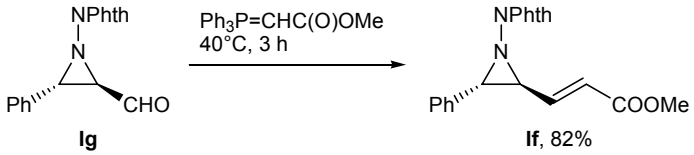
The reactions with unsymmetric 1,4-disubstituted dienes **IIb** and **IIc** afforded only addition products at the C=C bond neighboring to the carbonyl group; however, 1,1,4-trisubstituted compound **IId** gave rise to a mixture of regioisomeric aziridines **Id** and **Ie**

Scheme 2.



IId **Id**, 18% **Ie**, 7%

Scheme 3.



Ig **If**, 82%

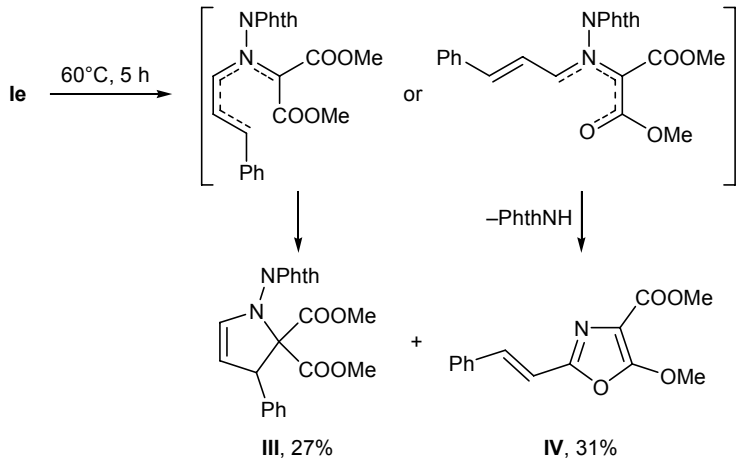
(Scheme 2) which were separated by column chromatography. Aziridine **If** was synthesized by the Wittig reaction of aldehyde **Ig** (Scheme 3) prepared as described in [12]. The vicinal coupling constant for the protons at the exocyclic double bond in **If** (^3J = 15.5 Hz) indicated (*E*) configuration of that bond.

N-Phthalimidoaziridines **Ia**–**Ig** were isolated as colorless, yellow, or greenish–yellow crystalline substances. Compounds **Ib**–**If** were not reported previously and were characterized by elemental analyses, ^{1}H and ^{13}C NMR spectra, and exact weights of quasimolecular ions determined from the high-resolution ESI mass spectra. We failed to obtain satisfactory elemental analysis data for aziridine **Ie** due to its instability under the isolation and purification conditions. *trans* Orientation of protons at the double bond in initial unsaturated compounds **IIb**–**IId** was retained in aziridines **Ib**–**Id**, as followed from the low values of the corresponding vicinal coupling constants (^3J = 4.4–5.8 Hz).

N-Aminoaziridine derivatives often display in the NMR spectra signals from two invertomers due to slow (on the NMR time scale) inversion of the endocyclic nitrogen atom at room temperature [13, 14]. The ratio of invertomers of **If** was 10 : 1, whereas the fraction of the minor invertomer of **Ie** was so small that it cannot be detected by NMR spectroscopy. On the basis of steric considerations we presumed that the phthalimido group in the only spectrally detectable invertomer of **Ie** occupies *syn* position with respect to the proton in the aziridine ring, and in the major invertomer of **If**, *anti* position with respect to the phenyl group as the bulkier substituent. Aziridines **Ia**–**Id** were equilibrium mixtures of two invertomers in comparable amounts, which suggests similar effective volumes of the corresponding substituents.

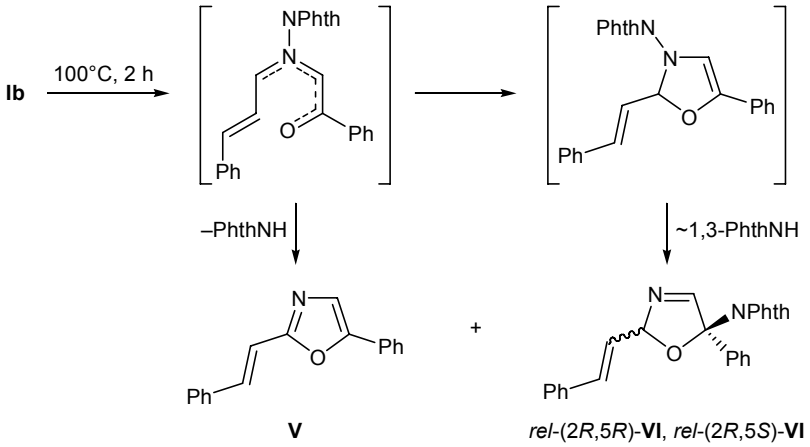
The structure of adducts **Ic**–**Ie** unambiguously follows from the multiplicity of signals from the aziridine proton in the ^{1}H NMR spectra; however, regioisomeric aziridination products of diene **IIb** cannot be distinguished in such a way. For this purpose, 2D ^{1}H NOESY experiment was performed. The NOESY spectrum contained cross peaks for readily identifiable *ortho*-protons in the benzoyl group (down-

Scheme 4.



III, 27% **IV**, 31%

Scheme 5.



V *rel*-(2*R*,5*R*)-**VI**, *rel*-(2*R*,5*S*)-**VI**

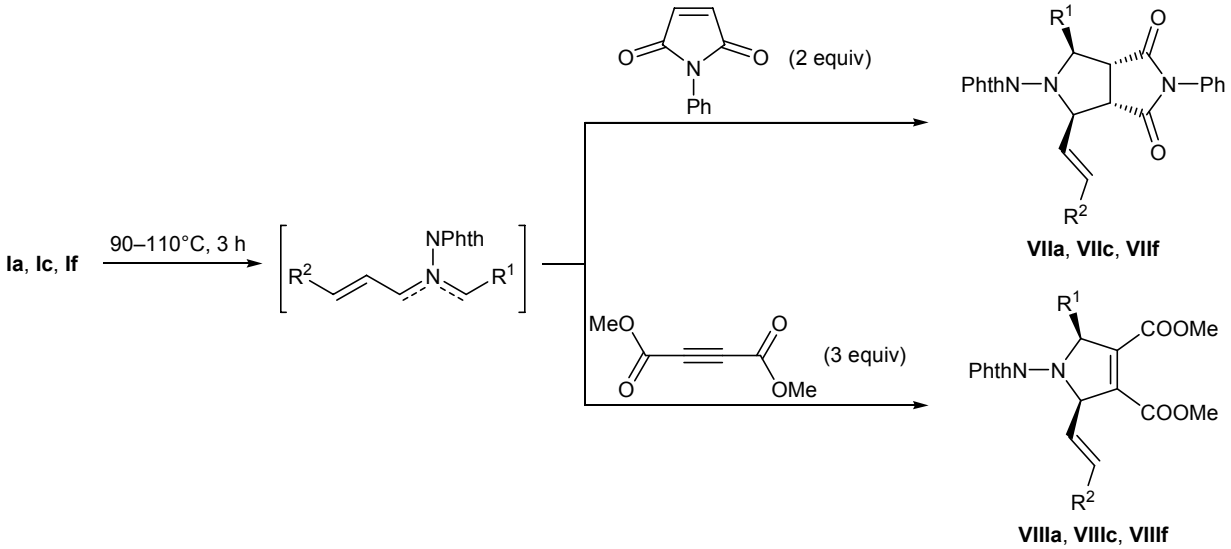
field signals) and aziridine ring proton (doublet) for both invertomers, which reliably proved structure **Ib**.

1,5-Electrocyclization of *N*-phthalimidoaziridines **Ia**–**If** with participation of the double carbon–carbon bond was studied by heating these compounds in the absence of dipolarophiles. Thermolysis of **Ie** gave expected dihydropyrrole **III** and oxazole **IV**, the latter being formed via 1,5-electrocyclization involving the C=O bond (Scheme 4).

By heating aziridine **Ib** we obtained only 1,5-electrocyclization products at the carbonyl group, 5-phenyl-2-styryloxazole (**V**) and two diastereoisomers of dihydrooxazole **VI** at a ratio of 4:1 (Scheme 5). This cyclization could be expected to produce 2,3-dihydrooxazole having a phthalimido group on the nitrogen atom; however, the position of some signals in the ^{1}H and ^{13}C NMR spectra of **VI** was consistent only with structures where the phthalimido group is attached to C^5. The NOESY spectrum of stereoisomer mixture **VI** showed that the styryl and phenyl substituents in the major isomer [*rel*-(2*R*,5*S*)-**VI**] are oriented *cis*, and in the minor isomer [*rel*-(2*R*,5*R*)-**VI**], *trans*.

The thermolysis of aziridines **Ia**, **Ic**, **Id**, and **If** was accompanied by appreciable tarring. In each case, the conversion of the initial compound was complete, but chromatographic separation of the reaction mixtures gave only fractions containing mixtures of products and phthalimide. A new compound was detected by TLC in the reaction mixture obtained by thermolysis of **Id**; however, we succeeded in isolating only phthalimide, benzaldehyde, and tarry fractions with intractable ^{1}H NMR spectra.

Scheme 6.



VIIa, **VIIc**, **VIIf** **VIIIa**, **VIIIc**, **VIIIf**

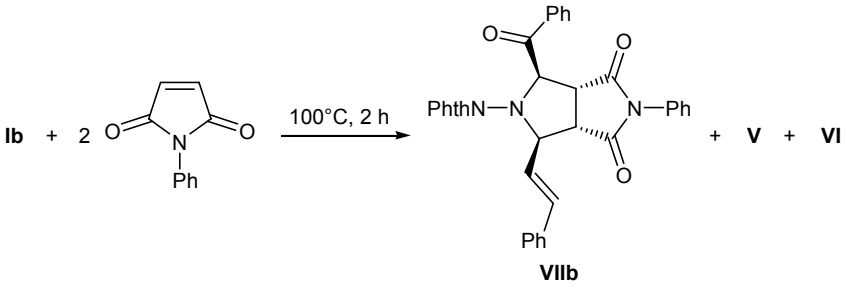
$R^1 = R^2 = Ph$ (**a**); $R^1 = MeOC(O)$, $R^2 = Me$ (**c**); $R^1 = Ph$, $R^2 = MeOC(O)$ (**f**).

Heating of aziridines **Ia**, **Ic**, and **If** under analogous conditions but with addition of *N*-phenylmaleimide or dimethyl acetylenedicarboxylate smoothly afforded the corresponding 1,3-dipolar cycloaddition products whose spatial structure was determined on the basis of the NOESY data. The reactions with PMI gave expected (cf. [8–10]) bicyclic *exo*-adducts **VIIa**, **VIIc**, and **VIIf** with *cis* orientation of the substituents in the former aziridine ring. The thermolysis in the presence of DMAD produced 2,5-dihydro-1*H*-pyrrole derivatives **VIIIa**, **VIIIc**, and **VIIIf** with *cis* orientation of the same substituents as well (Scheme 6). The structure of adducts **VII** and **VIII** is very consistent with the generally accepted reaction mechanism [1, 2, 8–11] including allowed (by the Woodward–Hoffmann orbital symmetry rules) conrotatory opening of the *trans*-2,3-disubstituted aziridine ring to form *W*-ylide and concerted addition of the latter to the dipolarophile (see below).

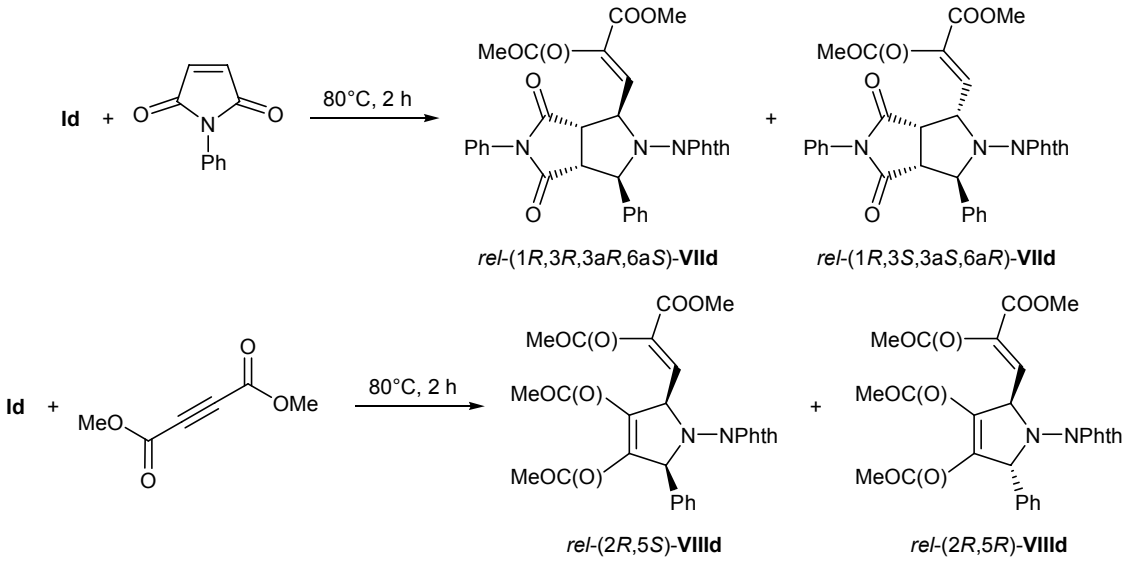
By contrast, aziridines **Ib** and **Ie** which underwent 1,5-electrocyclization on heating in the absence of dipolarophiles were generally converted into the same products in the presence of dipolarophiles. Only in the reaction of **Ib** with PMI we succeeded in isolating cycloadduct **VIIb** in a poor yield (Scheme 7).

Quite unexpected results were obtained in the reactions of dipolarophiles with aziridine **Id** (Scheme 8). In both cases, mixtures of stereoisomeric cycloadducts with both *cis* and *trans* configuration of the substituents in the former aziridine ring were formed. The steric structure of the products was determined using NOESY experiments. The major product of the reaction with PMI, *rel*-(1*R*,3*R*,3a*R*,6a*S*)-**VIId**, was isolated as individual substance and completely characterized. The second stereoisomer was not isolated pure, but the NMR spectra of a 2:1 mixture of *rel*-(1*R*,3*S*,3a*S*,6a*R*)-**VIId** and *rel*-(1*R*,3*R*,3a*R*,6a*S*)-**VIId** were fully consistent with the assumed structures, and the elemental analysis data for that mixture and its mass spectrum corresponded to the general formula. The adducts formed by aziridine **Id** with DMAD were separated neither by chromatography nor by recrystallization; therefore, only their mixture was analyzed and characterized by spectral data; the ratio *rel*-(2*R*,5*S*)-**VIIId**–

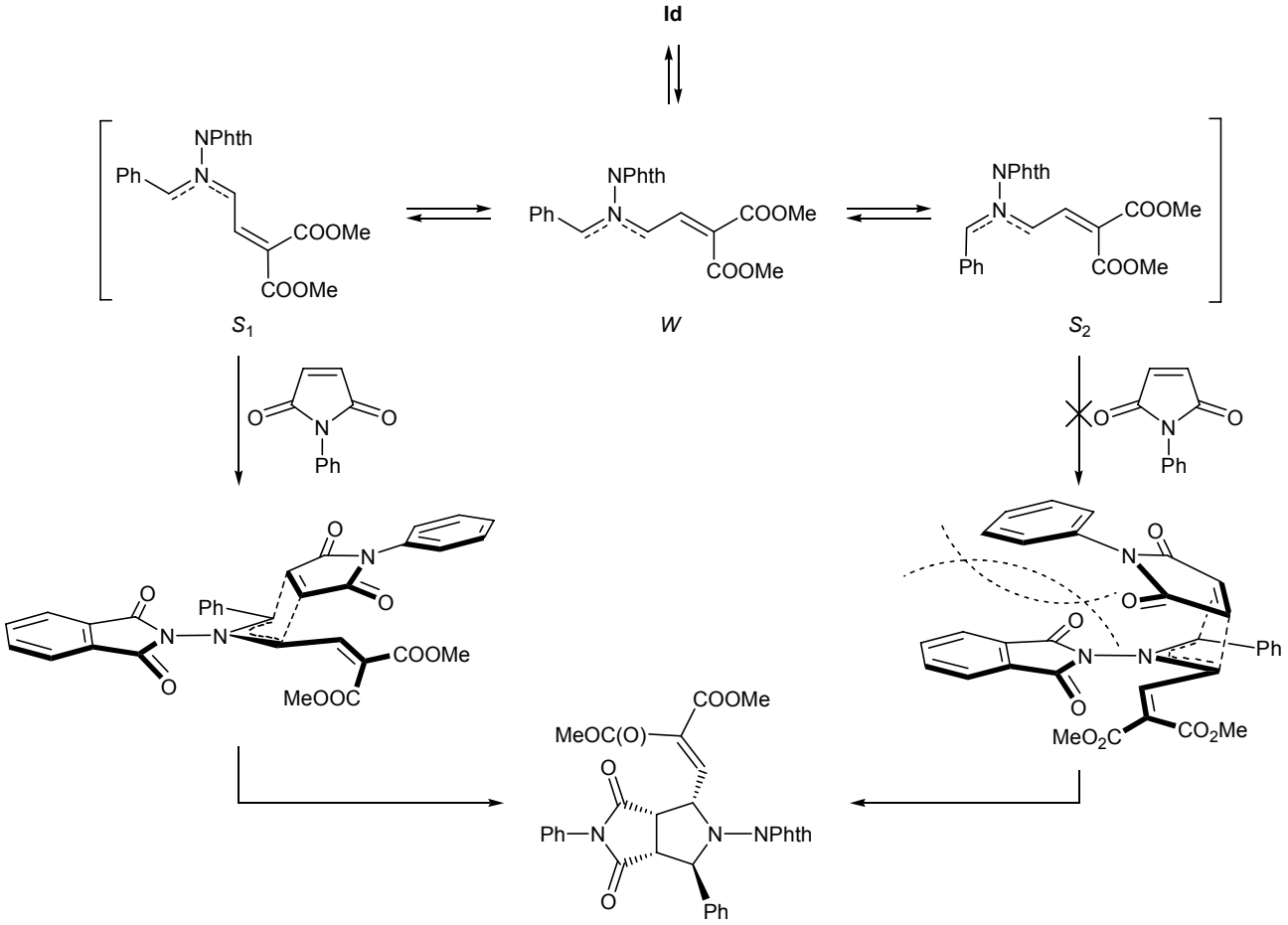
Scheme 7.



Scheme 8.



Scheme 9.



rel-(2*R*,5*R*)-**VIIId** was 7 : 1. Adducts **VII** and **VIII** specifically featured slow (on the NMR time scale) rotation about the N–N bond in the hydrazine fragment. As a result, their ^{13}C NMR spectra displayed broadening or doubling of signals from carbon atoms in the phthalimide fragment. The same factor is responsible for symmetry distortion of the multiplet signal from protons in the phthaloyl group in the ^{1}H NMR spectra of some adducts.

The results obtained in the present work are somewhat surprising. In all cases studied previously, thermally induced 1,3-dipolar cycloaddition of disubstituted *N*-phthalimidoaziridines was stereospecific, and only adducts arising from conrotatory opening of the three-membered ring were formed [8–10]. Here, we were the first to obtain mixtures of stereoisomeric products. As before, their major components correspond to conrotatory opening of the aziridine ring to generate *W*-dipole and subsequent concerted cycloaddition, while the formation of minor stereoisomers may be due to partial isomerization of *W*-ylide into *S*-ylide. On the other hand, stepwise addition of intermediate ylide to dipolarophile cannot be ruled out, which should lead to violation of stereospecificity.

Theoretically, adducts with *trans* orientation of the substituents in the former aziridine ring may be formed from *S*-dipoles S_1 and S_2. As shown in Scheme 9, the formation of *trans*-adduct *rel*-(1*R*,3*S*,3a*S*,6a*R*)-**VIId** from *N*-phenylmaleimide and S_2 implies approach of the dipolarophile from the side of the bulky phthalimide group, whereas the interaction of PMI with S_1 does not involve appreciable steric hindrances. Therefore, it is more probable that *trans*-adducts are formed via rearrangement of *W*-ylide into S_1.

Presumably, the presence of two electron-withdrawing groups in the $NCHCH{=}C(CO_2Me)_2$ fragment of intermediate ylide favors charge delocalization in such a way that the order of the C–N bond in the above fragment decreases, which reduces the barrier to rotation about the C–N bond. As a result, the rate of isomerization of *W*-dipole into S_1 becomes comparable to the rate of cycloaddition, and mixtures of stereoisomeric products are formed.

To conclude, it should be noted that alkenyl derivatives of *N*-phthalimidoaziridine undergo intramolecular transformations and react with dipolarophiles at a considerably lower temperature (60–110°C) than do analogous derivatives with acyl, alkoxycarbonyl, aryl, and cyano groups (130–220°C [7–11]). This fact indicates efficient stabilization of intermediate azomethine ylides by alkenyl groups.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-300 spectrometer (300 and 75 MHz, respectively) from solutions in $CDCl_3$ using the residual proton (δ 7.26 ppm) and carbon signals (δ_C 77.16 ppm) of the solvent as reference [15]. The elemental compositions were determined on an HP-185B automatic CHN analyzer. The high-resolution mass spectra (electrospray ionization) were obtained on a Bruker micrOTOF instrument. The composition of the reaction mixtures and fractions obtained after their separation, as well as the purity of the isolated compounds, were monitored by TLC on Polygram SIL G/UV_{254} and Alugram SIL G/UV_{254} plates (Macherey-Nagel). *N*-Aminophthalimide was synthesized according to the procedure described in [16].

***N*-Phthalimidoaziridines Ia–Ie and Ig (*general procedure*).** Anhydrous potassium carbonate, 1.863 g (13.5 mmol), was dispersed in a solution of 3.0 mmol of the corresponding 1,3-diene in 30 ml of anhydrous methylene chloride, and *N*-aminophthalimide and lead tetraacetate were added one by one in 7–15-mg portions (4.5 mmol each in the synthesis of **Ia**–**Ie** and 3 mmol each in the synthesis of **Ig**) under stirring over a period of 20 min. The mixture was then stirred for 20–30 min more at room temperature and filtered through a 1.5-cm layer of silica gel, the precipitate was washed with 40–150 ml of methylene chloride, the filtrate was combined with the washings and evaporated under reduced pressure at room temperature (18–23°C), and the residue was subjected to column chromatography on silica gel.

***rel*-(2*R*,3*R*)-2-Phenyl-3-styryl-1-phthalimidoaziridine (Ia)** was synthesized from (1*E*,3*E*)-1,4-diphenylbuta-1,3-diene **IIa** at –20°C. After removal of the solvent, the residue was subjected to chromatography on 40 g of silica gel using ethyl acetate–hexane (1:8 to 1:4) as eluent. Yield 538 mg (49%), greenish–yellow crystals, mp 138°C; published data [13]: mp 138–139°C. According to the ^{1}H NMR data, the product was a mixture of two invertomers at a ratio of 8:2; the ^{1}H NMR spectrum was very consistent with that given in [17].

***rel*-(2*R*,3*S*)-2-Benzoyl-3-styryl-1-phthalimidoaziridine (Ib)** was synthesized from (2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-one (**IIb**) [18] at –20°C. After removal of the solvent, the residue was subjected to chromatography on 40 g of silica gel using ethyl acetate–hexane (1:6 to 1:3) as eluent. Yield 627 mg (53%), greenish–yellow crystals, mp 146°C. ^{1}H NMR spectrum (a mixture of two invertomers at a ratio of 8:2), δ, ppm: 3.83 d.d (3-H, minor, J = 8.0, 5.1 Hz) and 4.34 d.d (3-H, major, J = 7.3, 5.1 Hz) (1H); 4.28 d (2-H, major, J = 5.1 Hz) and 4.87 d (2-H, minor, J = 5.1 Hz) (1H); 6.05 d.d (**H**C=CHPh, minor, J = 16.0, 8.0 Hz) and 6.19 d.d (**H**C=CHPh, major, J = 16.0, 7.3 Hz) (1H); 6.92 d (HC=C**H**Ph, minor, J = 16.0 Hz) and 7.01 d (HC=C**H**Ph, major, J = 16.0 Hz) (1H); 7.25–7.81 m (12H, H_{arom}); 8.06–8.09 m (*o*-H in COPh, major) and 8.23–8.26 m (*o*-H in COPh, minor) (2H). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 47.92 and 50.56 (C^2, C^3), 123.25 and 123.46 (C^b, H**C**=CHPh); 126.74, 128.76, 128.83, 128.90 (C^m, C^o); 128.39 and 129.02 (C^p), 130.38 (C^a), 133.71 (HC=**C**HPh), 134.09 (C^c), 135.83 and 137.50 (C^i), 164.47 (NCO), 190.85 (CO). Found, %: C 76.06; H 4.47; N 7.10. *m*/*z* 417.1191 $[M + Na]^+$. $C_{21}H_{18}N_2O_3$. Calculated, %: C 76.13; H 4.60; N 7.10. (M + Na) 417.1210.

Methyl *rel*-(2*R*,3*S*)-3-[(*E*)-prop-1-en-1-yl]-1-phthalimidoaziridine-2-carboxylate (Ic) was synthesized from methyl (2*E*,4*E*)-hexa-2,4-dienoate (**IIc**) [19] at –20°C. After removal of the solvent, the residue was subjected to chromatography on 30 g of silica gel using ethyl acetate–hexane (1:6) as eluent. Yield 345 mg (40%), light yellow crystals, mp 95–96°C. ^{1}H NMR spectrum (a mixture of two invertomers at a ratio of 7:3), δ, ppm: 1.68 d.d (CH_3, minor, J = 6.6, 1.5 Hz) and 1.79 d.d (CH_3, major, J = 6.6, 1.5 Hz) (3H); 3.23 d (2-H, major, J = 5.0 Hz), 3.45 d.d (3-H, minor, J = 7.7, 5.1 Hz), and 3.78–3.81 m (3-H, major and 2-H, minor) (2H); 3.70 s (OCH_3, major) and 3.84 s (OCH_3, minor) (3H); 5.28 d.d.d (**H**C=$CHCH_3$, minor, J = 15.2, 7.7, 1.5 Hz) and 5.39 d.d.d (**H**C=$CHCH_3$, major, J = 15.4, 7.4, 1.5 Hz) (1H); 5.97–6.17 m (1H, HC=C**H**CH_3); 7.65–7.80 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 18.14 and 18.33 (CH_3); 44.15, 44.97, 48.87, 49.29 (C^2, C^3); 52.87 and 52.97 (OCH_3), 121.31 (HC=**C**$CHCH_3$); 123.19, 123.36, 124.97 (C^b, H**C**=$CHCH_3$); 130.36 (C^a), 133.40 and 136.02 (H**C**=$CHCH_3$), 134.09 and 134.33 (C^c), 164.81 and 165.22 (NCO), 167.14 and 168.37 (COO); signals

from C^a in the phthalimido group of both invertomers coincided. Found, %: C 63.16; H 5.02; N 9.64. *m*/*z* 287.1006 $[M + H]^+$. $C_{15}H_{14}N_2O_4$. Calculated, %: C 62.93; H 4.93; N 9.79. (*M* + H) 287.1026.

Aziridines **Id** and **Ie** were synthesized from dimethyl 2-(3-phenylprop-2-en-1-ylidene)malonate (**IId**) [20] at 13°C. After removal of the solvent, the residue was subjected to chromatography on 40 g of silica gel using ethyl acetate–hexane (1:4 to 1:0) as eluent to isolate 450 mg (37%) of a mixture of **Id** and **Ie** at a ratio of 2:1 (^{1}H NMR). Repeated chromatography on 50 g of silica gel (ethyl acetate–hexane, 1:8 to 1:1) gave fractions enriched in aziridines **Id** and **Ie** due to their close R_f values.

Dimethyl {[*rel*-(2*R*,3*R*)-3-phenyl-1-phthalimidoaziridin-2-yl]methylidene}malonate (Id). Yield 219 mg (18%), colorless crystals, mp 103–104°C. ^{1}H NMR spectrum (a mixture of two invertomers at a ratio of 3:1), δ, ppm: 3.74 s (OCH_3, major), 3.82–3.88 m (OCH_3, major; OCH_3, minor, 2-H, major, 3-H, minor), 4.15 d (3-H, major, *J* = 5.1 Hz), 5.09 d.d (2-H, minor, *J* = 8.0, 5.8 Hz) (8H); 6.75 d (CH=C, major, *J* = 10.2 Hz) and 6.79 d (CH=C, minor, *J* = 8.0 Hz) (1H); 7.24–7.49 m (5H, Ph), 7.60–7.61 (PhthN, minor) and 7.71–7.83 (PhthN, major) (4H). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 47.35, 51.10, 52.77 (C^2, C^3, OCH_3); 123.57 (C^b), 128.42 and 128.79 (C^m, C^o), 128.65 (C^p), 130.31 (CH=**C**), 130.47 (C^a), 134.12 (C^c), 134.57 (C^i), 142.85 (**C**H=C); 163.92, 164.76, 165.44 (NCO, COO). Found, %: C 65.41; H 4.24; N 6.83. *m*/*z* 429.1020 $[M + Na]^+$. $C_{22}H_{18}N_2O_6$. Calculated, %: C 65.02; H 4.46; N 6.89. (*M* + Na) 429.1057.

Dimethyl 1-phthalimido-3-styrylaziridine-2,2-dicarboxylate (Ie). Yield 85 mg (7%), yellow crystals, mp 120–121°C. ^{1}H NMR spectrum, δ, ppm: 3.77 s and 3.88 s (3H each, OCH_3), 4.39 d (1H, 3-H, *J* = 6.2 Hz), 5.97 d.d (1H, **H**C=CHPh, *J* = 16.0, 6.2 Hz), 7.05 d (1H, HC=C**H**Ph, *J* = 16.0 Hz), 7.26–7.38 m (5H, Ph), 7.70–7.85 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 53.49, 53.90, 54.10 (C^3, OCH_3); 119.38 (H**C**=CHPh), 123.45 (C^b), 126.94 and 128.74 (C^m, C^o), 128.62 (C^p), 130.22 (C^a), 134.36 (C^c), 135.89 (C^i), 137.63 (HC=**C**HPh); 163.43, 163.82, 164.30 (NCO, COO). Found: *m*/*z* 407.1213 $[M + H]^+$. Calculated: (*M* + H) 407.1238.

***rel*-(2*R*,3*S*)-3-Phenyl-1-phthalimidoaziridine-2-carbaldehyde (Ig)** was synthesized from cinnamaldehyde at 0°C. The residue was subjected to chromatography on 20 g of silica gel using methylene chloride as eluent. Yield 745 mg (85%), greenish–yellow crystals, mp 172–174°C; published data [21]: mp 176°C. The ^{1}H NMR spectrum of **Ig** was very consistent with that given in [21].

Methyl (2*E*)-3-[*rel*-(2*R*,3*R*)-3-phenyl-1-phthalimidoaziridin-2-yl]acrylate (If). A solution of 585 mg (2 mmol) of compound **Ig** and 0.8 g (2.4 mmol) of methyl (triphenyl-λ^5-phosphanylidene)acetate [22] in 5 ml of methylene chloride was heated for 4 h under reflux, the progress of the reaction being monitored by TLC. The resulting solution (without evaporation) was applied to a column charged with 20 g of silica gel, and the column was eluted with ethyl acetate–hexane (1:4) to isolate 573 mg (82%) of **If** as greenish–yellow crystals with mp 130–132°C. ^{1}H NMR spectrum (a mixture of two invertomers at a ratio of 10:1), δ, ppm: 3.46 d.d (2-H, major, *J* = 9.5, 5.1 Hz) and 4.76 d.d (2-H, minor, *J* = 8.7, 5.4 Hz) (1H); 3.70 s (OCH_3, major) and 3.77 s (OCH_3, minor) (3H); 4.04 d (3-H, minor, *J* = 5.4 Hz) and 4.19 d (3-H, major, *J* = 5.4 Hz) (1H); 6.28 d (CH=C**H**CO_2CH_3, major, *J* = 15.5 Hz) and 6.38 d (CH=C**H**CO_2CH_3, minor, *J* = 15.7 Hz) (1H); 6.68 d.d (C**H**=$CHCO_2CH_3$, major, *J* = 15.5, 9.5 Hz) and 6.99 d.d (C**H**=$CHCO_2CH_3$, minor, *J* = 15.7, 8.7 Hz) (1H); 7.33–7.54 m (5H, Ph), 7.61–7.62 m (PhthN, minor) and 7.69–7.82 m (PhthN, major) (4H). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 50.24, 50.58, 51.89 (C^2, C^3, OCH_3); 123.46 (C^b), 125.66 (CH=**C**HCO_2CH_3), 127.07 and 128.79 (C^m, C^o), 128.50 (C^p), 130.84 (C^a), 134.43 (C^c), 135.41 (C^i), 140.53 (**C**H=$CHCO_2CH_3$), 165.49 and 165.92 (NCO, COO). Found, %: C 69.09; H 4.55; N 8.16. *m*/*z* 349.1188 $[M + H]^+$. $C_{20}H_{16}N_2O_4$. Calculated, %: C 68.96; H 4.63; N 8.04. (*M* + H) 349.1183.

Thermolysis of aziridines Ib and Ie in the absence of dipolarophiles (*general procedure*). A solution of aziridine **Ib** or **Ie** in 10 ml of anhydrous toluene in a thick-walled glass reactor was heated on a silicone bath. When the initial compound disappeared (TLC), the mixture was cooled, the solvent was distilled off under reduced pressure, and the residue was treated as described below.

a. Aziridine **Ib**, 394 mg (1 mmol), was heated for 2 h at 100°C. The residue was subjected to chromatography on 20 g of silica gel using hexane–ethyl acetate (8:1 to 2:1) as eluent. Fractions containing dihydrooxazole **VI** and contaminated with phthalimide were combined and evaporated, and the residue was subjected to repeated chromatography on silica gel using methylene chloride as eluent. We isolated 96 mg (39%) of **V** and 158 mg (40%) of a 1:4 mixture of diastereoisomers *rel*-(2*R*,5*R*)-**VI** and *rel*-(2*R*,5*S*)-**VI**.

5-Phenyl-2-styryloxazole (V). Yellow crystals, mp 101–103°C; published data [23]: mp 102–104°C. The ^{1}H and ^{13}C NMR spectra of the product were in good agreement with published data [23, 24].

Stereoisomer mixture **VI** was dissolved in 10 ml of ethyl acetate, 40 ml of hexane was added, and the mixture was evaporated under reduced pressure until crystallization started. After 2 h, the precipitate was filtered off and dried in air. We thus isolated 110 mg (28%) of pure isomer *rel*-(2*R*,5*S*)-**VI**. The mother liquor was evaporated under reduced pressure to obtain 42 mg of a 3:1 mixture of *rel*-(2*R*,5*R*)-**VI** and *rel*-(2*R*,5*S*)-**VI** as colorless crystals.

***rel*-(2*R*,5*S*)-5-Phenyl-5-phthalimido-2-styryl-2,5-dihydrooxazole (VI).** Colorless needles, mp 176–178°C. ^{1}H NMR spectrum, δ, ppm: 6.32 d.d (1H, **H**C=CHPh, *J* = 15.9, 6.4 Hz), 6.55 d.d (1H, 2-H, *J* = 6.4, 2.5 Hz), 6.92 d (1H, HC=C**H**Ph, *J* = 15.9 Hz), 7.29–7.53 m (10H, Ph), 7.75–7.87 m (4H, PhthN), 8.14 d (1H, 4-H, *J* = 2.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 98.50 (C^5), 107.58 (C^2), 123.84 (C^b), 124.91 (H**C**=CHPh); 125.39, 127.11, 128.76, 129.06 (C^m, C^o); 128.53 and 128.93 (C^p), 131.82 (C^a), 134.67 (C^c), 134.92 (HC=**C**HPh), 136.06 and 137.59 (C^i), 159.70 (C^4), 167.31 (NCO). Found, %: C 76.14; H 4.50; N 7.23. *m*/*z* 417.1228 [*M* + Na]$^+$. $C_{25}H_{18}N_2O_3$. Calculated, %: C 76.13; H 4.60; N 7.10. (*M* + Na) 417.1210.

Diastereoisomer mixture *rel*-(2*R*,5*R*)-VI/*rel*-(2*R*,5*S*)-VI (3:1). Found, %: C 76.44; H 4.42; N 7.03. *m*/*z* 417.1179 [*M* + Na]$^+$. $C_{25}H_{18}N_2O_3$. Calculated, %: C 76.13; H 4.60; N 7.10. (*M* + Na) 417.1210. Analysis of the NMR spectra of the mixture allowed us to identify the following spectral parameters of *rel*-(2*R*,5*R*)-5-phenyl-5-phthalimido-2-styryl-2,5-dihydrooxazole (**VI**). ^{1}H NMR spectrum, δ, ppm: 6.18 d.d (1H, **H**C=CHPh, *J* = 16.0, 6.5 Hz), 6.58 d.d (1H, 2-H, *J* = 6.5, 2.0 Hz), 6.81 d (1H, HC=C**H**Ph, *J* = 16.0 Hz), 7.24–7.51 m (10H, Ph), 7.72–7.85 m (4H, PhthN), 8.11 d (1H, 4-H, *J* = 2.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 97.78 (C^5), 108.16 (C^2), 123.90 (C^b); 125.01, 127.06, 128.60, 129.16 (C^m, C^o); 125.29 (H**C**=CHPh), 128.37 and 128.99 (C^p), 131.78 (C^a), 134.02 (HC=**C**HPh), 134.68 (C^c), 135.97 and 137.42 (C^i), 159.21 (C^4), 167.18 (NCO).

b. Aziridine **Ie**, 203 mg (0.5 mmol), was heated for 5 h at 60°C. The residue was subjected to chromatography on 15 g of silica gel using hexane–ethyl acetate (6:1 to 2:1) as eluent. Fractions containing compound **III** were combined and evaporated, the residue was dissolved in 3 ml of diethyl ether, and hexane was added dropwise until crystallization started. After 1 h, the precipitate was filtered off and dried in air. We isolated 55 mg (27%) of **III** and 40 mg (31%) of **IV**.

Dimethyl 3-phenyl-1-phthalimido-2,3-dihydro-1*H*-pyrrole-2,2-dicarboxylate (III). Yellow crystals, mp 135°C. ^{1}H NMR spectrum, δ, ppm: 3.07 s and 3.69 s (3H each, OCH_3), 5.09 d.d (1H, 3-H, *J* = 4.1, 2.2 Hz), 5.13 d.d (1H, 4-H, *J* = 4.1, 4.1 Hz), 6.20 d.d (1H, 5-H, *J* = 4.1, 2.2 Hz), 7.21–7.33 m (3H, *m*-H, *p*-H), 7.39–7.42 m (2H, *o*-H), 7.75–7.88 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 51.92 and 53.56 (OCH_3), 55.46 (C^3), 79.75 (C^2), 105.18 (C^4), 123.79 (C^b), 127.80 (C^p), 128.30 and 129.41 (C^m, C^o), 130.03 (C^a), 134.65 (C^c), 136.14 (C^5), 138.52 (C^i); 166.43, 166.68, 167.26 (COO, NCO). Found, %: C 65.21; H 4.56; N 6.73. *m*/*z* 407.1189 [*M* + H]$^+$. $C_{22}H_{18}N_2O_6$. Calculated, %: C 65.02; H 4.46; N 6.89. (*M* + H) 407.1238.

Methyl (*E*)-5-methoxy-2-styryloxazole-4-carboxylate (IV). Yellow oily substance. ^{1}H NMR spectrum, δ, ppm: 3.89 s (3H, OCH_3), 4.25 s (3H, OCH_3), 6.78 d (1H, **H**C=CHPh, *J* = 16.4 Hz), 7.32–7.39 m (4H, *m*-H, *p*-H, HC=C**H**Ph), 7.46–7.50 m (2H, *o*-H). ^{13}C NMR spectrum, δ_C, ppm: 51.92 ($CO_2\mathbf{C}H_3$), 59.93 (OCH_3), 113.04 (H**C**=CHPh), 127.18 and 129.03 (C^m, C^o, C^4), 129.45 (C^p), 135.24 (C^i), 135.90 (HC=**C**HPh), 150.90 (C^5), 161.54 and 161.91 (C^2, C=O). Found: *m*/*z* 260.0904 [*M* + H]$^+$. Calculated: (*M* + H) 260.0917.

Reactions of aziridines Ia–Id and If with *N*-phenylmaleimide (*general procedure*). A solution of 0.5 mmol of aziridine **Ia**–**Id** or **If** and 173 mg (1 mmol) of *N*-phenylmaleimide in 10 ml of anhydrous toluene was heated in a thick-walled glass reactor at a required temperature on a silicone bath. When the initial compound disappeared (TLC), the mixture was cooled, the solvent was distilled off under reduced pressure, and the residue was subjected to column chromatography on silica gel.

a. The residue obtained after heating a mixture of aziridine **Ia** and PMI for 3 h at 90°C was separated using hexane–ethyl acetate (6:1 to 3:1) as eluent to isolate 175 mg (65%) of *rel*-(3a*R*,4*S*,6*S*,6a*S*)-2,4-diphenyl-5-phthalimido-6-[(*E*)-styryl]tetrahydropyrrolo-[3,4-*c*]pyrrole-1,3(2*H*,3a*H*)-dione (**VIIa**) as colorless crystals with mp 245°C. ^{1}H NMR spectrum, δ, ppm: 3.49–3.62 m (2H, 3a-H, 6a-H), 4.80 d.d (1H, 6-H, *J* = 8.2, 8.2 Hz), 5.36 d (1H, 4-H, *J* = 7.2 Hz), 6.39 d.d (1H, **H**C=CHPh, *J* = 15.8, 8.2 Hz), 6.72 d (1H, HC=C**H**Ph, *J* = 15.8 Hz), 7.21–7.72 m (19H, Ph, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 47.85 and 50.33

(C^{3a}, C^{6a}), 67.18 and 67.31 (C^4, C^6), 123.19 and 124.01 (C^b); 125.99, 128.38, 128.82, 128.91 (HC=**C**HPh, C^p); 126.64, 127.02, 127.83, 128.65, 128.99, 129.33 (C^m, C^o); 129.45 and 129.75 (C^a); 131.66, 135.93, 137.72 (C^i); 134.42 and 134.61 (C^c), 136.39 (H**C**=CHPh), 165.86 and 168.11 (NCO), 174.85 and 175.10 (C^1, C^3). Due to restricted rotation about the N–N bond, all carbon nuclei in the phthalimide fragment are nonequivalent, and they give 8 signals. Found, %: C 75.65; H 4.69; N 7.60. *m*/*z* 540.1896 $[M + H]^+$. $C_{34}H_{25}N_3O_4$. Calculated, %: C 75.68; H 4.67; N 7.79. (*M* + H) 540.1918.

b. The residue obtained after heating a mixture of **Ib** with PMI for 2 h at 100°C was separated by chromatography on silica gel using hexane–ethyl acetate (8:1 to 2:1) as eluent to isolate 28 mg (10%) of adduct **VIIb**, 32% of **V**, and 34% of **VI**.

***rel*-(3a*R*,4*R*,6*R*,6a*S*)-4-Benzoyl-2-phenyl-5-phthalimido-6-[(*E*)-styryl]tetrahydropyrrolo[3,4-*c*]-pyrrole-1,3(2*H*,3a*H*)-dione (VIIb).** Colorless crystals, mp 247–248°C. ^{1}H NMR spectrum, δ, ppm: 3.64 d.d (1H, 6a-H, *J* = 8.7, 8.7 Hz), 4.20 d.d (1H, 3a-H, *J* = 8.7, 5.3 Hz), 4.76 d.d (1H, 6-H, *J* = 8.7, 8.7 Hz), 5.80 d (1H, 4-H, *J* = 5.3 Hz), 6.33 d.d (1H, **H**C=CHPh, *J* = 15.8, 8.7 Hz), 6.64 d (1H, HC=C**H**Ph, *J* = 15.8 Hz), 7.19–7.68 m (13H, Ph, *m*-H, *p*-H in COPh), 7.64–7.70 m (4H, PhthN), 7.98 d (2H, *o*-H in COPh). ^{13}C NMR spectrum, δ_C, ppm: 40.50 and 48.75 (C^{3a}, C^{6a}), 65.31 and 66.63 (C^4, C^6), 132.72 (C^b); 125.26, 128.43, 129.08 (HC=**C**HPh, C^p in Ph); 126.70, 127.07, 128.63, 128.76, 129.03, 129.45 (C^m, C^o); 131.69, 135.89, 135.77 (C^i); 133.77, 134.68, 136.40 (H**C**=CHPh, C^c, C^p in COPh), 174.28 and 175.78 (C^1, C^3), 194.54 (CO); signals from C^a and NCO in the phthalimide fragment were not identified because of strong broadening. Found, %: C 74.42; H 4.33; N 7.29. *m*/*z* 568.1830 $[M + H]^+$. $C_{35}H_{25}N_3O_5$. Calculated, %: C 74.06; H 4.44; N 7.40. (*M* + H) 568.1867.

c. The residue obtained after heating a mixture of **Ic** and PMI for 3 h at 130°C was separated by chromatography on silica gel using hexane–ethyl acetate (4:1 to 1:2) as eluent to isolate 143 mg (62%) of methyl *rel*-(1*R*,3*R*,3a*S*,6a*R*)-4,6-dioxo-5-phenyl-2-phthalimido-3-[(*E*)-prop-1-en-1-yl]octahydropyrrolo[3,4-*c*]pyrrole-1-carboxylate (**VIIc**) as colorless crystals with mp 149–150°C. ^{1}H NMR spectrum, δ, ppm: 1.62 d.d (3H, CH_3, *J* = 5.8, 1.3 Hz), 3.44 d.d (1H, 3a-H, *J* = 9.0, 9.0 Hz), 3.72 s (3H, OCH_3), 4.07 d.d (1H, 6a-H, *J* = 9.0, 5.7 Hz), 4.47 d.d (1H, 3-H, *J* = 9.0, 9.0 Hz), 4.78 d (1H, 1-H, *J* = 5.7 Hz), 5.58 d.d.q (1H, **H**C=CHCH$_3$, *J* = 15.1, 9.0, 1.3 Hz), 5.74 d.q (1H, HC=C**H**CH$_3$, *J* = 15.1, 5.8 Hz), 7.36–7.53 m (5H, Ph), 7.75–7.87 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 17.98 (CH_3), 45.14 and 47.63 (C^{3a}, C^{6a}), 53.24 (OCH_3), 63.14 and 68.64 (C^1, C^3), 123.79 (C^b), 126.59 and 129.33 (C^m, C^o), 127.11 and 128.94 (HC=**C**HCH$_3$, C^p), 129.77 (C^a), 131.58 (C^i), 134.00 and 134.75 (H**C**=CHCH$_3$, C^c); 169.35, 174.28, 175.03 (C^4, C^6, COO). Signals from the NCO carbon atoms in the phthalimide group were not identified because of strong broadening. Found, %: C 65.32; H 4.54; N 8.88. *m*/*z* 460.1483 $[M + H]^+$. $C_{25}H_{21}N_3O_6$. Calculated, %: C 65.35; H 4.61; N 9.15. (*M* + H) 460.1503.

d. The residue obtained after heating a mixture of aziridine **Id** and PMI for 2 h at 80°C was subjected to chromatographic separation using hexane–ethyl acetate (3:1) as eluent to isolate 252 mg (87%) of a mixture of *rel*-(1*R*,3*R*,3a*R*,6a*S*)-**VIId** and *rel*-(1*R*,3*S*,3a*S*,6a*R*)-**VIId**. Repeated chromatography on silica gel using hexane–ethyl acetate (4:1) as eluent gave 148 mg (51%) of pure isomer (1*R*,3*R*,3a*R*,6a*S*)-**VIId** and 75 mg (26%) of a 2:1 mixture of *rel*-(1*R*,3*R*,3a*R*,6a*S*)-**VIId** and *rel*-(1*R*,3*S*,3a*S*,6a*R*)-**VIId**.

Dimethyl {[*rel*-(1*R*,3*R*,3a*R*,6a*S*)-4,6-dioxo-3,5-diphenyl-2-phthalimidooctahydropyrrolo[3,4-*c*]pyrrol-1-yl]methylidene}malonate (VIId). Colorless crystals, mp 138–140°C. ^{1}H NMR spectrum, δ, ppm: 3.49–3.60 m (2H, 3a-H, 6a-H), 3.67 s and 3.77 s (3H each, OCH_3), 5.07 d.d (1H, 1-H, *J* = 9.9, 6.6 Hz), 5.39 d (1H, 3-H, *J* = 7.1 Hz), 7.16 d (1H, CH=C, *J* = 9.9 Hz), 7.29–7.55 m (8H, NPh, *m*-H, *p*-H in NCHPh), 7.60 d (2H, *o*-H in NCHPh, *J* = 6.8 Hz), 7.66–7.78 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 47.86 and 50.73 (C^{3a}, C^{6a}), 52.76 and 52.78 (OCH_3), 62.02 and 67.88 (C^1, C^3), 123.07 and 124.14 (C^b); 126.54, 127.68, 128.97, 129.04, 129.35 (C^m, C^o, C^p); 129.67 and 129.77 (C^a); 131.57, 133.00, 137.14 (CH=**C**, C^i); 134.50 and 134.62 (C^c), 143.26 (**C**H=C), 163.28 and 164.34 (COO), 165.38 and 167.72 (NCO), 173.88 and 174.41 (C^4, C^6). Due to restricted rotation about the N–N bond, all carbon nuclei in the phthalimide fragment are nonequivalent, and they give 8 signals; two signals in the region δ_C 126.54–129.35 overlapped each other. Found, %: C 66.09; H 4.46; N 7.10. *m*/*z* 580.1720 $[M + H]^+$. $C_{32}H_{25}N_3O_8$. Calculated, %: C 66.32; H 4.35; N 7.25. (*M* + H) 580.1714.

Mixture (1*R*,3*S*,3a*S*,6a*R*)-VIId/(1*R*,3*R*,3a*R*,6a*S*)-VIId (2:1). Found: *m/z* 580.1683 $[M + H]^+$. Calculated: (*M* + H) 580.1714. Analysis of the NMR spectra of that mixture allowed us to identify signals belonging

to dimethyl {[*rel*-(1*R*,3*S*,3a*S*,6a*R*)-4,6-dioxo-3,5-diphenyl-2-phthalimidooctahydropyrrolo[3,4-*c*]pyrrol-1-yl]methylidene}malonate (**VIId**). ^{1}H NMR spectrum, δ, ppm: 3.66 d.d (1H, 3a-H, J = 9.1, 5.7 Hz), 3.70 s and 3.76 s (3H each, OCH_3), 4.13 d.d (1H, 6a-H, J = 9.1, 9.1 Hz), 5.36 d.d (1H, 1-H, J = 11.1, 9.1 Hz), 5.64 d (1H, 3-H, J = 5.7 Hz), 7.11 d (1H, CH=C, J = 11.1 Hz), 7.29–7.55 m (8H, NPh, *m*-H, *p*-H in NCHPh), 7.60 d (2H, *o*-H in NCHPh, J = 6.9 Hz), 7.64–7.74 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 46.36 and 50.47 (C^{3a}, C^{6a}), 52.78 and 52.90 (OCH_3), 60.46 and 65.05 (C^1, C^3), 123.41 and 123.59 (C^b), 126.56 and 127.69 (C^p); 126.66, 127.71, 129.18, 129.46 (C^m, C^o); 129.60 and 129.69 (C^a); 131.59, 132.61, 137.35 (CH=**C**, C^i); 134.51 and 134.53 (C^c), 140.63 (**C**H=C), 163.34 and 164.34 (COO), 166.15 and 167.52 (NCO), 173.13 and 175.31 (C^4, C^6). Due to restricted rotation about the N–N bond, all carbon nuclei in the phthalimide fragment are nonequivalent, and they give 8 signals.

e. The residue obtained after heating a mixture of **If** and PMI for 3 h at 110°C was subjected to chromatographic separation on silica gel using hexane–ethyl acetate (4:1 to 2:1) as eluent to isolate 212 mg (81%) of methyl (*E*)-[*rel*-(1*R*,3*R*,3a*R*,6a*S*)-4,6-dioxo-3,5-diphenyl-2-phthalimidooctahydropyrrolo[3,4-*c*]pyrrol-1-yl]acrylate (**VIIf**) as colorless crystals with mp 222–224°C. ^{1}H NMR spectrum, δ, ppm: 3.50–3.56 m (2H, 3a-H, 6a-H), 3.70 s (3H, OCH_3), 4.84 d.d (1H, 1-H, J = 7.5, 7.5 Hz), 5.30 d (1H, 3-H, J = 6.9 Hz), 6.29 d (1H, CH=C**H**CO_2CH_3, J = 15.6 Hz), 7.09 d.d (1H, C**H**=$CHCO_2CH_3$, J = 15.6, 7.5 Hz), 7.19–7.68 m (8H, NPh, *m*-H, *p*-H in NCHPh), 7.60 d (2H, *o*-H in 3-Ph, J = 7.5 Hz), 7.65–7.75 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 47.77, 50.37, 51.95 (C^{3a}, C^{6a}, OCH_3); 65.16 and 67.95 (C^1, C^3); 123.38, 124.14, 126.00, 128.98 (C^b, CH=**C**HCO_2CH_3, C^p); 126.59, 127.82, 129.00, 129.37 (C^m, C^o); 129.61 (C^a), 131.50 and 137.16 (C^i), 134.59 and 134.79 (C^c), 143.61 (**C**H=$CHCO_2CH_3$); 165.29, 165.89, 167.76 (NCO, COO); 174.48 and 174.66 (C^4, C^6). Due to restricted rotation about the N–N bond, the C^c carbon nuclei in the phthalimide fragment are nonequivalent, and they give two signals. Found, %: C 69.25; H 4.42; N 8.06. m/z 544.1452 $[M + Na]^+$. $C_{30}H_{23}N_3O_6$. Calculated, %: C 69.09; H 4.45; N 8.06. (M + Na) 544.1479.

Thermal reactions of aziridines Ia, Ic, Id, and If with dimethyl acetylenedicarboxylate (*general procedure***).** A solution of 0.5 mmol of aziridine **Ia**, **Ic**, **Id**, or **If** and 213 mg (1.5 mmol) of DMAD in 10 ml of anhydrous toluene was heated in a thick-walled glass reactor on a silicone bath. When the initial aziridine disappeared (TLC), the mixture was cooled, the solvent was distilled off under reduced pressure, and the residue was subjected to column chromatography on silica gel.

a. A mixture of aziridine **Ia** and DMAD was heated for 3 h at 90°C, and the product was isolated by chromatography on silica gel using hexane–ethyl acetate (6:1 to 4:1) as eluent. Yield of dimethyl *rel*-(2*R*,5*S*)-2-phenyl-1-phthalimido-5-(*E*)-styryl-2,5-dihydro-1*H*-pyrrole-3,4-dicarboxylate (**VIIIa**) 97 mg (38%), colorless crystals, mp 179–181°C. ^{1}H NMR spectrum, δ, ppm: 3.60 s and 3.77 s (3H each, OCH_3), 5.48 d.d (1H, 5-H, J = 7.9, 5.5 Hz), 5.89 d (1H, 2-H, J = 5.5 Hz), 6.40 d.d (1H, **H**C=CHPh, J = 15.8, 7.9 Hz), 6.37 d (1H, HC=C**H**Ph, J = 15.8 Hz), 7.22–7.40 m (8H, HC=CH**Ph**, *m*-H, *p*-H in 5-Ph), 7.56 d (2H, *o*-H in 5-Ph, J = 7.1 Hz), 7.67–7.79 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 52.33 and 52.57 (OCH_3), 70.74 and 71.90 (C^2, C^5); 126.32, 127.06, 128.09, 128.35, 128.62, 128.75 (H**C**=CHPh, C^m, C^o, C^p); 129.89 (C^a), 134.45 (C^c), 134.53 (HC=**C**HPh); 136.41, 136.75, 137.38, 138.95 (C^3, C^4, C^i); 164.32 and 163.39 (COO); signals from C^a and C^c were strongly broadened, while signals from C^b and NCO were not identified; two signals in the region δ_C 127.06–128.75 overlapped each other. Found, %: C 70.90; H 4.75; N 5.70. m/z 547.1296 $[M + K]^+$. $C_{30}H_{24}N_2O_6$. Calculated, %: C 70.86; H 4.76; N 5.51. (M + K) 547.1266.

b. A mixture of aziridine **Ic** and DMAD was heated for 3 h at 130°C, and the residue was subjected to chromatography on silica gel using hexane–ethyl acetate (6:1 to 3:1) as eluent. Fractions containing compound **VIIIc** were combined and concentrated under reduced pressure until a viscous oily material was obtained, 1 ml of diethyl ether and 3 ml of hexane were added, and the resulting emulsion was left to stand in a refrigerator. After 12 h, the precipitate was filtered off and dried in air. Yield of trimethyl *rel*-(2*R*,5*R*)-1-phthalimido-5-[(*E*)-prop-1-en-1-yl]-2,5-dihydro-1*H*-pyrrole-2,3,4-tricarboxylate (**VIIIc**) 107 mg (50%), light yellow crystals, mp 110°C. ^{1}H NMR spectrum, δ, ppm: 1.62 d (3H, CH_3, J = 6.0 Hz), 3.72 s (3H, OCH_3), 3.76 s (3H, OCH_3), 3.82 s (3H, OCH_3), 5.14 d (1H, 2-H, J = 4.5 Hz), 5.20 d.d (1H, 5-H, J = 7.6, 4.5 Hz), 5.55 d.d (1H, **H**C=CHCH_3, J = 15.2, 7.6 Hz), 5.63–5.75 m (1H, HC=C**H**CH_3), 7.75–7.86 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 17.76 (CH_3); 52.62, 52.67, 52.92 (OCH_3); 70.06 and 73.57 (C^2, C^5), 123.81 (C^b), 126.98 (HC=**C**HCH_3), 128.82 and 143.76 (C^3, C^4), 129.98 (C^a), 132.24

(H**C**=CHCH$_3$), 134.70 (C^c); 161.91, 163.64, 169.10 (COO). Signals from the carbonyl carbon atoms in the phthalimide group were not identified because of strong broadening. Found, %: C 65.35; H 4.83; N 9.00. *m*/*z* 429.1302 [*M* + H]$^+$. $C_{25}H_{21}N_3O_6$. Calculated, %: C 65.35; H 4.61; N 9.15. (*M* + H) 429.1292.

c. A mixture of aziridine **Id** and DMAD was heated for 2 h at 80°C, and the residue was subjected to chromatography on silica gel using hexane–ethyl acetate (4:1) to isolate a mixture of *rel*-(2*R*,5*R*) and *rel*-(2*R*,5*S*) isomers of dimethyl 2-[2,2-bis(methoxycarbonyl)ethenyl]-5-phenyl-1-phthalimido-2,5-dihydro-1*H*-pyrrole-3,4-dicarboxylate (**VIIId**) at a ratio of 1:7 (according to the ^{1}H NMR data). Yield 110 mg (40%), light yellow crystals, mp 71–78°C. ^{1}H NMR spectrum, δ, ppm: 3.52 (OCH_3, major), 3.60 (OCH_3, major), 3.61 (OCH_3, minor), 3.69 (OCH_3, minor), 3.748 (OCH_3, minor), 3.754 (OCH_3, major), 3.78 (OCH_3, major), 3.84 (OCH_3, minor) (12H); 5.67 d.d (2-H, minor, *J* = 10.8, 5.8 Hz), 5.68 d.d (2-H, major, *J* = 10.4, 5.1 Hz) (2H); 5.98 d (5-H, major, *J* = 5.1 Hz), 6.38 d (5-H, minor, *J* = 5.8 Hz) (2H); 7.10 d (CH=C, major, *J* = 10.4 Hz), 7.12 d (CH=C, minor, *J* = 10.8 Hz) (2H); 7.25–7.35 m (3H, *m*-H, *p*-H), 7.42 d.d (*o*-H, minor, *J* = 8.0, 2.0 Hz), 7.51 d.d (*o*-H, major, *J* = 8.0, 1.6 Hz) (2H); 7.66–7.75 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: major isomer: 52.50, 52.54, 52.70, 52.82 (OCH_3); 65.40 and 73.33 (C^2, C^5), 128.37 and 128.60 (C^m, C^o), 129.05 (C^p); 130.01, 130.70, 131.25, 136.20, 143.93 (C^a, C^3, C^4, C^i, CH=**C**); 134.50 (C^c), 143.55 (**C**H=C); 161.89, 163.33, 163.66, 164.70 (COO); signals from the C^c atoms were strongly broadened, while those corresponding to C^b and NCO were not identified. Found, %: C 61.42; H 4.24; N 5.17. *m*/*z* 571.1298 [*M* + Na]$^+$. $C_{28}H_{24}N_2O_{10}$. Calculated, %: C 61.31; H 4.41; N 5.11. (*M* + Na) 571.1323.

d. A mixture of aziridine **If** and DMAD was heated for 3 h at 110°C, and the residue was subjected to chromatography on silica gel using hexane–ethyl acetate (6:1 to 3:1) as eluent. Fractions containing compound **VIIIf** were combined and evaporated under reduced pressure, and the residue was crystallized by cooling the flask with liquid nitrogen. Diethyl ether and hexane (2 ml each) were added to the solid material, and the mixture was left to stand in a refrigerator. After 12 h, the precipitate was filtered off and dried in air. Yield of dimethyl *rel*-(2*R*,5*S*)-2-[(*E*)-2-(methoxycarbonyl)ethenyl]-5-phenyl-1-phthalimido-2,5-dihydro-1*H*-pyrrole-3,4-dicarboxylate (**VIIIf**) 105 mg (43%), light yellow crystals, mp 78–80°C. ^{1}H NMR spectrum, δ, ppm: 3.59 s (3H, OCH_3), 3.73 s (3H, OCH_3), 3.79 s (3H, OCH_3), 5.50 d.d (1H, 2-H, *J* = 5.5, 5.5 Hz), 5.84 d (1H, 5-H, *J* = 5.5 Hz), 6.49 d (1H, CH=C**H**CO_2CH_3, *J* = 15.5 Hz), 7.14 d.d (1H, C**H**=$CHCO_2CH_3$, *J* = 15.5, 5.5 Hz), 7.28–7.30 m (3H, *m*-H, *p*-H), 7.47 d (2H, *o*-H, *J* = 7.4 Hz), 7.71–7.75 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: 51.86, 52.48, 52.70 (OCH_3); 69.00 and 73.42 (C^2, C^5), 123.80 (C^b), 124.37 (**C**H=$CHCO_2CH_3$), 128.50 and 128.54 (C^m, C^o), 128.98 (C^p), 129.77 (C^a); 132.40, 136.63, 142.05 (C^3, C^4, C^i); 134.66 (C^c), 143.75 (CH=**C**HCO_2CH_3); 162.27, 163.41, 166.60 (COO); signals from the C^b atoms were strongly broadened, while those corresponding to the carbonyl groups in the phthalimide fragment were not identified. Found, %: C 63.62; H 4.56; N 5.72. *m*/*z* 513.1251 [*M* + Na]$^+$. $C_{26}H_{22}N_2O_8$. Calculated, %: C 63.67; H 4.52; N 5.71. (*M* + Na) 513.1268.

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