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INTRAMOLECULAR THERMAL TRANSFORMATIONS OF *N*-PHTHALIMIDOAZIRIDINES: 1,3-DIPOLAR CYCLO-ADDITION AND REARRANGEMENTS*

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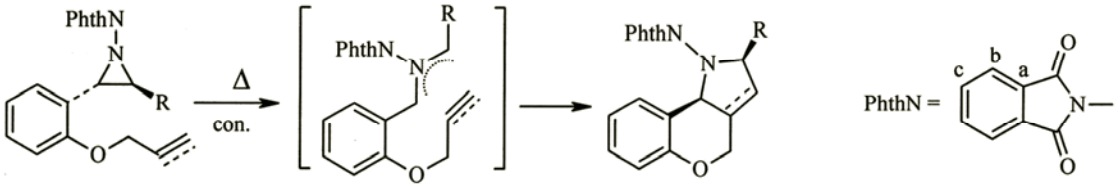
The intramolecular thermal cycloaddition of N-phthalimidoaziridines at multiple bonds of substituents with the intermediate formation of azomethine ylides leads to condensed pyrrole derivatives, in which the five-membered ring is adjacent to a five-, six-, or seven-membered ring. Rearrangements, which sometimes become the predominant reactions, compete with cycloaddition. Thus, aziridines with aryl substituents readily isomerize to give imines with a 1,2-shift of the phthalimide group to one of the carbon atoms. Aziridines with one electron-withdrawing substituent probably do not open to give 1,3-dipoles but rather undergo a Cope-type rearrangement involving the three-membered ring and C=O bond of the second substituent. Even in intramolecular reactions, very low activity is found for the cyano group triple bond and aromatic ring bonds as dipolarophiles.

Keywords: aziridines, azomethine ylides, benzoxepinopyrrole, chromenoimidazole, hexahydro-indenopyrroles, 1,3-dipolar cycloaddition, rearrangements.

Intramolecular 1,3-dipolar cycloaddition of azomethine ylides at carbon–carbon multiple bonds is commonly used in the synthesis of various heterocyclic compounds with condensed rings [1]. In previous work [2], we showed that *N*-aminoaziridine derivatives may serve as azomethine ylides precursors in such reactions. We found that heating a series of 2-allyl- and 2-propargyloxyphenyl-*N*-phthalimidoaziridines gave products containing partially hydrogenated chromeno[4,3-*b*]pyrrole fragment with condensed five- and six-membered rings.



*Dedicated to Academician M. G. Voronkov on his 90th birthday.

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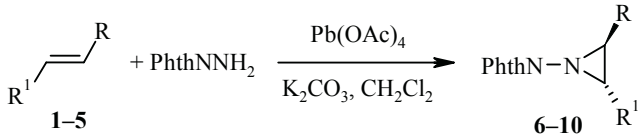
Aim of the present work was to study the feasibility of using intramolecular thermal reactions of substituted *N*-phthalimidoaziridines for constructing condensed structures, in which the five-membered ring is fused not only with six-membered rings but also with five- and seven-membered rings. Furthermore, since even unactivated multiple bonds often participate in intramolecular cycloaddition reactions [2-4], we hoped to effect reactions of such inactive dipolarophiles as aromatic rings and C≡N multiple bonds.

We have studied *trans*-2,3-disubstituted *N*-phthalimidoaziridines **6-10**, which were selected for the following reasons. Firstly, all these compounds contain two (compounds **6-9**) or, at least, one substituent (compound **10**) at carbon atoms of three-membered ring capable of stabilizing an intermediate azomethine ylide and, thereby, activate opening of the aziridine ring at the C–C bond. Secondly, the side chains of these compounds have various types of multiple bonds (including aromatic system bonds), which are sterically accessible for reaction with the expected 1,3-dipoles obtained upon opening of the aziridine ring, leading us to expect the formation of polycyclic condensed cycloadducts in these thermal reactions.



1–5 **6–10**

1, 6 a R = CO_2Me, R^1 = 2-$AllC_6H_4$, **b** R = CN, R^1 = 2-$AllC_6H_4$;
2, 7 a R = CN, R^1 = 2-$PropOCH_2C_6H_4$, **b** R = CN, R^1 = 2-$AllOCH_2C_6H_4$;
3, 8 a R = CO_2Me, R^1 = 2-$BnOC_6H_4$, **b** R = CN, R^1 = 2-$BnOC_6H_4$,
c R = CN, R^1 = 2-$NCCH_2OC_6H_4$;
4, 9 a R = Ph, R^1 = CO_2All, **b** R = Ph, R^1 = CO_2Prop;
5, 10 a R = Ph, R^1 = Ph–C≡C–CO_2CH_2, **b** R = Ph, R^1 = 2-$FurCO_2CH_2$,
c R = Ph, R^1 = $PhCO_2CH_2$, **d** R = Ph, R^1 = 4-$O_2NC_6H_4CO_2CH_2$

All = $-CH_2$ H-a / H-b Prop = $-CH_2C{\equiv}CH$

Aziridines **6-10** were synthesized by the oxidative addition of *N*-aminophthalimide to alkenes **1-5** according to the standard procedure [5]. This reaction is usually carried out at reduced temperature but in many cases better yields of aziridines **6-10** are obtained at 13°C. As a consequence of the low activity of triple and unconjugated terminal double bonds in oxidative aminoaziridination reactions [6], the addition of *N*-aminophthalimide to compounds **1a,b, 2a,b, 4a,b,** and **5a** proceeded only at the double bonds of the styrene fragment.

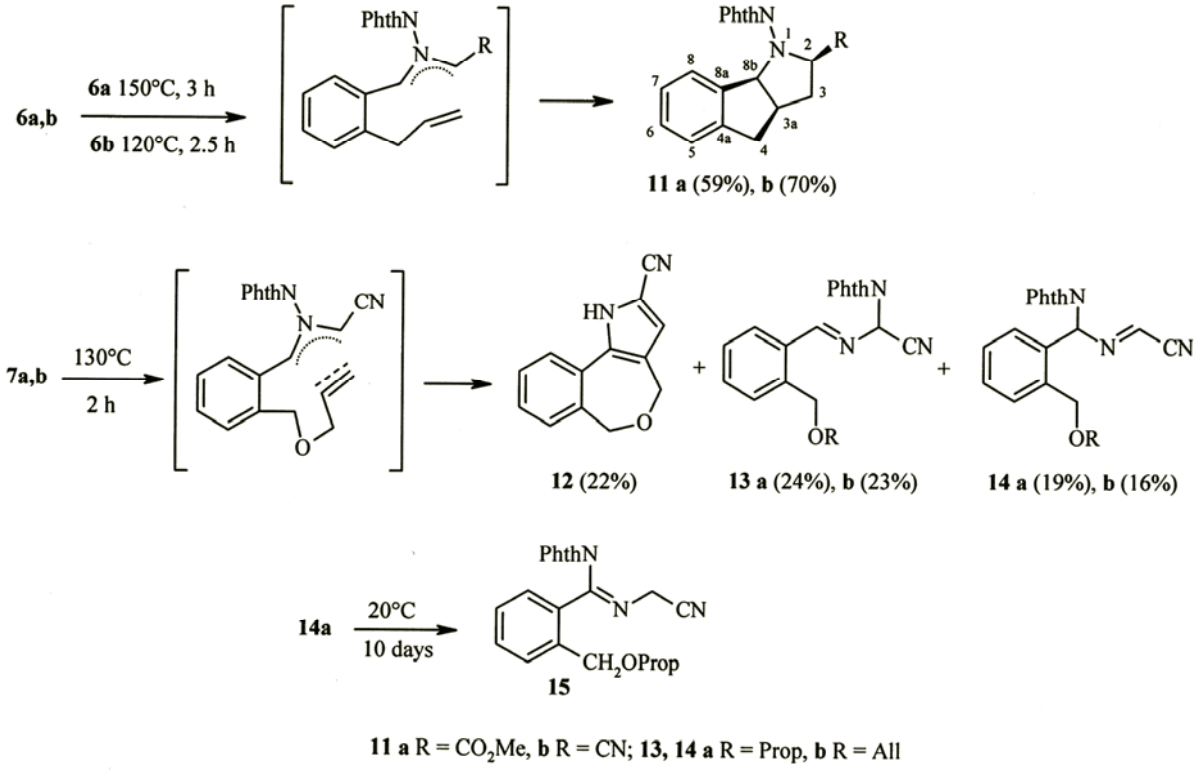
N-Phthalimidoaziridines **6-10** are colorless or yellow crystalline compounds stable under usual conditions. Aziridines **9a,b** and **10a** form glassy masses, which foam with solidification only at high vacuum. The structures and compositions of products **6-10** were supported by ^1H and ^{13}C NMR spectroscopy, mass spectrometry, and/or elemental analysis.

The *trans* configuration of the double bond in the starting alkenes is retained in the products of their oxidative aminoaziridination **6-10**, which is indicated by the small vicinal coupling constants of the aziridine protons (4.6-5.5 Hz). As the result of slow inversion of the endocyclic nitrogen atom (relative to the NMR time scale) [7, 8], the ^1H NMR spectra indicate the existence of aziridines **6a, b** at room temperature as a mixture of two invertomers. One of these invertomers is clearly predominant (the invertomer ratio was 1:≤0.12). The content of the minor invertomer for aminoaziridines **7-9** is evidently so low that its signals could not be observed in the NMR spectra. We can assume that the phthalimide group in the major or only spectrally detected invertomer of compound **6-9** is in the *anti* position related to the aryl group, which is the bulkier of the two substituents at the carbon atoms. The two invertomers for aziridines **10a-d** exist in comparable amounts, indicating similar effective bulk of the substituents.

The proton signal of the major or only observed invertomer in the ^{1}H NMR spectra of aziridines **6-9** at 4.40-4.76 ppm is lower and broader relative to the signal at 3.14-3.57 ppm. In our view, this broadening is a manifestation of long-range spin-spin coupling of the proton geminal to the aryl group with the *o*-protons of this aryl group and, thus, we assign the downfield signal to H-3 proton. The upfield signal is assigned to proton H-2.

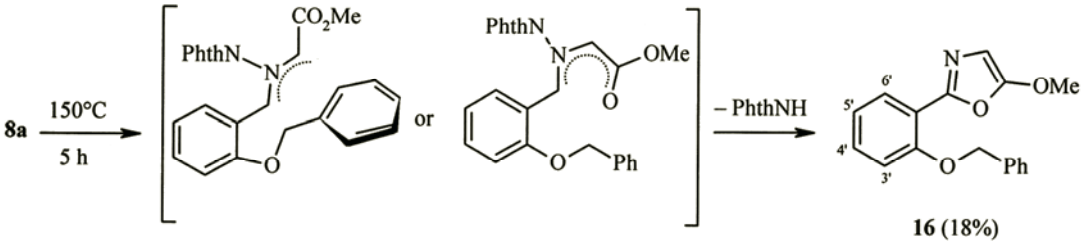
The thermal transformations of *N*-phthalimidoaziridines **6-10** were carried out in a sealed, heat-stable glass reactor in absolute benzene or toluene solutions. The optimal temperature for the reaction was determined by thin-layer chromatographic monitoring of the change in the composition of the reaction mixture at approximately 30 min intervals upon heating at constant temperature. The temperature was raised from 80°C in steps of about 10°C until onset of the reaction. The ^{1}H NMR spectrum of the reaction mixture was taken upon the cessation of heating.

Heating of aziridines **6a,b** led to good yields of the expected cycloadducts with two condensed five-membered rings, namely, hexahydroindenopyrroles derivatives **11a,b**. The three-dimensional structure of these products was proved by two-dimensional ^{1}H-^{1}H NOESY spectroscopy and corresponds to thermally-allowed conrotatory opening of the aziridine ring with subsequent concerted [3+2] cycloaddition. In this case, as usually observed (see our previous work [2]), the yield of adduct **11b** with a cyano group, which strongly stabilizes the intermediate ylide, is slightly higher than for its analog **11a** with an ester group and the required temperature and reaction time for **11b** are lower.



We expected to obtain benzoxepinopyrrole derivatives with a seven-membered ring from aziridines **7a,b**. However, chromatographic separation of the reaction mixture obtained upon heating aziridine **7a** gave only dihydrobenzoxepinopyrrole **12** with 22% yield, which was probably formed as the result of the loss of phthalimide from the initial intramolecular cycloaddition product. ^{1}H and ^{13}C NMR spectroscopy indicated the major

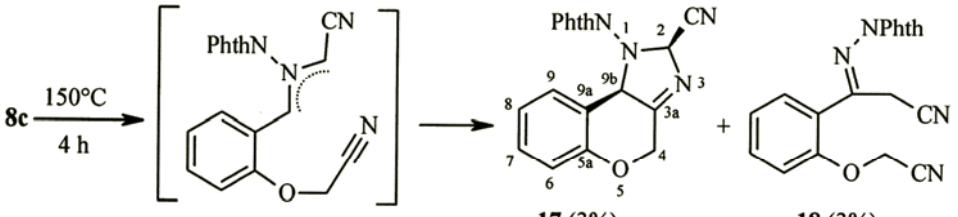
fraction is a mixture of isomeric imines **13a** and **14a***. This mixture could not be separated by either chromatography or recrystallization but we observed that one of its components completely converted to amidine **15** over the course of a few days at room temperature with access to the air. Separation of the new mixture resulted in isolation of pure crystalline compounds **13a** and **15**. Doublets for the protons of the NCHN and CH=N fragments in the downfield region of the ^{1}H NMR spectrum as well as corresponding signals in the ^{13}C NMR spectrum are characteristic for imine **13a**. Cross peaks corresponding to NOE of the CH=N proton with the *o*-proton of the adjacent phenyl ring and with the NCHN proton, which is spatially-proximate in the (*E*)-isomer, are seen in the ^{1}H-^{1}H NOESY spectrum of compound **13a**. We note that the formation of such imines has been observed previously upon heating several tri- and tetrasubstituted *N*-phthalimidoaziridines [9].



16 (18%)

The thermolysis of aziridine **7b** with a double bond less active as a dipolarophile did not lead to the expected cycloadduct. Only a mixture of imines **13b** and **14b** could be isolated in this case, which was confirmed by elemental analysis and mass spectrometry. The ^{1}H NMR spectra of this mixture showed two sets of signals for the allyloxymethylene group, two doublets in the downfield region corresponding to the CH=N-CH< fragment of imine **13b** (by analogy with imine **13a**), and a doublet of one of these protons in **14b** (the second doublet is apparently superposed by the aromatic proton signals) in addition to the aromatic proton multiplets. Thus, the intramolecular 1,3-cycloaddition of azomethine ylides at unactivated double bond with concurrent formation of a seven-membered ring proves so unfavorable that rearrangements of such compounds with migration of the phthalimide fragment leading to imines **13** and **14** become the major reactions for these compounds.

The thermolysis of aziridine **8a** did not lead to products of the 1,3-dipolar cycloaddition of the azomethine ylide at a formal multiple bond of the phenyl ring. 5-Methoxyoxazole **16**, which may be seen as the product of the 1,5-electrocyclization of the intermediate azomethine ylide with subsequent loss of a phthalimide molecule and formation of the aromatic oxazole system (see our previous works [10, 11]) was isolated from the reaction mixture in addition to phthalimide and 2-benzyloxybenzaldehyde.



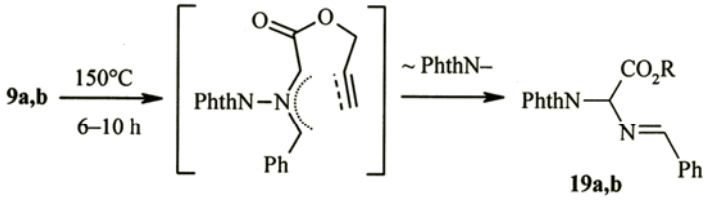
17 (3%) **18** (3%)

This is the first report of the preparation of 5-methoxyoxazole **16** but due to the instability of this compound at room temperature, we were able to record only its ^{1}H NMR spectrum displaying a singlet at

*The yields of imines **13a** and **14a** were calculated using the ^{1}H NMR spectrum of the reaction mixture relative to isolated product **12**, while the yields of imines **13b** and **14b** were calculated from the ^{1}H NMR spectrum of their mixture.

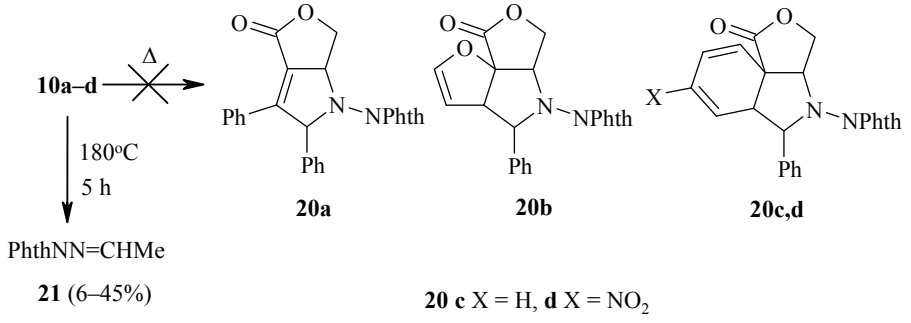
6.26 ppm assigned to proton H-4 of the heterocycle and signals for the aromatic protons and OCH_3 group in their usual regions.

Thermolysis of the analogous aziridine **8b** with a cyano group, which facilitates generation of the azomethine ylide but is incapable of participating in 1,5-electrocyclization, led only to decomposition products, namely, phthalimide and 2-benzyloxybenzaldehyde. Heating aziridine **8c**, which proceeds with considerable tar formation, gave a low yield of the product of the intramolecular cycloaddition of the intermediate ylide, namely, tetrahydrochromenoimidazole **17** as well as hydrazone **18**. Thus, the usually inert C≡N bond proved nevertheless a better dipolarophile than the aromatic system multiple bond.



19 a R = All (40%), **b** R = Prop (41%)

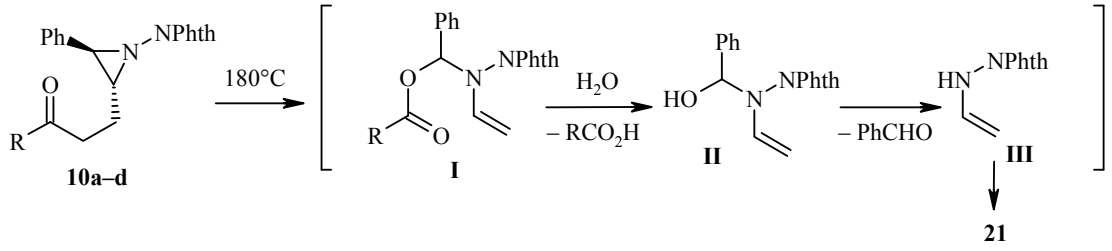
Attempting to carry out the intramolecular 1,3-dipolar cycloaddition in aziridines **9a,b** with a more flexible unsaturated side chain than in previously studied **6a,b**, we have observed only isomerization to imines **19a,b**. These imines could not be isolated as pure compounds and thus we estimated their yield from the ^{1}H NMR spectra of the reaction mixtures using an internal standard.



20 c X = H, **d** X = NO_2

The ^{1}H NMR spectra of imines **19a,b** display characteristic signals for the alcoholic residues of the ester groups, while the NCHN and CH=N protons signals appear in vicinity of 6.12 and 8.40 ppm, respectively. The structure of imine **19a** was confirmed by its ^{1}H-^{1}H NOESY spectrum, in which, as in the spectrum of compound **13a**, cross peaks are seen corresponding to NOE of the CH=N proton with the *o*-protons of the adjacent phenyl ring and with the NCHN proton.

We expected that heating aziridines **10a-d** would yield products of the intramolecular cycloaddition at the triple bond (compound **20a**), at the C=C bond of the slightly aromatic furan ring (compound **20b**), and even at the formally multiple bonds of aryl substituents (compounds **20c,d**) since Henke et al. [4] had already reported the synthesis of similar compounds from *N*-alkylaziridines through flash vacuum pyrolysis.

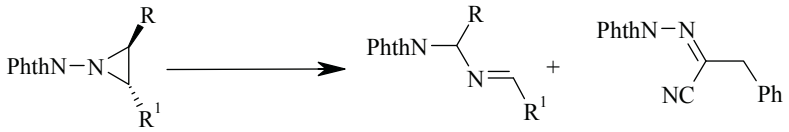


However, although starting aziridines **10a-d** were no longer detected in the reaction mixtures upon heating for 5 h at 180°C, the ^{1}H NMR spectra of these mixtures lacked signals of the expected cycloadducts in the region of 2-6 ppm. Furthermore, in all cases, we observed characteristic multiplets of the aliphatic protons of acetaldehyde phthaloylhydrazone (**21**) (quartet at 8.66 ppm and doublet with triple intensity at 2.21 ppm), which we have isolated from the reaction mixture with aziridine **10a** and identified by comparison with an authentic sample.

Our proposed reaction scheme for formation of this rather unexpected product features a key step of the starting aziridine conversion into the compound **I** through a hetero-Cope rearrangement (the three-membered ring here is a double bond analog) followed by hydrolysis to give aminal **II**. Then, compounds **II** decomposes to give enhydrazine **III**, which isomerizes to hydrazone **21**.

Aziridines **10a-d** differ significantly from compounds **6-9** in that the aziridine ring carbon atom in compounds **10a-d** has only a single phenyl substituent capable of stabilizing the intermediate azomethine ylides. Thus, formation of 1,3-ylides in the case of compounds **10a-d** is energetically unfavored and thermolysis of these aziridines probably proceeds without the participation of such ylides.

With the exception of the latter reaction, the rearrangement of *N*-phthalimidoaziridines to give imines almost always proceeds along with intramolecular 1,3-dipolar cycloaddition or instead of this process. In order to clarify how common this rearrangement is, we carried out the thermolysis of previously known *N*-phthalimidoaziridines **22a-c** [12-14], which possess substituents incapable of participating in other intramolecular transformations.



22a 120°C, 6 h — **23a** (~100%)
b 180°C, 5 h
c 120°C, 5 h — **23c** (23%) — **24** (6%)

22, 23 a R = R^1 =Ph; **22b** R = R^1 = CN; **22, 23 c** R = CN, R^1 = Ph

The thermolysis results indicated that 2,3-diphenylaziridine **22a** converts upon heating quantitatively to corresponding imine **23a**: the ^{1}H and ^{13}C NMR spectra of the reaction mixture show signals only for compound **23a**. In absolute benzene, imine **23a** remains unchanged for a rather long period, but only phthalimide in almost quantitative yield could be isolated in attempts to separate out this compound by chromatography or crystallization. However, heating aziridine **22b**, which has two cyano groups, led only to complete decomposition of the starting compound and tar formation; formation of rearrangement products could not be detected in this case.

In the case of unsymmetrical aziridine **22c,** the reaction is also accompanied by heavy tar formation but products **23c** and **24** could be isolated as pure compounds after chromatography. The ^{1}H NMR spectrum of the reaction mixture showed that these compounds were formed in ~4:1 ratio, which corresponds to the amounts isolated. The ^{1}H and ^{13}C NMR spectra of imine **23c** are similar to the spectra of compounds **13, 19,** and **23a**. Structures of compounds **23a,c** were additionally confirmed by 2D ^{1}H-^{1}H NOESY spectroscopy.

The ^{1}H NMR spectrum of hydrazone **24** displays a singlet for the CH_2 group protons at δ 4.48 ppm in addition to the signals for the phthalimide and phenyl group protons. Chemical shift of the CH_2 group carbon atom at 39.8 ppm corresponds to a position adjacent to a phenyl substituent since this atom would appear at much higher field if it were adjacent to a cyano group (~20 ppm). The ^{1}H NMR spectrum of hydrazone **24** could also correspond to the structure of the imine obtained as a result of migration of the double bond in compound **23c** to a carbon atom at the phthalimide and cyano group. However, the signal of the CH_2 group carbon atom in the ^{13}C NMR spectrum would be found at much lower field (~50 ppm). Since it is more favorable for the bulky

phthalimide group to be located near the small cyano group, we propose (*Z*)-configuration for the C=N bond in hydrazone **24**. We attribute the formation of phthaloylhydrazones **18** and **24** to opening of the aziridine ring at a C–N bond under the rigorous reaction conditions.

Thus, isomerization to imines is indeed a common feature of the thermal transformations of disubstituted *N*-phthalimidoaziridines. Aryl substituents at the aziridine ring facilitate this process. Opening of the three-membered ring to give the corresponding azomethine ylide evidently precedes this isomerization, while at least three mechanisms for shifting the phthalimide fragment to the adjacent carbon atom are theoretically possible: a concerted 1,2-shift and cleavage of the phthalimide group with subsequent recombination of the two species through an ion or radical pair. Person et al. [9] presented experimental data serving as evidence against mechanisms involving participation of an ion or radical pair in their work on a similar isomerization of tri- and tetrasubstituted *N*-phthalimidoaziridines. These authors found no cross reactions, a high reaction rate in nonpolar solvents, and the lack of EPR signals. Thus, we consider that this reaction in our case as well proceeds as a 1,2-shift of the phthalimide group from the nitrogen atom to a carbon atom in the azomethine ylide, most likely through a concerted mechanism.

Summarizing, we conclude that heating *N*-phthalimidoaziridines with unsaturated substituents leads to intramolecular cycloaddition at the multiple bonds of these substituents competing with rearrangements. The ratio of these processes depends both on the steric accessibility and activity of the multiple bond serving as the dipolarophile and the nature of the aziridine ring substituents. Five-membered rings form smoothly from (2-allylphenyl)aziridines, while heating esters of aziridinecarboxylic acid with a side chain of the same length leads only to rearrangement products. Seven-membered rings, as might have been expected, close with greater difficulty than five- and six-membered rings [see, 2] and rearrangements become predominant in this case. Very low activity is found for the cyano group triple bond and phenyl ring formal multiple bonds as dipolarophiles, even in intramolecular reactions. Adducts in these cases either are not formed at all or are obtained with extremely low yields. Aziridines possessing an aryl substituent readily isomerize to give imines *via* a 1,2-shift of the phthalimide group to one of the carbon atoms in the intermediate azomethine ylide. Phthalimidoaziridines with only one substituent capable of stabilizing the azomethine ylide do not give 1,3-dipoles upon heating but rather undergo a Cope type rearrangement.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300 and 75 MHz, respectively, in $CDCl_3$ solution with the signal of the residual protons (δ 7.26 ppm) as internal standard for the ^{1}H NMR spectra and solvent carbon atom signal at δ 77.2 ppm as internal standard for the ^{13}C NMR spectra. The high-resolution ESI mass spectra were performed on a Bruker micrOTOF spectrometer. The elemental analyses were taken on a Hewlett-Packard HP-185B automatic CHN analyzer. The composition of reaction mixtures and the fractions obtained upon separation as well as the purity of the isolated compounds were monitored by thin-layer chromatography on Macherey-Nagel Polygram SIL G/UV254 and Alugram SIL G/UV254 plates.

N-Aminophthalimide was obtained according to Drew and Hatt [15].

***N*-Phthalimidoaziridines 6-10 (General Method)**. *N*-Aminophthalimide (0.729 g, 4.5 mmol) and $Pb(OAc)_4$ (1.995 g, 4.5 mmol) were added consecutively in 7-15-mg portions to a stirred suspension of anhydrous K_2CO_3 (1.863 g, 13.5 mmol) in a solution of alkene **1-5** (3.0 mmol) in anhydrous CH_2Cl_2 (30 ml) at the indicated temperature over 20 min. The mixture was then stirred for an additional 20-30 min at the same temperature and filtered through a 1.5-cm-thick silica gel layer. The residue was washed with 40-150 ml CH_2Cl_2. The combined filtrates were treated as described below.

Methyl (2*R*′,3*S*′)-3-(2-Allylphenyl)-1-phthalimidoaziridine-2-carboxylate (6a). The reaction was carried out at -20°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a column packed with 30 g silica gel using CH_2Cl_2 as the eluent to give compound **6a.** Yield

1.065 g (98%). Colorless crystals, mp 107-108°C. The ^{1}H NMR spectrum indicates that this compound exists as a 25:1 mixture of two invertomers. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.26 (0.96H, d, *J* = 5.1, H-2); 3.49 (1H, dd, *J* = 16.0, *J* = 6.2) and 3.56 (1H, dd, *J* = 16.0, *J* = 6.2, CH_2); 3.74 (2.88H, s) and 3.90 (0.12H, s,CH_3); 4.38 (0.04H, d, *J* = 5.5) and 4.80 (0.04H, d, *J* = 5.5, H-2,3); 4.45 (0.96H, d, *J* = 5.1, H-3); 4.95 (1H, dd, *J* = 17.4, *J* = 1.5, H-a); 5.06 (1H, dd, *J* = 10.2, *J* = 1.5, H-b); 5.94 (1H, ddt, *J* = 17.4, *J* = 10.2, *J* = 6.2, CH); 7.20-7.30 (3H, m) and 7.48 (1H, dd, *J* = 7.2, *J* = 2.0, H Ar); 7.66-7.79 (4H, m, H PhthN). ^{13}C NMR spectrum of major invertomer, δ, ppm: 37.5 (CH_2); 46.7, 47.8 (C-2,3); 53.0 (CH_3); 116.3 (=CH_2); 123.3 (C-b); 126.5, 127.0, 128.5, 129.7 (C-3',4',5',6'); 130.4 (C-a); 133.3, 138.3 (C-1',2'); 134.2 (C-c); 136.4 (CH=CH_2); 164.8 (NCO); 166.9 (CO_2). Found, *m/z*: 363.1310 $[M+H]^+$. $C_{21}H_{19}N_2O_4$. Calculated, *m/z*: 363.1340. Found, %: C 69.42; H 4.80; N 7.92. $C_{21}H_{18}N_2O_4$. Calculated, %: C 69.60; H 5.00; N 7.73.

(2*R'*,3*S'*)-3-(2-Allylphenyl)-1-phthalimidoaziridine-2-carbonitrile (6b). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a column packed with 30 g silica gel using CH_2Cl_2 as the eluent to give compound **6b.** Yield 0.495 g (50%). Colorless crystals, mp 122-123°C. The ^{1}H NMR spectrum indicates that compound **6b** exists as an 8.3:1 mixture of two invertomers. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.14 (0.89H, d, *J* = 5.0, H-2); 3.54 (1H, dd, *J* = 16.0, *J* = 6.2) and 3.63 (1H, dd, *J* = 16.0, *J* = 6.2, CH_2); 4.52 (0.11H, d, *J* = 5.1) and 4.56 (0.11H, d, *J* = 5.1, H-2,3); 4.61 (0.89H, d, *J* = 5.0, H-3); 5.06 (1H, dd, *J* = 17.2, *J* = 1.5, H-a); 5.18 (1H, dd, *J* = 10.2, *J* = 1.5, H-b); 6.02 (1H, ddt, *J* = 17.2, *J* = 10.2, *J* = 6.2, CH); 7.23-7.42 (4H, m, H Ar); 7.75-7.89 (4H, m, H PhthN). ^{13}C NMR spectrum of major invertomer, δ, ppm: 35.4 (C-2); 37.5 (CH_2); 47.6 (C-3); 114.9 (CN); 116.9 (=CH_2); 123.9 (C-b); 126.3, 127.2, 129.3, 130.1 (C-3',4',5',6'); 130.2 (C-a); 131.5, 138.5 (C-1',2'); 136.1 (CH=CH_2); 164.9 (NCO). Found, *m/z*: 352.1010 $[M+Na]^+$. $C_{20}H_{15}N_3NaO_2$. Calculated, *m/z*: 352.1057. Found, %: C 73.01; H 4.53; N 12.68. $C_{20}H_{15}N_3O_2$. Calculated, %: C 72.94; H 4.59; N 12.76.

(2*R'*,3*S'*)-3-[2-(Propargyloxymethyl)phenyl]-1-phthalimidoaziridine-2-carbonitrile (7a). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a column packed with 30 g silica gel using CH_2Cl_2 as the eluent to give compound **7a**. Yield 0.579 g (54%). Yellow crystals, mp 165°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 (1H, t, *J* = 2.3, ≡CH); 3.24 (1H, d, *J* = 5.0, H-2); 4.27 (2H, d, *J* = 2.3, CH_2C≡); 4.71 (1H, d, *J* = 11.4) and 4.91 (1H, d, *J* = 11.4, OCH_2Ar); 4.76 (1H, d, *J* = 5.0, H-3); 7.34-7.45 (4H, m, H Ar); 7.75-7.89 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 35.6 (C-2); 47.4 (C-3); 57.7 (CH_2C≡); 69.9 (CH_2Ar); 75.7 (C≡CH); 79.2 (C≡CH); 114.9 (CN); 123.9 (C-b); 126.5, 129.1, 129.1, 130.0 (C-3',4',5',6'); 130.2 (C-a); 132.7, 135.9 (C-1',2'); 134.8 (C-c); 164.9 (NCO). Found, *m/z*: 358.1119 $[M+H]^+$. $C_{21}H_{16}N_3O_3$. Calculated, *m/z*: 358.1186. Found, %: C 70.63; H 4.26; N 11.50. $C_{21}H_{15}N_3O_3$. Calculated, %: C 70.58; H 4.23; N 11.76.

(2*R'*,3*R'*)-3-(2-Allyloxymethyl)phenyl)-1-phthalimidoaziridine-2-carbonitrile (7b). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a column packed with 30 g silica gel using CH_2Cl_2 as the eluent to give compound **7b**. Yield 0.496 g (46%). Colorless crystals, mp 121-122°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.23 (1H, d, *J* = 5.0, H-2); 4.07 and 4.13 (total 2H, two dddd, *J* = 12.5, *J* = 5.8, *J* = 1.3, *J* = 1.3, CH_2CH=); 4.57 (1H, d, *J* = 11.5) and 4.81 (1H, d, *J* = 11.5, H-b); 4.73 (1H, d, *J* = 5.0, H-3); 5.24 (1H, ddt, *J* = 10.3, *J* = 1.3, *J* = 1.3, H-b); 5.33 (1H, ddt, *J* = 17.2, *J* = 1.3, H-a); 5.99 (1H, ddt, *J* = 17.2, *J* = 10.3, *J* = 5.8, CH=CH_2); 7.32-7.36 (3H, m) and 7.42-7.46 (1H, m, H Ar); 7.57-7.89 (4H, m, PhthN). ^{13}C NMR spectrum, δ, ppm: 35.5 (C-2); 47.5 (C-3); 70.7 (OCH_2); 71.8 (OCH_2); 115.0 (CN); 118.1 (CH=CH_2); 123.8 (C-b); 126.5, 128.8, 129.0, 129.7 (C-3',4',5',6'); 130.2 (C-a); 132.5, 136.8 (C-1',2'); 134.3 (CH=CH_2); 134.8 (C-c); 164.9 (NCO). Found, *m/z*: 398.0900 $[M+K]^+$. $C_{21}H_{17}KN_3O_3$. Calculated, *m/z*: 398.0902. Found, %: C 70.05; H 4.80; N 11.65. $C_{21}H_{17}N_3O_3$. Calculated, %: C 70.58; H 4.77; N 11.69.

Methyl (2*R'*,3*S'*)-3-(2-Benzyloxyphenyl)-1-phthalimidoaziridine-2-carboxylate (8a). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was dissolved in a minimal amount of dichloromethane and hexane was added dropwise until the onset of crystallization. The precipitate formed was filtered off and dried in the air to give compound **8a**. Yield 0.964 g (75%). Yellow

crystals, mp 172-174°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.32 (1H, d, *J* = 5.1, H-2); 3.66 (3H, s, OCH_3); 4.57 (1H, d, *J* = 5.1, H-3); 5.14 (2H, s, OCH_2); 6.99-7.10 (2H, m, H-3',5'); 7.26-7.41 (6H, m, H Ph, H-4'); 7.53 (1H, dd, *J* = 7.3, *J* = 1.5, H-6'); 7.66-7.80 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 46.0, 46.5 (C-2,3); 52.8 (CH_3); 70.2 (OCH_2); 111.8 (C-3'); 121.2 (C-5'); 123.2 (C-b); 123.9 (C-1'); 127.1, 127.9, 128.0, 128.6,129.5(C-4',6', *m,o,p*-C); 130.5 (C-a); 134.1 (C-c); 137.0 (*i*-C); 157.0 (C-2'); 164.8 (NCO); 167.2 (CO_2). Found, *m/z*: 429.1455 $[M+H]^+$. $C_{25}H_{21}N_2O_5$. Calculated, *m/z*: 429.1455. Found, %: C 70.08; H 4.61; N 4.61. $C_{25}H_{20}N_2O_5$. Calculated, %: C 70.08; H 4.71; N 6.54.

(2*R′*,3*S′*)-3-(2-Benzyloxyphenyl)-1-phthalimidoaziridine-2-carbonitrile (8b). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was dissolved in a minimal amount of dichloromethane and hexane was added until the solution became turbid. The mixture was then left overnight in a refrigerator. The precipitate was filtered off and dried in the air to give compound **8b**. Yield 0.403 g (34%). Colorless crystals. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.22 (1H, d, *J* = 5.1, H-2); 4.73 (1H, d, *J* = 5.1, H-3); 5.19 (2H, s, OCH_2); 6.93-7.03 (2H, m, H-3',5'); 7.28-7.50 (7H, m, H Ph, H-4',6'); 7.70-7.90 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 34.9 (C-2); 46.1 (C-3); 70.4 (OCH_2); 112.1 (C-3'); 115.1 (CN); 121.3 (C-5'); 121.9 (C-1'); 123.8 (C-b); 127.2 (*o*-C); 127.7, 128.2 (C-4',6', *p*-C); 128.8 (*m*-C); 130.3 (C-a); 134.7 (C-c); 136.6 (*i*-C); 157.2 (C-2'); 164.9 (CO). Found, *m/z*: 396.1313 $[M+H]^+$. $C_{24}H_{18}N_3O_3$. Calculated, *m/z*: 396.1343.

(2*R′*,3*S′*)-3-[2-(Cyanomethoxy)phenyl]-1-phthalimidoaziridine-2-carbonitrile (8c). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was dissolved in a minimal amount of dichloromethane and hexane was added dropwise until the onset of crystallization. After several hours, the precipitate formed was filtered off and dried in vacuum to give compound **8c**. Yield 0.837 g (81%). Colorless crystals, mp 127-129°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.25 (1H, d, *J* = 5.1, H-2); 4.69 (1H, d, *J* = 5.1, H-3); 4.92 (1H, d, *J* = 16.4) and 4.93 (1H, d, *J* = 16.4, OCH_2); 7.07 (1H, d, *J* = 8.7, H-3'); 7.14 (1H, dd, *J* = 7.3, *J* = 7.3, H-5'); 7.38-7.47 (2H, m, H-4',6'); 7.75-7.88 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 35.1 (C-2); 45.1 (C-3); 54.2 (CH_2O); 112.3 (C-3'); 114.8 (CN); 114.9 (CN); 121.5 (C-5'); 123.6, 123.9 (C-b, C-1'); 128.0 (C-6'); 130.2, 130.6 (C-4', C-a); 134.8 (C-c); 155.2 (C-2'); 164.8 (CO). Found, *m/z*: 345.0968 $[M+H]^+$. $C_{19}H_{13}N_4O_3$. Calculated, *m/z*: 345.0983. Found, %: C 66.38; H 3.52; N 16.22. $C_{19}H_{12}N_4O_3$. Calculated, %: C 66.28; H 3.51; N 16.27.

Allyl (2*R′*,3*S′*)-3-Phenyl-1-phthalimidoaziridine-2-carboxylate (9a). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a column packed with 30 g silica gel using dichloromethane as the eluent to give compound **9a**. Yield 0.627 g (60%). A yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.55 (1H, d, *J* = 4.6, H-2); 4.40 (1H, d, *J* = 4.6, H-3); 4.56-4.68 (2H, m, OCH_2); 5.25 (1H, ddt, *J* = 10.4, *J* = 1.2, *J* = 1.2, H-b); 5.34 (1H, ddt, *J* = 17.2, *J* = 1.4, *J* = 1.4, H-a); 5.90 (1H, ddt, *J* = 17.2, *J* = 10.4, *J* = 5.9, C<u>H</u>=CH_2); 7.28-7.48 (5H, m, H Ph); 7.65-7.81 (4H, m, H PhthN). ^{13}C NMR, δ, ppm: 46.3, 49.8 (C-2,3); 66.8 (OCH_2); 119.3 (CH=<u>C</u>H_2); 123.3 (C-b); 127.3, 128.8 (*m,o*-C, <u>C</u>H=CH_2, signals overlap); 130.4 (C-a); 131.3 (*p*-C); 134.2 (C-c); 134.6 (*i*-C); 164.8 (NCO); 166.1 (CO_2). Found, *m/z*: 349.1136 $[M+H]^+$. $C_{20}H_{17}N_2O_4$. Calculated, *m/z*: 349.1183.

Propargyl (2*R′*,3*S′*)-3-Phenyl-1-phthalimidoaziridine-2-carboxylate (9b). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a column packed with 30 g silica gel using from 3:1 to 5:1 dichloromethane−hexane as the eluent to give compound **9b**. Yield 0.770 g (74%). A pale-yellow glassy substance. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.48 (1H, t, *J* = 2.4, C≡CH); 3.57 (1H, d, *J* = 4.9, H-2); 4.41 (1H, d, *J* = 4.9, H-3); 4.63 (1H, dd, *J* = 15.5, *J* = 2.4) and 4.81 (1H, dd, *J* = 15.5, *J* = 2.4, OCH_2); 7.34-7.48 (5H, m, H Ph); 7.66-7.81 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 45.9, 50.0 (C-2,3); 53.6 (OCH_2); 75.8 (C≡<u>C</u>H); 123.3 (C-b); 127.4, 128.8 (*m,o*-C); 128.9 (*p*-C); 130.3 (C-a); 134.2 (C-c); 134.3 (*i*-C); 164.7 (NCO); 165.7 (CO_2). The <u>C</u>≡CH signal is apparently overlapped by the solvent signal. Found, *m/z*: 385.0513 $[M+K]^+$. $C_{20}H_{14}KN_2O_4$. Calculated, *m/z*: 385.0586.

(2*R′*,3*S′*)-(3-Phenyl-1-phthalimidoaziridin-2-yl)methyl 3-Phenylprop-2-ynoate (10a). The reaction was carried out at 0°C. The combined filtrates were evaporated in vacuum. The residue was separated by chromatography on a silica gel column with 350:1 dichloromethane−methanol as the eluent to give compound

10a. Yield 0.620 g (49%). A pale-yellow glassy substance, mp 76-77°C. The ^{1}H NMR spectrum indicated a 1:0.58 mixture of two invertomers. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.21-3.26 (0.37H, m) and 4.38-4.43 (0.63H, m, H-2); 3.80 (0.63H, d, *J* = 5.5) and 4.14 (0.37H, d, *J* = 5.5, H-3); 4.48 (0.37H, dd, *J* = 12.5, *J* = 5.2); 4.77 (0.37H, dd, *J* = 12.5, *J* = 5.8); 4.57 (0.63H, dd, *J* = 11.9, *J* = 6.0) and 4.69 (0.63H, dd, *J* = 11.9, *J* = 4.9, OCH_2); 7.22-7.65 (12.52H, m, H Ph, H PhthN maj.); 7.68-7.83 (1.48H, m, H Ph, H PhthN min.). ^{13}C NMR spectrum, δ, ppm: 42.3; 46.2; 47.0 and 49.6 (C-2,3); 62.1 (OCH_2 min.); 65.5 (OCH_2 maj.); 80.0 (C≡<u>C</u>CO_2 min.); 80.4 (C≡<u>C</u>CO_2 maj.); 87.4 (<u>C</u>≡CCO_2 maj.); 87.8 (<u>C</u>≡CCO_2 min.); 119.4 and 119.6 (*i*-C Ph at C≡C); 123.0 and 123.4 (C-b); 127.3; 128.3; 128.4; 128.7; 129.0; 129.6, 130.9; 131.0 and 133.2 (*m,o,p*-C); 130.1, 130.4, 130.6, and 135.8 (C-a, *i*-C 3-Ph); 134.0 and 134.4 (C-c); 153.9 (CO_2); 165.5 and 165.9 (NCO). Found, *m/z*: 445.1198 $[M+Na]^+$. $C_{26}H_{18}N_2NaO_4$. Calculated, *m/z*: 445.1159. Found, %: C 74.22; H 4.37; N 6.61. $C_{26}H_{18}N_2O_4$. Calculated, %: C 73.92; H 4.29; N 6.63.

(2*R′*,3*S′*)-(3-Phenylphthalimidoaziridin-2-yl)methyl Furan-2-carboxylate (10b). The reaction was carried out at 13°C. The combined filtrates were evaporated in vacuum but not to dryness. Hexane was added dropwise to the residue until the onset of crystallization with concurrent rubbing the walls of the flask using a glass rod. The precipitate was filtered off to give compound **10b**. Yield 0.594 g (51%). Yellow crystals, mp 150-151°C. The ^{1}H NMR spectrum indicated the existence of a 1.3:1 mixture of two invertomers. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.24-3.28 (0.43H, m) and 4.38-4.44 (0.57H, m, H-2); 3.79 (0.57H, d, *J* = 5.7, H-3) and 4.24 (0.43H, d, *J* = 5.5, H-3); 4.53-4.59 (0.86H, m) and 4.64-4.81 (1.14H, m, OCH_2); 6.48 (0.43H, dd, *J* = 3.5, *J* = 1.7) and 6.53 (0.57H, dd, *J* = 3.5, *J* = 1.7, H-4'); 7.15-7.52 (7H, m, H-3',5' and H Ph); 7.57-7.64 (2.28H, m) and 7.68-7.81 (1.72H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 42.8; 45.5; 47.4 and 49.5 (C-2,3); 60.8 and 64.6 (OCH_2); 112.1 (C-4'); 118.8 (C-3'); 123.0 and 123.3 (C-b); 127.3, 128.3. 128.4, 128.7, 129.0 and 129.6 (*m,o,p*-C); 130.1, 130.5, 130.6, and 135.9 (C-a and *i*-C); 134.0 and 134.3 (C-c); 144.0 and 144.4 (C-2'); 146.8 and 146.9 (C-5'); 158.0 and 158.6 (CO_2); 165.5 and 165.9 (NCO). Found, *m/z*: 411.1027 $[M+Na]^+$. $C_{22}H_{16}N_2NaO_5$. Calculated, *m/z*: 411.0952. Found, %: C 68.11; H 4.08; N 7.09. $C_{22}H_{16}N_2O_5$. Calculated, %: C 68.04; H 4.15; N 7.21.

(2*R′*,3*S′*)-(3-Phenyl-1-phthalimidoaziridin-2-yl)methyl Benzoate (10c). The reaction was carried out at 0°C. The combined filtrates were evaporated in vacuum but not to dryness. Hexane was added to the residue until the onset of crystallization. The precipitate formed was filtered off and discarded. Diethyl ether was added to the remaining solution and cooled to 0°C. The precipitate formed was filtered off and washed with diethyl ether to give compound **10c**. Yield 0.560 g (47%). Colorless flakes with a greenish tinge, mp 123-124°C. The ^{1}H NMR spectrum indicated the existence of a 1.4:1 mixture of two invertomers. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.27-3.32 (0.42H, m) and 4.44-4.50 (0.58H, m, H-2); 3.80 (0.58H, dd, *J* = 5.5) and 4.25 (0.42H, d, *J* = 5.5, H-3); 4.56 (0.58H, dd, *J* = 11.7, *J* = 6.6); 4.82 (0.58H, dd, *J* = 11.7, *J* = 4.1) and 4.68-4.76 (0.84H, m, OCH_2); 7.21-7.64 (10.32H, m, H Ar, H PhthN maj.); 7.67-7.80 (1.68H, m, H PhthN min.); 7.97 (0.84H, d, *J* = 7.4) and 8.16 (1.16H, d, *J* = 7.3, *o*-H $PhCO_2$). ^{13}C NMR spectrum, δ, ppm: 42.9, 45.5, 47.6, 49.5 (C-2,3); 60.9, 64.9 (OCH_2); 123.0, 123.3, 127.3, 128.3, 128.5, 128.7, 128.9, 129.7, 129.8, 130.0, 133.2 and 133.4 (C-b, *m,o,p*-C); 130.1, 130.5, 130.6 and 135.9 (C-a, *i*-C); 134.0 and 134.3 (C-c); 165.5, 165.9, 166.1 and 166.6 (NCO, CO_2). Found, *m/z*: 421.1139 $[M+Na]^+$. $C_{24}H_{18}N_2NaO_4$. Calculated, *m/z*: 421.1158.

(2*R′*,3*S′*)-(3-Phenyl-1-phthalimidoaziridin-2-yl)methyl 4-Nitrobenzoate (10d). The reaction was carried out at 0°C. The combined filtrates were evaporated in vacuum but not to dryness. Hexane was added dropwise to the residue until the onset of crystallization with concurrent rubbing the walls of the flask using a glass rod. The precipitate was filtered off to give compound **10d**. Yield 0.652 g (49%). Yellowish flake crystals, mp 159°C. The ^{1}H NMR spectrum indicated a 1.9:1 mixture of two invertomers. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.32 (0.35H, ddd, *J* = 7.3, *J* = 5.5, *J* = 3.9) and 4.96 (0.65H, ddd, *J* = 9.1, *J* = 7.3, *J* = 4.8, H-2); 3.79 (0.65H, d, *J* = 4.8) and 4.24 (0.35H, dd, *J* = 5.5, H-3); 4.43-4.48 (1.30H, m); 4.64 (0.35H, dd, *J* = 12.9, *J* = 7.3) and 4.84 (0.35H, dd, *J* = 12.9, *J* = 3.9, OCH_2); 7.20-7.48 and 8.19-8.38 (9H, m, H Ar); 7.61 (2.60H, br. s) and 7.70-7.81 (1.40H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 42.8, 45.3, 47.2 and 49.3 (C-2,3); 61.7 (OCH_2 min.); 65.9 (OCH_2 maj.); 123.7 (C-b maj.); 123.1, 123.3, 127.3, 128.4, 128.5, 128.7, 129.1 and 129.6 (C-b min., *o*-C Ar, *m,o,p*-C Ph both invertomers); 131.0 (*m*-C Ar min.); 131.2 (*m*-C Ar maj.); 134.1 (C-c maj.);

134.5 (C-c min.); 130.0, 130.2, 130.5, 135.0, 135.4 and 135.6 (C-a, *i*-C); 150.7 (*p*-C Ar); 164.4, 164.8, 165.4 and 165.9 (NCO, CO_2). Found, *m/z*: 444.1222 $[M+H]^+$. $C_{24}H_{18}N_3O_6$. Calculated, *m/z*: 444.1196. Found, %: C 64.97; H 3.96; N 9.26. $C_{24}H_{17}N_3O_6$. Calculated, %: C 65.01; H 3.86; N 9.48.

Thermolysis of Aziridines 6 and 7 (General Method). A solution of aziridine **6** or **7** (1 mmol) in anhydrous toluene (10 ml) was heated in a thick-walled glass reactor. The solvent was then distilled off in vacuum. The residue was separated by chromatography on a silica gel column using from 6:1 to 3:1 hexane–ethyl acetate mixture as eluent.

Methyl (2*R′*,3a*R′*,8b*S′*)-1-phthalimido-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole-2-carboxylate (11a) was obtained after 3 h heating of aziridine **6a** at 150°C. Yield 213 mg (59%). Colorless crystals, mp 133°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.96 (1H, ddd, *J* = 11.0, *J* = 11.0, *J* = 11.0, *endo*-H-3); 2.51-2.60 (1H, m, *exo*-H-3); 2.85 (1H, d, *J* = 16.4, *endo*-H-4); 3.15 (1H, dd, *J* =16.4, *J* = 8.0, *exo*-H-4); 3.42-3.47 (1H, m, H-3a); 3.56 (3H, s, CH_3); 4.72 (1H, dd, *J* = 11.0, *J* = 6.4, H-2); 5.03 (1H, d, *J* = 8.6, H-8b); 7.18-7.20 (3H, m) and 7.29-7.31 (1H, m, H Ar); 7.75-7.91 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 34.3, 36.6 (C-3,4); 40.2 (C-3a); 52.1 (CH_3); 64.9 (C-2); 75.0 (C-8b); 123.6 (C-b); 125.4, 125.7, 127.4, 128.2 (C-5',6',7',8'); 130.3 (C-a); 134.5 (C-c); 141.2, 142.7 (C-4a,8a); 167.0 (NCO); 171.3 (CO_2). Found, *m/z*: 385.1157 $[M+Na]^+$. $C_{21}H_{18}N_2NaO_4$. Calculated, *m/z*: 385.1164. Found, %: C 69.45; H 5.21; N 7.71. $C_{21}H_{18}N_2O_4$. Calculated, %: C 69.60; H 5.01; N 7.73.

(2*R′*,3a*R′*, 8b*S′*)-1-Phthalimido-1,2,3,3a,4,8b-hexahydroindeno[1,2-*b*]pyrrole-2-carbonitrile (11b) was obtained after 2.5 h heating aziridine **6b** at 120°C. Yield 230 mg (70%). Colorless crystals, mp 188-189°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.09 (1H, ddd, *J* = 11.2, *J* = 11.2, *J* = 11.2, *endo*-H-3); 2.65-2.74 (1H, m, *exo*-H-3); 2.89 (1H, d, *J* = 16.4, *endo*-H-4); 3.19 (1H, dd, *J* = 16.4, *J* = 8.0, *exo*-H-4); 3.41-3.53 (1H, m, H-3a); 4.86 (1H, dd, *J* = 11.2, *J* = 6.1, H-2); 5.02 (1H, d, *J* = 8.4, H-8b); 7.21-7.32 (4H, m, H Ar); 7.81-7.95 (4H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 36.0, 36.3 (C-3,4); 40.8 (C-3a); 53.8 (C-2); 74.4 (C-8b); 118.3 (CN); 123.9 (C-b); 125.5, 125.7, 127.6, 128.6 (C-5',6',7',8'); 129.9 (C-a); 134.9 (C-c); 140.6, 141.7 (C-4a,8a). The phthalimide group NCO signals are not visible due to strong broadening attributed to slow rotation about the N–N bond. Found, *m/z*: 368.0774 $[M+K]^+$. $C_{20}H_{15}KN_3O_2$. Calculated, *m/z*: 368.0801. Found, %: 72.95; H 4.52; N 12.52. $C_{20}H_{15}N_3O_2$. Calculated, %: C 72.94; H 4.59; N 12.76.

4,6-Dihydro-1*H*-[2]benzoxepino[5,4-*b*]pyrrole-2-carbonitrile (12) was obtained after 2 h heating aziridine **7a** at 130°C. Yield 46 mg (22%). Colorless crystals, mp 196-198°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.69 (2H, s, OCH_2); 4.98 (2H, s, OCH_2); 6.72 (1H, d, *J* = 2.6, H-3); 7.23-7.30 (2H, m, H-7,9); 7.37 (1H, ddd, *J* = 7.0, *J* = 7.0, *J* = 2.4, H-8); 7.49 (1H, d, *J* = 7.6, H-10); 9.41 (1H, br. s, NH). ^{13}C NMR spectrum, δ, ppm: 69.5, 72.9 (C-4,6); 102.1 (C-2); 114.6 (CN); 118.5 (C-3); 123.9 (C-3a); 124.1, 128.0, 128.8, 129.1 (C-7',8',9',10'); 129.9, 132.0, 138.2 (C-6a,10a,10b). Found, *m/z*: 233.0648 $[M+Na]^+$. $C_{13}H_{10}N_2NaO$. Calculated, *m/z*: 233.0691. Found, %: C 74.39; H 4.76; N 13.12. $C_{13}H_{10}N_2O$. Calculated, %: C 74.27; H 4.79; N 13.33.

The fractions containing imines **13a** and **14a** were combined, concentrated in vacuum, and left for 10 days at room temperature. The product was separated by chromatography on a silica gel column using 4:1 hexane–ethyl acetate as eluent. Products **13a** and **15** were dissolved in a minimal amount of methylene chloride. Diethyl ether and hexane were added in volumes equal to the volume of the methylene chloride solution. After 1.5-2.0 h, the precipitates were filtered off and dried in the air.

(*E*)-2-[2-(Propargyloxymethyl)benzylidenamino]-2-phthalimidoacetonitrile (13a). Yield 55 mg (15%). Colorless crystals, mp 103-105°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.47 (1H, t, *J* = 2.4, C≡CH); 4.24 (2H, d, *J* = 2.4, $OCH_2C{\equiv}$); 4.80 (1H, d, *J* = 12.4) and 4.90 (1H, d, *J* = 12.4, $ArCH_2$); 6.78 (1H, d, *J* = 1.4, NCHN); 7.35-7.46 (4H, m, H Ar); 7.78-7.95 (4H, m, H PhthN); 9.10 (1H, *J* = 1.4, CH=N). ^{13}C NMR spectrum, δ, ppm: 57.8 ($O\underline{C}H_2C{\equiv}$); 59.6 (NCHN); 69.3 ($OCH_2Ar$); 75.4 ($C{\equiv}\underline{C}H$); 79.3 ($\underline{C}{\equiv}CH$); 112.9 (CN); 124.3 (C-b); 128.6, 129.3, 129.7, 132.2 (C-3',4',5',6'); 131.5 (C-a); 132.5, 138.4 (C-1',2'); 135.0 (C-c); 164.8 (CH=N); 165.5 (NCO). Found, *m/z*: 358.1182 $[M+H]^+$. $C_{21}H_{16}N_3O_3$. Calculated, *m/z*: 358.1192. Found, %: C 70.48; H 4.32; N 11.49. $C_{21}H_{15}N_3O_3$. Calculated, %: C 70.58; H 4.23; N 11.76.

The following signals of **(*E*)-{[2-(propargyloxymethyl)phenyl](phthalimido)methyl}iminoacetonitrile (14a)** were identified in the ^{1}H NMR spectrum of the mixture of imines **13a** and **14a**, δ, ppm (*J*, Hz): 2.37 (1H, t, *J* = 2.4, C≡CH); 3.99 (2H, d, *J* = 2.4, OCH_2C≡); 4.53 (1H, d, *J* = 11.1) and 4.69 (1H, d, *J* = 11.1, $ArCH_2$); 7.22 (1H, d, *J* = 2.3, HCHN or CH=N).

({(*Z*)-[2-(Propargyloxymethyl)phenyl](phthalimido)methylidene}aminoacetonitrile (15). Yield 20 mg (6%). Colorless crystals, which turn pink over time, mp 126°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.37 (1H, t, *J* = 2.2, C≡C<u>H</u>); 3.94 (2H, d, *J* = 2.2, O<u>CH$_2$</u>C≡CH); 4.54 (2H, s) and 4.72 (2H, s, $ArCH_2$, NCH_2); 7.35-7.55 (4H, m, H Ar); 7.81-7.95 (4H, m, H PhthN). ^{13}C NMR spectrum in DMSO-d_6, δ, ppm: 40.3 (NCH_2); 57.2 (O<u>C</u>H$_2$C≡); 68.6 (OCH_2Ar); 77.4 (C≡<u>C</u>H); 79.7 (<u>C</u>≡CH); 117.9 (CN); 124.1 (C-b); 127.9, 129.0, 129.5, 130.9 (C-3',4',5',6'); 131.5 (C-a); 133.4, 136.9 (C-1',2'); 135.3 (C-c); 149.6 (NC=N); 165.3 (NCO). Found, *m/z*: 358.1162 $[M+H]^+$. $C_{21}H_{16}N_3O_3$. Calculated, *m/z*: 358.1192. Found, %: C 70.37; H 4.28; N 11.23. $C_{21}H_{15}N_3O_3$. Calculated, %: C 70.58; H 4.23; N 11.76.

A mixture of (*E*)-2-[2-(allyloxymethyl)benzylideneamino]-2-phthalimidoacetonitrile (13b) and (*E*)-{[2-(allyloxymethyl)phenyl](phthalimido)methyl}iminoacetonitrile (14b) was obtained after 2 h heating of aziridine **7b** at 130°C. Yield 140 mg (39%) of a 3:2 mixture of **13b** and **14b.** Yellow crystals, mp 79-82°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.87-3.90 (0.8H, m, C<u>H$_2$</u>CH=CH_2 **14b**); 4.09-4.11 (1.2H, m, C<u>H$_2$</u>CH=CH_2 **13b**); 4.46 (0.4H, d, *J* = 11.2) and 4.59 (0.4H, d, *J* = 11.2, $ArCH_2$ **14b**); 4.70 (0.6H, d, *J* = 12.3) and 4.80 (0.6H, d, *J* = 12.3, $ArCH_2$ **13b**); 5.03 (0.4H, ddt, *J* = 10.4, *J* = 1.5, *J* = 1.5, H-b **14b**); 5.14 (0.4H, ddt, *J* = 17.2, *J* = 1.5, *J* = 1.5, H-a **14b**); 5.20 (0.6H, ddt, *J* = 10.4, *J* = 1.6, *J* = 1.6, H-b isomer **13b**); 5.31 (0.6H, ddt, *J* = 17.2, *J* = 1.6, *J* = 1.6, H-a **13b**); 5.67 (0.4H, ddt, *J* = 17.2, *J* = 10.4, *J* = 5.7, C<u>H</u>=CH_2 **14b**); 5.98 (0.6H, ddt, *J* = 17.2, *J* = 10.4, *J* = 5.7, C<u>H</u>=CH_2 **13b**); 6.78 (0.6H, d, *J* = 1.9, NCHN **13b**); 7.24 (0.4H, d, *J* = 2.4); 7.28-7.45 (m) and 7.72-7.96 (total 8.4H, m, NCHN and CH=N **14b**, H Ar and H PhthN of both isomers); 9.12 (0.6H, d, *J* = 1.9, CH=N isomer **13b**). ^{13}C NMR spectrum, δ, ppm: 59.6, 70.7 (NCHN); 70.0, 70.6, 71.6, 71.8 (OCH_2); 112.9, 114.2 (CN); 117.5, 117.8 (CH=<u>C</u>H$_2$); 123.8, 124.3 (C-b); 128.3, 128.8, 129.1, 130.5, 130.8, 132.1, 134.0, 134.4, 134.6, 135.0 (C-3',4',5',6', C-b, <u>C</u>H=CH_2); 131.4, 131.6 (C-a); 132.4, 134.6, 135.6, 139.3 (C-1',2'); 137.6 (CH=N **14b**); 164.9 (CH=N **13b**); 165.5, 167.1 (NCO). Several signals in the ^{13}C NMR spectrum overlap. Found, *m/z*: 398.0885 $[M+K]^+$. $C_{21}H_{17}KN_3O_3$. Calculated, *m/z*: 398.0907. Found, %: C 70.33; H 4.75; N 11.56. $C_{21}H_{17}N_3O_3$. Calculated, %: C 70.18; H 4.77; N 11.69.

Thermolysis of Aziridine 8a. A solution of aziridine **8a** (0.860 g, 2 mmol) in anhydrous benzene (12 ml) was heated for 5 h at 150°C. The solvent was distilled off in vacuum. The residue was separated chromatographically on silica gel using 1:1 hexane–ethyl acetate as the eluent to give 100 mg (18%) **2-(2-benzyloxyphenyl)-5-methoxyoxazole (16)** as a green oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 3.91 (3H, s, OCH_3); 5.24 (2H, s, OCH_2); 6.26 (1H, s, H-4); 7.00-7.05 (2H, m, H-3',5'); 7.29-7.40 (5H, m, H Ph); 7.52-7.59 (2H, m, H-4',6').

Thermolysis of Aziridine 8b. A solution of aziridine **8b** (534 mg, 1.4 mmol) in anhydrous benzene (15 ml) was heated for 4 h at 150°C. The ^{1}H NMR spectrum of the reaction mixture showed only signals of phthalimide and 2-benzyloxybenzaldehyde (identified by comparison with the spectra of authentic samples).

Thermolysis of Aziridine 8c. The reaction was carried out twice, isolating one of the products in each case. A solution of aziridine **8c** (650 mg, 1.9 mmol) in anhydrous benzene (15 ml) was heated for 4 h at 150°C. The solvent was distilled off in vacuum. The residue was dissolved in 50 ml methylene chloride and washed with 0.025 M NaOH (8×30 ml). The organic layer was separated and dried over sodium sulfate. The solvent was distilled off in vacuum. The residue was subjected to chromatography on silica gel using from 2:1 to 1:2 hexane–ethyl acetate as the eluent.

(2*R′*,9b*S′*)-1-Phthalimido-1,2,4,9b-tetrahydrochromeno[3,4-*d*]imidazole-2-carbonitrile (17) was additionally purified by recrystallization from ethanol. Yield 20 mg (3%).Colorless crystals, mp 200-202°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.84 (1H, dd, *J* = 16.7, *J* = 1.8, *endo*-H-4); 5.17 (1H, dd, *J* = 3.2, *J* = 3.1, *exo*-H-4); 5.67 (1H, d, *J* = 2.8, H-2); 6.33 (1H, ddd, *J* = 3.2, *J* = 2.8, *J* = 1.8, H-9b); 7.01 (1H, d, *J* = 7.9, H-6); 7.11 (1H, dd, *J* = 7.5, *J* = 7.1, H-8); 7.20-7.30 (1H, m, H-7); 7.58 (1H, d, *J* = 7.7, H-9); 7.80-8.00 (4H, m,

H PhthN). ^{13}C NMR spectrum, δ, ppm: 66.9 (C-4); 69.7 (C-9b); 83.6 (C-2); 115.6 (C-6); 117.9 (CN); 124.1 (C-9a); 124.3, 124.6 (C-8, C-b); 126.2, 129.6 (C-7,9); 129.7 (C-a); 135.4 (C-c); 153.2 (C-5a); 165.9 (NCO); 177.7 (C-3a). Found, *m/z*: 345.0971 $[M+H]^+$. $C_{19}H_{13}N_4O_3$. Calculated, *m/z*: 345.0982. Found, %: C 66.34; H 3.56; N 16.38. $C_{19}H_{12}N_2O_3$. Calculated, %: C 66.28; H 3.51; N 16.27.

3-[2-(Cyanomethoxy)phenyl]-3-(2-phthalimidoimino)propanenitrile (18). A solution of aziridine **8c** (343 mg, 1 mmol) in anhydrous benzene (15 ml) was heated for 4 h at 150°C. The solvent was distilled off in vacuum. The residue was separated chromatographically on silica gel using pure methylene chloride as the eluent. Isolated hydrazone **18** was further purified by recrystallization from ethanol. Yield 10 mg (3%). Colorless crystals. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.46 (2H, s, OCH_2CN); 4.58 (2H, s, CCH_2CN); 6.85 (1H, d, *J* = 8.0, H-3); 7.24-7.29 (1H, m, H-5); 7.51 (1H, dd, *J* = 7.3, *J* = 7.3, H-4); 7.82-8.01 (5H, m, H PhthN, H-6). ^{13}C NMR spectrum, δ, ppm: 40.1 ($C\underline{C}H_2CN$); 54.1 (OCH_2); 112.3 (C-3'); 113.7 (CN); 116.6 (CN); 124.0 (C-5'); 124.3 (C-1'); 124.8 (C-b); 131.7 (C-a); 132.9, 133.3 (C-4',6'); 135.5 (C-c); 154.5 (C-2'); 162.5 (C=N); 165.5 (NCO). Found, *m/z*: 345.0979 $[M+H]^+$. $C_{19}H_{13}N_4O_3$. Calculated, *m/z*: 345.0982.

Determination of the Aziridines 9 and 10 Thermolysis Products Yield by ^{1}H NMR Spectroscopy with Internal Standard. After heating the starting aziridine, the solvent was distilled off in vacuum. The residue was dissolved in $CDCl_3$ and the ^{1}H NMR spectrum was recorded. Then, 1 eq. *N*-benzylmaleimide was added into ampule and the ^{1}H NMR spectrum was recorded again.

Thermolysis of Aziridines 9a,b. A solution of aziridine **9a,b** (0.3 mmol) in anhydrous benzene (5 ml) was heated at 150°C. After 6 h heating of aziridine **9a**, the spectral yield of the **allyl (*E*)-2-benzylideneamino-2-phthalimidoacetate (19a)** was 40%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 4.73 (2H, dd, *J* = 5.8, *J* = 1.3, OCH_2); 5.21 (1H, ddt, *J* = 10.3, *J* = 1.2, *J* = 1.2, H-b); 5.30 (1H, ddt, *J* = 17.2, *J* = 1.4, *J* = 1.4, H-a); 5.86 (1H, ddt, *J* = 17.2, *J* = 10.3, *J* = 5.8, $C\underline{H}{=}CH_2$); 6.11 (1H, d, *J* = 0.9, NCHN); 7.35-7.90 (9H, m, H Ph, H PhthN). 8.40 (1H, s, CH=N).

After 10 h heating of aziridine **9b**, the spectral yield of the **propargyl (*E*)-2-benzylideneamino-2-phthalimidoacetate (19b)** was 41%. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49 (1H, t, *J* = 2.5, C≡CH); 4.80 (1H, dd, *J* = 15.5, *J* = 2.5) and 4.89 (1H, dd, *J* = 15.5, *J* = 2.5, OCH_2); 6.13 (1H, s, NCHN); 7.35-7.90 (9H, m, H Ph, H PhthN); 8.40 (1H, s, CH=N).

Thermolysis of aziridine 10a. A solution of aziridine **10a** (210 mg, 0.5 mmol) in anhydrous benzene (10 ml) was heated for 5 h at 180°C. The solvent was then distilled off in vacuum. The residue was separated chromatographically on silica gel using from 1:0 to 100:1 dichloromethane–methanol as the eluent. The yield of ***N*-ethylideneaminophthalimide** was 35 mg (37%, spectral yield 43%). Colorless crystals, subl.p 168-172°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.21 (3H, d, *J* = 5.3, CH_3); 7.72-7.77 (2H, m) and 7.83-7.88 (2H, m, H PhthN); 8.66 (1H, q, *J* = 5.3, CH=N). The structure of product **21** was confirmed by counter synthesis from acetaldehyde and *N*-aminophthalimide.

Thermolysis of Aziridines 10b-d. A solution of aziridine **10b-d** (15-17 mg) in anhydrous benzene (2 ml) was heated for 5 h at 180°C. The spectral yield of ***N*-ethylideneaminophthalimide (21)** for aziridines **10b, 10c,** and **10d** was 13, 6, and 45%, respectively.

Thermolysis of aziridines 22a-c. A solution aziridine **22a-c** [12-14] (0.7 mmol) in anhydrous benzene (10 ml) was heated in a thick-walled reactor and the solvent was then distilled off in vacuum. After 6 h heating aziridine **22a** at 120°C, the ^{1}H NMR spectrum of the reaction mixture showed only signals for ***N*-[(*E*)-1-(benzylideneamino)benzyl]phthalimide (23a)** but this product could not be isolated as a pure compound due to its instability. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.87 (1H, d, *J* = 1.4, NCHN); 7.30-7.46 (6H, m, *m,p*-H); 7.58 (2H, d, *J* = 7.3, *o*-H benzyl); 7.70-7.74 (2H, m) and 7.84-7.90 (4H, m, H PhthN, *o*-H benzylidene); 8.40 (1H, d, *J* = 1.4, CH=N). ^{13}C NMR spectrum, δ, ppm: 73.9 (NCHN); 123.6 (C-b); 127.6, 128.4, 128.7, 129.0 (*m,o*-C); 128.3 and 131.6 (*p*-C); 131.9 (C-a); 134.3 (C-c); 135.4 and 138.8 (*i*-C); 162.7 (CH=N); 167.5 (NCO).

Heating aziridine **22b** for 2 h at 180°C leads to its complete decomposition and tar formation. Only signals for phthalimide could be identified in the ^{1}H NMR spectrum of the reaction mixture.

The residue obtained after heating aziridine **22c** at 120°C was separated on silica gel using 1.7:1 dichloromethane–hexane as the eluent. The fractions containing major products were combined and evaporated in vacuum. The residues were dissolved in dichloromethane and the products were precipitated from solution by adding hexane to give 45 mg (23%) **(*E*)-2-benzylideneamino-2-phthalimidoacetonitrile 23c** and 12 mg (6%) **(*Z*)-2-(phthalimido)imino-3-phenylpropanenitrile (24).**

(*E*)-2-Benzylideneamino-2-phthalimidoacetonitrile (23c). Colorless crystals, mp 145-146°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.78 (1H, d, *J* = 1.4, NCHN); 7.41-7.53 (3H, m, *m,p*-H); 7.78-7.84 (4H, m) and 7.91-7.96 (2H, m, H PhthN, *o*-H Ph); 8.77 (1H, d, *J* = 1.4, CH=N). ^{13}C NMR spectrum, δ, ppm: 59.3 (NCHN); 112.8 (CN); 124.3 (C-b); 128.9 and 129.6 (*m,o*-C); 131.5 (C-a); 132.7 (*p*-C); 134.0 (*i*-C); 135.0 (C-c); 165.6 (NCO); 165.9 (CH=N). Found, *m/z*: 328.0481 $[M+K]^+$. $C_{17}H_{11}KN_3O_2$. Calculated, *m/z*: 328.0482.

(*Z*)-2-(Phthalimido)imino-3-phenylpropanenitrile (24). Colorless needles, mp 185-186°C. ^{1}H NMR spectrum, δ, ppm: 44.8 (2H, s, CH_2); 7.39-7.45 (2H, m, *m*-H Ph); 7.50-7.55 (1H, m, *p*-H Ph); 7.72 (2H, m, *o*-H Ph); 7.86-7.91 (2H, m) and 7.96-8.02 (2H, m, H PhthN). ^{13}C NMR spectrum, δ, ppm: 39.8 (CH_2); 116.4 (CN); 124.8 (C-b); 128.2 and 129.0 (*m,o*-C); 131.4 (C-a); 132.5 (*p*-C); 133.3 (*i*-C, C=N); 135.5 (C-c); 165.4 (NCO). Found, *m/z*: 290.0914 $[M+H]^+$. $C_{17}H_{12}N_3O_2$. Calculated, *m/z*: 290.0925.

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