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Synthesis of Oxazoles from α,β-Unsaturated Carbonyl Compounds through 2-Acylaziridines

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Abstract—Oxidative addition of *N*-aminophthalimide to benzylideneacetone and chalcones followed by thermolysis of the arising 2-aryl-3-acyl-1-phthalimidoaziridines led to the formation of 2,5-disubstituted oxazoles in an overall yield 30–55%. Electron-donor substituents in the aryl fragment of 2-aryl-3-aroyl-1-phthalimidoaziridines accelerate their conversion into oxazoles, and similar substituents in the aroyl fragment retard this process. The possibility was demonstrated of going over to oxazoles from α,β-unsaturated carbonyl compounds via 2-acyl-1-sulfonylaziridines employing chloramine-B. However ethyl 2 cyanocinnamate reacted with chloramine-B with the rupture of the C=C bond and the formation of *N*-benzylidene-benzenesulfamide.

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The conversion of 2-acylaziridines into oxazoles was described 49 years ago [1]. It was shown that at 220°C in the vaporizer of the gas chromatograph 2 benzoyl-1-*tert*-butyl-3-phenylaziridine materially completely (to 96%) decomposed into 2,5 diphenyl-oxazole. Later the 2,5-diphenyloxazole was also obtained at the photolysis of this aziridine however in a lower yield (38%) [2].

Some years later a report appeared on the formation of oxazoles from 2 acylaziridines under far milder conditions [3]. It turned out that if 1-phthalimidoaziridines had at the C^2 atom two electron-acceptor groups, at least one of these groups was a carbonyl, and to the C^3 was attached an aryl substituent, these compounds already at 20–80°C decomposed along two competing routes leading to oxazolines and oxazoles. Therewith the oxazoles fraction in the reaction mixture grew with increasing temperature.

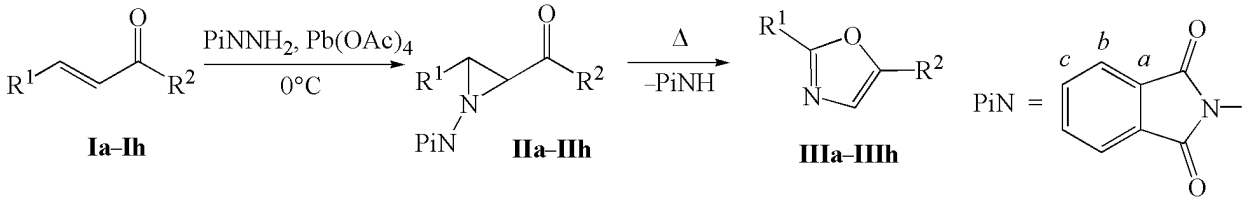
Thus up till now the fundamental possibility of oxazoles preparation from 2 acyl-1-phthalimidoaziridines was shown only for a narrow choice of compounds containing an additional electron-acceptor moiety. Meanwhile the conversion of α,β-unsaturated carbonyl compounds into aziridines with an appropriate leaving group on the nitrogen atom combined with subsequent thermolysis of these aziridines might become a general two-stage method of the synthesis of oxazoles, compounds exhibiting versatile biological activity [4], and also widely used in the organic synthesis [5], for instance, like latent equivalent of a carboxy group [6] or azadiene components in the Diels–Alder reaction [7].

Therefore the target of this research was the establishment of the preparative possibility of the transition from α,β-unsaturated carbonyl compounds to oxazoles via 2-acyl-1 phthalimidoaziridines lacking an additional electron-acceptor moiety. We selected as objects of the study easily available compounds like benzylideneacetone (**Ia**), chalcones **Ib–If**, vinylmethyl ketone (**Ig**), and ester of cynnamic acid **Ih** which by oxidative addition of *N*-aminophthalimide were converted into the corresponding *N*-phthalimidoaziridines **IIa–IIh** (Scheme 1).

Yields of *N*-phthalimidoaziridines **II** were 52–75%, except for adduct **IIg** with vinyl methyl ketone (35%). Aziridines **IIa, IIf–IIh** were not previously described or were just mentioned in the literature, and compounds **IIb–IIe** were not always adequately described, therefore they all were characterized by the data of elemental analysis, NMR and mass spectra.

Owing to the slow in the NMR time scale inversion of the endocyclic nitrogen characteristic of *N*-aminoaziridine

Scheme 1.



R^1 = Ph, R^2 = Me (**a**), Ph (**b**), *p*-$MeOC_6H_4$ (**c**), *p*-$NO_2C_6H_4$ (**d**); R^2 = Ph, R^1 = *p*-$MeOC_6H_4$ (**e**), *p*-$NO_2C_6H_4$ (**f**); R^1 = Me, R^2 = H (**g**); R^1 = Ph, R^2 = OEt (**h**).

derivatives [8] the middle region of the ^{1}H NMR spectra (δ 2.8–5.6 ppm) of compounds **IIa–IIf** and I**Ih** contains two pairs of doublets corresponding to the protons of the aziridine rings of two invertomers (in the spectrum of aziridine **IIg** the signals of the methylene protons of two invertomers are overlapping). The observed vicinal coupling constants (4.4–5.8 Hz) indicate the *trans*-position of the aziridine protons which is not surprising for the configuration of the double bond is always retained at the oxidative aziridination. The content of the minor invertomer varies from 2% for 3-(4-nitrophenyl)-substituted aziridine **IId** to 15% for 3 methyl derivative **IIg**, with a common value of 6–7%. The comparison of the substituents at the carbon atoms of the aziridine ring suggests that in all events the prevailing invertomer contains the phthalimide group in the *cis*-position with respect to the smaller COR^2 group.

The signals of the aziridine protons belonging to the major and minor invertomers differ notably and regularly in chemical shifts. For instance, in the ^{1}H NMR spectra of aziridines **IIb–IIf** prepared from chalcones the signals of the major invertomer are located at δ 4.37–4.40 and 4.65–4.75 ppm, and those of the minor invertomer, in the region δ 3.65–4.32 and 5.48–5.56 ppm. These differences originate from the relative location of the phthalimide fragment and its effect on the chemical shifts (deshielding of the *syn*-proton [8]). In the ^{13}C NMR spectra the carbon atoms of the aziridine ring give rise to signals around δ 50 ppm.

Mass spectra of *N*-phthalimidoaziridines **IIb–IIf** alongside the peaks of molecular ions contain characteristic peaks originating from the presence in their molecules of a phthalimide fragment: $[M - 146]^+$ ($[M - PiN]^+$), $[M - 147]^+$ ($[M - PiNH]^+$), $[147]^+$ ($[PiNH]^+$), $[146]^+$ ($[PiN]^+$), and $[104]^+$ ($[C_6H_4CO]^+$). In the mass spectra of aziridines **IIb–IIf** also peaks $[M - ArCO]^+$ and $[ArCO]^+$ are observed.

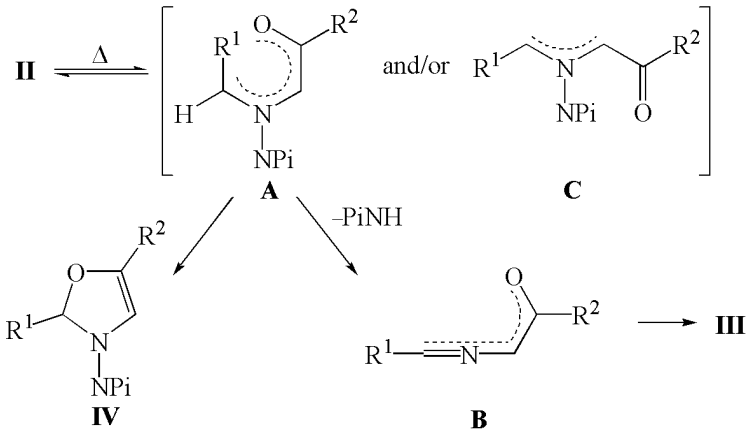
The thermolysis of aziridines **IIa–IIf** in toluene solution at 140–170°C in pressure-tight vessels for 1–5 h led to the formation of the corresponding oxazoles **IIIa–IIIf** in 54–86% yields. All the latter compounds were already known, and we identified them by comparison of their melting points and/or NMR spectra with the published data.

By analogy with the mechanism advanced in [3] we assume that in the thermolysis of aziridines **II** first occurs the conrotatory opening, probably reversible, of the C–C bond in the three-membered ring giving azomethine ylides of *U*- or *W*-type. *U*-Azomethine ylide **A** may undergo further cyclization into the corresponding 4-oxazoline (2,3-dihydrooxazole) **IV** and also a transfer of the hydrogen atom marked in the scheme to the oxygen of the phthalimide moiety resulting in the elimination of a phthalimide molecule from the azomethine ylide. The new 1,3-dipole (nitrile ylide **B**) arising in this process may further undergo cyclization directly into oxazole **III** (Scheme 2).

For *W*-dipole **C** both these processes are impossible for the sterical reasons. It probably either suffers cyclization into the initial aziridine, or undergoes stereoisomerization at the C–N bonds into the azomethine ylides of *S*-type, one of which is able to cyclize into oxazoline, and another to eliminate the phthalimide molecule converting into nitrile ylide.

From the thermolysis products of aziridine **IIa** we additionally isolated in a low yield 5-methyl-2-phenyl-3-phthalimido-2,3-dihydrooxazole (**IVa**), the cyclization product of the *U*-azomethine ylide **A**. In the ^{1}H NMR spectrum of this compound a multiplet in observed in the region δ 7.7–7.9 ppm showing the retention of the phthalimide fragment. The protons of the oxazoline ring appear as doublets at δ 6.8 and 8.0 ppm with a characteristic long-range coupling constant 3 Hz. In the ^{13}C NMR spectrum the signal of C^2 atom is observed at

Scheme 2.

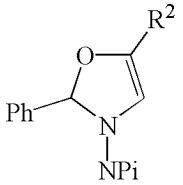


R^2 = Me (a), OEt (h).

δ 107 ppm, of C^4 atom, around δ 126–129 ppm, of C^5 atom, at δ 160 ppm.

Aziridine **IIg** did not visibly change even after heating for 5 h at 180°C. The low reactivity of this compound is apparently due to the fact that the hydrogen atom unlike the aryl substituents of aziridines **IIa**–**IIf** cannot stabilize the transition state of the reaction by the conjugation with the orbitals of the opening C–C bond.

The heating of ester **IIh** at 160°C resulted in its complete decomposition. However we failed to isolate from the reaction mixture the expected heterocyclic compounds apparently due to their instability during the chromatography on silica gel. The only substance obtained from this experiment after column chromatography was benzaldehyde (52%), probably formed by the hydrolysis of the initially arising 5-ethoxy-oxazoline (**IVh**).



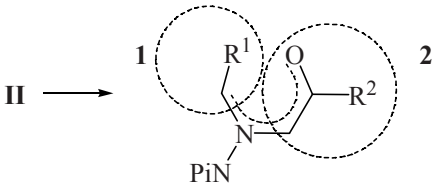
IVa, IVh

Thus in the majority of cases it is actually possible to go over from α,β-unsaturated carbonyl compounds to oxazoles in two steps with the overall yield 30–52%. Therewith the close values of yields were obtained for 2,5-diaryloxazoles both with electron-donor and electron-acceptor aromatic substituents. The good yield of oxazole **IIIa** suggests that this method might be suitable for the synthesis of other and alkyl-substituted oxazoles. Yet we failed to obtain by this method an oxazole lacking a substituent at the C^2 atom.

The estimation of the effect of the electronic character of substituents in the acylaziridines on the rate of their conversion into oxazoles we performed the thermolysis of mixtures of aziridines **IIb–IIf** with various substituents in the aryl and the aroyl fragments. The change in the ratio of these aziridines in the course of the thermolysis was monitored by ^{1}H NMR spectroscopy. As a result it turned out, that the rate of consumption of initial aziridines decreased in the series (**IIc**)> (**IIb**) > (**IId**), and also in the series (**IIf**) > (**IIb**) > (**IIe**). Consequently, the decomposition of aziridines is accelerated by introducing electron-donor groups in the aryl substituent or electron-acceptor groups in the aroyl substituent. This fact suggests that in the rate-limiting stage of the reaction on the carbon atom attached to the aryl substituent appears a partial positive charge, and on the carbon atom at the aroyl substituent, a partial negative charge.

These findings are well consistent with the assumption that the limiting stage of the whole process is the cleavage of the aziridine C–C bond resulting in the azomethine ylide. In the first approximation in the π-system of azomethine ylide the positive charge is localized on the nitrogen, and the negative charge is distributed between the fragments **1** and **2**. Due to the different nature of substituents the distribution of the negative charge is evidently unsymmetrical: It should be larger on fragment **2**. Inasmuch as in the initial aziridine all the three parts of the molecule formally bear no charge, in the transition state the negative charge on fragment **2** also should be larger. Therewith in the transition state because of the large angle between the axis of the orbital of the unshared

electron pair and the orbitals of the opening σ-bond, and consequently, because of their small overlapping, the nitrogen atom should bear only a small positive charge, and its main fraction should be located on fragment **1**. In keeping with this reasoning the donor substituents in the aryl ring accelerate the reaction, and in the aroyl ring retard it.



We further attempted to extend the already tested procedure to the conversion of conformationally rigid spiro-joined benzylideneindandiones **Ii–Il** into the corresponding fused oxazoles. By analogy with the behavior of 3-aryl-2,2-dibenzoyl-1-phthalimidoaziridines [3] we expected that the corresponding aziridines would be far more active than their 2,3-disubstituted analogs, and their conversion into oxazoles would occur in milder conditions.

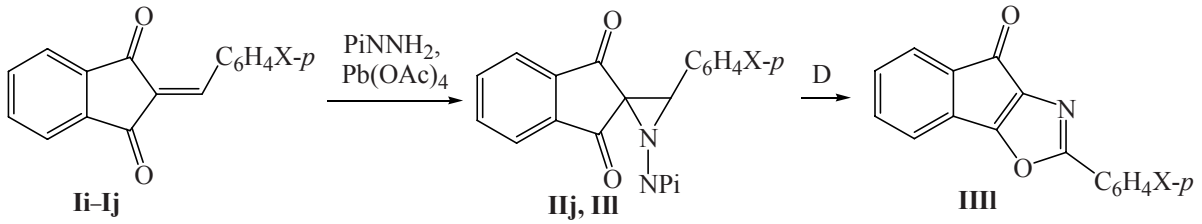
However another side of the high reactivity of these phthalimidoaziridines proved to be their low stability: we succeeded to obtain pure spiroaziridines only from compounds **Ik** and **Il** with electron-acceptor groups in the aryl substituent. Evidently like in the previous reaction series the introduction of these groups into the aryl substituent retards the opening of the aziridine ring (Scheme 3).

Compounds **Ik** and **Il** are stable in crystals, but in solutions they decomposed even at room temperature. Their composition is confirme by elemental analysis, and their structure, by mass and NMR spectra which show that both aziridines exist in the form of a single invertomer, evidently with the *syn*-location of the phthalimide group and the aziridine hydrogen. In the ^{1}H NMR spectra of these compounds the characteristic signal is the singlet of the aziridine proton in the region δ 5.0 ppm. In the ^{13}C NMR spectra the signals of the aziridine carbons in the region δ 50–60 ppm and of two carbonyl atoms of indandione at δ 190 ppm are easy to identify. Due to the typical for the sterically loaded phthalimidoaziridines slow rotation of the phthalimide fragment around the N–N bond in the ^{13}C NMR spectrum of compound **III** the signals of phthalimide atoms C^a at δ 130 ppm and NCO around δ 165 ppm are considerably broadened, and in the spectrum of compound **IIk** the NCO signal coincides with the base line. In the mass spectra of phthalimidoaziridines **Ik** and **Il** the molecular ion peak is weak or lacking, but peaks characteristic of phthalimidoaziridins $[M - 147]^+$ ($[M - \mathrm{PiNH}]^+$), $[147]^+$ ($[\mathrm{PiNH}]^+$), and $[104]^+$ ($[C_6H_4CO]^+$) are present.

We failed to obtain the corresponding spiroaziridines from arylideneindandiones **Ii** and **Ij** with electron-donor groups in the aryl ring. Yet at the oxidative addition of *N* aminophthalimide to the *para*-tolyl derivative **Ij** the TLC monitoring of the reaction mixture showed the disappearance of the initial compound and the presence of a single product. Assuming that this was the desired aziridine we left the mixture standing for two days at room temperature hoping to obtain the product of its decomposition, the corresponding oxazole. Finally the ^{1}H NMR spectrum revealed the presence in the solution of a single compound containing a methyl group, but it turned out to be not oxazole but *p*-toluic aldehyde. In the reaction mixture with compound **Ii** according to the ^{1}H NMR spectrum alongside the *p* methoxybenzaldehyde (43% of the overall intensity of the methoxy groups) another product containing methoxy groups was present in a significant amount (about 30% of the overall intensity of the methoxy groups) that we failed to isolate due to its instability.

The boiling in benzene of nitro-substituted spiroaziridine **III** resulted in the formation of a product insoluble in common organic solvents, whose composition and mass

Scheme 3.



X = MeO (**i**), Me (**j**), Cl (**k**), NO_2 (**l**).

spectrum corresponded to the structure of expected oxazole **IIIl**. In particular, its mass spectrum contained a strong peak of molecular ion and no peaks characteristic of phthalimide derivatives with *m/z* 146 and 147 indicating the absence of this fragment in the obtained compound.

Yet as a result of heating spiroaziridine **IIk** at 80°C till its complete disappearance from the reaction mixture (TLC monitoring) after the subsequent chromatographic separation of the reaction mixture we only obtained an instable compound whose structure was not established.

Inasmuch as in the transition from unsaturated carbonyl compounds to oxazoles we used relatively expensive *N*-aminophthalimide and lead tetraacetate, and the phthalimide moiety was not present in the final product we started to look for cheaper reagents for the preparation of 2-acylaziridines with a good leaving gtoup at the nitrogen atom and assumed that this could be an arylsulfonyl group.

In the last decade several publications reported on the synthesis of tosylaziridines from unsaturated compounds with the use of chloramine-T. The process required a catalyst, the role of which played sources of molecular bromine [9, 10] or iodine [11], and also some compounds of Cu(I) [12]. However in the most cases alkenes and styrenes were used as substrates, and only in [10] the tosylaziridines were obtained from α,β-unsaturated carbonyl compounds.

Therefore we decided to synthesize sulfonylaziridines from chalcones and chloramine-B we possessed along the procedure of [10]. As a result from chalcones **Ib** and **Ie** we actually obtained benzenesulfonylaziridines **IVb** and **IVd**, although in a low yield. Therewith in the experiments with benzalacetophenone (**Ib**) we used as catalyst both pyridinium tribromide [10] and tetramethylammonium tribromide recommended in [9]. According to ^{1}H NMR of the reaction mixtures the analytical yields of sulfonylaziridine **Vb** in both cases attained ~32% (Scheme 4).

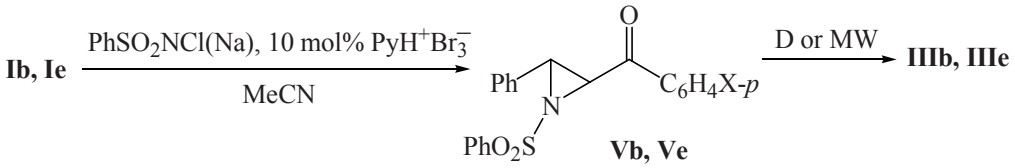
The composition of *N*-benzenesulfonylaziridines **Vb** and **Ve** was confirmed by elemental analyses, and their structure, by ^{1}H, ^{13}C NMR and mass spectra. In the ^{1}H NMR spectra in the region δ 4.3–4.6 ppm pairs of doublets corresponding to the protons of the aziridine ring appeared in due course, and the values of the vicinal coupling constants (4.4–5.8 Hz) revealed the *trans*-position of the aziridine protons. The signals of the aziridine carbon atoms were observed in the ^{13}C NMR spectra in their usual region δ ~50 ppm. The molecular ion peaks were absent from the mass spectra of compounds **Vb** and **Ve**, but appeared the characteristic fragment ions $[M - 141]^+$ ($[M - C_6H_5SO_2]^+$). Besides also peaks appeared corresponding to the fragment $[ArCO]^+$.

The only products that we succeeded in separating from the thermolysis of sulfonylaziridines **Vb** and **Ve** at 160–170°C were the expected oxazoles **IIIb** and **IIIe**, but their yields were considerably worse than from the corresponding phthalimidoaziridines. This may be ascribed to the stronger electron-acceptor properties of the sulfonyl group compared to the phthalimide moiety that lead to a greater number of side processes with the opening of C–N bond. However applying the microwave irradiation we succeeded in reducing the decomposition temperature of aziridine **Vb** to 135°C and hence increasing the yield of oxazole **IIIb** nearly 1.5-fold.

It would be interesting to prepare benzenesulfonylaziridines from α,β-unsaturated carbonyl compounds with an additional electron-acceptor group in the α-position for by analogy to the corresponding 1-phthalimidoaziridines [3] it is expectable to convert them into the oxazoles under mild conditions. It proved however that both in the presence and in the absence of bromine source the ethyl 2-cyanocinnamate **Im** reacted with chlor-amine-B to give *N*-benzylidenebenzenesulfamide (**VI**) and not aziridine or oxazole (Scheme 5).

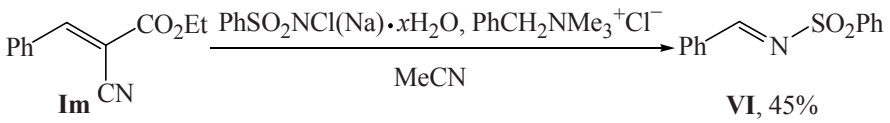
We presume that here first occurs the nucleophilic attack of the anion of chloramine-B on the electron-

Scheme 4.

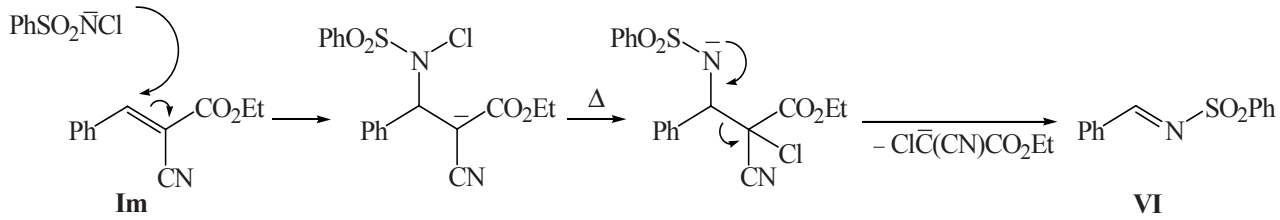


X = H (**b**), OMe (**e**).

Scheme 5.



Scheme 6.



deficient C=C bond of ester **Im** (Scheme 6). The arising anion apparently transforms into the anion analogous in structure to the intermediate suggested for the reaction of unsaturated compounds with chloramine-T in the presence of trimethylphenylammonium tribromide [9], but further instead of intramolecular nucleophilic substitution of chlorine providing aziridine occurs the cleavage of the C–C bond facilitated by the high stability of the leaving anion.

Despite these drawbacks we can state that we suggested and carried out by two examples a two-stage process of the conversion of α,β-unsaturated carbonyl compounds into oxazoles with the use of a cheap reagent, chloramine-B. We regard the results obtained as hopeful for further research directed to the optimization of this reaction and the estimation of the range of its applicability. Yet apparently this reaction is not feasible for the synthesis of oxazoles with alkenyl and some heteroaromatic and aromatic substituents with elevated electron density for they themselves can react with bromine catalyzing the aziridination stage. Besides the last example shows that the reaction is hardly suitable for compounds containing at the C=C bond simultaneously two electron-acceptor moieties.

EXPERIMENTAL

^{1}H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra were registered on a spectrometer Bruker DPX-300 from solutions in $CDCl_3$, DMSO-d_6, or CD_3CN using for internal reference in the ^{1}H NMR spectra the signals of the residual protons of the solvent (δ 7.26, 2.50, and 1.96 ppm), and in the ^{13}C NMR spectra, carbon signals of the solvents (δ 77.16, 39.52, and 1.32 ppm respectively). The assignment of signals in the ^{13}C NMR spectra was made with the help of DEPT spectra. Mass spectra were measured on an instrument Finnigan MAT INCOS-50 (Electron impact, 70 eV, direct admission into the ion source). Elemental analysis was carried out on an automatic CHN-analyzer HP-185B. The composition of the reaction mixtures and the purity of compounds obtained was controlled by TLC on ALUGRAM SIL G/UV_{254} plates.

The reactions under microwave activation were performed in a monomode microwave installation Minotavr (maximum power 200 W) of Lyumeks Co.

N-Aminophthalimide was prepared by procedure [13], chalcones **Ic–If**, by general method [14]. Arylideneindandiones **Ii–Il** were kindly provided by Professor of Voronezh State University Kh.S.Shikhaliev to whom the authors are deeply grateful. Toluene was dried with metal sodium [15]. Acetonitrile was distilled over phosphorus(V) oxide [15]. Chloramine-B was dried till constant weight at 80°C and the pressure 10 mm Hg.

Oxidative addition of *N*-aminophthalimide to α,β-unsaturated ketones. *General procedure.* To a solution of 6 mmol of unsaturated compound in 20 ml of dichloromethane containing a dispersion of 3 g of potassium carbonate was added while stirring at cooling to 0°C within 10 min by alternating small portions 972 mg (6 mmol) of *N*-aminophthalimide and 2.66 g (6 mmol) of lead tetraacetate. The mixture was stirred for another 5 min, filtered through a bed of silica gel (1 cm), and washed with 20 ml of dichloromethane. The solvent was distilled off in a vacuum, 30 ml of ethyl ether was added

to the residue, and the separated precipitate was filtered off.

***trans*-2-Acetyl-3-phenyl-1-phthalimidoaziridine (IIa)**,[a] mixture of two invertomers in a ratio 94:6. Charge of reagents 10 mmol each. Yield 2.31 g (75%), white powder, mp 192–193°C (from butanol). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.47 C and 2.55 C–CH_3 of minor and of major invertomer respectively, overall 3H; 3.72 d (*J* 4.4 Hz) and 4.37 d (*J* 4.4 Hz) – NCH of major invertomer, 4.02 d (*J* 5.8 Hz) and 4.54 d (*J* 5.8 Hz) – NCH of minor invertomer, overall 2H; 7.37–7.43 m (5H, Ph), 7.66–7.77 m (4H, PiN). ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 31.51 (CH_3), 49.92 (NCH), 51.07 (NCH), 123.07 (PiN, C^b), 127.06 and 128.60 (Ph, C^o and C^m), 128.52 (Ph, C^p), 130.18 (PiN, C^a), 133.98 (PiN, C^c), 134.91 (Ph, C^i), 164.67 (NCO), 198.50 (CO). Mass spectrum, *m/z* (I_{rel}, %): 307 (0.3), 306 (2) $[M]^+$, 265 (11), 264 (62) $[M - CH_2CO]^+$, 263 (11) $[M - MeCO]^+$, 130 (18), 118 (41), 117 (64), 116 (22), 105 (18), 104 (60) $[C_6H_4CO]^+$, 103 (20), 91 (26), 90 (28), 89 (17), 77 (39), 76 (83), 75 (12), 74 (10), 63 (11), 51 (23), 50 (43), 43 (100) $[MeCO]^+$. Found, %: C 70.5; H 4.63; N 9.30. $C_{18}H_{14}N_2O_3$. Calculated, %: C 70.6; H 4.61; N 9.15. Compound **IIa** was mentioned in [16], however none of its characteristics was reported.

***trans*-2-Benzoyl-3-phenyl-1-phthalimidoaziridine (IIb),** mixture of two invertomers in a ratio 94:6. Charge of reagents 10 mmol each. Yield 2.17 g (60%), white powder, mp 126–127°C (from ethanol) (mp 121–123°C [17], 124°C [18]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.28 d (*J* 4.8 Hz) and 5.56 d (*J* 4.8 Hz) – NCH of minor invertomer, 4.40 d (*J* 4.8 Hz) and 4.70 d (*J* 4.8 Hz) – NCH of major invertomer, overall 2H; 7.26–7.74 m (12H, H_{arom}); 8.10 d (*J* 7.2 Hz[b]) and 8.32 d (*J* 7.2 Hz) – PhCO, H^o of major and of minor invertomer respectively, overall 2H. ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 48.65 (NCH), 50.58 (NCH), 123.12 (PiN, C^b), 127.17, 128.56, 128.65, 128.72, 128.78, 130.24 (PiN, C^a), 133.59, 133.95 (PiN, C^c), 135.15 (C^i), 137.29 (C^i), 164.57 (NCO), 190.53 (CO). ^{1}H and ^{13}C NMR spectra of major invertomer are well consistent with the published data [17, 19]. Mass spectrum, *m/z* (I_{rel}, %): 368 (2) $[M]^+$, 263 (16) $[M - PhCO]^+$, 222 (13) $[M - PiN]^+$, 167 (10), 116 (10), 106 (14), 105 (100) $[PhCO]^+$, 104 (36) $[C_6H_4CO]^+$, 103 (13), 77 (82), 76 (50), 51 (31), 50 (31). Found, %: C 75.1; H 4.44; N 7.41. $C_{23}H_{16}N_2O_3$. Calculated, %: C 75.0; H 4.35; N 7.61.

***trans*-2-Benzoyl-3-(4-methoxyphenyl)-1-phthalimidoaziridine (IIc)**, mixture of two invertomers in a ratio 93:7. Yield 1.24 g (52%), white powder, mp 154–155°C (ethanol–butanol, 1:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.73 s and 3.82 s – MeO of minor and of major invertomer respectively, overall 3H; 4.21 d (*J* 5.1 Hz) and 5.48 (*J* 5.1 Hz) – NCH of minor invertomer, 4.39 d (*J* 4.4 Hz) and 4.65 d (*J* 4.4 Hz) – NCH of major invertomer, overall 2H; 6.79 d (*J* 8.7 Hz) and 6.94 d (*J* 8.7 Hz) – C_6H_4, H^m of minor and of major invertomer respectively, overall 2H; 7.32 d (*J* 8.7 Hz) – C_6H_4, H^o of minor invertomer and 7.43–7.74 m (H_{arom}), overall 9H; 8.10 d (*J* 7.4 Hz) and 8.32 d (*J* 7.2 Hz) – PhCO, H^o of minor and of major invertomer respectively, overall 2H. ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 48.55 (NCH), 50.45 (NCH), 55.33 (OMe), 114.11 (*p*-C_6H_4, C^m), 123.08 (PiN, C^b), 127.12 (*p*-C_6H_4, C^i), 128.43, 128.68, 128.72, 130.24 (PiN, C^a), 133.53, 133.92 (PiN, C^c), 137.34 (PhCO, C^i), 159.87 (C–O), 164.59 (NCO), 190.68 (CO). Mass spectrum, *m/z* (I_{rel}, %): 398 (11) $[M]^+$, 293 (34) $[M - PhCO]^+$, 252 (22) $[M - PiN]^+$, 251 (21) $[M - PiNH]^+$, 238 (10), 237 (12), 147 (17) $[PiNH]^+$, 146 (31) $[PiN]^+$, 105 (100) $[PhCO]^+$, 104 (29) $[C_6H_4CO]^+$, 77 (47), 76 (34), 51 (14), 50 (18). Found, %: C 72.4; H 4.54; N 6.81. $C_{24}H_{18}N_2O_4$. Calculated, %: C 72.4; H 4.52; N 7.04. ^{1}H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [19].

***trans*-2-Benzoyl-3-(4-nitrophenyl)-1-phthalimidoaziridine (IId)**, mixture of two invertomers in a ratio 98:2. Yield 1.52 g (61%), light-yellow powder, mp 192–193°C (butanol–DMF, 10:1). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.65 d (*J* 5.1 Hz) and 5.53 d (*J* 5.1 Hz) – aziridine protons of minor invertomer; 4.39 d (*J* 5.1 Hz) and 4.75 d (*J* 5.1 Hz) – aziridine protons of major invertomer, overall 2H; 7.50–7.71 m (9H), 8.10 d (2H, PhCO, H^o, *J* 7.3 Hz), 8.26 (2H, *p*-C_6H_4, H^m, *J* 8.7 Hz). ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 48.83 (NCH), 49.18 (NCH); 123.27, 123.85 (*p*-C_6H_4, C^m and PiN, C^b); 128.16, 128.82, 128.84, 130.05 (PiN, C^a), 133.92, 134.16, 136.89 (PhCO, C^i), 142.49 (*p* C_6H_4, C^i), 147.95 (CNO_2), 164.40 (NCO), 189.58 (CO). Mass spectrum, *m/z* (I_{rel}, %): 413 (0.8) $[M]^+$, 308 (25) $[M - PhCO]^+$, 267 (19) $[M - PiN]^+$, 266 (29) $[M - PiNH]^+$, 212 (29), 178

[a] Adducts **IIa** and **IIg** were first synthesized and described in the graduation thesis of the student of our team Yu.A. Titarev, St. Petersburg State University.

[b] Here and hereinafter in the description of the signals of aromatic substituents appearing as the second order spectra we present the apparent multiplicity of complex signals and the distance between the main peaks of the complex multiplets and not the real coupling constants.

(11), 165 (18), 147 (28) $[PiNH]^+$, 130 (28), 116 (13), 115 (11), 106 (61), 105 (71) $[PhCO]^+$, 104 (27) $[C_6H_4CO]^+$, 103 (28), 102 (46), 89 (37), 77 (100), 76 (43), 75 (49), 74 (37), 64 (11), 63 (38), 62 (19), 51 (74), 50 (83), 39 (29), 38 (12), 37 (10). Found, %: C 66.9; H 3.76; N 10.2. $C_{23}H_{15}N_3O_5$. Calculated, %: C 66.8; H 3.63; N 10.2. ^1H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [19].

***trans*-2-(4-Methoxybenzoyl)-3-phenyl-1-phthalimidoaziridine (IIe)**, mixture of two invertomers in a ratio 94:6. We used 1.33 equiv of *N*-aminophthalimide and lead tetraacetate. Yield 1.30 g (54%), glassy substance. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.87 s and 3.89 s (3H, OMe) – MeO of major and of minor invertomer respectively, overall 3H; 4.27 d (*J* 5.1 Hz) and 5.50 d (*J* 5.1 Hz) – NCH of minor invertomer, 4.37 d (*J* 4.4 Hz) and 4.70 d (*J* 4.4 Hz) – NCH of major invertomer, overall 2H; 6.99 d (*J* 8.7 Hz) and 7.05 d (*J* 8.7 Hz) – C_6H_4, H^m of major and of minor invertomer respectively, overall 2H; 7.37–7.74 m (9H); 8.08 d (*J* 8.7 Hz) and 8.32 d (*J* 7.2 Hz) – C_6H_4, H^o of major and of minor invertomer respectively, overall 2H. ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 48.40 (NCH), 50.05 (NCH), 55.49 (OMe), 113.99 (C_6H_4, C^m), 123.04 (PiN, C^b), 124.65 (C^i), 127.13, 128.43, 128.59, 130.22 (PiN, C^a), 131.05, 133.86 (PiN, C^c), 135.22 (C^i), 163.99 (CO), 164.54 (NCO), 188.53 (CO). Mass spectrum, *m/z* (I_{rel}, %): 398 (4) $[M]^+$, 263 (27) $[M - MeOC_6H_4CO]^+$, 252 (34) $[M - PiN]^+$, 251 (24) $[M - PiNH]^+$, 237 (11), 197 (48), 146 (29) $[PiN]^+$, 136 (84) $[MeOC_6H_4CO]^+$, 135 (75), 130 (14), 116 (20), 107 (30), 105 (20), 104 (94) $[C_6H_4CO]^+$, 103 (27), 102 (14), 92 (49), 90 (38), 89 (22), 77 (93), 76 (100), 75 (23), 74 (21), 64 (30), 63 (31), 51 (29), 50 (69), 39 (19). Found, %: C 72.2; H 4.59; N 7.02. $C_{24}H_{18}N_2O_4$. Calculated, %: C 72.4; H 4.52; N 7.04. ^1H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [19].

***trans*-2-(4-Nitrobenzoyl)-3-phenyl-1-phthalimidoaziridine (IIf)**, mixture of two invertomers in a ratio 94:6. Yield 1.81 g (73%), light-yellow crystalline powder, mp 183–184°C (butanol–DMF, 10:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.32 d (*J* 5.1 Hz) and 5.50 d (*J* 5.1 Hz) – NCH of minor invertomer, 4.38 d (*J* 5.1 Hz) and 4.68 d (*J* 5.1 Hz) – NCH of major invertomer, overall 2H; 7.38–7.54 m (5H), 7.65–7.74 m (4H), 8.26 d (2H, C_6H_4, *J* 8.7 Hz); 8.37 d (*J* 8.7 Hz) and 8.53 d (*J* 8.7 Hz) – C_6H_4, signals of major and of minor invertomer respectively, overall 2H. ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 49.05 (NCH), 51.11 (NCH); 123.24, 123.90 (C_6H_4, C^m and PiN, C^b); 127.11, 128.75, 128.83, 129.82, 130.02 (PiN, C^a), 134.18 (PiN, C^c), 134.51 (C^i), 141.69 (C_6H_4, C^i), 150.42 (CNO_2), 164.54 (NCO), 189.08 (CO). Mass spectrum, *m/z* (I_{rel}, %): 413 (11) $[M]^+$, 267 (25) $[M - PiN]^+$, 266 (55) $[M - PiNH]^+$, 264 (45), 251 (12), 252 (39), 236 (42), 221 (22), 220 (18), 206 (10), 178 (11), 165 (31), 151 (46), 150 (14), 147 (55) $[PiNH]^+$, 132 (19), 131 (19), 130 (43), 120 (23), 117 (61), 106 (45), 105 (14), 104 (56) $[C_6H_4CO]^+$, 103 (64), 102 (29), 92 (42), 91 (21), 90 (64), 89 (93), 77 (84), 76 (61), 75 (69), 74 (57), 64 (26), 63 (72), 62 (27), 52 (17), 51 (28), 50 (100), 39 (50), 38 (28), 37 (21). Found, %: C 66.6; H 3.80; N 10.2. $C_{23}H_{15}N_3O_5$. Calculated, %: C 66.8; H 3.63; N 10.2.

2-Acetyl-1-phthalimidoaziridine (IIg), mixture of two invertomers in a ratio 85:15 in $CDCl_3$, 93:7 in DMSO-d_6. Charge of reagents 10 mmol each. Vinyl methyl ketone was used in 10% excess. Yield 810 mg (35%), white powder, mp 136–137°C (ethanol). ^1H NMR spectrum, δ, ppm, in $CDCl_3$: 2.34 s and 2.52 s – CH_3 of major and of minor invertomer respectively, overall 3H; 2.80–2.82 m (2H) – NCH_2 of both invertomers; 3.16 t (*J* 6.5 Hz) and 3.48 t (*J* 5.8 Hz) – NCH of major and of minor invertomer respectively, overall 1H; 7.69–7.79 m (4H, PiN); in DMSO-d_6: 2.19 s and 2.42 s – CH_3 of major and of minor invertomer respectively, overall 3H; 2.84–2.87 m (2H) – NCH_2 of both invertomers; 3.25 d.d (J_1 8.3, J_2 5.5 Hz) and 3.69 t (*J* 5.8 Hz) – NCH of major and of minor invertomer respectively, overall 1H; 7.81 C (4H, PiN). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm, major invertomer: 27.19 (CH_3), 36.58 (NCH_2), 46.28 (NCH), 123.28 (PiN, C^b), 129.97 (PiN, C^a), 134.34 (PiN, C^c), 164.52 (NCO), 202.90 (CO); minor invertomer: 31.52 (CH_3), 36.80 (NCH_2), 42.07 (NCH), 123.01 (PiN, C^b), 133.95 (PiN, C^c).

Ethyl *trans*-3-phenyl-1-phthalimidoaziridine-2-carboxylate (IIh), mixture of two invertomers in a ratio 93:7. Charge of reagents 5 mmol each. Yield 850 mg (57%), colorless crystals, mp 96–97°C (ether–hexane, 1:1). ^1H NMR spectrum ($CDCl_3$), δ, ppm: – 1.28 t (*J* 7.3 Hz) and 1.37 t (*J* 6.5 Hz) – CH_3 of major and of minor invertomer respectively, overall 3H; 3.53 d (*J* 5.1 Hz) and 4.40 d (*J* 5.1 Hz) – NC^2H and NC^3H of major invertomer, 4.07 d (*J* 5.8 Hz) and 4.59 d (*J* 5.8 Hz) – NCH of minor invertomer, overall 2H; 4.19 q (*J* 7.3 Hz) and 4.36 q (*J* 6.5 Hz) – CH_2 of major and of minor invertomer respectively, overall 2H; 7.37–7.78 m (9H). ^{13}C NMR spectrum of major invertomer ($CDCl_3$), δ, ppm: 13.90 (CH_3), 46.28 (NCH), 49.47 (NCH), 62.05 (OCH_2), 123.08 (PiN, C^b), 127.19, 128.59

(C^p), 128.62, 130.22 (*Pi*N, C^a), 134.00 (PiN, C^c), 134.51 (Ph, C^i), 164.60 (NCO), 166.17 (COO). Found, %: C 67.81; H 4.88; N 8.28. $C_{19}H_{16}N_2O_4$. Calculated, %: C 67.86; H 4.76; N 8.33.

5-Methyl-2-phenyloxazole (IIIa). A solution of 306 mg (1 mmol) of aziridine **IIa** in 10 ml of anhydrous toluene was heated for 5 h at 160°C in a glass reactor with a pressure-tight screw-top. On cooling the reaction mixture the solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 20 g of silica gel (eluent dichloromethane), and the main fraction was evaporated in a vacuum. Yield 96 mg (60%). Colorless oily substance (colorless oily substance [20]). ^{1}H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [20].

The small first fraction containing the mixture of oxazole **IIIa** and **5-methyl-2-phenyl-3-phthalimido-2,3-dihydrooxazole (IVa)** was evaporated in a vacuum to the volume of 5 ml, and 10 ml of hexane was added. The separated precipitate of oxazoline **IVa** was filtered off. Yield 10 mg (3%). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 (3H, CH_3), 6.77 d (1H, H^4, *J* 3.0 Hz), 7.36–7.44 m (5H, Ph), 7.74–7.88 m (4H, PiN), 8.06 d (1H, H^2, *J* 3.0 Hz). ^{13}C NMR spectrum (as the difference of spectra of the mixture of compounds **IIIa** and **IVa** and pure oxazole **IIIa**) ($CDCl_3$), δ, ppm: 24.09 (Me), 107.26 (C^2), 123.48 (PiN, C^b), 125.9 (C^o), 126.42 (C^p or C^4), 128.46 (C^m), 128.74 (C^4 or C^p), 131.70 (PiN, C^a), 134.39 (PiN, C^c), 137.83 (C^i), 159.95 (C^5), 167.48 (NCO).

2,5-Diphenyloxazole (IIIb). A solution of 368 mg (1 mmol) of aziridine **IIb** in 10 ml of anhydrous toluene was heated for 2 h at 160°C. The solvent was distilled off in a vacuum. The oily residue was extracted with hexane which was later distilled off in a vacuum. Yield 191 mg (86%), colorless crystals, mp 73–74°C (mp 72–74°C [21]). ^{1}H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [21].

2-(4-Methoxyphenyl)-5-phenyloxazole (IIIc). A solution of 398 mg (1 mmol) of aziridine **IIc** in 10 ml of anhydrous toluene was heated for 2 h at 140°C. The solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 20 g of silica gel (eluent dichloromethane–ethyl ether, 20:1). Yield 135 mg (54%), colorless crystals, mp 98–99°C (103°C [22]). ^{1}H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [23].

2-(4-Nitrophenyl)-5-phenyloxazole (IIId). A solution of 413 mg (1 mmol) of aziridine **IId** in 10 ml of anhydrous toluene was heated for 2 h at 170°C. The precipitate formed on cooling was filtered off and subjected to chromatography on a column packed with 20 g of silica gel (eluent dichloromethane–ethyl ether, 20:1). Yield 160 mg (60%), yellow powder, mp 207–208°C (mp 204.5°C [24]). ^{1}H NMR spectrum of compound we obtained is well consistent with published data [25].

5-(4-Methoxyphenyl)-2-phenyloxazole (IIIe). A solution of 398 mg (1 mmol) of aziridine **IIe** in 10 ml of anhydrous toluene was heated for 4 h at 160°C. The solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 20 g of silica gel (eluent dichloromethane–ethyl ether, 20:1). Yield 180 mg (75%), colorless crystals, mp 83–84°C (80°C [22]). ^{1}H and ^{13}C NMR spectra of compound we obtained are well consistent with published data [26].

5-(4-Nitrophenyl)-2-phenyloxazole (IIIf). A solution of 413 mg (1 mmol) of aziridine **IIf** in 10 ml of anhydrous toluene was heated for 2 h at 160°C. The solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 20 g of silica gel (eluent dichloromethane–ethyl ether, 20:1). The product contained about 5% of unidentified impurity. Yield 201 mg (76%). Analytically pure sample was obtained by recrystallization from a mixture ethanol–butanol, 1:2. Yield 150 mg (56%), yellow powder, mp 197–198°C (mp 194–196°C [27]). ^{1}H NMR spectrum of compound we obtained is well consistent with published data [25].

Thermolysis of aziridine IIg. A solution of 230 mg (1 mmol) of aziridine **IIg** in 10 ml of anhydrous toluene was heated for 5 h at 180°C. The solvent was distilled off in a vacuum. According to the data of ^{1}H NMR spectroscopy and TLC the residue contained only the initial compound.

Thermolysis of aziridine IIh. A solution of 336 mg (1 mmol) of aziridine **IIh** in 10 ml of anhydrous toluene was heated for 3 h at 160°C. In keeping with TLC the initial compound disappeared from the reaction mixture. The solvent was distilled off in a vacuum. The column chromatography (eluent dichloromethane) provided 55 mg (52%) of benzaldehyde that was absent in the reaction mixture according to ^{1}H NMR spectroscopy.

Estimation of substituents effect on the rate of conversion acylaziridine – oxazole. Weighed portions of aziridines **IIb–IIf** were dissolved in 10 ml of anhydrous toluene and heated at 140°C. After 30 and 60 min of heating the aziridines ratio in the reaction mixture was measured by the intensity of the corresponding aziridine

protons of the main invertomers in the ^{1}H NMR spectra ($CDCl_3$) taking into account the fraction of these invertomers.

Run no. *1*. Initial mixture of aziridines: 83.3 mg (**IIb**), 71.9 mg (**IIc**), 63.6 mg (**IId**) (molar ratio 1:0.79:0.68). As analytical the following signals were used: at δ 4.70, 4.65 and 4.75 ppm respectively. After 30 min the ratio of aziridines was 1:0.30:0.84, after 60 min, 1:0.1:1.15.

Run no. *2*. Initial mixture of aziridine: 57.2 mg (**IIb**), 87.8 mg (**IIe**) (molar ratio 1:1.42). Analytical signals at δ 4.40 and 4.37 ppm respectively. After 30 min the ratio of aziridines was 1:1.66, after 60 min, 1:1.90.

Run no. *3*. Initial mixture of aziridine: 57.3 mg (**IIb**), 68.8 mg (**IIf**) (molar ratio 1:1.07). Analytical signals at δ 4.40 and 4.38 ppm respectively. After 30 min the ratio of aziridinee was 1:0.67, after 60 min, 1:0.37.

1-Phthalimido-3-(4-chlorophenyl)spiro[aziridine-2,2'-indene]-1',3'-dione (IIk). To a solution of 269 mg (1 mmol) of 2-(4-chlorobenzylidene)indan-1,3-dione (**Ik**) in 10 ml of dichloromethane containing a dispersion of 0.5 g of potassium carbonate was added while stirring at cooling to 0°C within 10 min by alternating small portions 176 mg (1.1 mmol) of *N*-aminophthalimide and 488 mg (1.1 mmol) of lead tetraacetate. The mixture was stirred for another 5 min, filtered through a bed of silica gel (1 cm), and washed with 20 ml of dichloromethane. The solution was evaporated to a volume of 5 ml, 10 ml of ethyl ether was added, and the precipitated product was filtered off. Yield 329 mg (77%), light-pink powder, t.decomp. 120–130°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.94 s (1H, CHN), 7.36 d (2H, C_6H_4, *J* 7.9 Hz), 7.57 d (2H, C_6H_4, *J* 7.9 Hz), 7.65–8.00 m (8H). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 54.43 (C–N), 56.10 (CHN); 123.42 and 123.46 (PiN, C^b and $C^{4',7'}$), 128.47 (C_6H_4, C^o or C^m), 129.34 (C_6H_4, C^i or C^p), 129.73 (PiN, C^a and C_6H_4, C° or C^m), 134.33 (PiN, C^C), 134.91 (C_6H_4, C^i or C^p); 135.82 and 135.97 ($C^{5',6'}$); 190.04 (CO), 190.62 (CO). Mass spectrum, *m/z* (I_{rel}, %): 283 (10) [*M* – PiNH]$^+$, 281 (32) [*M* – PiNH]$^+$, 190 (18), 147 (33) [PiNH]$^+$, 114 (16), 104 (72) [C_6H_4CO]$^+$, 103 (26), 88 (33), 87 (16), 77 (16), 76 (100), 75 (36), 74 (35), 73 (12), 63 (13), 62 (25), 61 (10), 50 (73), 43 (10), 39 (12), 38 (17), 37 (16). Found, %: C 66.9; H 3.08; N 6.32. $C_{24}H_{13}ClN_2O_4$. Calculated, %: C 67.2; H 3.06; N 6.53.

3-(4-Nitrophenyl)-1-phthalimidespiro[aziridine-2,2'-indene]-1',3'-dione (IIl). To a solution of 488 mg (1.75 mmol) of 2-(4-nitrobenzylidene)indan-1,3-dione (**Il**) in 20 ml of a mixture dichloromethane–THF, 1:1 containing a dispersion of 1 g of potassium carbonate was added while stirring at cooling to 0°C within 10 min by alternating small portions 340 mg (2.1 mmol) of *N*-aminophthalimide and 930 mg (2.1 mmol) of lead tetraacetate. The mixture was stirred for another 5 min, filtered, and the solvent was distilled off in a vacuum. Then 10 ml of dichloromethane was added, the solution was filtered through a bed of silica gel (1 cm), and washed with 20 ml of dichloromethane. The solvent was distilled off in a vacuum. The residue was washed with 10 ml of ethyl ethera. Yield 605 mg (79%), white powder, t.decomp. 155–160°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.01 s (1H, CHN), 7.73–8.01 m (10H), 8.27 d (2H, C_6H_4, H^m, *J* 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 54.19 (CN), 57.01 (CHN), 123.42, 123.45, 123.60, 123.62, 129.46, 129.90 (PiN, C^a), 134.49, 136.11, 136.19, 136.22, 137.99, 141.54, 141.96, 148.14 (CNO_2), 164.82 (NCO), 189.47 (CO), 190.32 (CO). Mass spectrum, *m/z* (I_{rel}, %): 439 (0.4) [*M*]$^+$, 293 (21), 292 (100) [*M* – PiNH]$^+$, 262 (10), 190 (41), 147 (36) [PiNH]$^+$, 104 (56) [C_6H_4CO]$^+$, 103 (16), 77 (11), 76 (77), 75 (21), 74 (20), 62 (14), 50 (48), 39 (11), 38 (11), 37 (10). Found, %: C 65.52; H 3.27; N 9.30. $C_{24}H_{13}N_3O_6$. Calculated, %: C 65.60; H 2.99; N 9.58.

Oxidative addition of *N*-aminophthalimide to 2-(4-methoxybenzylidene)-indan-1,3-dione (Ii).To a solution of 132 mg (0.5 mmol)of compound **Ii** in 5 ml of a mixture dichloromethane–THF, 1:1, containing a dispersion of 1 g of potassium carbonate was added while stirring at cooling to –15°C within 5 min by alternating small portions 82 mg (0.5 mmol) of *N*-aminophthalimide and 222 mg (0.5 mmol) of lead tetraacetate. The mixture was stirred for another 5 min, filtered, and kept for 2 days at 5°C in the dark place. According to ^{1}H NMR spectrum the final reaction mixture contained 43% of *p*-methoxybenzaldehyde. By column chromatography on 15 g of silica gel (eluent dichloromethane) 22 mg of unstable substance was isolated whose structure we failed to establish.

Oxidative addition of *N*-aminophthalimide to 2-(4-methylbenzylidene)indan-1,3-dione (Ij). To a solution of 124 mg (0.5 mmol) of compound **Ij**) in 5 ml of a mixture dichloromethane–THF, 1:1, containing a dispersion of 1 g of potassium carbonate was added while stirring at cooling to 0°C within 5 min by alternating small portions 82 mg (0.5 mmol) of N aminophthalimide and 222 mg (0.5 mmol) of lead tetraacetate. The mixture was stirred for another 5 min. The monitoring by TLC showed the absence in the reaction mixture of the initial compound

and the presence of a single reaction product. The reaction mixture was filtered, and kept for 2 days at 5°C in the dark place. According to ^{1}H NMR spectrum the only reaction product containing a methyl group was the *p*-toluic aldehyde separated by chromatography on a column packed with 15 g of silica gel (eluent dichloromethane). Yield 47 mg (81%).

Thermolysis of spiroaziridine IIk. A solution of 107 mg (0.25 mmol) of aziridine **IIk** in 5 ml of anhydrous toluene was heated for 1.5 h at 80°C. By chromatography on a column packed with 10 g of silica gel (eluent hexane–ethyl acetate, from 2:1 to 1:1) 30 mg of unstable substance was isolated whose structure we failed to establish.

2-(4-Nitrophenyl)-4*H*-indeno[2,1-*d*]oxazol-4-one (IIIl). A solution of 100 mg (0.23 mmol) of spiroaziridine **IIl** in 10 ml of anhydrous benzene was boiled for 5 h. The precipitate formed was filtered off and washed with 10 ml of ethyl ether. Yield 37 mg (56%), red powder virtually insoluble in common organic solvents, mp 271–274°C. Mass spectrum, *m/z* (I_{rel}, %): 293 (19), 292 (100) $[M]^+$, 262 (15), 234 (10), 218 (13), 191 (15), 190 (89), 189 (12), 164 (13), 163 (25), 114 (17), 104 (67), 102 (25), 88 (82), 87 (40), 86 (19), 77 (14), 76 (97), 75 (57), 74 (39), 63 (26), 62 (65), 61 (21), 51 (23), 50 (84), 46 (10), 39 (36), 38 (19), 37 (14). Found, %: C 65.67; H 2.77; N 9.37. $C_{16}H_8N_2O_4$. Calculated, %: C 65.75; H 2.74; N 9.59.

***trans*-2-Benzoyl-1-benzenesulfonyl-3-phenylaziridine (Vb).** To a solution of 4.16 g (20 mmol) of benzylideneacetophenone (**Ib**) in 50 ml of anhydrous acetonitrile was added 4.69 g (22 mmol) of chloramine-B and 620 mg (2.2 mmol) of tetramethylammonium tribromide. The reaction mixture was stirred for 3 days at room temperature. The solvent was distilled off in a vacuum. The residue was passed through a short column packed with silica gel, eluent eluent hexane–ethyl acetate, 3:1. The precipitated reaction product was filtered off. Yield 990 mg (14%), white powder, mp 139–140°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.33 d (1H, NCH, *J* 4.4 Hz), 4.56 d (1H, NCH, *J* 4.4 Hz), 7.32–7.36 m (5H, 3-Ph), 7.42–7.65 m (6H), 7.86 d (2H, $PhSO_2$, H^o, *J* 7.6 Hz), 8.06 d (2H, PhCO, H^o, *J* 7.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 47.58 (NCH), 50.26 (NCH), 127.45, 127.59, 128.62, 128.78, 128.86, 128.87, 128.90, 132.78 (3-Ph, C^i), 133.34, 134.08, 135.91 (PhCO, C^i), 139.63 ($PhSO_2$, C^i), 190.18 (CO). Mass spectrum, *m/z* (I_{rel}, %): 222 (43) $[M - SO_2C_6H_5]^+$, 167 (21), 105 (100) $[PhCO]^+$, 90 (14), 89 (24), 77 (97), 51 (41), 50 (12). Found, %: C 69.3; H 4.71; N 3.79. $C_{21}H_{17}NO_3S$. Calculated, %: C 69.4; H 4.68; N 3.86.

***trans*-1-Benzenesulfonyl-2-(4-methoxybenzoyl)-3-phenylaziridine (Ve).** To a solution of 640 mg (2.70 mmol) of chalcone **Ie** in 15 ml of anhydrous acetonitrile was added 639 mg (3.0 mmol) of chloramine-B and 95 mg (0.30 mmol)of pyridinium tribromide. The reaction mixture was kept for 3 days at room temperature. The solvent was distilled off in a vacuum. The residue was passed through a short column packed with silica gel, eluent hexane–ethyl acetate, from 3:1 to 2:1. The product precipitated from the second fraction was filtered off. Yield 180 mg (14%), white powder, mp 142–143°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.88 s (3H, OMe), 4.30 d (1H, NCH, *J* 4.8 Hz), 4.53 d (1H, NCH, *J* 4.8 Hz), 6.95 d (2H, C_6H_4, H^m, *J* 8.6 Hz), 7.31–7.35 m (5H, 3-Ph), 7.36–7.43 m (2H, $PhSO_2$, H^m), 7.46–7.56 m (1H, $PhSO_2$, H^p), 7.85 d (2H, $PhSO_2$, H^o, *J* 7.6 Hz), 8.05 d (2H, *p*-C_6H_4, H^o, *J* 8.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 47.50 (NCH), 50.17 (NCH), 55.56 (OMe), 114.04 (C_6H_4, C^m), 127.50, 127.61, 128.59, 128.84, 129.10 (C_6H_4, C^i), 131.34, 131.38, 132.93 (3-Ph, C^i), 133.29, 139.71 ($PhSO_2$, C^i), 164.36 (CO), 188.32 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 252 (50) $[M - SO_2C_6H_5]^+$, 197 (42), 135 (100) $[MeOC_6H_4CO]^+$, 107 (10), 92 (18), 89 (11), 90 (11), 77 (71), 64 (13), 63 (10), 51 (27), 50 (12). Found, %: C 67.0; H 4.90; N 3.51. $C_{22}H_{19}NO_4S$. Calculated, %: C 67.2; H 4.83; N 3.56.

Reaction of chloramine-B with ethyl (*E*)-2-cyanocinnamate (Im). To a solution of 201 mg (1 mmol) of ester **Im** and 23 mg (0.1 mmol) of benzyltrimethylammonium chloride in 5 ml of acetonitrile was added at stirring 322 mg (1.2 mmol) of chloramine-B hydrate. The reaction mixture was stirred for 15 min. The solvent was distilled off in a vacuum. The residue was passed through a thin bed of silica gel in a mixture hexane–ethyl acetate, 1:1. The solvent was distilled off in a vacuum. The reaction mixture was found to contain *N*-benzylidenebenzenesulfamide (**VI**). Yield 45% (by ^{1}H NMR data). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.08 s (CH=N) (9.07 [28]). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm (published data are given in parentheses [28]): 127.93 (128.2), 129.11 (129.30), 129.20 (129.34), 131.29 (131.5), 132.25 (132.6), 133.50 (133.7), 134.99 (135.2), 138.32 (138.5), 170.56 (170.7) (CH=N).

Thermolysis of sulfonylaziridine Vb. A solution of 182 mg (0.5 mmol) of aziridine **Vb** in 5 ml of anhydrous toluene was heated for 1 h at 160°C. The solvent was distilled off in a vacuum. The residue was passed through a bed of neutral aluminum oxide (1 cm) and washed with 20 ml of mixture dichloromethane–hexane, 1:1. The

solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 15 g of silica gel (eluent dichloromethane –ethyl ether, 1:20). We obtained 42 mg (38%) of 2,5-diphenyl-oxazole (**IIIb**).

Thermolysis of sulfonylaziridine Ve. A solution of 131 mg (0.33 mmol) of aziridine **Ve** in 3 ml of anhydrous toluene was heated for 2 h at 170°C. The solvent was distilled off in a vacuum. The residue was passed through a bed of neutral aluminum oxide (1 cm) and washed with 20 ml of mixture dichloromethane–hexane, 1:1. The solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 15 g of silica gel (eluent dichloromethane–ethyl ether, 1:20). We obtained 26 mg (31%) of 5-(4-methoxyphenyl)-2-phenyloxazole (**IIIe**).

Microwave irradiation of sulfonylaziridine Vb. A solution of 254 mg (0.7 mmol) of aziridine **Vb** in a mixture of 4 ml of *p*-xylene and 0.5 ml of DMF was irradiated for 1 h with microwave radiation of 180 W power. The temperature of the reaction mixture attained 135°C. The solution was washed with water (3 × 1 ml). The solvent was distilled off in a vacuum. The residue was passed through a bed of neutral aluminum oxide (1 cm) and washed with 20 ml of mixture dichloromethane–hexane, 1:1. The solvent was distilled off in a vacuum. The residue was subjected to chromatography on a column packed with 15 g of silica gel (eluent dichloromethane –ethyl ether, 1:20). We obtained 84 mg (54%) of 2,5-diphenyloxazole (**IIIb**).

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