ISSN 1070-4280, Russian Journal of Organic Chemistry, 2007, Vol. 43, No. 7, pp. 1042–1047. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © O.A. Ignatenko, M.A. Kuznetsov, S.I. Selivanov, 2007, published in Zhurnal Organicheskoi Khimii, 2007, Vol. 43, No. 7, pp. 1048–1053.

Oxidative Addition of *N*-Aminophthalimide to 2-Alkenyl-1,3,4-oxadiazoles. Synthesis of Aziridinyloxadiazoles

O. A. Ignatenko, M. A. Kuznetsov, and S. I. Selivanov

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: mak@org.chem.lgu.spb.su

Received June 21, 2006

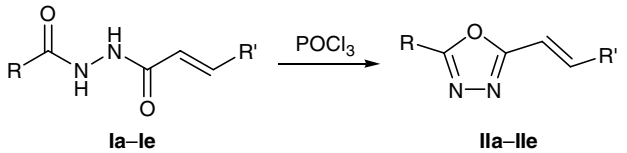
Abstract—Oxidation of *N*-aminophthalimide with lead tetraacetate in the presence of 2-[(*E*)-2-arylethenyl]-5-phenyl-1,3,4-oxadiazoles gives the corresponding 2-(3-aryl-1-phthalimidoaziridin-2-yl)-5-phenyl-1,3,4-oxadiazoles. From 2-phenyl-5-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-1,3,4-oxadiazole only the addition product at both C=C bonds was obtained, while in the reaction with 2,5-bis[(*E*)-2-phenylethenyl]-1,3,4-oxadiazole both mono- and bis-adducts were isolated.

DOI: 10.1134/S1070428007070172

We recently reported on a sharp difference in the results of oxidative phthalimidoaziridination of alkenyldihydropyrazoles and alkenylpyrazoles, which confirmed our assumption that the reaction successfully occurs with unsaturated compounds having a C=N bond only if the latter is a part of an aromatic system [1]. Presumably, in other cases intermediate aminonitrenoid (or aminonitrene) attacks primarily just the C=N bond (most probably, at the lone electron pair on the nitrogen atom) to give a product incapable of forming adducts at C=C bonds. In order to verify whether the observed relation is general we examined analogous reactions with alkenyl-substituted 1,3,4-oxadiazoles. Unlike pyrazoles, the heteroring in 1,3,4-oxadiazoles is π-acceptor; in addition, it contains one more heteroatom (oxygen) whose lone electron pair may also be attacked by intermediate nitrenoid.

Initial alkenyl-substituted 1,3,4-oxadiazoles **IIa**–**IId** were synthesized by cyclization of diacylhydrazines **Ia**–**Id** according to known procedures [2, 3] (Scheme 1). Compounds **Ia**–**Ic** were prepared in turn by acylation of benzohydrazide with the corresponding substituted cinnamoyl chlorides; hydrazide **Id** was obtained from cinnamoyl chloride and hydrazine hydrate. Oxadiazole **IIe** was synthesized following the same scheme from 5-phenylpenta-2,4-dienoic acid and benzohydrazide without isolation of intermediate diacylhydrazine.

Scheme 1.



Ia–Ie **IIa–IIe**

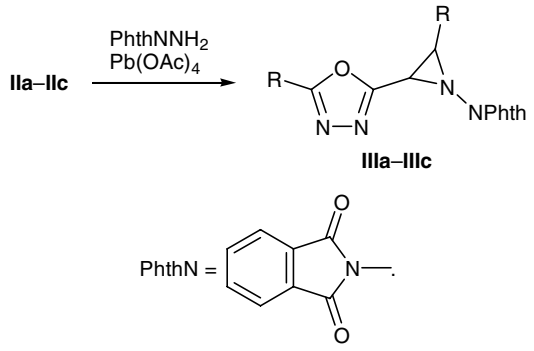
R = Ph, R′ = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-$O_2NC_6H_4$ (**c**), PhCH=CH (**e**); R = PhCH=CH, R′ = Ph (**d**).

Styryl-substituted oxadiazoles **IIa**–**IIe** showed in the ^{1}H NMR spectra doublets due to olefinic protons in the region δ 6.6–7.9 ppm with a coupling constant ^3J of about 16 Hz, indicating that their original *trans*-orientation did not change during the cyclization process. The ^{13}C NMR spectra of newly synthesized compounds **IIb** and **IIe** characteristically contained signals at δ_C 160–165 ppm from carbon atoms in the oxadiazole ring.

The oxidative addition of *N*-aminophthalimide to alkenyloxadiazoles **IIa**–**IIe** was carried out by adding alternately in small portions *N*-aminophthalimide and lead tetraacetate to a solution of unsaturated substrate in methylene chloride. In first experiments, the reaction mixture was cooled to –15°C (as in reactions with styrylpyrazoles [1]); however, in these cases the conversion of initial unsaturated compounds **II** was poor, and the yield of adducts **III** did not exceed 15–20%. When the reactions were performed at room temperature (18–23°C), the conversion of styryloxadiazoles and the yield of compounds **IIIa**–**IIIf** increased considerably. The product structure was confirmed by elemental analysis, ^{1}H and ^{13}C NMR spectroscopy, and mass spectrometry. From monostyryl-substituted oxadia-

zoles **IIa–IIc** we obtained 42–46% of the corresponding addition products at the exocyclic C=C bonds, first representatives of the aziridinyloxadiazole series **IIIa–IIIc** (Scheme 2).

Scheme 2.

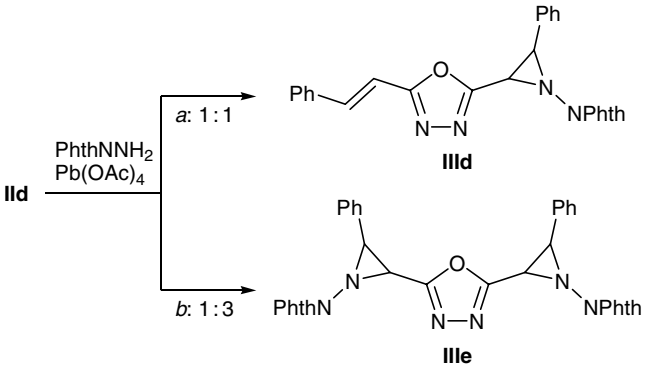


R = Ph (**a**), 4-$MeOC_6H_4$ (**b**), 4-$O_2NC_6H_4$ (**c**).

In the ^{1}H NMR spectra of compounds **IIIa–IIIc** we observed four doublets in the region δ 3.9–5.3 ppm, which belong to protons in the aziridine ring of two invertomers (due to low inversion of the aziridine nitrogen atom on the NMR time scale [4]). The corresponding vicinal coupling constants (^3J = 5.3–5.8 Hz) indicate *trans* orientation of protons in the aziridine ring. This is not surprising, for oxidative aminoaziridination is known to always retain original configuration of substituents at the double bond in the addition products [5, 6]. The invertomer ratio ranges from ~5:1 to ~20:1, and signals from the aziridine protons of the major invertomer appear in a stronger field relative to the corresponding signals of the minor one. Taking into account that the effective volume of the five-membered heteroring is clearly smaller than that of the aryl group, the major invertomers in solution are likely to be those with *syn* orientation of the heteroring and phthalimide fragment.

In the ^{13}C NMR spectra of aziridinyloxadiazoles **IIIa–IIIc** we clearly distinguished signals from the phthaloyl carbonyl carbon atoms (δ_C 165–166 ppm), carbon atoms in the aziridine ring (δ_C 41–51 ppm), and carbon atoms in the five-membered heteroring (δ_C 160–165 ppm). The other signals are located in the region typical of aromatic carbon atoms (δ_C 114–141 ppm). Compounds **IIIa–IIIc** showed in the electron impact mass spectra fairly strong molecular ion peaks, peaks of the $[M - 146]^+$ and/or $[M - 147]^+$ ions arising from elimination of the phthalimide fragment (which are characteristic of *N*-phthalimidoaziridines), and the phthalimide ion peak with *m*/*z* 147.

Scheme 3.

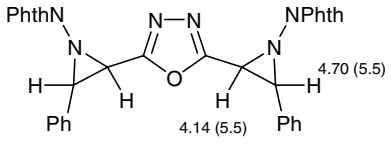


The reaction of 2,5-distyryloxadiazole **IId** with equimolar amounts of *N*-aminophthalimide and lead tetraacetate (*a*) gave only the corresponding adduct **IIId** at one C=C bond of the substrate (yield 46%), while in the reaction with 3 equiv of *N*-aminophthalimide and 3 equiv of the oxidant (*b*) we succeeded in isolating 37% of bis-adduct **IIIe** (Scheme 3). The spectral parameters of compounds **IIId** and **IIIe** were analogous to those of aziridinyloxadiazoles **IIIa–IIIc** with the difference that the ^{1}H NMR spectrum of **IIIe** contained at least three pairs of doublets from aziridine protons with an intensity ratio of ~84:8:8. In all cases, the corresponding coupling constants did not exceed 6 Hz, indicating *trans* orientation of protons in the three-membered rings. This means that the presence of several signals does not result from the lack of *cis*-stereoselectivity in the addition process but from (1) formation of two diastereoisomeric adducts (addition at the same or different sides of the formal plane of distyryloxadiazole molecule **IId**) and/or (2) slow inversion of the aziridine nitrogen atoms. Each of the two diastereoisomers could give rise to three invertomers which, in keeping with the relative orientation of the heteroring and phthalimido groups, may be denoted as *anti–anti*, *anti–syn*, and *syn–syn*. The *anti–syn* invertomer should display in the ^{1}H NMR spectrum two pairs of signals with equal intensities from the aziridine protons, while the symmetrical structures (*anti–anti* and *syn–syn*) should be characterized by a single pair of signals. Obviously, the stronger doublets at δ 4.14 and 4.67 ppm in the ^{1}H NMR spectrum of **IIIe** belong to more stable symmetric invertomer of one diastereoisomer; on the basis of steric considerations, we can presume that the major invertomer in solution has *syn–syn* structure.

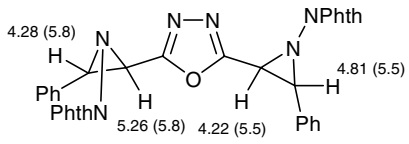
Our attempts to separate product **IIIe** into two possible diastereoisomers by chromatography using several solvent systems were unsuccessful. Therefore, it

seemed more probable that we have not a mixture of diastereoisomers but a mixture of invertomers of only one diastereoisomer. This assumption is confirmed by the two-dimensional EXSY-NOESY data for a solution of bis-aziridine **IIIe** in $CDCl_3$ at 45°C. At that temperature, the rate of inversion of the aziridine nitrogen atoms is still insufficient to induce appreciable changes in a routine ^{1}H NMR spectrum but sufficient to distinguish signals from protons belonging to different interconvertible forms. Raising the temperature to 60°C leads to appreciable broadening of signals from aziridine protons, but their complete coalescence is not achieved.

The EXSY-NOESY data showed that the doublet at δ 4.14 ppm, belonging to the major invertomer, correlates with signals at δ 4.22 and 5.26 ppm and that the doublet at δ 4.70 ppm is related to signals at δ 4.28 and 4.81 ppm. This means that two low-intense pairs of doublets correspond to the *anti–syn* invertomer of the same diastereoisomer as for the *syn–syn* invertomer. Insofar as inversion of the nitrogen atom should strongly affects the chemical shifts of protons just in the corresponding ring, while variations of the chemical shifts of protons in the other ring should be small, we assigned doublets at δ 4.22 and 4.81 ppm to the *syn*-fragment, and those at δ 5.26 and 4.28 ppm, to the *anti*-fragment of the *anti–syn* invertomer. It is seen that the inversion leads to transposition of signals from protons in the inverted ring: the upfield signal in the *syn*-fragment (δ 4.14 ppm for the *syn–syn* invertomer) becomes the most downfield (δ 5.26 ppm), whereas the downfield signal (δ 4.67 ppm) shifts upfield to δ 4.28 ppm. Taking into account that the phthalimide fragment in *N*-phthalimidoaziridines usually strongly deshields protons oriented *syn* with respect to it and shields *anti*-oriented protons [4], signals from the aziridine protons in the *syn–syn* and *anti–syn* invertomers of bis-adduct **IIIe** were assigned as follows:



syn–syn

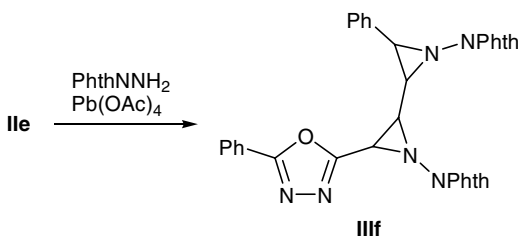


anti–syn

The fraction of the *anti–syn* invertomer of **IIIe** in solution is approximately 5 times lower (16:84) than that of the more stable *syn–syn* invertomer. With account taken of statistical factor (*anti–syn* invertomer is identical to *syn–anti*), these data are very consistent with the *syn*/*anti* ratio found for aziridine **IIIa** (9:1). The fraction of the least stable *anti–anti* invertomer should be lower by a factor of ~20 than the fraction of *anti–syn* (<1%); therefore, it is not surprising that we failed to distinguish signals from the *anti–anti* invertomer. Nevertheless, the ^{1}H NMR spectrum of **IIIe** contained a weak doublet signal at δ 4.02 ppm (^3J = 5.3 Hz) which is likely to correlate with the signal at δ 4.79 ppm, the latter being partially overlapped by the signal at δ 4.81 ppm from the *anti–syn* invertomer. Since both these signals showed no correlation with the other aziridine proton signals in the EXSY-NOESY spectrum, they may be assigned to the *syn–syn* invertomer of the other diastereoisomer whose concentration does not exceed 3%. The reason for the high diastereoselectivity in the formation of compound **IIIe** still remains unclear.

In the reaction with oxadiazole **IIe** having a diene fragment, as with similarly substituted 5-phenyl-3-(4-phenylbuta-1,3-dien-1-yl)pyrazole [1], we succeeded in isolating in a poor yield only the addition product at both C=C bonds, despite equimolar reactant ratio. The use of 2 equiv of the reagents allowed us to raise the yield of bis-adduct **IIIf** to 32% (Scheme 4). No olefinic proton signals were present in the ^{1}H NMR spectrum of **IIIf**, and in the region δ 3–5 ppm we observed three sets of aziridine proton signals with an intensity ratio of ~10:10:1, the overall intensity corresponding to four rather than two protons. The coupling constants for all doublets ranged from 5 to 6 Hz, in keeping with *trans* arrangement of protons in the aziridine rings. As in the reaction with **IId**, the formation of two diastereoisomers of **IIIf** is possible, and each of them may be a mixture of four invertomers.

Scheme 4.



The ratio of stereoisomeric bis-adducts **IIIf** is fairly similar to the ratio of structurally related bis-adducts

obtained from 5-phenyl-3-(4-phenylbuta-1,3-dien-1-yl)pyrazole (~6:6:1 [1]). The coupling constants for protons in the neighboring aziridine rings in the two major structures differ by a factor of more than 1.5 (8.5 and 5.4 Hz), indicating different equilibrium conformations of these stereoisomers. We made no attempts to separate possible diastereoisomers of **IIIf** by chromatography because of the low stability of this compound over silica gel.

Thus oxidative phthalimidoaziridination of alkenyl-substituted 1,3,4-oxadiazoles **IIa–IIe** gives the corresponding aziridinyloxadiazoles rather than products resulting from attack by phthalimidonitrene or the corresponding nitrenoid at the lone electron pairs on the nitrogen or oxygen atoms in the heteroring. Comparison of the reaction conditions and yields shows that the C=C bond in alkenyloxadiazoles **IIa** and **IIb** is less reactive than the same bond in similarly substituted pyrazoles [1], which may be due to stronger π-acceptor power of the 1,3,4-oxadiazole ring.

EXPERIMENTAL

The elemental analyses were obtained on a Hewlett–Packard 185B C,H,N analyzer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer at 300 and 75.4 MHz, respectively, using $CDCl_3$ as solvent and reference (δ 7.26 ppm; δ_C 77.0 ppm). Signals in the ^{13}C NMR spectra were assigned using DEPT technique. The mass spectra were run on MKh-1321 (electron impact, 70 eV) and Finnigan MAT 95 instruments (electrospray ionization; solvent methanol). The reaction mixtures were analyzed, and the purity of the products was checked, by TLC on Alugram SIL G/UV plates. *N*-Aminophthalimide was synthesized as described in [7].

Styryl-1,3,4-oxadiazoles IIa–IId (*general procedure*). A mixture of 10 mmol of diacylhydrazine **Ia–Id** and 20 ml (32.9 g, 0.21 mol) of $POCl_3$ was heated for 2 h under reflux, cooled, and poured onto ice. The precipitate was filtered off and dried in air. The crude product was purified by flash chromatography, followed by recrystallization from ethanol.

2-Phenyl-5-[(*E*)-2-phenylethenyl]-1,3,4-oxadiazole (IIa). Yield 83%, mp 122–123°C; published data [8]: mp 128°C. ^{1}H NMR spectrum, δ, ppm: 7.25 d (1H, =CH, J = 16.2 Hz), 7.37–7.70 m (9H, 8H$_{arom}$, =CH), 8.08 m (2H, 5-Ph, o-*H*).

2-[(*E*)-2-(4-Methoxyphenyl)ethenyl]-5-phenyl-1,3,4-oxadiazole (IIb). Yield 64%, mp 118–119°C. ^{1}H NMR spectrum, δ, ppm: 3.84 s (3H, MeO), 6.95 d (1H, =CH, J = 15.8 Hz), 6.97–7.60 m (8H, 7H$_{arom}$, =CH), 8.10 d (2H, 5-Ph, *o*-H, J = 7.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 55.34 (MeO); 107.51 (2-CH=); 114.43 (*p*-C_6H_4, C^m); 123.92 (C^i); 126.82, 127.49 (C^i); 128.98, 129.02, 131.55, 138.48 (=CHAr); 161.07, 162.26, 163.72 (CO, C=N). Mass spectrum (EI), m/z (I_{rel}, %): 278 (33) $[M]^+$, 277 (100) $[M - H]^+$, 161 (15), 105 (23), 77 (21). Found, %: C 73.34; H 5.18; N 10.10. $C_{17}H_{14}N_2O_2$. Calculated, %: C 73.37; H 5.04; N 10.07.

2-[(*E*)-2-(4-Nitrophenyl)ethenyl]-5-phenyl-1,3,4-oxadiazole (IIc). Yield 75%, mp 242–244°C; published data [9]: mp 247–249°C. ^{1}H NMR spectrum, δ, ppm: 7.57–7.63 m (4H, 3H$_{arom}$, =CH), 7.84 d (1H, =CH, J = 16.0 Hz), 8.03 d (2H, 4-$O_2NC_6H_4$, 2-H, J = 8.7 Hz), 8.11 m (2H, 5-Ph, *o*-H), 8.26 d (2H, 4-$O_2NC_6H_4$, 3-H, J = 8.7 Hz). Found, %: C 65.69; H 4.01; N 14.10. $C_{16}H_{11}N_3O_3$. Calculated, %: C 65.53; H 3.75; N 14.33.

2,5-Bis[(*E*)-2-phenylethenyl]-1,3,4-oxadiazole (IId). Yield 70%, mp 152–153°C; published data [10]: mp 150–151°C. ^{1}H NMR spectrum, δ, ppm: 7.05 d (2H, =CH, J = 16.0 Hz), 7.39–7.64 m (12H, Ph, =CH).

2-Phenyl-5-[(1*E*,3*E*)-4-phenylbuta-1,3-dien-1-yl]-1,3,4-oxadiazole (IIe). 5-Phenylpenta-2,4-dienoic acid, 3.48 g (20 mmol), was dispersed in 30 ml of methylene chloride, 1.5 ml (2.5 g, 21 mmol) of $SOCl_2$ and a few drops of DMF were added, and the mixture was heated for 30 min under reflux. The solvent was evaporated, the residue was dissolved in 10 ml of dioxane, and a solution of 2.72 g (20 mmol) of benzohydrazide and 2.5 ml (2.3 g, 22.8 mmol) of *N*-methylmorpholine in 20 ml of dioxane were added. The mixture was heated to the boiling point, cooled, and diluted with 150 ml of water. The residue was filtered off, dried, and transferred into a round-bottom flask, 20 ml (32.9 g, 0.21 mol) of phosphoryl chloride was added, and the mixture was heated to the boiling point (it became homogeneous) and was then heated under reflux for 20 min. The solution was cooled, poured onto ice, and treated with 50 ml of methylene chloride. The organic phase was separated, and the aqueous phase was extracted with methylene chloride (2× 50 ml). The extracts were combined with the organic phase, dried over $MgSO_4$, and passed through a layer of silica gel. The solvent was removed, and the residue was recrystallized from ethanol. Yield 1.09 g (20%), mp 103–104°C. ^{1}H NMR spectrum, δ, ppm: 6.63 d (1H, =CH, J = 16.0 Hz), 6.87–7.03 m (2H, =CH),

7.30–7.51 m (9H, 8H_{arom}, =CH), 8.10 m (2H, 2-Ph, *o*-H). ^{13}C NMR spectrum, δ_C, ppm: 112.74 (=CH), 123.82 (C^i), 126.78, 126.84, 127.05, 128.79, 128.91, 128.99, 131.62 (=CH), 136.00 (4-Ph, C^i), 138.99 (=CH), 139.07 (=CH), 163.86 (C_{Ht}), 164.22 (C_{Ht}). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 275 (4), 274 (23) $[M]^+$, 273 (8) $[M - H]^+$, 198 (14), 197 (100), 128 (10), 105 (10), 77 (10). Found, %: C 78.70; H 5.19; N 10.16. $C_{18}H_{14}N_2O$. Calculated, %: C 78.81; H 5.14; N 10.21.

General procedure for the oxidative addition of *N*-aminophthalimide to styryl-substituted 1,3,4-oxadiazoles IIa–IId. Compound **IIa**–**IId**, 1 mmol, was dissolved in 50 ml of methylene chloride, 0.69 g (5 mmol) of potassium carbonate was added, and 162 mg (1 mmol) of *N*-aminophthalimide and 443 mg (1 mmol) of lead tetraacetate were added alternately in small portions to the suspension over a period of 15 min under stirring at room temperature. The mixture was stirred for 30 min, and the inorganic precipitate was filtered off and washed with methylene chloride until colorless filtrate. The solvent was removed, and the residue was treated with diethyl ether for crystallization. The product was filtered off, washed with diethyl ether, and recrystallized from ethanol. Compound **IIIc** was purified by flash chromatography, followed by recrystallization. Compound **IIId** was repeatedly recrystallized until complete removal of the initial olefin impurity.

2-Phenyl-5-[(*E*)-3-phenyl-1-phthalimidoaziridin-2-yl]-1,3,4-oxadiazole (IIIa). Yield 44%, mp 155–156°C, a mixture of two invertomers (90:10). ^1H NMR spectrum, δ, ppm: 4.20 d and 4.86 d (H_{azir}, major invertomer, J = 5.5 Hz), 4.47 d and 5.45 d (H_{azir}, minor, invertomer, J = 5.7 Hz), 7.4–7.6 m (8H, 3-Ph and 2-Ph, *m*-H, *p*-H), 7.63–7.75 m (4H, PhthN), 8.03 m and 8.14 m (2H, 2-Ph, *o*-H, major and minor invertomers, respectively). ^{13}C NMR spectrum (major invertomer), δ, ppm: 41.95 and 50.33 ($2C_{azir}$), 123.28 (C^b), 126.99, 127.19, 128.77, 128.83, 129.04, 129.98 (C^a), 134.16 (C^c); 160.31 and 164.8 ($2C_{Ht}$), 165.73 (C=O). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 408 (11) $[M]^+$, 407 (3), 305 (35), 262 (29), 248 (12), 236 (21), 203 (12), 173 (14), 147 (44), 130 (11), 103 (100), 90 (8), 76 (65), 63 (7), 50 (25). Found, %: C 70.36; H 4.08; N 13.53. $C_{24}H_{16}N_4O_3$. Calculated, %: C 70.58; H 3.95; N 13.72.

2-[(*E*)-3-(4-Methoxyphenyl)-1-phthalimidoaziridin-2-yl]-5-phenyl-1,3,4-oxadiazole (IIIb). Yield 46%, mp 149–150°C, a mixture of two invertomers (83:17). ^1H NMR spectrum, δ, ppm: 3.83 s and 3.85 s (3H, MeO, major and minor invertomers), 4.17 d and 4.79 d (H_{azir}, major invertomer, J = 5.6 Hz), 4.40 d and 5.37 d (H_{azir}, minor invertomer, J = 5.8 Hz), 6.81 d and 6.96 d (2H, *p*-C_6H_4, 3-H, minor and major invertomers, J = 8.7 Hz), 7.33 d (*p*-C_6H_4, 2-H, minor invertomer, J = 8.7 Hz), 7.50 d (*p*-C_6H_4, 2-H, major invertomer, J = 8.7 Hz), 7.4–7.6 m (5H, 5-Ph, *m*-H, *p*-H); 7.64–7.72 m (4H, PhthN), 8.01 m and 8.12 m (2H, 5-Ph, *o*-H, major and minor invertomers). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 41.78, 50.17 ($2C_{azir}$); 55.32 (MeO), 114.22 (*p*-C_6H_4, C^m), 123.37 (C^b), 126.96, 128.50, 129.03, 129.98 (C^a), 130.86, 131.94, 134.14 (C^c); 160.06 (C_{Ht}), 160.41, 162.28 (C_{Ht}); 165.66 (C=O). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 438 (6) $[M]^+$, 305 (56), 291 (56), 271 (20), 266 (11), 188 (9), 161 (8), 147 (60), 133 (100), 113 (9), 105 (40), 103 (29), 90 (17), 76 (56), 63 (8), 50 (24). Found, %: C 68.51; H 4.28; N 12.68. $C_{25}H_{18}N_4O_4$. Calculated, %: C 68.49; H 4.14; N 12.78.

2-[(*E*)-3-(4-Nitrophenyl)-1-phthalimidoaziridin-2-yl]-5-phenyl-1,3,4-oxadiazole (IIIc). Yield 42%, mp 209–210°C (decomp.); a mixture of two invertomers (~95:5). ^1H NMR spectrum, δ, ppm: 4.17 d and 4.92 d (H_{azir}, major invertomer, J = 5.3 Hz), 4.53 d and 5.42 d (H_{azir}, minor invertomer, J = 5.5 Hz); 7.45–7.62 m (3H, 5-Ph, *m*-H, *p*-H), 7.66–7.77 m (6H, PhthN, 4-$O_2NC_6H_4$, 2-H), 8.02 m and 8.12 m (2H, 5-Ph, *o*-H, major and minor invertomers), 8.31 d (2H, 4-$O_2NC_6H_4$, 3-H, J = 8.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 41.24, 48.40 ($2C_{azir}$), 122.46, 122.84, 122.94, 125.92, 127.60, 128,30, 128.75, 129.78 (C^a), 133.69 (C^c), 140.71; 163.64, 164.77 ($2C_{Ht}$), 165.21 (C=O). Mass spectrum (EI), *m*/*z* (I_{rel}, %): 454 (5) $[M + 1]^+$, 453 (20) $[M]^+$, 435 (5), 307 (20), 306 (17), 305 (66), 304 (5), 248 (7), 173 (11), 148 (18), 147 (11), 144 (7), 132 (17), 130 (11), 105 (100), 104 (76), 103 (37), 90 (8), 77 (46), 76 (34), 51 (5), 50 (8). Found, %: C 63.68; H 3.47; N 15.22. $C_{24}H_{15}N_5O_5$. Calculated, %: C 63.58; H 3.33; N 15.45.

2-[(*E*)-3-Phenyl-1-phthalimidoaziridin-2-yl]-5-[(*E*)-2-phenylethenyl]-1,3,4-oxadiazole (IIId). Yield 46%, mp 143–145°C; a mixture of two invertomers (90:10). ^1H NMR spectrum, δ, ppm: 4.14 d and 4.81 d (H_{azir}, major invertomer, J = 5.5 Hz), 4.43 d and 5.42 d (H_{azir}, minor invertomer, J = 5.8 Hz), 6.96 d (J = 16.5 Hz, =CHPh, major invertomer), 7.26–7.58 m (12H, 2Ph, =CHPh, minor invertomer, =CHHt), 7.61–7.75 m (4H, PhthN). ^{13}C NMR spectrum, δ_C, ppm: major invertomer: 41.93, 50.32 ($2C_{azir}$); 109.38, 123.29

(C^b), 128.46, 128.76, 128.83, 128.94, 129.49, 129.95, 130.11, 134.18 (C^c), 161.60, 164.78 ($2C_{Ht}$), 165.37 (C=O). Mass spectrum (ES), *m*/*z* (I_{rel}, %): 923 (21) $[2M + Na + MeOH]^+$, 891(100) $[2M + Na]^+$, 489 (9) $[M + Na + MeOH]^+$, 457(21) $[M + Na]^+$. Found, %: C 71.68; H 4.36; N 12.59. $C_{26}H_{18}N_4O_3$. Calculated, %: C 71.88; H 4.18; N 12.90.

2,5-Bis[(*E*)-3-phenyl-1-phthalimidoaziridin-2-yl]-1,3,4-oxadiazole (IIIe). Potassium carbonate, 5 mmol, was dispersed in a solution of 274 mg (1 mmol) of oxadiazole **IId** in 50 ml of methylene chloride, 486 mg (3 mmol) of *N*-aminophthalimide and 1.329 g (3 mmol) of lead tetraacetate were added alternately in small portions over a period of 15 min under stirring at room temperature, and the mixture was stirred for 30 min. The inorganic precipitate was filtered off and washed with methylene chloride until colorless filtrate, the solvent was removed, and the residue was recrystallized from ethanol with addition of DMF. Yield 220 mg (37%), mp 220–222°C (decomp.); a mixture of three stereoisomers (~82:15:3). ^{1}H NMR spectrum, δ, ppm: 4.14 d and 4.70 d (H_{azir}, major isomer, J = 5.5 Hz); 4.22 d (J = 5.5 Hz), 4.28 d (J = 5.8 Hz), 4.79 d (J 5.5 Hz), and 5.26 d (J = 5.8 Hz) (H_{azir}, medium-fraction component); 4.03 d (J = 5.3 Hz) and ~4.79 d (H_{azir}, minor isomer) (4H total); 7.26–7.57 m (10H, 2Ph), 7.60–7.77 m (8H, 2PhthN). ^{13}C NMR spectrum, δ_C, ppm: major component: 41.59, 50.30 ($2C_{azir}$); 123.32 (C^b), 127.20, 128.75, 128.94, 129.94 (C^a), 133.86, 134.20 (C^c); 161.59 and 164.73 ($2C_{Ht}$). Mass spectrum (ES), *m*/*z* (I_{rel}, %): 1869 (18) $[3M + Na + 2MeOH]^+$, 1837 (38) $[3M + Na + MeOH]^+$, 1805 (38) $[3M + Na]^+$, 1275 (36) $[2M + Na + 2MeOH]^+$, 1243 (84) $[2M + Na + MeOH]^+$, 1211 (80) $[2M + Na]^+$, 681 (15) $[M + Na + 2MeOH]^+$, 649 (64) $[M + Na + MeOH]^+$, 617 (100) $[M + Na]^+$. Found, %: C 68.60; H 3.70; N 14.13. $C_{34}H_{22}N_6O_5$. Calculated, %: C 68.68; H 3.73; N 14.13.

2-{(*E*)-3-[(*E*)-3-Phenyl-1-phthalimidoaziridin-2-yl]-1-phthalimidoaziridin-2-yl}-5-phenyl-1,3,4-oxadiazole (IIIf). Potassium carbonate, 0.69 g (5 mmol), was dispersed in a solution of 274 mg (1 mmol) of oxadiazole **IIe** in 50 ml of methylene chloride, 324 mg (2 mmol) of *N*-aminophthalimide and 886 mg (2 mmol) of lead tetraacetate were added alternately in small portions over a period of 15 min under stirring at room temperature, and the mixture was stirred for 30 min. The inorganic precipitate was filtered off and washed with methylene chloride until colorless filtrate. The solvent was removed, the residue was treated with 5 ml of methylene chloride, and the precipitate was filtered off. Yield 32%, mp 242–245°C (decomp.); a mixture of three stereoisomers (~10:10:1). The product decomposed on attempted recrystallization from ethanol. ^{1}H NMR spectrum, δ, ppm: 2.88 d.d (J = 8.5, 5.0 Hz), 3.78 d.d (J = 8.5, 5.5 Hz), 4.26 d (J = 5.5 Hz), and 4.57 d (J = 5.0 Hz) (H_{azir}, major stereoisomer); 4.13 d (J = 5.7 Hz), 4.21 d.d (J = 5.4, 5.4 Hz), 4.44 d.d and 4.45 d (overlapping signals, J = 5.4–5.9 Hz) (H_{azir}, another major stereoisomer); 3.65 m, 3.95 d (J = 5.2 Hz), 4.50 m, and 5.05 d (J = 4.9 Hz) (H_{azir}, minor isomer), (4H total); 7.25–7.78 m (16H, 5-Ph, *m*-H, *p*-H, Ph, 2PhthN); 8.03–8.07 m (5-Ph, *o*-H, major stereoisomers) and 8.11 m (5-Ph, *o*-H, minor stereoisomer) (2H total). ^{13}C NMR spectrum, δ_C, ppm: two major stereoisomers: 38.12, 40.66, 43.01, 47.11, 48.51, 49.14, 49.20, 50.15 ($8C_{azir}$), 122.99, 123.23, 123.33 (2C), 123.41 (C^b), 127.06, 127.14, 127.24, 128.22, 128.27, 128.59, 129.07, 129.57, 129.81 (2C), 129.97 (2C, C^a), 130.47, 131.98, 132.03, 134.01 (2C), 134.20 (2C, C^c), 159.86, 160.07, 164.77, 164.62 ($4C_{Ht}$); 165.38 (C=O). Mass spectrum (ES), *m*/*z* (I_{rel}, %): 1869 (18) $[3M + Na + 2MeOH]^+$, 1837 (14) $[3M + Na + MeOH]^+$, 1805 (7) $[3M + Na]^+$, 1275 (66) $[2M + Na + 2MeOH]^+$, 1243 (68) $[2M + Na + MeOH]^+$, 1211 (22) $[2M + Na]^+$, 681 (38) $[M + Na + 2MeOH]^+$, 649 (100) $[M + Na + MeOH]^+$, 617 (55) $[M + Na]^+$. Found, %: C 68.69; H 3.69; N 14.01. $C_{34}H_{22}N_6O_5$. Calculated, %: C 68.68; H 3.73; N 14.13.

REFERENCES

1. Ignatenko, O.A., Blandov, A.N., and Kuznetsov, M.A., *Russ. J. Org. Chem*., 2005, vol. 41, p. 1793.
2. Grekov, A.P. and Azen, R.S., *Zh. Obshch. Khim*., 1961, vol. 31, p. 407.
3. Kerr, V.N., Ott, D.G., and Hayes, F.N., *J. Am. Chem. Soc*., 1960, vol. 82, p. 186.
4. Atkinson, R.S. and Malpass, J.R., *J. Chem. Soc., Perkin Trans. 1*, 1977, p. 2242.
5. Jones, D.W. and Thornton-Pett, M., *J. Chem. Soc., Perkin Trans. 1*, 1995, p. 809.
6. Atkinson, R.S. and Barker, E., *J. Chem. Soc., Chem. Commun*., 1995, p. 819.
7. Drew, N.D.K. and Hatt, N.H., *J. Chem. Soc*., 1937, p. 16.
8. Milcent, R., *Ann. Chim*., 1967, p. 169.
9. JPN Patent Appl. no. 70-02765, 1966; *Chem. Abstr*., 1970, vol. 72, no. 134169g.
10. Hayes, F.N., Rogers, B.S., and Ott, D.G., *J. Am. Chem. Soc*., 1955, vol. 77, p. 1851.