Russian Journal of Organic Chemistry, Vol. 39, No. 4, 2003, pp. 559–573. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 4, 2003, pp. 595–609.

Dedicated to Full Member of the Russian Academy of Sciences I. P. Beletskaya on occasion of her jubilee

Cascade Transformations of (2,2-Diaryl-3,3-dichloroaziridin-1-yl)acetates

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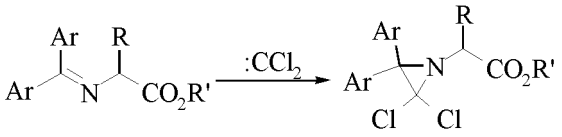
Received December 4, 2002

Abstract—Esters of (2,2-diaryl-3,3-dichloroaziridin-1-yl)acetic acid prepared from glycine derivatives under alkylation conditions afford esters of 2-[*N*-alkyl-*N*-(2,2-diaryl-1-cyanovinyl)amino]-3,3-diarylacrylic acid in 20–40% yield. The reaction resulting in these compounds proceeds through a cascade of 3-chloro-2-azadiene and ylide intermediates. 3-Chloro-2-azadienes originating from (2,2-diaryl-3,3-dichloroaziridin-1-yl)-acetates react with primary and secondary amines at the carbon atom of imine group providing ketenimines which undergo ketenimine-nitrile rearrangement or fragmentation. The other bases (KOH, MeONa, DBU) effect dehydrochlorination of the mentioned 3-chloro-2-azadienes giving nitrile-ylides which are trapped by nucleophilic reagents. The 3-chloro-2-azadiene obtained from methyl (2,2-diaryl-3,3-dichloroaziridin-1-yl)-acetate and DBU was relatively stable and was isolated as an individual compound. (2,2-diaryl-3,3-dichloro-aziridin-1-yl)propionates behave as nonfunctionalized dichloroaziridines.

Aziridines due to their high reactivity are widely used in the syntheses of versatile nitrogen-containing compounds. The readily available gem-dihaloaziridines take a special place in this respect for the presence of halogen atoms results in unusual transformations. Therefore dihaloaziridines are convenient precursors of various acyclic (2-halo or 2-hydroxyacetamides, amidines, imidoesters, phenethylamines, ketenimines etc.) and also heterocyclic (pyrroles, isoquinolinecarboxylic acids, pyridines, azepines etc.) compounds. By now reactions of dihaloaziridines with aryl and alkyl substituents attached to the aziridine ring are studied in detail [1–18]. These reactions as a rule involve the acid-catalyzed opening of the three-membered ring. Recently by treating imino derivatives of amino acids with dihalocarbenes were prepared functionalized dihaloaziridines with a fragment $CHRCO_2Me$ attached to the nitrogen in the ring [19]. A transformation of these compound useful for synthesis is their dehalogenation affording uncommon ketenimines, *N*-(diphenylvinylidene)-amino acids [20].

Analysis of the structure of aziridines **IIa–e** and comparison of pK_a of the corresponding imines $Ph_2C{=}NCHRCO2Et$ (**I**) (DMSO, 25°C; R = H, 18.7; R = Me, 22.8; R = Ph, 21.2 [21]) shows that compounds **IIa–c** should possess sufficiently high CH-acidity (**IIa** ≈ **IIb** ≈ **IIc** > **IIe** > **IId**). This characteristic of glycines **IIa–c** suggests that they may be alkylated under conditions used in alkylation of imines $Ph_2C{=}NCH_2CO_2R$ [19, 20].

Aiming at investigation of these transformations we prepared gem-dichloroaziridines **IIa–e** from imino derivatives of glycine, alanine, and phenylglycine (**Ia–e**) by reaction with dichlorocarbene.



Ia–e **IIa–e**

Ar = Ph, R = H, R' = Me (**a**), Ar = Ph, R = H, R' = Et (**b**), Ar = *p*-ClC_6H_4, R = H, R' = Me (**c**), Ar = Ph, R = Me, R' = Et (**d**), Ar = Ph, R' = Ph, R' = Me (**e**).

Alkylation of compounds **IIa–c** with methyl iodide, allyl bromide, and benzyl bromide was carried out in acetonitrile in the presence of powdered potassium hydroxide and benzyltriethylammonium chloride (TEBA) as a phase-transfer catalyst. However the analysis of spectra of compounds **III–VII** isolated from the reaction mixtures revealed that the expected alkylated aziridines of **IIf** type did not form

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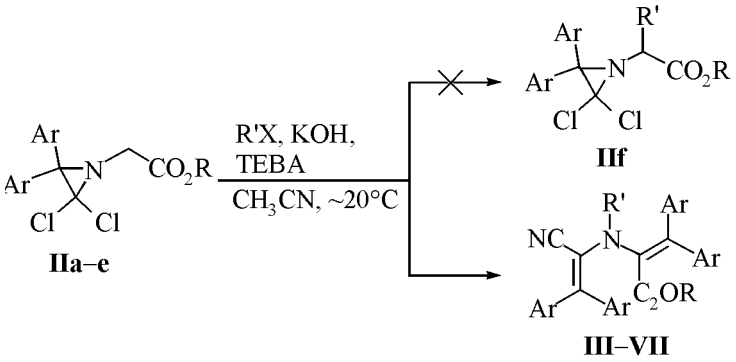
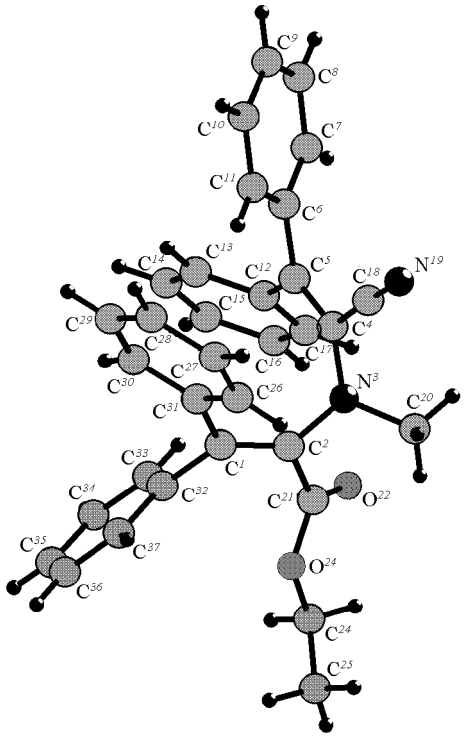
under the conditions of the process. The replacement of solvent (DMSO instead of acetonitrile) and of base (NaH instead of KOH) did not change the direction of reaction.



R'X = MeI, $H_2C{=}CHCH_2Br$, $PhCH_2Br$; **III**, Ar = Ph, R = R' = Me, **IV**, Ar = Ph, R = Et, R' = Me, **V**, Ar = *p*-ClC_6H_4, R = R' = Me, **VI**, Ar = Ph, R = Me, R' = $H_2C{=}CHCH_2$, **VII**, Ar = Ph, R = Me, R' = $PhCH_2$.

The structure of compounds **III–VII** was confirmed by spectral data, and their composition was determined from elemental analysis and mass spectra. The structure of compound **IV** was established by X-ray diffraction analysis (see figure, Tables 1, 2). In the UV spectra of compounds **III, IV, VI, VII** long-wave bands are observed in the region 393–415 nm indicating the presence in the molecules of a prolonged conjugation system. In the IR spectra of compounds **III–VII** appear bands of stretching vibrations of the ester groups at 1714–1740 cm^{-1} and cyano groups at 2208–2215 cm^{-1}. In the ^1H NMR spectra signals from aromatic protons and from protons of N-alkyl (alkenyl) and alkoxy groups are present. In the ^{13}C NMR spectra appear the characteristic peaks of carbon atoms in cyano groups at 115–116 ppm, of carbonyl carbons, δ 165–167 ppm, and also of CH_3N groups, δ 39 ppm, CH_2N, δ 55 ppm, and AlkO. In the mass spectrum of compound **III** appeared a peak of the molecular ion whose composition was confirmed by precise mass measuring, and also $[M\text{-}59]^+$ ($[M\text{-}CO_2Me]^+$). The structure of compounds **III–VII** evidenced that the molecules of the initial aziridines suffered fundamental transformation and also that in formation of a single product molecule took part two molecules of the initial compound. The probable route leading to compounds **II–VI** is shown on Scheme 1.



General view of a molecule of ethyl-2-[*N*-(2,2-diphenyl-1-cyanovinyl)-*N*-methylamino]-3,3-diphenylacrylate (**IV**).

The suggested mechanism on the one hand assumes that the aziridine is deprotonated by a base, the anion transforms into 3-chloro-2-azabuta-1,3-diene A which in keeping with the chemical behavior of α-chloroenamines [22] is able to exist in equilibrium with the corresponding keteniminium salt B. In the presence of a sufficiently strong base the latter can suffer dehydrochlorination into a nitrile-ylide C that should be relatively stable because of the charge delocalization. On the other hand, aryl- and alkyl-substituted aziridines are capable at heating to undergo cleavage of any among the three non-equivalent bonds [1–18]. Therewith the cleavage of

Table 1. Main bond lengths (*d*, Å) in the molecule of compound **IV**

Bond	*d*	Bond	*d*	Bond	*d*
O^{22}–C^{21}	1.202 (12)	C^{5}–C^{6}	1.49 (1)	C^{26}–C^{27}	1.390 (13)
O^{24}–C^{21}	1.327 (11)	C^{6}–C^{7}	1.388 (11)	C^{26}–C^{31}	1.396 (11)
O^{24}–C^{24}	1.468 (14)	C^{6}–C^{11}	1.394 (14)	C^{27}–C^{28}	1.393 (10)
N^{3}–C^{2}	1.403 (4)	C^{7}–C^{8}	1.389 (10)	C^{28}–C^{29}	1.384 (11)
N^{3}–C^{4}	1.408 (10)	C^{8}–C^{9}	1.382 (14)	C^{29}–C^{30}	1.389 (13)
N^{3}–C^{20}	1.462 (14)	C^{9}–C^{10}	1.383 (11)	C^{30}–C^{31}	1.40 (1)
N^{19}–C^{18}	1.147 (7)	C^{10}–C^{11}	1.392 (10)	C^{32}–C^{33}	1.391 (5)
C^{1}–C^{2}	1.353 (19)	C^{12}–C^{13}	1.398 (14)	C^{32}–C^{37}	1.393 (13)
C^{1}–C^{31}	1.485 (14)	C^{12}–C^{17}	1.390 (15)	C^{33}–C^{34}	1.389 (6)
C^{1}–C^{32}	1.490 (6)	C^{13}–C^{14}	1.383 (9)	C^{34}–C^{35}	1.375 (13)
C^{2}–C^{21}	1.512 (14)	C^{14}–C^{15}	1.359 (16)	C^{35}–C^{36}	1.388 (6)
C^{4}–C^{5}	1.352 (12)	C^{15}–C^{16}	1.388 (15)	C^{36}–C^{37}	1.385 (6)
C^{4}–C^{18}	1.448 (9)	C^{16}–C^{17}	1.407 (9)		
C^{5}–C^{12}	1.481 (9)	C^{24}–C^{25}	1.441 (14)		

Table 2. Main bond angles (Å, deg) in the molecule of compound **IV**

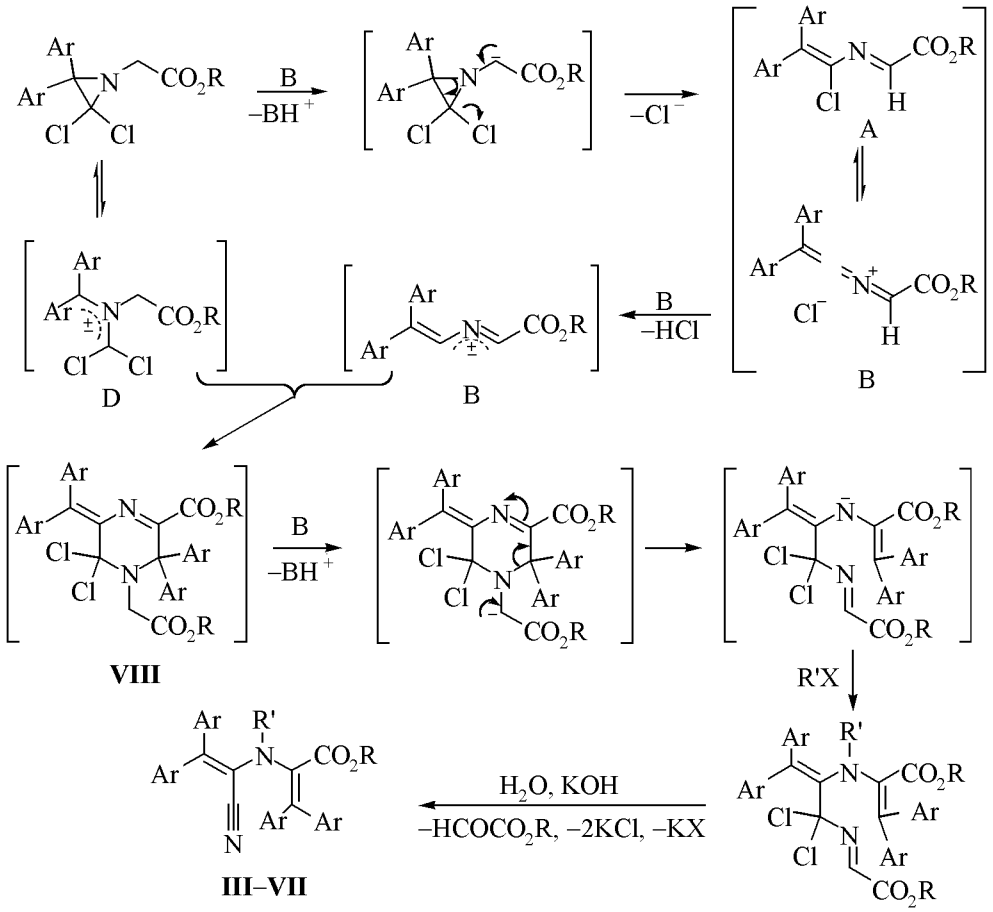
Angle	ω	Angle	ω	Angle	ω
$O^{22}C^{21}O^{24}$	123.38 (20)	$C^{2}C^{1}C^{31}$	122.67 (16)	$C^{13}C^{12}C^{17}$	118.92 (22)
$C^{21}O^{24}C^{24}$	113.74 (19)	$C^{2}C^{1}C^{32}$	120.86 (16)	$C^{13}C^{14}C^{15}$	120.53 (30)
$C^{25}C^{24}O^{24}$	108.31 (25)	$C^{4}C^{5}C^{12}$	123.97 (16)	$C^{14}C^{15}C^{16}$	120.09 (35)
$O^{22}C^{21}C^{2}$	124.71 (20)	$C^{4}C^{5}C^{6}$	120.36 (16)	$C^{15}C^{16}C^{17}$	120.24 (26)
$O^{24}C^{21}C^{2}$	111.88 (16)	$C^{5}C^{4}C^{18}$	118.65 (16)	$C^{26}C^{27}C^{28}$	120.46 (19)
$C^{2}N^{3}C^{4}$	123.54 (15)	$C^{5}C^{6}C^{7}$	118.44 (16)	$C^{26}C^{31}C^{30}$	118.48 (16)
$C^{2}N^{3}C^{20}$	118.50 (15)	$C^{5}C^{6}C^{11}$	122.75 (16)	$C^{27}C^{26}C^{31}$	120.55 (17)
$C^{4}N^{3}C^{20}$	116.90 (14)	$C^{5}C^{12}C^{13}$	119.31 (17)	$C^{27}C^{28}C^{29}$	119.33 (19)
$C^{1}C^{2}N^{3}$	126.02 (16)	$C^{5}C^{12}C^{17}$	121.63 (17)	$C^{28}C^{29}C^{30}$	120.43 (19)
$N^{3}C^{2}C^{21}$	112.42 (15)	$C^{6}C^{5}C^{12}$	115.64 (15)	$C^{29}C^{30}C^{31}$	120.75 (17)
$C^{5}C^{4}N^{3}$	126.66 (16)	$C^{6}C^{7}C^{8}$	120.96 (18)	$C^{31}C^{1}C^{32}$	116.42 (15)
$N^{3}C^{4}C^{18}$	114.66 (15)	$C^{6}C^{11}C^{10}$	120.16 (18)	$C^{32}C^{33}C^{34}$	120.57 (19)
$N^{19}C^{18}C^{4}$	176.89 (20)	$C^{7}C^{6}C^{11}$	118.81 (17)	$C^{32}C^{37}C^{36}$	120.41 (17)
$C^{1}C^{2}C^{21}$	121.48 (16)	$C^{7}C^{8}C^{9}$	119.86(19)	$C^{33}C^{32}C^{37}$	118.68 (18)
$C^{1}C^{31}C^{26}$	121.27 (16)	$C^{8}C^{9}C^{10}$	119.84 (20)	$C^{33}C^{34}C^{35}$	120.4 (2)
$C^{1}C^{31}C^{30}$	120.21 (16)	$C^{9}C^{10}C^{11}$	120.37 (19)	$C^{34}C^{35}C^{36}$	119.53 (21)
$C^{1}C^{32}C^{33}$	121.23 (16)	$C^{12}C^{13}C^{14}$	120.78 (22)	$C^{37}C^{36}C^{35}$	120.4 (2)
$C^{1}C^{32}C^{37}$	120.08 (16)	$C^{12}C^{17}C^{16}$	119.43 (21)		

C–N bonds gives ylide D that is in equilibrium with the initial aziridine. Further the reaction between the nitrile-ylide C with the azomethine-ylide D affords pyrazine **VIII** whose transformations under attack of the base and the alkylating agent (see Scheme 1) furnish the final products, the corresponding esters of 2-[*N*-alkyl-*N*-(2,2-diaryl-1-cyanovinyl)-amino]-3,3-diarylacrylic acid **III**–**VII**.

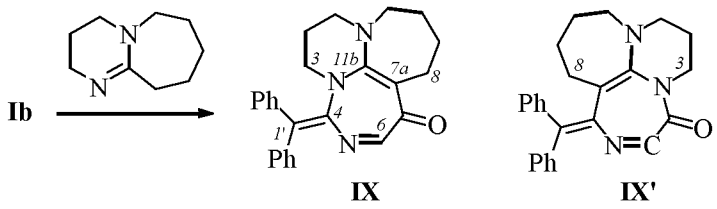
In order to refine the assumed scheme of reactions leading to compounds **III**–**VII**, to prove the existence of the mentioned intermediates A–D, and also to look for synthetically useful transformations of 2,2-diaryl-3,3-dichloroaziridines (amino acids derivatives) we investigated reactions of aziridines **Ia**–**e** in the presence of bases of different strength and nucleophilicity: sodium methylate, primary, secondary, and tertiary amines, amidines.

We planned to isolate chloroazadiene A from reaction of aziridine **IIb** with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) known as strong base (pK_aH 12.5,

Scheme 1.



H_2O, 20–25°C) but weak nucleophile. We unexpectedly obtained compound **IX** in high yields: from 57% in acetonitrile to 93% in cyclohexene). The formation of compound **IX** evidenced that in this reaction the DBU behaved not only as a base, but also as nucleophile.

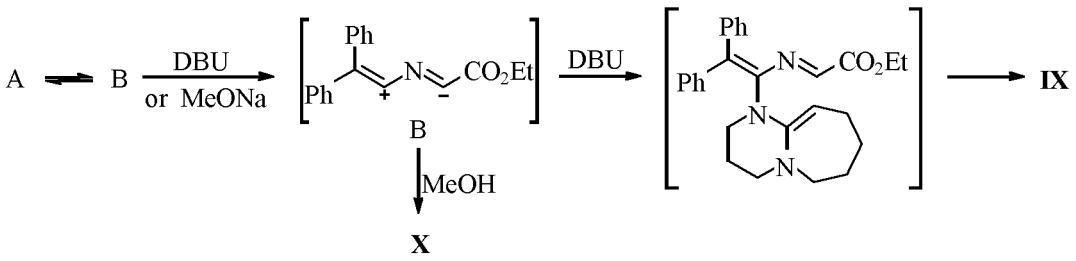


The structure and composition of compound **IX** was derived from the data of IR and NMR (^{1}H, ^{13}C, NOESY) spectroscopy, mass spectrometry, and elemental analysis. In ^{13}C NMR spectrum was present a characteristic signal from a carbonyl carbon at 173.9 ppm, the signals of olefin carbons were observed at 138.4 ($C^{1'}$), 147.3 (C^{4}), 94.8 (C^{7a}), 162.8 (C^{11b}) ppm, and the signal of C^{6} at 131.8 ppm. In the mass spectrum was present the molecular ion peak and that of ion $[M\text{-}77]^+$ ($[M\text{-Ph}]^+$).

The selection between the structures **IX** and **IX'** in favor of the former was based on the NOESY ^{1}H NMR spectrum. The analysis of this spectrum revealed the interaction between aromatic protons and the proton attached C^{3} and the lack of their interaction with the proton at C^{8}.

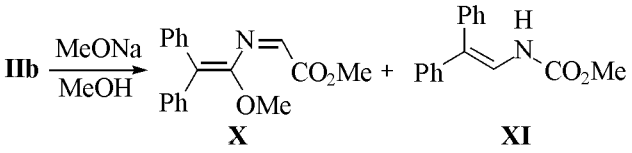
The probable pathway of compound **IX** formation is presented in Scheme 2. The DBU is sufficiently strong base to be able to effect dehydrochlorination of

Scheme 2.



intermediates A (B) providing ylide C that further is attacked by DBU giving rise to an intermediate compound containing a strongly nucleophilic (β-endiamine) carbon atom facilitating 7-*endo*-trig cyclization.

At treating aziridine **IIb** with sodium methylate in methanol arise compounds **X** and **XI** in 42 and 6% yield respectively.

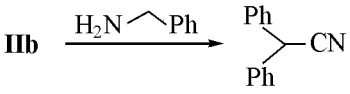


X **XI**

In the IR spectrum of compound **X** appear the bands of stretching vibrations of the ester group at 1750 cm^{-1} and of C=C bond at 1640 cm^{-1}. In the ^{13}C NMR spectrum the peak of the carbonyl carbon is located at 158.3 ppm, the signal of imine carbon 148.9 ppm, signals of the olefin carbon atoms at 141.2 (=COMe) and 127.1 (CPh_2) ppm The mass spectrum of compound **X** contained the peak of the molecular ion and also those of ions $[M\text{-}15]^+$ ($[M\text{-}Me]^+$) and $[M\text{-}59]^+$ ($[M\text{-}CO_2Me]^+$). In the ^1H NMR spectrum of compound **XI** is observed a characteristic NH signal at 8.80 ppm split into a doublet. In the ^{13}C NMR spectrum appear the signals of carbonyl carbon at 160.4 ppm, of olefin carbons at 117.6 and 152.7 ppm In the IR spectrum the absorption band of ester group stretching vibrations is present at 1718 cm^{-1}, of C=C bond at1640 cm^{-1}, and of NH group at 3385 cm^{-1}.

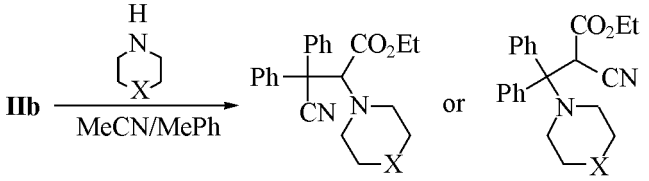
The reaction of aziridine **IIb** in the presence of sodium methylate is similar to those at the use of the other bases (KOH, DBU) sufficiently strong for dehydrochlorination of intermediate A (B) into ylide C (Scheme 2).

In reaction of aziridine **IIb** with benzylamine diphenylacetonitrile **XII** was isolated in 10% yield. Its structure was derived from IR and NMR spectra and was confirmed by the melting point consistent with the published one.



XII

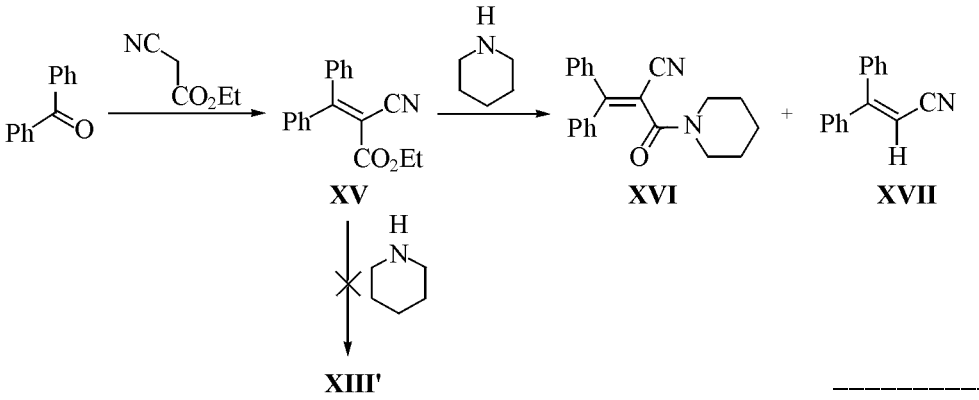
Reaction of aziridine **IIb** with piperidine and morpholine gave rise to nitriles **XIII** and **XIV** in 56 and 38% yield respectively. The IR spectra of these compounds contain bands of carbonyl stretching vibrations at 1750 cm^{-1} and those of cyano groups in the region 2250 cm^{-1}. In the ^{13}C NMR spectrum of compound **XIII** besides the signals from the carbons from two phenyl groups are present characteristic carbon peaks from cyano group at 121.3 ppm and from carbonyl group at 167.7 ppm In the upfield part of the spectrum appear signals of the methyl group (13.8 ppm), OCH_2 group (60.4 ppm), methylene groups in the piperidine ring (23.7, 26.2, 53.0 ppm), and also of a quaternary carbon (53.6 ppm) and methine carbon (74.6 ppm). These data and the results of the elemental analysis suffice for ascribing the product structure **XIII** or **XIII'**, although the chemical shift of the methine carbon is in better agreement with structure **XIII**. The choice between structures **XIII** and **XIII'** was based on chemical reactions.



XIII, XIV **XIII', XIV'**

X = CH_2 (**XIII, XIII'**), O (**XIV, XIV'**).

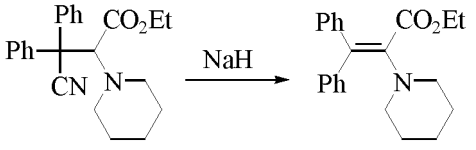
The attempt to prepare compound **XIII'** from ethyl benzhydrylidenecyanoacetate **XV** and piperidine was unsuccessful, and piperidide **XVI** and diphenylacrylonitrile (**XVII**) were isolated as reaction products. Apparently structure **XIII'** did not form due to steric



hindrance to conjugate addition of piperidine to ester **XV**.

In the IR spectrum of compound **XVI** are observed the bands of stretching vibrations of the ester group at 1640 cm^{-1}, of cyano group at 2219 cm^{-1} (in the spectrum of compound **XVII** at 2223 cm^{-1}), and of C=C bond at 1600 cm^{-1}. In the ^{13}C NMR spectrum are present the characteristic signals of the cyano group carbon with the chemical shift of 116.4 ppm (117.5 ppm for compound **XVII**), of carbonyl carbon (161.3 ppm), of olefin carbons (106.0, 159.3 ppm) and of carbons in the piperidine ring (23.7, 24.5, 25.1, 42.5, 47.3 ppm).

When cyano and ester groups are vicinal, as in compound **XIII**, elimination of hydrogen cyanide is possible. Actually at treatment of compound **XIII** with sodium hydride in acetonitrile compound **XVIII** was separated. In the IR spectrum of compound **XVIII** are observed the bands of stretching vibrations of the conjugated ester group at 1720 cm^{-1}, and in the ^{13}C NMR spectrum appear characteristic signals of the carbonyl carbon (168.3 ppm), benzene rings carbons, olefin carbons (127.5, 140.8 ppm), and those from the piperidine ring (25.8, 51.4, 60.3 ppm).

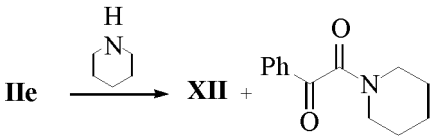


XIII **XVIII**

The above data permitted assignment to the compounds synthesized structures **XIII** and **XIV** with the vicinal location of the cyano and ester groups.

The probable paths of products formation in reactions of aziridine **IIb** with piperidine, morpholine, and benzylamine are shown on Scheme 3. In the first stage amine acting as a base brings about formation of azadiene A (or salt B) which is attacked by a nucleophile at the electrophilic imine carbon giving rise to the corresponding ketenimine **XIXa–c**. According to published data [23–26] ketenimines (e.g., diphenyl-*N*-benzylketenimine) capable to homolysis of the C–N bond providing relatively stable free radicals are prone at 25–65°C to undergo ketenimine-nitrile rearrangement that occurs presumably through formation and recombination of the corresponding radical pair in the solvent cage. Apparently this type rearrangement occurs on the path leading to formation of nitriles **XIII** and **XIV** in reaction of aziridine **IIb** with piperidine and morpholine. In the case of benzylamine the corresponding ketenimine **XIXc** provided at homolysis radicals that due to the presence of the N–H bond easier underwent disproportionation affording diphenylacetonitrile **XII** and compound **XX** which was lost because of hydrolysis on silica gel during the chromatographic separation. However in this case the reaction might follow the retroene mechanism that for instance was assumed for thermal transformation of *N*-(*tert*-butyl)diphenylketenimine into diphenylacetonitrile and isobutylene [27].

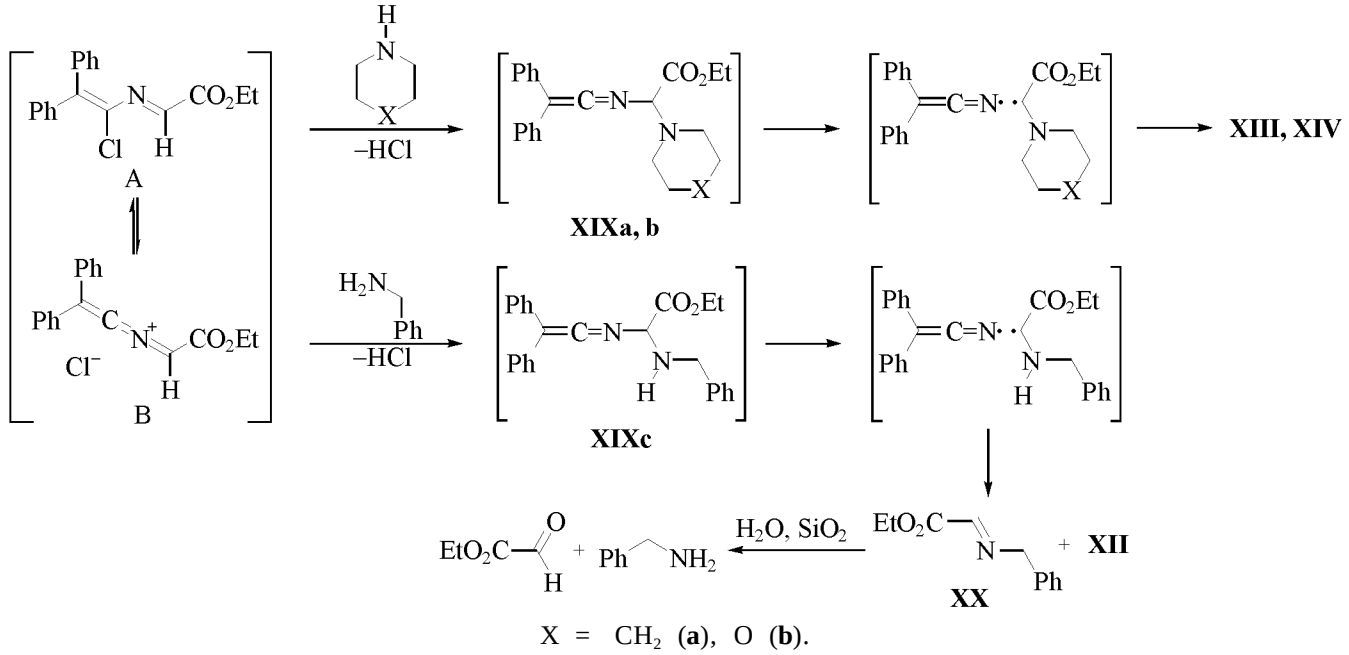
In reactions of aziridines **IId, e** with piperidine, as in reaction of aziridine **IIb** with benzylamine formed diphenylacetonitrile **XII** in 5 and 30% yield respectively, but here the reaction proceeded considerably slower. In reaction with aziridine **IIe** alongside diphenylacetonitrile **XII** was isolated compounds **XXI** in 18% yield.



XXI

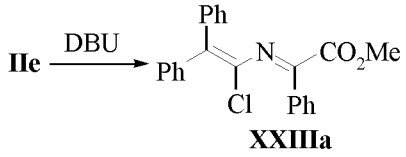
The data obtained do not contradict the mechanism presented in Scheme 4. No intermediate **XXII** forms apparently due to the steric hindrance to attack of a rather bulky piperidine nucleophile on the imine carbon which in **IId, e** possesses a methyl or a phenyl substituent. Intermediate **XXIIIa/XXIIIb** in

Scheme 3.



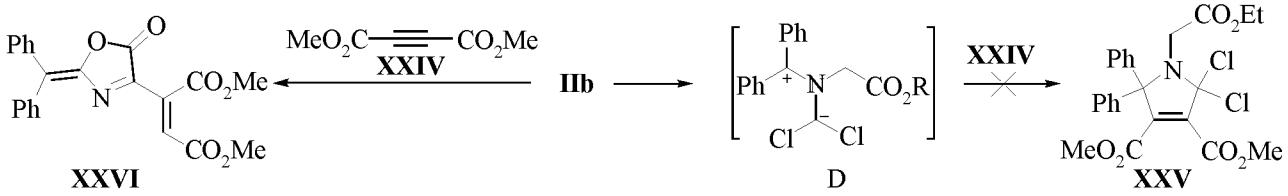
this case reacts with water present in the reaction mixture in small amount, and then as shown in Scheme 4.

In chloroazadiene **XXIIIa** arising from aziridine **IIe** the hydrogen atom providing the possibility of dehydrochlorination to intermediate C is lacking; at the same time this chloroaziridine is relatively inert with respect to weak nucleophiles, e.g., to DBU. Therefore in this case we succeeded in isolation of the chloroazadiene thus directly confirming the assumption on formation of this type intermediates in reactions of aziridines **II** with bases.



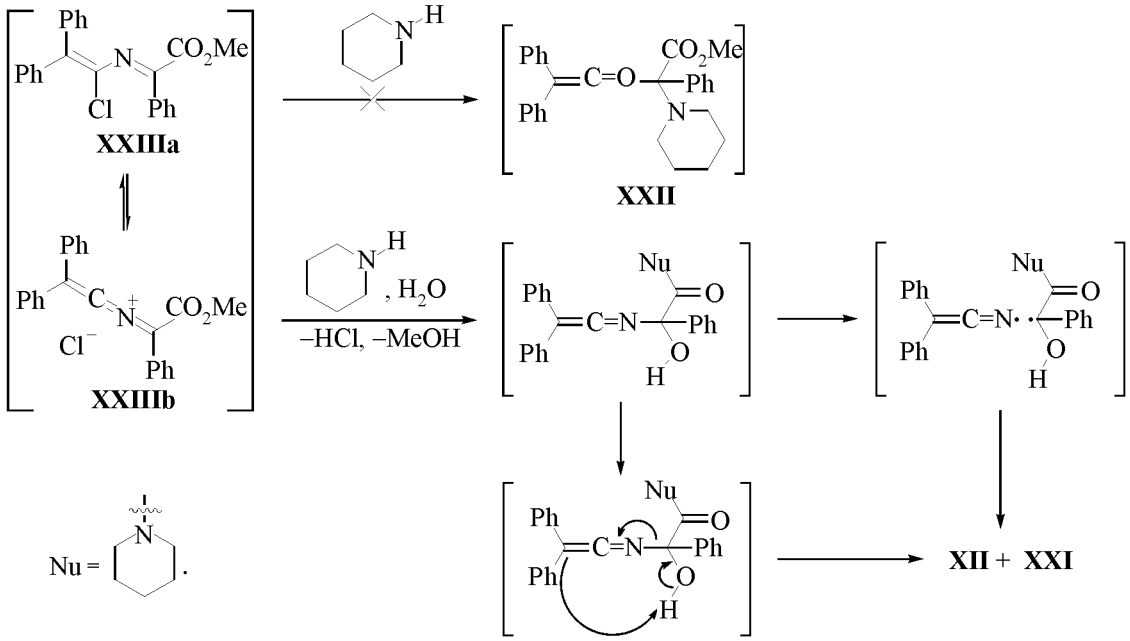
In the IR spectrum of compound **XXIIIa** are present bands of stretching vibtations of the ester group at 1745 cm^{-1} and of C=C bond at 1590 cm^{-1}. In the ^{13}C NMR spectrum appear signals at 153.8 (C=N), 166.5 (C=O) ppm, signals of olefin carbons at 139.8 (=CCl), 129.5 (CPh_2) ppm.

We attempted to trap ylide D by reaction of 1,3-dipolar cycloaddition applying dimethyl acetylenedicarboxylate **XXIV** as dipolarophile by analogy with published data [18]. However the attempt failed, and heating of aziridine **IIb** with dipolarophile **XXIV** in toluene did not lead to compound **XXV**, but instead compound **XXVI** was isolated in 6% yield.

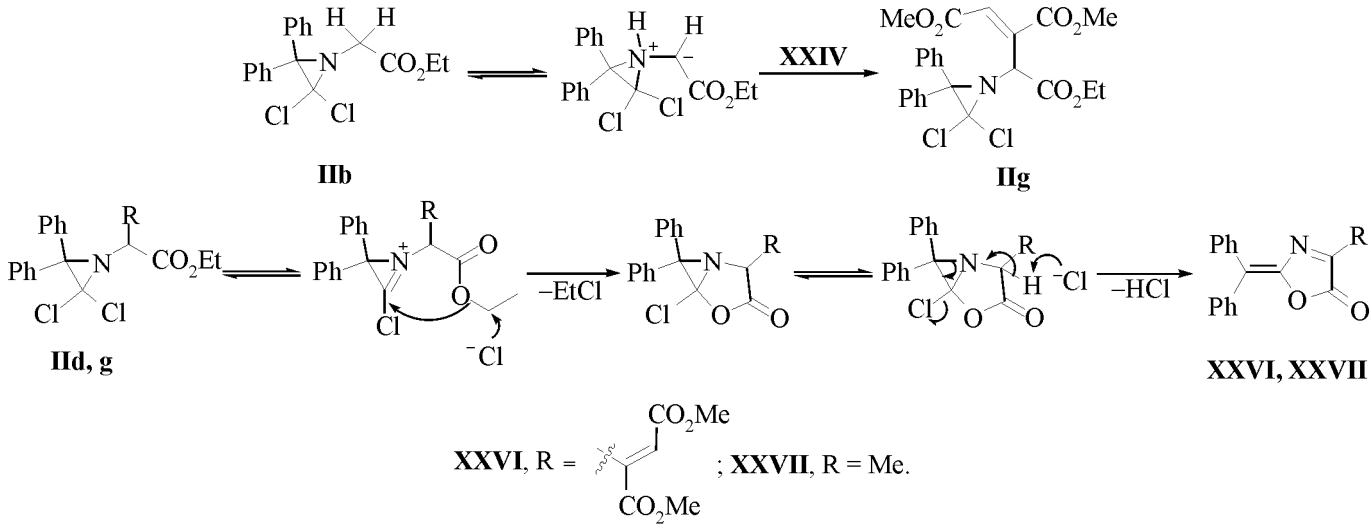


The IR spectrum of compound **XXVI** contains bands of ester group stretching vibrations at 1760 and 1735 cm^{-1}, of lactone group C=O (1808 cm^{-1}), and of C=C bond (1600 cm^{-1}). In the ^{13}C NMR spectrum the signals of carbons from ester carbonyls and lactone carbonyl are present at 163.3, 163.6 and 163.7 ppm, the carbon of the C=N group gives peak at 157.7 ppm, and the olefin carbon signals appear at 155.3 (=C–N), 125.7 (=CPh_2), 129.6, and 135.8 ppm. In the mass spectrum of compound **XXVI**

Scheme 4.



Scheme 5.



is present the molecular ion peak and that of ion $[M-59]^+$ ($[M-CO_2Me]^+$).

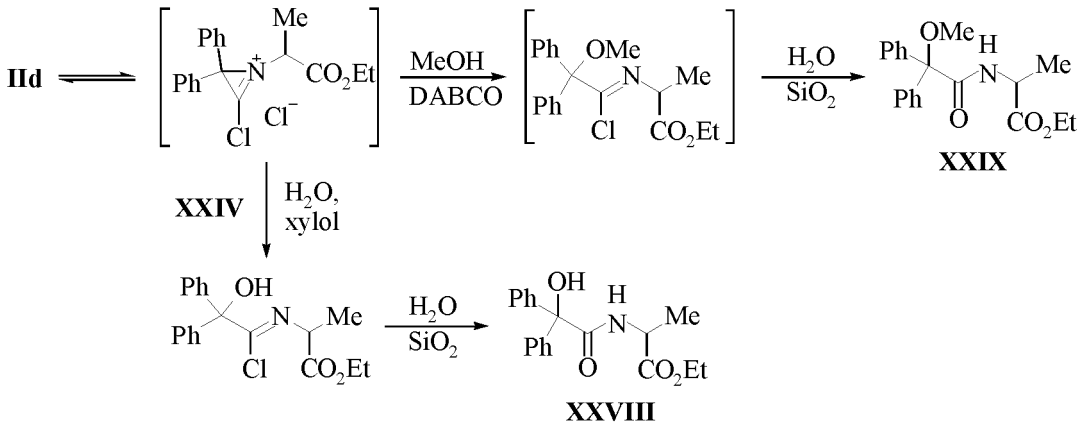
Proceeding from literature analogies [28, 29] we suggest the following scheme of compound **XXVI** formation (Scheme 5).

Compound of type **XXV** did not form either in reaction of dipolarophile **XXIV** with aziridine **IId**. At the same time at heating azridine **IId** with DBU in acetonitrile we obtained oxazolone **XXVII** similar in structure to compound **XXVI** which was separated after reaction of aziridine **IIb** with dipolarophile **XXIV** in 11% yield (Scheme 5).

The IR spectrum of compound **XXVII** contains bands of stretching vibrations of the lactone C=O group at 1790 cm^{-1} and of C=C bond at 1630 cm^{-1}. In the ^{13}C NMR spectrum the signal of lactone carbonyl carbon signal appears at 163.8, that of the carbon from C=N group at 157.2 ppm, and peaks of olefin carbons at 125.4 (=CPh_2), 151.0 (=C–N) ppm.

At the same time for aziridine **IId** possessing the lowest C–H acidity among all aziridines **II** under study the most characteristic are the reactions common to nonfunctionalized dichloroaziridines, namely, opening of the three-membered ring by the

Scheme 6.



rupture of the C–N bond opposite to the dichloromethylene group (Scheme 6).

The reaction of aziridine **IId** with water in the presence of compound **XXIV** in *o*-xylene gave reaction product **XXVIII** in 9% yield. In the reaction of aziridine **IId** with methanol in the presence of 1,4-diazabicyclo[2.2.2]octane compound **XXVIII** formed in 93% yield.

Although we have failed to detect ylide D by trapping it through reaction of 1,3-dipolar addition to alkyne **XXIV** it does not mean that ylide D cannot be present in the reaction mixture for the ylides of this type generated from benzophenone and dichlorocarbene readily cyclize into aziridines and do not take part in cycloaddition reactions [19]. At the same time the corresponding difluoroylides which are not prone to cyclization into aziridines furnish products of 1,3-dipolar cycloaddition. It is however possible that this reaction is not concerted [30, 31].

EXPERIMENTAL

IR spectra of substances dissolved in $CHCl_3$ or CCl_4 were recorded on spectrophotometer UR-20 in a cell with absorbing layer of 400 μm. NMR spectra were registered on spectrometer Bruker DPX-300 at operating frequencies 300 (^{1}H) and 75 (^{13}C) MHz. Elemental analysis was carried out on CHN-analyzer HP-185B. Mass spectra were measured on MKh-1303 and HP-59970C instruments (ionizing energy 70 eV). The reaction progress was monitored by TLC on Silufol254 plates. The reaction mixtures were separated by column chromatography on silsca gel LS 5/40 (Chemapol).

Methyl *N*-benzhydrylidenephenylglycinate (IIe) was obtained along procedure from [32], mp 76–78°C (from hexane). IR spectrum ($CHCl_3$), cm^{-1} 3070, 2955, 1750 (C=O), 1630, 1450, 1180. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.71 s (3H, MeO), 5.20 s (1H, CH), 7.12 d (2H, *J* 3.1 Hz), 7.33–7.49 m (11H), 7.76 d (2H, *J* 6.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.0 (OCH_3), 69.3 (CH), 127.3, 127.5, 127.6, 127.7, 128.2, 128.2, 128.5, 128.7, 130.2, 135.8, 138.8, 139.1 (CPh); 170.0 (C=N), 171.7 (C=O). Found, %: C 80.47; H 5.82; N 4.26. $C_{22}H_{19}NO_2$. Calculated, %: C 80.22; H 5.81; N 4.25.

Aziridines (IIa–c). To a weakly boiling solution of imine **Ia–c** (0.064 mol), benzyltriethylammonium chloride (1.6 g, 0.007 mol) in 200 ml of chloroform (purified from stabilizer) was added by small portions at vigorous stirring within 3 h sodium trichloroacetate (32.4 g, 0.175 mol). The mixture was filtered, the solvent was evaporated, the products were purified by column flash-chromatography followed by crystallization from pentane. Yields were 50, 47, and 40% respectively. Physical constants and spectral data of aziridines **IIb, c** are in agreement with the published data [19].

Methyl 2-[2,2-dichloro-3,3-bis(4-chlorophenyl)-aziridine-1-yl]acetate (IIc). mp 78–80°C (ether–hexane). IR spectrum ($CHCl_3$), cm^{-1} 3030, 2955, 1760 (C=O), 1445, 1095. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.53 s (2H, CH_2), 3.86 s (3H, MeO), 7.34 d (4H, Ar, *J* 8.4 Hz), 7.46 d (4H, Ar, *J* 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 49.8 (CH_2N), 52.1 (OCH_3), 57.1 (CAr_2), 80.8 (CCl_2), 127.3, 128.5, 130.4, 131.00, 134.0, 134.1 (CPh); 169.2 (C=O). Found, %: C 50.35; H 3.22; N 3.20. $C_{17}H_{13}Cl_4NO_2$. Calculated, %: C 50.40; H 3.23; N 3.46.

Aziridines (IId, e). To a mixture of imine **Id, e** (6 mmol), benzyltriethylammonium chloride (0.3 g, 1.32 mmol) in chloroform (30 ml) under vigorous stirring was added powdered potassium hydroxide

(2.2 g, 38.6 mmol), maintaining the temperature at 21–23°C with the use of a cooling bath. The mixture was stirred at this temperature for 6 h (for 2 h at the synthesis of aziridine **IIe**). Then pentane was added (100 ml), the mixture was stirred for 30 min, filtered through 3 mm bed of Celite, the solvent was evaporated, and the residue was crystallized from pentane. Physical constants and spectral data of aziridine **IId** are consistent with those published in [19].

Methyl 2-(2,2-diphenyl-3,3-dichloroaziridin-1-yl)-2-phenylacetate (IIe). Yield 64%, mp 76–78°C (hexane). IR spectrum ($CHCl_3$), cm^{-1} 3070, 2955, 1760 (C=O), 1330, 1180. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.78 s (3H, MeO), 4.19 s (1H, CH), 7.34 d (6H, *J* 6.2 Hz), 7.43–7.48 m (7H), 7.72 d (2H, *J* 6.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.4 (CHN), 58.9 (OCH_3), 66.4 (CPh2), 81.4 (CCl_2), 127.8, 127.8, 127.9, 128.2, 128.5, 128.5, 128.9, 129.5, 135.3 (CPh); 170.4 (C=O). Found, %: C 67.25; H 4.72; N 3.38. $C_{23}H_{19}Cl_2NO_2$. Calculated, %: C 67.00; H 4.64; N 3.40.

Methyl 3,3-diphenyl-2-[*N*-(2,2-diphenyl-1-cyanovinyl)-*N*-methylamino]acrylate (III). To a mixture of aziridine **IIa** (0.772 g, 2.3 mmol), methyl iodide (1.42 g, 10 mmol), benzyltriethylammonium chloride (0.15 g, 0.66 mmol) in acetonitrile (3 ml) was added at vigorous stirring the powdered potassium hydroxide (0.415 g, 7.4 mmol), maintaining the temperature at 21–23°C with the use of a cooling bath. The mixture was stirred at this temperature for 1.2 h, then 30 ml of ether was added, and the mixture was filtered. The filtrate was washed with cold water (3 × 20 ml), dried over $MgSO_4$, the solvent was evaporated to give orange oily substance (390 mg). From this residue compound **III** was isolated by crystallization from ethanol. [Yield 0.185 g, 34% (62%, recalculated with accounting for 55% conversion according to ^1H NMR data)]. mp 178–180°C (EtOH). UV spectrum, λ_{max}, nm (log ε): 258 (4.20), 309 (3.87), 413 (3.66). IR spectrum ($CHCl_3$), cm^{-1}: 2209 (CN), 1721 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.06 s (3H, MeN), 3.31 s (3H, MeO), 6.25 d (2H, Ph, *J* 7.2 Hz), 6.48 d (2H, Ph, *J* 7.4 Hz), 7.24–7.00 m (10H, Ph), 7.45–7.34 m (6H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm:, 39.2 (CH_3N), 51.2 (CH_3O), 115.9, 116.9, 127.0 127.1, 127.2, 127.7, 127.9, 128.1, 128.2, 128.6, 128.8, 130.2, 132.7, 135.5, 137.8, 138.7, 138.8, 141.3, 140.4 (CN, C=C, CPh); 166.8 (C=O). Found, %: C 81.36; H 5.25; N 5.65. $C_{32}H_{26}N_2O_2$. Calculated, %: C 81.68; H 5.57; N 5.95. Mass spectrum, *m/z* (I_{rel}, %): 470 (51) $[M]^+$, 411 (100) $[M\text{-}CO_2Me]^+$, 395 (5) $[M\text{-}75]^+$, 319 (3), 207 (6), 165 (19), 77 (7). High-resolution mass spectrum: $[M]^+$, Found: 470.1994. $C_{32}H_{26}N_2O_2$. Calculated: 470.1994.
09.06.2003

Ethyl 3,3-diphenyl-2-[*N*-(2,2-diphenyl-1-cyanovinyl)-*N*-methylamino]acrylate (IV). To a mixture of aziridine **IIb** (0.403 g, 1.15 mmol), methyl iodide (1.85 g, 13 mmol), benzyltriethylammonium chloride (0.086 g, 0.38 mmol) in acetonitrile (4 ml) was added at vigorous stirring the powdered potassium hydroxide (0.304 g, 5.4 mmol), maintaining the temperature at 21–23°C with the use of a cooling bath. The mixture was stirred at this temperature for 3 h, then 30 ml of ether was added, and the mixture was filtered. The filtrate was washed with cold water (3 × 20 ml), dried over $MgSO_4$, the solvent was evaporated to give orange oily substance (295 mg). From this residue compound **IV** was isolated by crystallization from ethanol (0.085 g, 31%). mp 180–181°C (EtOH). UV spectrum, λ_{max}, nm (log ε): 256 (4.45), 316 (4.09), 414 (3.88). IR spectrum ($CHCl_3$), cm^{-1}: 2208 (CN), 1718 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.72 t (3H, MeC, *J* 7.0 Hz), 3.09 s (3H, MeN), 3.78 q (2H, CH_2O, *J* 7.0 Hz), 6.22 d (2H, Ph, *J* 7.0 Hz), 6.46 d (2H, Ph, *J* 7.4 Hz), 7.46–7.01 m (16H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 12.8 (CH_3), 39.2 (CH_3N), 60.4 (CH_2O), 116.2, 117.0, 126.9, 127.0, 127.2, 127.7, 127.8, 128.0, 128.1, 128.5, 129.0, 129.8, 130.2, 132.9, 135.3, 137.8, 138.7, 140.0, 140.4, 141.5 (CN, C=C, CPh); 165.2 (C=O). Found, %: C 81.54; H 5.95; N 5.43. $C_{33}H_{28}N_2O_2$. Calculated, %: C 81.79; H 5.82; N 5.78. The structure of compound **IV** was proved by X-ray diffraction analysis (see the figure). Parameters obtained by X-ray diffraction study: $C_{34}H_{28}N_2O_2$, M 496.61, a 10.124 (3), b 11.2924 (10), c 12.155 (2) Å, α 99.70 (1), β 91.70(1), γ 95.32 (2)°, *V* 1323.79 (50) $Å^3$, d_{calc} 1.246 g cm^{-3}, triclinic crystal, space group *P*1 (no. 2), Z 2, Enraf-Nonius CAD4 diffractometer, CuK_α radiation, γ 1.54178 Å, graphite monochromator, temperature –100°C, crystal habit 0.8 × 0.8 × 0.7 mm, R_{All} 0.065.

Methyl 3,3-bis(4-chlorophenyl)-2-[*N*-(2,2-bis(4-chlorophenyl)-1-cyanovinyl)-*N*-methylamino]acrylate (V). To a mixture of aziridine **IIc** (0.773 g, 2 mmol), methyl iodide (1.42 g, 10 mmol), benzyltriethylammonium chloride (0.15 g, 0.66 mmol) in acetonitrile (3 ml) was added at vigorous stirring the powdered potassium hydroxide (0.415 g, 7.4 mmol), maintaining the temperature at 21–23°C with the use of a cooling bath. The mixture was stirred at this temperature for 1.2 h, then 30 ml of ether was added,

and the mixture was filtered. The filtrate was washed with cold water (3 × 20 ml), dried over $MgSO_4$, the solvent was evaporated to give orange oily substance (390 mg). The residue was submitted to column chromatography that provided 0.125 g of compound **V**, yield 21%, mp 169–171°C (from ether–hexane). IR spectrum (CCl_4), cm^{-1}: 3030, 2950, 2215 (CN), 1740 (C=O), 1590, 1095. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.11 s (3H, CH_3), 3.39 s (3H, CH_3O), 6.15 d (2H, *J* 8.4 Hz), 6.40 d (2H, *J* 8.4 Hz), 7.00 d (2H, *J* 8.4 Hz), 7.08 d (2H, *J* 9.1 Hz), 7.12–7.18 m (4H), 7.35 d (2H, *J* 8.4 Hz), 7.46 d (2H, *J* 8.4 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 39.4 (CH_3N), 51.7 (OCH_3), 115.7 (CN), 127.8, 128.0, 128.3, 129.1, 130.0, 131.6, 132.8, 133.6, 134.6, 134.9, 135.0, 135.5, 136.4, 137.6, 138.1, 139.0 (C=C, CPh); 166.4 (C=O). Found, %: C 63.60; H 3.68; N 4.35. $C_{32}H_{22}Cl_4N_2O_2$. Calculated, %: C 63.18; H 3.64; N 4.60.

Methyl 3,3-diphenyl-2-[*N*-allyl-*N*-(2,2-diphenyl-1-cyanovinyl)amino]acrylate (VI). To a mixture of aziridine **IIa** (0.383 g, 1.14 mmol), allyl bromide (1.48 g, 12 mmol), and benzyltriethylammonium chloride (0.07 g, 0.31 mmol) in acetonitrile (3 ml) was added at vigorous stirring the powdered potassium hydroxide (0.225 g, 4 mmol), maintaining the temperature at 21–23°C with the use of a cooling bath. The mixture was stirred at this temperature for 2 h, then 30 ml of ether was added, and the mixture was filtered. The filtrate was washed with cold water (3 × 20 ml), dried over $MgSO_4$, the solvent was evaporated to give orange oily substance (210 mg). From this residue compound **VI** was isolated by crystallization from ethanol (0.103 g, 36 %). mp 166–168°C (EtOH). UV spectrum, λ_{max}, nm (log ε): 257 (4.43), 310 (4.10), 409 (3.83). IR spectrum ($CHCl_3$), cm^{-1}: 2210 (CN), 1721 (C=O). 1H NMR spectrum ($CDCl_3$), δ, ppm: 3.26 s (3H, MeO), 4.00 d (2H, CH_2N, *J* 6.7 Hz), 5.38–5.28 m (2H, CH_2=), 6.44–6.11 m (1H, CH=), 6.18 d (2H, Ph, *J* 7.0 Hz), 6.43 d (2H, Ph, *J* 7.3 Hz), 7.26–6.90 m (10H, Ph), 7.48–7.31 m (6H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 51.1 (CH_3O), 54.2 (CH_2N), 116.0, 116.1, 120.1, 126.9, 127.0, 127.2, 127.7, 127.9, 128.2, 128.6, 128.9, 129.8, 129.9, 130.2, 132.2, 133.2, 134.7, 137.6, 138.5, 140.3, 141.4, 142.0 (CN, C=C, CPh); 167.1 (C=O). Found, %: C 82.47; H 5.51; N 5.16. $C_{34}H_{28}N_2O_2$. Calculated, %: C 82.23; H 5.68; N 5.64.

Methyl 2-[*N*-benzyl-*N*-(2,2-diphenyl-1-cyanovinyl)amino]-3,3-diphenylacrylate (VII). To a mixture of aziridine **Ia** (0.383 g, 1.14 mmol), benzyl bromide (0.52 g, 3 mmol), and benzyltriethylammonium chloride (0.07 g, 0.31 mmol) in acetonitrile (3 ml) was added at vigorous stirring the powdered potassium hydroxide (0.225 g, 4 mmol), maintaining the temperature at 21–23°C with the use of a cooling bath. The mixture was stirred at this temperature for 2 h, then 30 ml of ether was added, and the mixture was filtered. The filtrate was washed with cold water (3 × 20 ml), dried over $MgSO_4$, the solvent was evaporated, and from the residue compound **VII** was isolated by crystallization (0.102 g, 33 %). mp 166–168°C (EtOH). UV spectrum, λ_{max}, nm (log ε): 257 (4.27), 313 (3.99), 393 (3.65). IR spectrum ($CHCl_3$), cm^{-1}: 2210 (CN), 1714 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.19 s (3H, MeO), 4.58 s (2H, CH_2), 6.24 d (2H, Ph, *J* 7.0 Hz), 6.43 d (2H, Ph, *J* 7.2 Hz), 7.58–6.99 m (21H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 50.8 (CH_3O), 55.5 (CH_2N), 116.6, (CN), 126.9, 127.0, 127.1, 127.5, 127.7, 127.9, 128.0, 128.2, 128.6, 128.9, 129.3, 129.8, 130.0, 132.7, 133.1, 135.9, 137.6, 138.5, 138.8, 140.2, 141.6, 142.7 (C=C, CPh); 167.3 (C=O). Found, %: C 83.56; H 5.64; N 4.81. $C_{38}H_{30}N_2O_2$. Calculated, %: C 83.49; H 5.53; N 5.12.

4-Benzhydrylidene-2,3,4,7,8,9,10,11-octahydro-1*H*-3a,5,11a-triazabenzo[ef]heptalen-7-one (IX). To a solution of aziridine **IIb** (155 mg, 0.46 mmol) in acetonitrile (1 ml) was added dropwise a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (70 mg, 0.46 mmol) in acetonitrile (1 ml). The mixture self-heated and gave rise to red compound **IX** which crystallized at completion of the reaction. Yield 100 mg (57%). The same reaction was carried out in cyclohexane using 140 mg, 0.92 mmol of DBU. The reaction continued for 3 h, and compound **IX** crystallized in the course of the process. Yield 163 mg (93%). mp 234–235°C (from ether). IR spectrum ($CHCl_3$), cm^{-1}: 3030, 2875, 1645, 1580 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.73 m (2H, CH_2), 1.89 m (2H, CH_2), 2.01 m (2H, CH_2), 2.47 t (2H, CH_2, *J* 5.9 Hz), 3.33 t (2H, CH_2, *J* 5.9 Hz), 3.42 m [4H, $(CH_2)2$], 7.24–7.46 m (10H, Ph), 9.22 s (1H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 20.5, 21.1, 25.6, 27.9, 35.9, 49.0, 54.4, 94.8 (C^{7a}), 126.5, 126.7, 126.8, 127.6, 128.2, 130.2, 131.1 (CPh); 131.8 (C6), 138.4 ($C^{1'}$), 139.8, 141.5(CPh); 147.3 (C^{4}), 162.8 (C^{11b}), 173.9 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 383(54) $[M]^+$, 354(4), 306(9) $[M\text{-Ph}]^+$, 177(8), 163(3), 152(100), 151(100), 137(36), 124(23), 123(46), 110(15), 109(11), 96(57), 95(13), 93(39), 89(7), 88(6), 86(7), 70(18), 69(23), 68(19), 66(13), 57(21), 55(32), 54(21), 43(50), 41(79), 39(18),

37(22). Found, %: C 78.20; H 6.84; N 11.37. $C_{25}H_{25}N_3O$. Calculated, %: C 78.30; H 6.57; N 10.96.

Reaction of aziridine IIb with sodium methylate. To a solution of aziridine **IIb** (420 mg, 1.2 mmol) in methanol (1 ml) was added dropwise at stirring a solution of sodium methylate (134 mg, 2.4 mmol) in methanol (1 ml). The mixture self-heated, NaCl precipitated, and the mixture turned yellow. The precipitate was filtered off, and from the filtrate by column chromatography were isolated compounds **X** (162 mg, 42.3%) and **XI** (20 mg, 6.3%).

Methyl (1-methoxy-2,2-diphenylvinylimino)-acetate (X). IR spectrum ($CHCl_3$), cm^{-1}: 3050, 2955, 1750 (C=O), 1650, 1595, 1310, 1165. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.74 s (3H, OMe), 3.92 s (3H, OMe), 7.28–7.43 m (10H, Ph), 7.75 s (1H, CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.4 (OCH_3), 53.9 (OCH_3), 126.9, 127.1, 127.1, 127.9, 128.2, 128.5, 130.7, 138.2, 138.6 (=CPh_2, CPh); 141.2 (C=N), 148.9 (=COMe), 158.3 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 295(31) $[M]^+$, 280(4) [*M*-Me]$^+$, 265(2), 252(2), 236(16) [*M*-CO2Me]+, 221(22), 220(19), 204(9), 193(16), 183(19), 182(34), 178(11), 165(25), 152(6), 139(2), 106(13), 105(100), 77(54), 59(15), 51(31), 49(8), 39(5).

Methyl (2,2-diphenylvinyl)carbamate (XI). mp 111–113°C (from ether). IR spectrum ($CHCl_3$), cm^{-1}: 3380 (NH), 3050, 2955, 1715 (C=O), 1645, 1300, 1165. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.91 s (3H, OMe), 7.28–7.54 m (^{11}H, Ph, CH), 8.80 d (^1H, NH, *J* 11.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 53.5 (OCH_3), 117.6 (=CPh2), 126.9, 127.3, 128.1, 128.2, 129.1, 129.3, 136.2, 139.0 (CPh); 152.7 (=C), 160.4 (C=O). Found, %: C 75.85; H 5.77; N 5.30. $C_{16}H_{15}NO_2$. Calculated, %: C 75.87; H 5.97; N 5.53.

Reaction of aziridine IIb with benzylamine. A mixture of aziridine **IIb** (420 mg, 1.2 mmol) and benzylamine (600 mg, 5.6 mmol) was heated in toluene to 100°C for 3 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated, and from the yellow oily residue diphenylacetonitrile **XII** was isolated by column chromatography (23 mg, 9.6%). Compound **XII**: mp 71–73°C (publ. mp 71–73°C [33]). IR spectrum ($CHCl_3$), cm^{-1}: 2255 (CN). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.15 s (1H, CH), 7.34–7.40 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 42.3 (CH), 119.3 (CN), 127.4, 127.9, 128.9, 135.6 (CPh).

Reaction of aziridine IId with piperidine. A mixture of aziridine **IId** (438 mg, 1.2 mmol) and piperidine (600 mg, 7 mmol) was heated in toluene to 100°C for 48 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated, and from the yellow oily residue diphenylacetonitrile **XII** was isolated by column chromatography (14 mg, 6%). mp 70–72°C.

Reaction of aziridine IIb with piperidine (morpholine). A mixture of aziridine **IIb** (420 mg, 1.2 mmol) and piperidine (morpholine) (7 mmol) was heated in toluene to 100°C for 0.5 h (3 h). The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated, and by crystallization from hexane was isolated compound **XIII** (250 mg, 56%) (**XIV**, 170 mg, 38%).

Ethyl 2-piperidino-3,3-diphenyl-3-cyanopropionate (XIII). mp 129–130°C (from ether–hexane). IR spectrum ($CHCl_3$), cm^{-1} 3030, 2940, 2820, 2250 (CN), 1750 (C=O), 1600, 1180. ^1H NMR spectrum ($CDCl_3$), δ, ppm 1.14 t (3H, CH_3, *J* 7.1 Hz), 1.38–1.45 m (6H, $(CH_2)3$), 2.19 m (2H, CH_2N), 3.12 m (2H, CH_2N), 4.00 s (1H, CH), 4.13 q (2H, CH_2O, *J* 7.1 Hz), 7.29–7.50 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm 13.8 (CH_3), 23.7 (CH_2), 26.2 (CH_2), 53.0 (CH_2), 53.6 (CH_2O), 60.4 (CH_2), 74.6 (CH), 121.3 (CN), 126.7, 127.3, 127.6, 127.6, 128.5, 138.0, 138.9 (CPh); 167.7 (C=O). Found, %: C 76.23; H 7.23; N 7.69. $C_{23}H_{26}N_2O_2$. Calculated, %: C 76.21; H 7.23; N 7.73.

Ethyl 2-morpholino-3,3-diphenyl-3 cyanopropionate (XIV). mp 153–154°C (from ether–hexane). IR spectrum ($CHCl_3$), cm^{-1} 3030, 2920, 2860, 2830, 2250 (CN), 1750 (C=O), 1120. ^1H NMR spectrum ($CDCl_3$), δ, ppm 1.17 t (3H, CH_3, *J* 7.1 Hz), 2.26 m (2H, CH_2), 3.18 m (2H, CH_2), 3.55–3.61 m (4H, CH_2, CH_2), 4.02 s (1H, CH), 4.16 q (2H, CH_2O, *J* 7.1 Hz), 7.28–7.51 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.8 (CH_3), 52.0 (CH_2), 53.6 (CH_2O), 60.8 (CH_2), 66.9 (CH_2), 74.0 (CH), 121.2 (CN), 126.5, 127.4, 127.5, 127.8, 127.9, 128.6, 137.6, 138.5 (CPh); 167.2 (C=O). Found, %: C 72.50; H 6.70; N 7.68. $C_{22}H_{24}N_2O_3$. Calculated, %: C 72.51; H 6.64; N 7.69.

Reaction of benzhydrylidenecyanoacetate (XV) with piperidine. A mixture of compound **XV** (343 mg, 1.2 mmol) prepared as described in [34] and piperidine (600 mg, 7 mmol) was heated in toluene to 100°C for 3 days. The reaction mixture was wash-

ed with water, dried over $MgSO_4$, the solvent was evaporated, and the yellow oily residue was subjected to column chromatography to isolate compounds **XVI** (0.041 g, 10.5%) and **XVII** (0.019 g, 7.5%).

2-(Piperidinocarbonyl)-3,3-diphenylacrylonitrile (XVI). mp 174–175°C (ether). IR spectrum ($CHCl_3$), cm^{-1}: 3030, 2945, 2860, 2220 (CN), 1640 (C=O), 1440. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.19 m (2H, CH_2 CH_2), 1.46 m (4H, CH_2, CH_2), 3.31 m (2H, CH_2), 3.48 m (2H, CH_2), 7.25-7.43 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 23.7 (CH_2), 24.5 (CH_2), 25.1 (CH_2), 42.5 (CH_2), 47.3 (CH_2), 106.0 (=C), 116.4 (CN), 128.1, 128.1, 129.2, 129.4, 130.0, 130.1, 137.4, 137.6 (CPh); 159.3 (CPh2), 161.3 (C=O). Found, %: C 79.77; H 6.34; N 8.94. $C_{21}H_{20}N_2O$. Calculated, %: C 79.72; H 6.37; N 8.85.

3,3-Diphenylacrylonitrile (XVII). IR spectrum ($CHCl_3$), cm^{-1}: 3060, 2940, 2220 (CN), 1595. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.77 s (1H, CH), 7.30–7.50 m (10H, HPh). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 94.6 (CH), 117.5 (CN), 128.1, 128.2, 128.3, 129.2, 129.7, 130.1, 136.7, 138.6 (CPh), 162.8 (CPh_2).

Ethyl 2-piperidino-3,3-diphenyl-acrylate (XVIII). To a solution of compound **XIII** (41 mg, 0.1 mmol) in acetonitrile (3 ml) was added NaH (15 mg of 60% suspension in mineral oil), and the mixture was boiled for 1 h. The mixture was cooled, diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, dried over $MgSO_4$, the solvent was evaporated, and from the yellow oily residue compound **XVIII** was isolated by crystallization from ethanol (0.03 g, 79%). mp 68–70°C (EtOH). IR spectrum ($CHCl_3$), cm^{-1}: 3060, 2940, 2850, 1720 (C=O), 1600. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.86 t (3H, CH_3, *J* 7.7 Hz), 1.48 m (6H, $(CH_2)3$), 2.70 m (4H, CH_2N, CH_2N), 3.92 q (2H, CH_2O, *J* 7.7 Hz), 7.10–7.33 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.2 (CH_3), 23.7 (CH_2), 25.8 (CH_2), 51.4 (CH_2), 60.3 (CH_2), 126.3, 126.4, 127.4, 127.5, 127.5, 129.6, 130.2, 140.8, 141.3, 142.6 (C=C, CPh); 168.3 (C=O). Found, %: C 78.62; H 7.66; N 4.15. $C_{22}H_{25}NO_2$. Calculated, %: C 78.77; H 7.51; N 4.18.

1-Piperidino-2-phenylethane-1,2-dione (XXI). A mixture of aziridine **IIe** (213 mg, 0.5 mmol), DBU (74 mg, 0.5 mmol), and piperidine (236 mg, 2.8 mmol) was heated in acetonitrile (4 ml) at 80°C for 48 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, dried over $MgSO_4$, the solvent was evaporated, and by means of column chromatography were isolated from the residue diphenylacetonitrile **XII** (30 mg, 30%) (mp 71–73°C) and compound **XXI** (20 mg, 18%). mp 99–101°C (from ether). IR spectrum ($CHCl_3$), cm^{-1}: 3030, 2945, 2885, 1680 (C=O), 1640 (C=O). 1H NMR spectrum ($CDCl_3$), δ, ppm: 1.56 m (2H, CH_2), 1.71 m [4H, $(CH_2)2$], 3.30 m (2H, CH_2), 3.72 m (2H, CH_2), 7.52 m (2H, Ph), 7.66 m (1H, Ph), 7.95 m (2H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 24.1 (CH_2), 25.1 (CH_2), 25.9 (CH_2), 41.8 (CH_2), 46.7 (CH_2), 128.7, 129.3, 133.0, 134.3 (CPh); 165.1 (C=O), 191.6 (C=O). Found, %: C 70.64; H 6.82; N 6.21. $C_{13}H_{15}NO_2$. Calculated, %: C 71.87; H 6.96; N 6.45.

Methyl 2-(2,2-diphenyl-1-chlorovinylimino)-2-phenylacetate (XXIIIa). A mixture of aziridine **IIe** (500 mg, 1.2 mmol) and DBU (553 mg, 3.6 mmol) was heated in acetonitrile (4 ml) at 80°C for 3 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated, and by means of column chromatography from the residue was isolated yellow compound **XXIII** (50 mg, 11%). mp 148–150°C (from ether). IR spectrum ($CHCl_3$), cm^{-1}: 3060, 2955, 1745 (C=O), 1595, 1200. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.97 s (3H, CH_3O), 7.31–7.69 m (15H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.5 (CH_3O), 127.0, 127.5, 127.6, 127.7, 128.2, 128.4, 129.5, 130.1, 131.2, 131.4, 133.9, 139.6, 139.8, 140.3, 153.8 (CPh, C=C); 166.5 (C=O). Found, %: C 73.62; H 4.88; N 3.74. $C_{23}H_{18}ClNO_2$. Calculated, %: C 73.50; H 4.83; N 3.73.

Dimethyl 2-(2-benzhydrylidene-5-oxo-2,5-dihydrooxazol-4-yl)but-2-endionate (XXVI). A mixture of aziridine **IIb** (364 mg, 1.1 mmol) and dimethyl acetylenedicarboxylate (DMAD) (568 mg, 4 mmol) was heated in *o*-xylene at 120°C for 3 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated, and by means of column chromatography from the yellow oily residue was isolated yellow product **XXVI** (25 mg, 6%). mp 127–128°C (from ether). IR spectrum ($CHCl_3$), cm^{-1}: 3030, 2955, 1810 (C=O), 1740 (C=O), 1760 (C=O), 1600, 1200, 1000. 1H NMR spectrum ($CDCl_3$), δ, ppm: 3.85 s (3H, OMe), 3.97 s (3H, OMe), 6.80 s (1H, CH), 7.32-7.56 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.4 (OCH_3), 52.9 (OCH_3), 125.7 ($=CPh_2$); 127.5, 127.9 (CPh); 129.6 ($=CCO_2Me$); 130.2, 130.3, 131.0, 132.8, 134.8 (CPh); 135.8 ($=CCO_2Me$); 137.6 (CPh);

155.3 (=C–N), 157.7 (C=N); 163.3, 163.6, 163.7 (C=O). Mass spectrum, *m/z* (I_{rel}, %): 391(11) $[M]^+$, 360(1), 332(2) $[M\text{-}CO_2Me]+$, 192(9), 190(6), 171(100),165(16), 140(4), 111(3), 99(3), 82(5), 75(5), 59(23), 53(12), 36(6). Found, %: C 67.06; H 4.37; N 3.32. $C_{21}H_{17}NO_6$. Calculated, %: C 67.52; H 4.38; N 3.58.

2-Benzhydrylidene-4-methyl-2,5-dihydrooxazol-5-one (XXVII). A mixture of aziridine **IId** (364 mg, 1 mmol) and DBU (152 mg, 1 mmol) was heated in acetonitrile (1 ml) at 80 C for 3 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated, and by means of column chromatography yellow product **XXVII** was isolated. Yield 30 mg (11%). mp 156–158°C (from ether). IR spectrum (CHCl3), cm^{-1}: 3060, 1780 (C=O), 1630, 1240. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 s (3H, CH_3), 7.40–7.49 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.5 (CH_3), 125.4 (=CPh_2), 127.7, 127.9, 128.7, 128.9, 131.0, 131.6, 136.1, 136.2 (CPh); 151.0 (=C-N), 157.3 (C=N), 163.8 (C=O). Found, %: C 77.59; H 5.00; N 5.30. $C_{17}H_{13}NO_2$. Calculated, %: C 77.55; H 4.98; N 5.32.

Ethyl 2-(2-hydroxy-2,2-diphenylacetylamino)-propionate (XXVIII). A mixture of aziridine **IId** (364 mg, 1 mmol) and compound **XXIV** (568 mg, 4 mmol) was heated in *o*-xylene at 120°C for 2 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated. From the residue compound **XXVIII** was isolated by column chromatography (40 mg, 18%). mp 100–101°C (from ether). IR spectrum (CHCl3), cm^{-1}: 3600 (OH), 3420 (NH), 3030, 1735 (C=O), 1690 (C=O), 1170. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t (3H, CH_3, *J* 7.1 Hz), 1.42 d (3H, CH_3, *J* 7.1 Hz), 3.89 s (1H, OH), 4.19 q (2H, CH_2O, *J* 7.5 Hz), 4.57 q (^1H, CH, *J* 6.6 Hz), 7.09 d (1H, NH, *J* 6.6 Hz), 7.33–7.49 m (10H, Ph). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.7 (CH_3), 17.8 (CH_3), 48.2 (CH_2), 61.2 (C–OH), 81.0 (C–NH), 127.1, 127.2, 127.8, 127.8, 127.9, 128.0, 142.1, 142.6 (CPh); 172.2 (C=O), 172.5 (C=O). Found, %: C 69.70; H 6.38; N 4.24. $C_{19}H_{21}NO_4$. Calculated, %: C 69.71; H 6.47; N 4.28.

Ethyl 2-(2-methoxy-2,2-diphenylacetylamino)-propionate (XXIX). A mixture of aziridine **IId** (364 mg, 1 mmol) and 1,4-diazabicyclo[2.2.2]octane (120 mg, 1 mmol) was heated in methanol (2 ml) for 2 h. The mixture was diluted with CH_2Cl_2, washed with 2% sodium carbonate solution, with water, dried over $MgSO_4$, the solvent was evaporated. From the residue oily compound **XXIX** was isolated by column chromatography (327 mg, 93%). IR spectrum ($CHCl_3$), cm^{-1}: 3410 (NH), 3030, 2940, 1750 (C=O), 1690 (C=O), 1150. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.28 t (3H, *J* 7.1 Hz, Me), 1.45 d (3H, *J* 7.5 Hz, Me), 3.08 s (3H, OMe), 4.21 q (2H, *J* 7.1 Hz, OCH_2), 4.56 q (1H, *J* 7.1 Hz, CH), 7.35–7.51 m (10H, Ph), 7.67 d (1H, *J* 7.1 Hz, NH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 13.8 (Me), 17.9 (Me), 47.7 (CH_2), 52.4 (OMe), 61.1 (CH), 86.8 (COMe), 127.5, 127.6, 127.7, 128.4, 129.0, 138.4, 138.7 (CPh); 171.7, 172.5 (C=O).

The study was carried out under financial support of the Russian Foundation for Basic Research (grant no. 02-03-32735a) and INTAS program (grant 00-0549).

REFERENCES

1. Brooks, R.E., Edwards, J.O., Levey, G., and Smyth, R., *Tetrahedron*, 1966, vol. 22, p. 1279.
2. Kostikov, R.R., Khlebnikov, A.F., and Oglobblin, K.A., *Dokl. Akad. Nauk SSSR*, 1975, vol. 223, p. 1375.
3. Kostikov, R.R., Khlebnikov, A.F., and Oglobblin, K.A., *Khim. Geterotsikl. Soed.*, 1978, p. 48.
4. Kostikov, R.R., Khlebnikov, A.F., and Oglobblin, K.A., *Zh. Org. Khim.*, 1975, vol. 11, p. 585.
5. Kozlov, N.S., Pak, V.D., Mashevskii, V.V., and Mashevskaya, M.S., *Izv. Akad. Nauk BSSR, Ser. Khim.*, 1980, p. 126.
6. Kostikov, R.R., Khlebnikov, A.F., and Oglobblin, K.A., *Zh. Org. Khim.*, 1973, vol. 9, p. 2346.
7. Seno, M., Shiraishi, S., Suzuki, Y., and Asahara, T., *Bull. Chem. Soc. Japan*, 1978, vol. 51, p. 1413.
8. Kostikov, R.R., Khlebnikov, A.F., and Oglobblin, K.A., *Zh. Org. Khim.*, 1977, vol. 13, p. 1857.
9. Khlebnikov, A.F., Kostikov, R.R., Shklyaev, V.S., Dormidontov, M.Yu., and Aleksandrov, B.B., *Khim. Geterotsikl. Soed.*, 1990, p. 1086.
10. Khlebnikov, A.F., Nikiforova, T.Yu., Novikov, M.S., and Kostikov, R.R., *Zh. Org. Khim.*, 1997, vol. 33, p. 951.
11. Khlebnikov, A.F., Nikiforova, T.Yu., Novikov, M.S., and Kostikov, R.R., *Synthesis*, 1997, p. 677.
12. Khlebnikov, A.F., Nikiforova, T.Yu., and Kostikov, R.R., *Zh. Org. Khim.*, 1996, vol. 32, p. 746.
13. Ichimura, K. and Ohta, M., *Bull. Chem. Soc. Japan*, 1967, vol. 40, p. 1933.
14. Khlebnikov, A.F. and Kostikov, R.R., *Khim. Geterotsikl. Soed.*, 1984, p. 912.

15. Seno, M., Shiraishi, S., Suzuki, Y., and Asahara, T., *Bull. Chem. Soc. Japan*, 1976, vol. 49, p. 1893.
16. Petrov, O.S., Ogniyanov, V.I., and Mollov, N.M., *Synthesis*, 1987, p. 637.
17. Seno, M., Shiraishi, S., Kise, H.S., and Suzuki, Y., *J. Org. Chem.*, 1978, vol. 43, p. 3402.
18. De Kimpe, N., Sulmon, P., De Buyck, L., Vehre, R., Schamp, N., Declery, J.P., and Van Meerssehe, M., *J. Chem. Res.*, 1984, p. 82.
19. Khlebnikov, A.F., Novikov, M.S., Nikiforova, T.Yu., and Kostikov, R.R., *Zh. Org. Khim.*, 1999, vol. 35, p. 98.
20. Khlebnikov, A.F., Novikov, M.S., and Kostikov, R.R., *Synlett*, 1997, p. 929.
21. O'Donnell, M.J., Bennet, W.D., Bruder, W.A., Jacobsen, W.N., Knuth, K., LeClef, B., Polt, R.L., Bordwell, F.G., Mrozack, S.R., and Cripe, T.A., *J. Am. Chem. Soc.*, 1988, vol. 110, p. 8520.
22. *Comprehensive Organic Synthesis*, Trost, B.M. and Fleming, I., Eds., Oxford: Pergamon, 1991, vol. 5, p. 109.
23. Singer, L.A. and Lee, K.-W., *Chem. Commun.*, 1974, p. 962.
24. Lee, K.-W. and Singer, L.A., *J. Org. Chem.*, 1974, vol. 39, p. 3780.
25. Lee, K.-W., Gorowitz, N., Ware, J., and Singer, L.A., *J. Am. Chem. Soc.*, 1977, vol. 99, p. 2622.
26. Clarke, L.F., Hegarty, A., and O'Neill, P., *J. Org. Chem.*, 1992, vol. 57, p. 362.
27. Ciganek, E., *Tetrahedron Lett.*, 1969, p. 5179.
28. Grigg, R., *Chem. Soc. Rev.*, 1987, vol. 16, p. 89.
29. Krapcho, A.P., *Synthesis*, 1982, p. 893.
30. Novikov, M.S., Khlebnikov, A.F., Krebs, A., and Kostikov, R.R., *Eur. J. Org. Chem.*, 1998, p. 133.
31. Novikov, M.S., Khlebnikov, A.F., and Kostikov, R.R., *Zh. Org. Khim. 2002, vol. 35, p. 710.*
32. *O*'Donnel, M.J. and Polt, R.L., *J. Org. Chem.*, 1982, vol. 47, p. 2663.
33. Grignard, M.V. and Ono, K., *Bull. Soc. Chim. France*, 1926, vol. 39, p. 1589.
34. Le Moal, H., Garrie, R., Fougaud, A., Bargain, M., and Sevelleg, G., *Bull. Soc. chim.*, 1966, p. 1033.