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Monofluoro-Substituted Azomethine Ylides in Fluorocarbene Reactions with Imines. Synthesis and Transformations of Monofluoroaziridines

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Abstract—*N*-Arylmethylene and *N*-benzhydrylideneamines react with fluorocarbene yielding fluoro-substituted azomethine ylides that undergo 1,3-π-cyclization into aziridines. Generation of fluoroylides in the presence of dipolarophiles (dimethyl maleate or dimethyl acetylenedicarboxylate) led to the reaction of 1,3-dipolar cycloaddition resulting in substituted 2-pyrrolines or pyrroles. 2-Fluoroaziridines, products of *N*-alkyl-*N*-benzhydrylideneamines 1,3-π-cyclization, in the presence of acid catalysts suffer isomerization into α-fluoroimines and 1,3-disubstituted indoles.

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Halosubstituted iminium ylides, reactive intermediates formed in reactions of halocarbenes with a C=N bond, are convenient synthetic building blocks for preparation of various nitrogen-containing heterocycles [1]. Especially interesting are fluoro-substituted iminium ylides utilized in the synthesis of fluoro-containing compounds [2–18]. Introducing one or several fluorine atoms into a molecule is known to lead as a rule to essential changes in its geometry and also in its chemical and physical properties [19]. Therewith the reactivity dependence of the fluoro-containing molecules on the number of fluorine atoms is often rather complex [20]. Therefore the chemical behavior of the fluoro-containing short-living intermediates, in particular, also ylides, is often difficultly predictable a priori based on the regular trends known for non-fluorinated or chloro- and bromo-containing analogs. For instance, the most thoroughly studied dichloro- and difluoro-substituted azomethine ylides are quite different in their chemical behavior [1, 2, 21]. In this connection monofluoro-substituted azomethine ylides that has not been previously investigated are interesting from the theoretical viewpoint since the study of their characteristics makes it possible to reveal the effect of fluorine atom on the reactivity of ylide intermediates and also for practice for their π-cyclization and cycloaddition reactions may present a simple route to some difficultly accessible fluoro-containing compounds.

We report here on results of the study of generation and chemical reactions of monofluoro-substituted azomethine ylides and also of the products of their 1,3-cyclization, monofluoroaziridines.

The only efficient method to generate halosubstituted ylides is based on reactions of halocarbenes with compounds containing a C=N bond. Several methods are known for generation of monofluorocarbene that has been applied to preparation of fluorocyclopropanes from alkenes [22–28]. However all these procedures involve the use of strongly basic and highly nucleophilic reagents, like dimethylzinc or butyllithium, which are incompatible with substrates containing the C=N bond. We developed a new method of monofluorocarbene generation under mild neutral conditions involving a reduction of dibromofluoromethane with active lead in the presence of tetrabutylammonium bromide under an ultrasonic irradiation [16]. The active lead was prepared by reducing lead acetate with sodium borohydride in aqueous acetic acid [5].

The ultrasonic irradiation of a mixture containing aromatic ketone imine **Ia–Id**, active lead, and tetrabutylammonium bromide in dichloromethane led to a succession

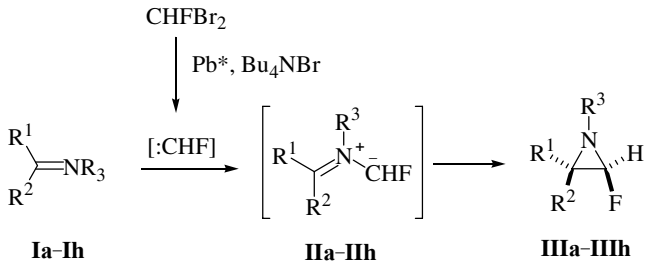
Table 1. Yields of fluoroaziridines in reaction of fluorocarbene with imines **Ia–Ih**

Imine	R^1	R^2	R^3	Aziridine	Yield, %
Ia	Ph	Ph	Me	**IIIa**	47
Ib	Ph	Ph	CH_2Ph	**IIIb**	34
Ic	Ph	Ph	CH_2CO_2Me	**IIIc**	47
Id	2,2′-biphenylene		CH_2CH_2Ph	**IIId**	19[a]
Ie	H	Ph	Ph	*cis*-**IIIe**	4
If	H	4-ClC_6H_4	4-ClC_6H_4	*cis*-**IIIf**	22
Ig	Ph	H	CH_2Ph	*trans*-**IIIg**	21[a]
Ih	Ph	H	CH_2CH_2Ph	*trans*-**IIIh**	Traces[b]

[a] Isolated with initial imine impurity.
[b] Detected by ^{1}H NMR spectroscopy.

of reactions including fluorocarbene generation, its addition to the nitrogen atom of the imine, and cyclization of the arising azomethine ylide **IIa–IId** (Scheme 1) resulting in the formation of aziridines **IIIa–IIId** in 19–47% yields (Table 1).

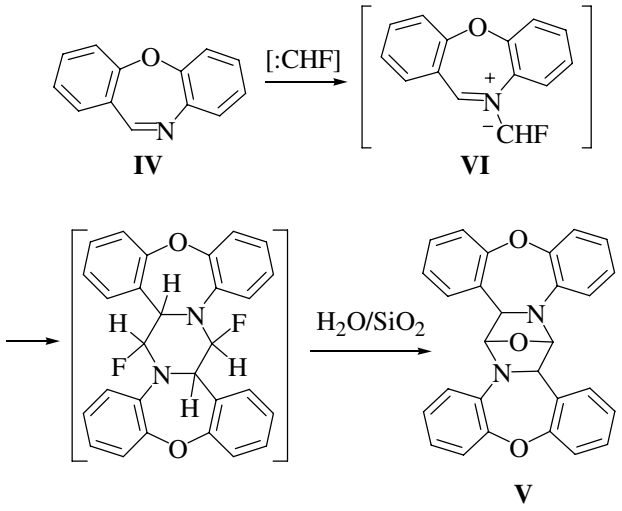
Scheme 1.



The structure of aziridines **IIIa–IIId** was established from the analysis of ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra of aziridines synthesized the signal of aziridine proton appeared as a doublet in the region 5.23–5.53 ppm ($^2J_{HF}$ 77.3–80.9 Hz). The ^{13}C NMR spectra contain two doublet signals belonging to C^F and C^{Ar} atoms of the aziridine ring in the region 87–90 (J_{CF} 243–254 Hz) and 52–56 ppm (J_{CF} 13–16 Hz).

Cyclizations of fluoroylides generated from aren-carbaldehydes imines **Ie–Ih** may give stereoisomeric aziridines. However in the reaction mixtures obtained from *N*-aryl-*N*-arylmethyleneamines **Ie** and **If** under the conditions of fluorocarbene generation we found by ^{1}H NMR method only *cis*-aziridines **IIIe** and **IIIf** ($^3J_{HH}$ 4.4, $^3J_{HF}$ 2.5, $^2J_{HF}$ 79 Hz). The stereochemistry of aziridines **IIIe** and **IIIf** follows from the value J_{HF} 2.5 Hz, since the *trans*- and *cis*-vicinal coupling constants $^3J_{HF}$ found in monofluoroaziridines are 2.4 and 8.1 Hz respectively [29].

Scheme 2.



It is known that dichloro-substituted ylides generated from dichlorocarbene and *N*-alkylimines of arenecarbaldehydes with the primary alkyl substituents do not undergo cyclization into aziridines [30]. In contrast, in the reaction mixtures of imines **Ig** and **Ih** with fluorocarbene we found by ^{1}H NMR spectroscopy aziridines **IIIg** and **IIIh** in the form of *trans*-isomers. Aziridine **IIIg** was isolated with an impurity of the initial *N*-benzyl-*N*-benzylideneamine in 21% yield.

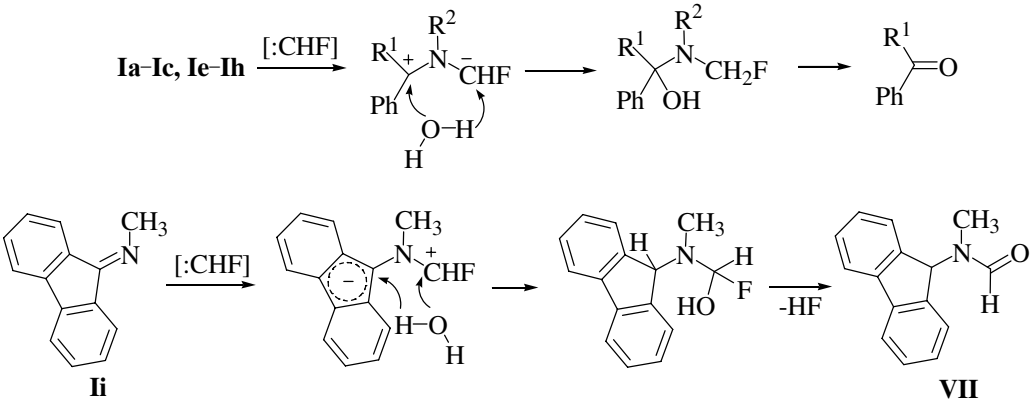
The configuration of fluoroaziridines **IIIg** and **IIIh** was established from comparison of coupling constants of vicinal H and F atoms ($^3J_{HF}$ 5.5 Hz) with the data published for monofluoroaziridines [29] and with values calculated by modified Karplus–Altona equation [31] ($^3J_{HF}$ 1.1–2.5 for *cis*- and 5.4–8.5 Hz for *trans*-isomers).

We obtained an unexpected result in the reaction of fluorocarbene with dibenzo[*b*,*f*][1,4]oxazepine (**IV**). Here instead of aziridine was obtained compound **V** in 17% yield which might be regarded as a hydrolysis product of ylide dimer **VI** (Scheme 2).

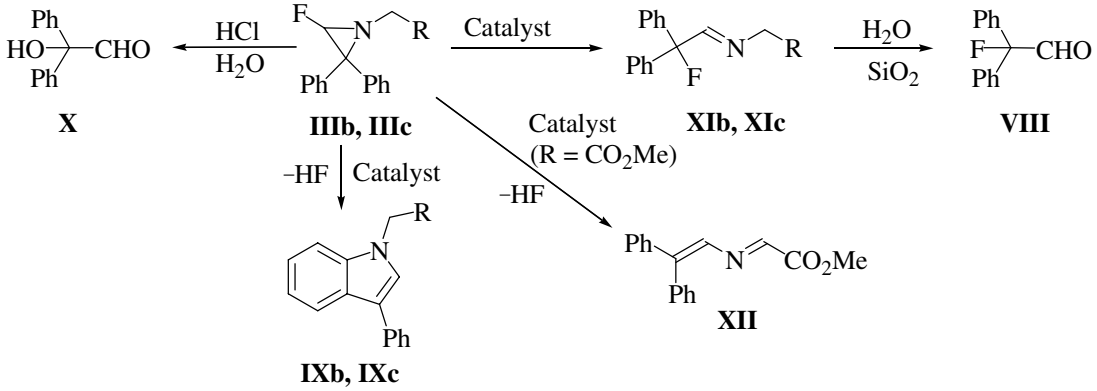
The yields of fluoroaziridines are strongly affected by two factors: the rate of 1,3-cyclization of the corresponding fluoroylide, and the stability of the formed aziridine. In event of relatively low rate of 1,3-cyclization one of the reasons of reduced yield of fluoroaziridines **IIIa–IIIi** may be a partial oligomerization of the intermediate azomethine ylides that is indirectly confirmed by formation of compound **V** resulting from dimerization of ylide **VI**.

At the presence of a little water in the initial compounds a fast hydrolysis occurs of the intermediate azomethine

Scheme 3.



Scheme 4.



ylide to a carbonyl compound. Actually, virtually in all performed reactions of imines **Ia–Ic, Ie–Ih** we isolated as side products or spectrally detected benzophenone or arenecarbaldehydes which apparently formed in the ylide reaction with water involving the protonation of ylide carbon attached to the fluorine atom (Scheme 3).

The fluorene iminium ylide generated from *N*-methylfluorene imine (**Ii**) because of additional stabilization of the negative charge by the fluorene system possessed an opposite polarization of the ylide fragment, and its hydrolysis in the reaction occurring in the presence of moisture proceeded through a protonation of the fluorenyl carbon atom. As a result *N*-methyl-*N*-fluorenylformamide (**VII**) formed in 13% yield.

There is no published data on the chemical properties of monofluoroaziridines, and we investigated some chemical reactions of these compounds in order to evaluate their synthetic potential. It was established that fluoroaziridines **IIIa–IIIh** are stable against heating: they survive two-hour boiling in dioxane (101°C) or xylene (144°C). Yet they considerably fast decompose on silica gel thus significantly reducing the preparative yields at purification by column chromatography. To decrease the losses at separating the reaction products we used silica gel treated with anhydrous triethylamine. Besides for crystalline aziridines an isolation procedure was developed avoiding the use of column chromatography that consisted in thorough washing of the reaction mixture with water solution of sodium carbonate followed by the aziridine crystallization.

We also established that fluoroaziridines **IIIa–IIIh** are sensitive to the action of Lewis and hydrogen acids. For instance, in the trifluoroacetic acid or in dichloromethane in the presence of boron trifluoride etherate aziridine **IIIb** suffered fast tarring without formation of any identifiable products. However after heating at reflux for 3 h solutions of aziridines **IIIb** and **IIIc** in dichloromethane in the presence of catalytic quantities of *p*-toluenesulfonic acid the subsequent chromatography on silica gel allowed separation of α-fluorodiphenylacetaldehyde (**VIII**) and indoles **IXb** and **IXc** (Scheme 4). At the use as catalyst of anhydrous zinc chloride or titanium tetrachloride only

indole derivative was obtained (Table 2). In aqueous dioxane in the presence of catalytic amounts of hydrochloric acid aziridine **IIIc** gave α-hydroxydiphenylacetaldehyde (**X**) in 77% yield.

Aldehyde **VIII** formed from hydrolysis of isomerization products of fluoroaziridines **III**, α-fluoroimines **XI**. Imines **XIb** and **XIc** were detected in the reaction mixtures at ring opening of aziridines **IIIb** and **IIIc** catalyzed by antimony trifluoride by means of ^{1}H NMR spectroscopy that revealed characteristic multiplet signals of the imine proton with the coupling constant $^3J_{HF}$ ~ 10 Hz. Similar opening of a three-membered ring with halogen migration was observed in *gem*-dihaloaziridines [32]. We failed to isolate pure imines **XI** using as catalysts for opening the fluoro-substituted aziridine ring TsOH, $ZnCl_2$, or $TiCl_4$. Antimony trifluoride proved to be exclusive catalyst: A treatment with the latter of aziridine **IIIb** in dichloromethane at reflux for 11 h led to a nearly quantitative formation of imine **XIb** containing 0.6% of indole **IXb** and 6% of the initial aziridine.A chromatographic purification on silica gel treated with anhydrous triethylamine provided analytically pure imine **XIb** in 55% yield. Under the same conditions we obtained from imine **IIIc** imine **XIc** in a nearly quantitative yield containing as an impurity 6 mol % of azadiene **XII**.

We showed with special experiments that imine **XIb** under treatment with SbF_3 or *p*-toluenesulfonic acid in boiling dichloromethane transformed into indole **IXb**, but the rate of indole **IXb** formation was here much slower than the rate of its formation from aziridine **IIIb**. At treating imine **XIb** with titanium tetrachloride indole **IXb** was found only in traces (^{1}H NMR data). These facts indicate that acid-catalyzed transformation of aziridine **IIIb** into indole **IXb** does not proceed through α-fluoroimine **XIb**.

The composition of products from aziridine **IIIc** transformation is strongly affected by the catalyst, for aziridine **IIIc** possesses considerable CH-acidity as compared to aziridine **IIIb**. In the presence of hydrogen acid alongside fluoroimine **XIc** formed indole **IXc**, and at the action of a Lewis acid the cyclization into indole was totally inhibited.

1,3-Cyclization into aziridines is the most characteristic behavior of *gem*-dichloro- and and fluorochloro-substituted azomethine ylides formed in the reaction of dihalocarbenes with *N*-alkyl-*N*-benzhydrylideneamines and benzylideneanilines [1]. On the contrary, ylides obtained from dihalocarbenes and *N*-alkyl-*N*-benzylidene-

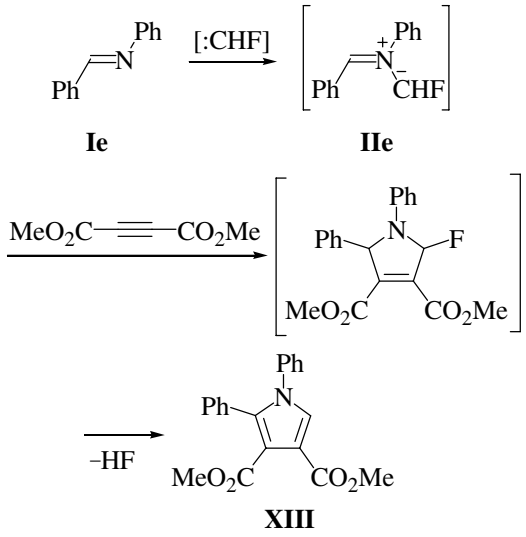
Table 2. Preparative yields of products of acid-catalyzed ring opening of aziridines **IIIb** and **IIIc** in CH_2Cl_2

Aziridine	Catalyst	Temperature and duration of reaction	Yield, %	
			VIII	**IXb** and **IXc**
IIIb	TsOH	40°C, 3 h	31	24
IIIb	$ZnCl_2$	20°C, 15 h	0	42
IIIb	$TiCl_4$	20°C, 15 min	0	60
IIIc	TsOH	40°C, 3 h	25	42

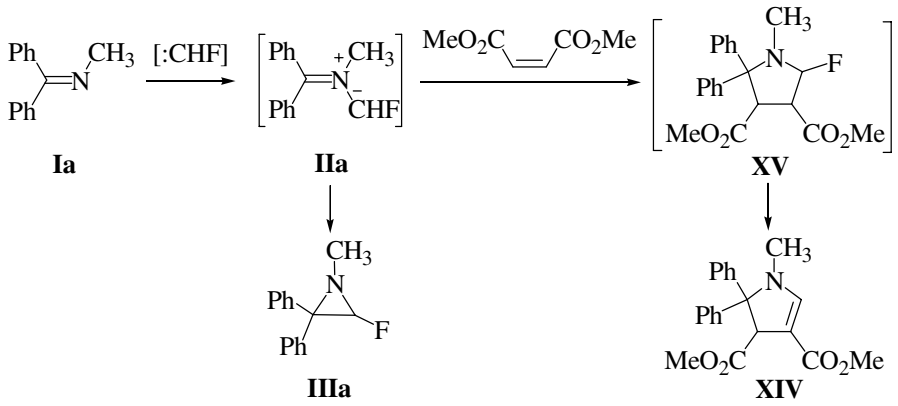
amines with primary alkyl substitiuents, and also *gem*-difluoro-substituted ylides do not undergo cyclization into aziridines, but readily provide products of 1,3-dipolar cycloaddition with dipolarophiles [1, 2, 30]. As seen from Table 1, cyclization of monofluoro-substituted analogs into monofluoroaziridines is hardly sensitive to the character of substituents at the ylide fragment. It is known that *gem*-dichloro-substituted azomethine ylides which easily cyclize into aziridines cannot be involved into 1,3-dipolar cycloaddition even with the most active dipolarophiles. To elucidate whether the monofluoro-substituted ylides can participate in cycloaddition reactions we have reacted imines **Ia**, **Ie**, **Ig**, and Ih with fluorocarbene in the presence of dimethyl acetylenedicarboxylate and dimethyl maleate, the moost often used dipole traps.

At ultrasonic irradiation of a mixture of imine **Ie**, active lead, tetrabutylammonium bromide, and dimethyl acetylenedicarboxylate in dichloromethane at 40°C for 100 h a mixture was obtained that was subjected to column chromatography to isolate pyrrole **XIII** in 32% yield (Scheme 5). Aziridine **IIIe** disappeared from the reaction mixture.

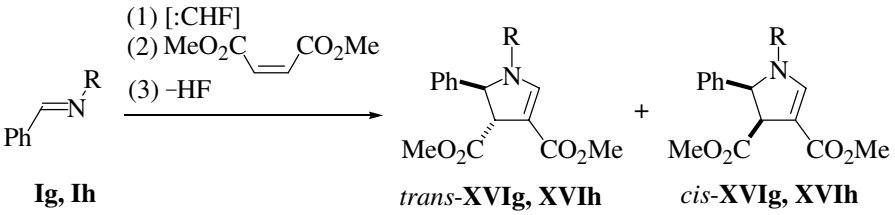
Scheme 5.



Scheme 6.



Scheme 7.



Similar reactions of imine **Ie** with dichloro- and difluorocarbenes in the presence of dimethyl acetylenedicarboxylate led to the formation of the corresponding chloro- and fluoropyrroles in 1.9 and 58% yield respectively, and therewith in the first case the main product was aziridine [5, 33]. Thus unlike dichloro-substituted analogs, both difluoro- and monofluoro-substituted azomethine ylides prepared from benzalanilines added to the triple bond of dimethyl acetylenedicarboxylate, the cycloaddition completely suppressing the 1,3-cyclization into aziridine.

From the products obtained in reaction of *N*-benzhydrylidene-*N*-methylamine (**Ia**) with fluorocarbene in the presence of less active dipolarophile, dimethyl maleate we isolated by column chromatography pyrroline **XIV** (10%) resulting from dehydrofluorination of pyrrolidine **XV**, the primary product of ylide **IIa** cycloaddition to the C=C bond (Scheme 6). The analysis of the reaction mixture by TLC and ^{1}H NMR showed alongside pyrroline **XIV** also aziridine **IIIa**, and the ratio pyrroline : aziridine was ~1:1, indicating that the rate of ylide **IIa** cycloaddition to the C=C bond of dimethyl maleate was comparable with the rate of its cyclization into aziridine. *gem*-Dichloro-substituted analog of ylide **IIa** does not enter into the cycloaddition reaction with dimethyl maleate.

In going from ylide **IIa** to ylides **IIg** and **IIh** due to removal of one phenyl substituents the steric hindrances to the dipolarophile approach were reduced, and this fact should favor the cycloaddition. Actually, in reactions of imines **Ig** and **Ih** with fluorocarbene in the presence of dimethyl maleate were obtained only cycloaddition products: pyrrolines **XVIg** and **XVIh** as mixtures of *cis*- and *trans*-isomers, the latter prevailing (Scheme 7). Compounds **XVIg** and **XVIh** were isolated by column chromatography in an overall yield of 32–35%.

Assignment of the configuration of pyrrolines *cis*- and *trans*- **XVIg** and **XVIh** was performed based on the analysis of the chemical shift values δ of methoxy groups in the ^{1}H NMR spectra. The proton signal of methoxy group at atom C^3 in the spectra of *cis*-2-phenyl-2,3-dihydropyrrole-3,4-dicarboxylates is shifted upfield on the average by 0.5 ppm compared to the usual value of 3.6–3.8 ppm due to the shielding effect of the *cis*-directed benzene ring [30, 34–37]. In the ^{1}H NMR spectra of stereoisomers **XVIg** and **XVIh** the δ values for the methoxy groups at C^3 were 3.12–3.15 for *cis*- and 3.66–3.67 ppm for *trans*-isomers.

Thus reaction of fluorocarbene with azomethines proceeds through intermediate formation of unstable azomethine ylides whose main transformations are 1,3-

cyclization into aziridines, 1,3-dipolar cycloaddition to electron-deficient multiple carbon–carbon bonds, and hydrolysis. Besides in some cases monofluoroylides are capable to give products of formal dimerization. The cyclization of fluoroylides occurs stereoselectively leading to the formation of *cis*-aziridines from *N*-aryl-substituted ylides and *trans*-aziridines from *N*-alkyl-substituted ylides. An efficient procedure has been found for selective ring opening in 2,2-diphenyl-3-fluoroaziridines catalyzed by antimony trifluoride, therefore the sequence "reaction of azomethines with fluorocarbene–opening of monofluoro-substituted aziridine ring" becomes a convenient method for the synthesis of α-fluoroimines, promising synthetic building blocks for fluorinated heterocycles. The cyclo-addition of fluoroylides to dimethyl acetylenedicarboxylate and dimethyl maleate results in formation of pyrroles and 2-pyrrolines, yet in the case of sterically loaded *C*,*C*-di-substituted ylides the cycloaddition to dipolarophiles suffers from competition with the cyclization into aziridines. By the chemical properties the monofluoro-substituted azomethine ylides take an intermediate position between difluoro-substituted ylides more prone to 1,3-dipolar cycloaddition to multiple bonds, and dichloro- and chlorofluoroylides whose more characteristic reaction is the 1,3-cyclization.

EXPERIMENTAL

Melting points of substances are measured on a Boëtius heating block and are reported without correction. NMR spectra were registered on a spectrometer Bruker DPX 300 at operating frequencies 300 (^{1}H) and 75 (^{13}C) MHz. Elemental analyses were performed on a CHN-analyzer HP-185B. Mass spectra were taken on MKh-1303 (ionizing electrons energy 70 eV). The monitoring of reaction progress was carried out by TLC on Silufol UV-254 plates. Reaction mixtures were separated by colum chromatography on silica gel Merck 60/200. Solvents (CH_2Cl_2, Et_2O, xylene, dioxane) were dried by standard procedures. Dimethyl acetylenedicarboxylate was distilled before use. Commercial tetrabutylammonium bromide was dried in a desiccator over P_2O_5 before use.

Dibromofluoromethane [38], imines **Ia–Ic** [39], **Id**, and **Ii** [40] were prepared by published procedures. Active lead was obtained by method from [5].

General procedure of reactions between dibromo-fluoromethate and actuve lead. Into a flask containing active lead was charged under an argon atmosphere anhydrous dichloromethane, tetrabutylammonium bromide, imine, and dibromofluoromethane (in a molar ratio Pb*–Bu_4NBr–imine–$CHFBr_2$ 4:4:1:5). On adding dibromofluoromethane the reaction mixture usually frothed and slightly heated. The flask was immediately stoppered, and the stopper was fixed to keep a slight excessive pressure in the flask. Then the flask was placed into an ultrasonic bath (160 W) and was subjected to irradiation at the bath temperature 40°C till total disappearance of lead. The products were isolated from the reaction mixtures by two procedures. *a.* On completion of the reaction 0.2 ml of triethylamine and silica gel in amount 2.5 g per 1 g of tetrabutylammonium bromide was added to the reaction mixture. The solvent was evaporated in a vacuum at room temperature, the dry residue was placed on the top of a chromatographic column packed with silica gel pretreated with triethyl-amine. The products were eluted by a mixture hexane–ethyl acetate containing 1 vol% of triethylamine.

b. The reaction mixture was shaken in a separatory funnel with a water solutio of sodium carbonate (0.02 mol l^{-1}, 70–80 ml per 50 ml of reaction mixture), the separated precipitate was filtered off. This procedure was repeated four times more. The filtrate was dried over Na_2SO_4, the solvent was removed in a vacuum, and the residue was recrystallized.

1-Methyl-2,2-diphenyl-3-fluoroaziridine (IIIa). A mixture of 0.64 g (3.3 mmol) of *N*-benzhydrylidene-*N*-methylamine (**Ia**), 2.87 g (14.9 mmol) of dibromo-fluoromethane, 2.5 g (12.1 mmol) of active lead, and 3.86 g (12.0 mmol) of Bu_4NBr in 40 ml of anhydrous dichloromethane was irradiated for 49 h in an ultrasonic bath. Yield 0.35 g (47%) by workup *a*. Characteristics of this compounds we reported in the preliminary communication [16].

1-Benzyl-2,2-diphenyl-3-fluoroaziridine (IIIb). A mixture of 0.83 g (3.1 mmol) *N*-benzhydrylidene-*N*-benzylamine (**Ib**), 2.94 g (15.3 mmol) of dibromo-fluoromethane, 2.56 g (12.4 mmol) of active lead, and 3.96 g (12.3 mmol) of Bu_4NBr in 10 ml of anhydrous dichloromethane was irradiated for 46 h in an ultrasonic bath. The reaction product was isolated by means of flash-chromatography on silica gel treated with triethylamine (eluent hexane–ethyl). On recrystallization of the crude product from a mixture ether–hexane, 10:1, we isolated 0.247 g of colorless crystals. Additional 0.032 g of compound **IIIb** was isolated from the mother liquor. Overall yield 0.279 g (30%). The workup of the reaction mixture by procedure *b* followed by recrystallization from ether resulted in the yield of aziridine **IIIb** of 34%. mp 114–115°C (Et_2O). IR spectrum ($CHCl_3$), cm^{-1}: 1500,

1180, 1150, 1100, 1090. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.53 d.d (1H, CH_2, J_{HH} 14.3, J_{HF} 3.7 Hz), 3.64 d.d (1H, CH_2, J_{HH} 14.3, J_{HF} 2.2 Hz), 5.44 d (1H, HCF, J_{HF} 79.2 Hz), 7.20–7.55 m ($15H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 53.7 d (CH_2, *J* 3.1 Hz), 55.5 d (C^2, *J* 14.5 Hz), 87.0 d (CHF, *J* 243.9 Hz), 126.8, 126.9, 127.58, 127.60, 128.0, 128.1, 128.3, 128.4 (C_{arom}), 130.2 d (C_{arom}, *J* 2.1 Hz), 134.8 d (C_{arom}, *J* 4.2 Hz), 137.9 (C_{arom}), 138.3 d (C_{arom}, *J* 3.1 Hz). Found, %: C 83.00; H 6.03; N 4.59. $C_{21}H_{18}FN$. Calculated, %: C 83.14; H 5.98; N 4.62.

Methyl (2,2-diphenyl-3-fluoroaziridin-1-yl)-acetate (IIIc). A mixture of 0.585 g (2.3 mmol) of methyl *N*-benzhydrylideneglycinate (**Ic**), 2.09 g (10.9 mmol) of dibromofluoromethane, 1.8 g(8.7 mmol) of active lead, and 2.82 g (8.7 mmol) of Bu_4NBr in 22 ml of anhydrous dichloromethane was irradiated for 70 h in an ultrasonic bath. The workup of the reaction mixture by procedure *b* followed by recrystallization from a mixture dichloromethane–ether, 2:5, we gave 0.309 g (47%) of compound **IIIc**, mp 120–121.5°C. IR spectrum ($CHCl_3$), cm^{-1}: 1750 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.04 d.d (1H, CH_2, J_{HH} 16.8, J_{HF} 3.6 Hz), 3.37 d.d (1H, CH_2, J_{HH} 16.8, J_{HF} 2.3 Hz), 3.76 (3H, CH_3), 5.42 d (1H, HCF, J_{HF} 77.3 Hz), 7.22–7.44 m ($8H_{arom}$), 7.56 m ($2H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 50.6 d (CH_2, *J* 4.0 Hz), 51.7 (CH_3), 55.4 d (C^2, *J* 14.0 Hz), 85.8 d (CHF, *J* 245.3 Hz), 127.1, 127.7, 128.3, 128.4, 128.6 (C_{arom}), 129.8 d (C_{arom}, *J* 2.0 Hz), 134.3 d (C_{arom}, *J* 4.0 Hz), 137.6 d (C_{arom}, *J* 4.0 Hz), 169.8 (C=O). Found %: C 71.43; H 5.62; N 5.17. $C_{17}H_{16}FNO_2$. Calculated %: C 71.57; H 5.65; N, 4.91.

1-Phenethyl-3-fluoro-9'*H*-spiro(aziridine-2,9'-fluorene) (IIId). A mixture of 1.2 g (4.2 mmol) of fluorenone *N*-phenethylimine (**Id**), 4 g (20.8 mmol) of dibromofluoromethane, 3.5 g (16.9 mmol) of active lead, and 5.4 g (16.7 mmol) of Bu_4NBr in 45 ml of anhydrous dichloromethane was irradiated for 36 h in an ultrasonic bath. The reaction mixture was worked up by procedure *a* to isolate 1.04 g of a mixture of aziridine (**IIId**) with the initial imine. Into the mixture obtained a crystal of the initial imine was seeded, the precipitated crystals were filtered off. The filtrate was subjected to chromatography on 10 g of silica gel pretreated with triethylamine (eluent hexane). On removing the solvent we obtained 0.36 g of viscous yellowish fluid containing 70% of aziridine **IIId** and 30% of initial imine (^{1}H NMR data). Yield of aziridine **IIId** 19%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.73 m (1H, CH_2), 2.87 m (1H, CH_2), 3.18 m (1H, CH_2), 3.46 m (1H, CH_2), 5.53 d (1H, HCF J_{HF} 80.9 Hz), 7.05–7.92 m ($10H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 35.9 ($PhCH_2$), 50.4 d (CH_2, *J* 3.3 Hz), 52.5 d (C^2, *J* 13.8 Hz), 89.5 d (CHF, *J* 253.8 Hz), the signals from the carbon atoms of aryl systems in the reaction product and the initial amine overlapped.

(2*RS*,3*SR*)-1,2-Diphenyl-3-fluoroaziridine (*cis*-IIIe). A mixture of 0.36 g (2.0 mmol) of *N*-benzylideneaniline (**Ie**), 1.91 g (10.0 mmol) of dibromofluoromethane, 1.64 g (7.9 mmol) of active lead, and 2.56 g (7.9 mmol) of Bu_4NBr in 22 ml of anhydrous dichloromethane was irradiated for 69 h in an ultrasonic bath. The reaction mixture was separated by means of flash-chromatography on silica gel treated with triethylamine (eluent hexane–ethyl acetate). On recrystallization of the crude product from hexane the yield was 0.015 g (3.5%). Colorless crystals, mp 62–64°C (66–68°C [16]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.34 d.d (1H, C^2-H, J_{HF} 2.4, J_{HH} 4.1 Hz), 5.23 d.d (1H, HCF, J_{HF} 79.2, J_{HH} 4.1 Hz), 7.05–7.60 m ($10H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 46.7 d (C^2, *J* 14.0 Hz), 83.9 d (CHF, *J* 245.3 Hz), 119.7, 124.1, 128.3, 128.5, 128.9, 130.0 (C_{arom}), 134.2 d (C_{arom}, *J* 4.0 Hz), 150.3 d (C_{arom}, *J* 2.0 Hz).

(2*RS*,3*SR*)-2-Fluoro-1,3-bis(4-chlorophenyl)-aziridine (*cis*-IIIg). A mixture of 0.5 g (2 mmol) of 4-chloro-*N*-(4-chlorobenzylidene)aniline (**If**), 3.67 g (19.1 mmol) of dibromofluoromethane, 3.2 g (15.5 mmol) of active lead, and 4.9 g (15.2 mmol) of Bu_4NBr in 15 ml of anhydrous dichloromethane was irradiated for 34 h in an ultrasonic bath. The reaction mixture was separated by means of flash-chromatography on silica gel treated with triethylamine (eluent hexane–ethyl acetate). Yield 0.126 g (22%), colorless crystals. Characteristics of this compounds we reported in the preliminary communication [16].

(2*RS*,3*RS*)-1-Benzyl-2-phenyl-3-fluoroaziridine (*trans*-IIIg). A mixture of 0.812 g (4.2 mmol) of *N*-benzyl-*N*-benzylideneamine (**Ig**), 6.7 g (34.9 mmol) of dibromofluoromethane, 3.5 g (16.9 mmol) of active lead, and 5.4 g (16.7 mmol) of Bu_4NBr in 45 ml of anhydrous dichloromethane was irradiated for 59 h in an ultrasonic bath. After workup of the reaction mixture by procedure *a* aziridine **IIIg** was obtained in a mixture (400 mg) with the initial imine. Yield of aziridine 21%. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.17 d (1H, C^2-H, J_{HF} 5.5 Hz), 3.88 d (1H, CH_2, *J* 14.0 Hz), 3.94 d (1H, CH_2, *J* 14.0 Hz), 5.17 d (1H, HCF, J_{HF} 78.5 Hz), 7.2–7.5 m (10H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 44.7 d (C^2, *J* 16.1 Hz), 52.4 d (CH_2, *J* 11.4 Hz), 84.3 d (CHF,

J 254.3 Hz), 126.7. 127.2, 127.5, 127.6, 127.7, 128.1, 128.3, 138.1 (C_{arom}).

(2*RS*,3*RS*)-1-Phenethyl-2-phenyl-3-fluoroaziridine (***trans*-IIIh**). A mixture of 1 g (4.8 mmol) of *N*-benzylidene-*N*-phenethylamine (**Ih**), 5.38 g (28.0 mmol) of dibromofluoromethane, 4.64 g (22.4 mmol) of active lead, and 7.24 g (22.4 mmol) of Bu_4NBr in 25 ml of anhydrous dichloromethane was irradiated for 57 h in an ultrasonic bath. After workup of the reaction mixture by procedure *a* (eluent hexane–ethyl acetate) we obtained 0.015 g of a mixture of compound **IIIh** with the initial imine. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.19 d (1H, C^2-H, *J* 5.5 Hz), 5.03 d (1H, CHF, J_{HF} 78.3 Hz).

6,17-Epoxy-6,6a,17,17a-tetrahydrodibenzo-[*b*,*f*]dibenzo[22 ,32 :62 ,72][1,4]oxazepino[42 ,52 :4,5]-pyrazino[1,2-*d*][1,4]oxazepine (V). A mixture of 1.14 g (5.9 mmol) of dibenzo[*b*,*f*][1,4]oxazepine (**IV**), 5.63 g (29.3 mmol) of dibromofluoromethane, 4.86 g (23.5 mmol) of active lead, and 7.58 g (23.5 mmol) of Bu_4NBr in 50 ml of anhydrous dichloromethane was irradiated for 10 h in an ultrasonic bath. After workup of the reaction mixture by procedure *b* we obtained 0.222 g (17.4%) of compound **V**, mp 272–273.5°C. IR spectrum ($CHCl_3$), cm^{-1}: 1610, 1500, 1460, 1390, 1320, 1285, 1250, 1180, 1110, 1060, 895. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.91 (1H, HCAr), 6.21 (1H, HCO), 6.55–7.40 m ($10H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 58.5 (HCAr), 70.1 (HCO), 116.8, 119.3, 120.4, 121.5, 124.7, 125.1, 125.9, 129.2, 129.5, 137.8, 144.7, 158.4 (C_{arom}). Mass spectrum, *m/z* (I_{rel}, %): 432 (0.1) $[M]^+$, 404 (7) $[M - CO]^+$, 209 (100) $[M - C_{13}H_{10}NO - CO]^+$, 181 (83). Found, %: C 77.55; H 4.89; N 6.50. $C_{28}H_{20}N_2O_3$. Calculated, %: C 77.76; H 4.66; N 6.48.

***N*-Methyl-*N*-(9*H*-fluoren-9-yl)formamide (VII).** A mixture of 0.186 g (1.0 mmol) *N*-methyl-*N*-fluorenylideenamine (**Ii**), 0.742 g (3.9 mmol) of dibromofluoromethane, 0.6 g (2.9 mmol) of active lead, and 0.94 g (2.9 mmol) of Bu_4NBr in 15 ml of anhydrous dichloromethane was irradiated in an ultrasonic bath for 67 h. After workup of the reaction mixture by procedure *b* using in chromatography eluent hexane–ethyl acetate we obtained compound **VII** in a yield 0.029 g (13%), mp 104–114°C. In a chloroform solution compound **VII** exists as a rotamers mixture. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.36 s (1.9H CH_3), 2.40 s (1.3H, CH_3), 5.57 s (0.6H, C^9–H), 6.69 s (0.4H, C^9-H), 7.30–7.50 m ($6H_{arom}$), 7.81–7.7 m ($2H_{arom}$), 8.48 s (0.4H, HCO), 8.71 s (0.6H, HCO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 25.4 (CH_3), 29.4 (CH_3), 56.7(C^9), 63.2 (C^9), 119.9, 120.1, 124.2, 124.5, 127.4, 127.6, 128.5, 129.0, 140.5, 140.8, 141.0, 141.1 (C_{arom}), 163.1 (HCO), 163.7 (HCO). Mass spectrum, *m/z* (I_{rel}, %): 223 (100) $[M]^+$, 208 (47.8) $[M - CH_3]^+$, 194 (13.8) $[M - HCO]^+$, 180 (68.5) $[M - HCO - CH_3]^+$, 165 (82.6) $[M - HCONCH_3]^+$.

1-Benzyl-3-phenylindole (IXb) and 2,2-diphenyl-2-fluoroacetaldehyde (VIII). *a*. A solution of 0.15 g (0.5 mmol) of aziridine **IIIb** in 10 ml of anhydrous dichloromethane in the presence of a catalytic quantity of *p*-toluenesulfonic acid (1 mg) was heated at reflux for 3 h. After separating the mixture by column chromatography (eluent hexane–dichloromethane) we obtained 0.033 g (24%) of compound **IXb** and 0.033 g (31%) of compound **VIII**.

Compound **IXb**, colorless crystals, mp 61–63°C. IR spectrum ($CHCl_3$), cm^{-1}: 3100–3010 w, 1610 s, 1620, 1550, 1500, 1480 s, 1465, 1400, 1390, 1360, 1340, 1310, 1275, 1260–1200, 1190 s, 1090, 1040. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 5.40 (2H, CH_2), 7.20–7.40 m ($10H_{arom}$), 7.43–7.53 m ($2H_{arom}$), 7.69–7.80 m ($2H_{arom}$), 8.00–8.05 m ($1H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 49.8 (CH_2), 109.7 (C^7), 117.1, 119.7, 119.8, 121.8, 125.5, 125.6, 126.1, 126.6, 127.1, 127.4, 128.4, 128.5, 135.2, 136.8, 136.9 (C_{arom}). Found, %: C 88.66; H 6.13; N 5.04. $C_{21}H_{17}N$. Calculated, %: C 89.01; H 6.05; N 4.94.

Compound **VIII**, colorless viscous fluid. IR spectrum ($CHCl_3$), cm^{-1}: 1760 (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.44 ($10H_{arom}$), 10.01 d (1H, HCO, J_{HF} 6.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 99.8 d (C^2, *J* 183.5 Hz), 126.6 d (C^o, *J* 7.0 Hz), 128.4 (C^p), 128.9 d (C^m, *J* 2.0 Hz), 135.8 d (C^i, *J* 22.9 Hz), 195.6 d (HCO, *J* 38.9 Hz).

b. With 1 ml of thionyl chloride 0.07 g of zinc chloride was boiled for 30 min, and then the excess thionyl chloride was removed in a vacuum. Anhydrous zinc chloride thus prepared (0.05 g, 0.4 mmol) was added to a solution of 0.15 g (0.5 mmol) aziridine **IIIb** and 0.057 g (0.5 mmol) of benzylamine in 5 ml of anhydrous dichloromethane, and the reaction mixture was left overnight. The reaction products were isolated by column chromatography on silica gel (eluent hexane–ethyl acetate). We obtained 0.059 g (42%) of 1-benzyl-3-phenylindole (**IXb**).

c. To a solution of 0.04 g (0.13 mmol) of aziridine **IIIb** in 5 ml of anhydrous dichloromethane was added one drop of titanium tetrachloride. The reaction mixture was stirred for 15 min at room temperature, and then was filtered through a silica gel bed. The silica gel was washed with 30 ml of dichloromethane, the filtrate was evaporated to dryness. We obtained 0.023 g (60%) of 1-benzyl-3-phenylindole (**IXb**).

Methyl (3-phenylindol-1-yl)acetate (IXc) and 2,2-diphenyl-2-fluoroacetaldehyde (VIII). A solution of 0.099 g (0.35 mmol) of aziridine **IIIc** in 25 ml of anhydrous dichloromethane containing a catalytic quantity of *p*-toluenesulfonic acid monohydrate (1 mg) was heated at reflux for 3 h. On separating the mixture by column chromatography (eluent hexane–ethyl acetate) we obtained 0.023 g (25%) of compound **IXc** and 0.031 g (42%) of compound **VIII**. Compound **IXc**, viscous fluid. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 (3H, CH_3), 4.93 (2H, CH_2), 7.20–7.60 m ($7H_{arom}$), 7.65–7.75 m ($2H_{arom}$), 7.95–8.05 m ($1H_{arom}$). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 47.5 (CH_2), 52.3 (CH_3), 108.9 117.9, 119.9, 120.1, 122.2, 125.70, 125.71, 126.2, 127.2, 128.4, 134.9, 136.9 (C_{arom}^-), 168.5 (C=O).

2-Hydroxy-2,2-diphenylacetaldehyde (X). To a solution of 0.105 g (0.37 mmol) of aziridine **IIIc** in 15 ml of 1,4-dioxane was added 15 ml of water and 8 drops of concn. HCl, the mixture obtained was maintained for 10 h at room temperature. The reaction mixture was diluted with 10 ml of CH_2Cl_2, the water layer was separated and washed with 10 ml of dichloromethane. Combined organic solutions were dried with Na_2SO_4, and the solvent was evaporated in a vacuum. The yellow-brown residue was subjected to column chromatography (eluent hexane–ethyl acetate) to give 0.06 g (77%) of compound **X**. Colorless crystals, mp 52–55°C [41]. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.43 (1H, OH), 7.36–7.47 m ($10H_{arom}$), 10.01 (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 83.4 (C–OH), 127.4, 128.5, 128.8, 139.3 (C_{arom}), 198.0 (CHO).

***N*-Benzyl-*N*-(2,2-diphenyl-2-fluoroethylidene)-amine (XIb).** A mixture of 0.096 g (0.32 mmol) of aziridine **IIIb** and 0.07 g (0.39 mmol) of SbF_3 as fine powder in 20 ml of dichloromethane was heated at reflux for 15 h. The mixture was cooled, SbF_3 was filtered off, the solution was evaporated in a vacuum, and the residue was subjected to column chromatography on silica gel treated with anhydrous triethylamine using as eluent a mixture hexane–ethyl acetate. Yield 0.053 g (55%). Colorless crystals, mp 29–30°C. IR spectrum (CCl_4), cm^{-1}: 3070, 3040, 1690 (C=N), 1500, 1460, 1005. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 4.81 (2H, CH_2), 7.2–7.5 m ($15H_{arom}$), 8.23 d.t (1H, H–CN, J_{HF} 10.2, J_{HH} 1.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 64.4 (CH_2), 98.1 d (CF, *J* 174.7 Hz), 127.0 d (C_{arom}, *J* 5.8 Hz), 127.1, 127.9, 128.2, 128.4, 128.5, 138.3 (C_{arom}), 139.8 d (C_{arom}, *J* 22.7 Hz), 164.3 d (C=N, *J* 32.5 Hz). Found, %: C 83.12; H 6.12; N 4.56. $C_{21}H_{18}FN$. Calculated, %: C 83.14; H 5.98; N, 4.62.

Methyl 2-[(2,2-diphenylvinyl)imino]acetate (XII). *a*. A mixture of 0.1 g (0.35 mmol) of aziridine **IIIc** and 0.057 g (0.32 mmol) of SbF_3 as fine powder in 20 ml of dichloromethane was heated at reflux for 6 h. Antimony trifluoride was filtered off, the solution was evaporated in a vacuum, anhydrous triethylamine was added to the residue, and the product was separated by column chromatography on silica gel treated with anhydrous triethylamine (eluent hexane– ethyl acetate). Yield 0.02 g (21%). Yellow crystals, mp 109–112°C. IR spectrum ($CHCl_3$), cm^{-1}: 1750, 1730, 1300. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.87 (3H, CH_3), 7.3–7.4 m ($11H_{arom}$, =CH), 7.79 (1H, =CH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.5 (CH_3), 127.7, 128.4, 128.6, 128.8, 129.0, 131.7, 137.41, 137.43, 140.7, 148.5, 150.9 (C_{arom}, =CH), 164.6 (C=O). Found %: C 77.18; H 5.92; N 5.23. $C_{17}H_{15}NO_2$. Calculated %: C 76.96; H 5.70; N 5.28.

b. A mixture of 0.112 g (0.39 mmol) of aziridine **IIIc** and 0.064 g (0.36 mmol) of SbF_3 as fine powder in 20 ml of dichloromethane was heated at reflux for 2 h. Antimony trifluoride was filtered off, the solution was evaporated in a vacuum. The obtained light-yellow oily residue (0.112 g) according to ^{1}H NMR spectrum was **methyl *N*-(2,2-diphenyl-2-fluoroethylidene)aminoacetate (XIc)** (94 mol %) containing as impurity 6 mol% of azadiene **XII**. Imine **XIc**. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.79 (3H, CH_3), 4.39 (2H, CH_2), 7.2–7.6 m ($10H_{arom}$), 8.18 d.d.d (1H, H–CN, J_{HF} 9.8, J_{HH} 2, J_{HH} 1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 52.2 (CH_3), 61.0 (CH_2), 98.3 d (CF, *J* 174.3 Hz), 127.2 d (C_{arom}, *J* 6.7 Hz), 128.3, 128.6 d (C_{arom}, *J* 2 Hz), 139.2 d (C_{arom}, *J* 22.7 Hz), 168.5 d (C=N, *J* 32.5 Hz), 169.8 (C=O).

Reaction of imine XIb with *p*-toluenesulfonic acid. A mixture of 0.02 g (0.07 mmol) of aziridine **IIIb** and 0.012 g (0.07 mmol) of SbF_3 as fine powder in 10 ml of dichloromethane was heated at reflux for 8 h. Antimony trifluoride was filtered off, the solution was evaporated in a vacuum, to the residue containing imine **XIb** 2 ml of dichloromethane and 1 mg of *p*-toluenesulfonic acid monohydrate was added, and the mixture obtained was boiled for 3 h. According to the ^{1}H NMR data the reaction mixture contained 93 mol% of imine **XIb** and 7% of indole **IXb**.

Reaction of imine XIb with SbF_3. A mixture of 0.009 g (0.03 mmol) of imine **XIb** and 0.007 g (0.04 mmol) of SbF_3 in 20 ml of dichloromethane was heated at reflux for 20 h, and the solvent was evaporated in a vacuum. According to the ^{1}H NMR data the reaction mixture contained 9 mol% of indole **IXb** and 91 mol% of imine **XIb**.

Dimethyl 1,2-diphenyl-1*H*-pyrrole-3,4-dicarboxylate (XIII). A mixture of 0.453 g (2.5 mmol) of *N*-benzylideneaniline, 2.4 g (12.5 mmol) of dibromofluoromethane, 0.703 g (5.0 mmol) of dimethyl acetylenedicarboxylate, 2.05 g (9.9 mmol) of active lead, and 3.20 g (9.9 mmol) of Bu_4NBr in 25 ml of anhydrous dichloromethane was irradiated for 100 h in an ultrasonic bath. On separating the reaction products by column chromatography (eluent hexane–ethyl acetate) the yield of compound **XIII** was 0.266 g (32%). Colorless crystals, mp 114–119°C. IR spectrum ($CHCl_3$), cm^{-1}: 1730 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.77 (3H, CH_3), 3.87 (3H, CH_3), 7.11–7.05 m ($2H_{arom}$), 7.32–7.18 m ($8H_{arom}$), 7.5 (1H, H^5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 51.2 (CH_3O), 51.7 (CH_3O), 115.1, 116.4, 125.53, 127.54, 127.60, 127.62, 127.9, 128.8, 129.5, 130.0, 135.1, 138.2 (C_{arom}), 163.6 (C=O), 165.6 (C=O). Found, %: C 71.76; H 5.23; N, 4.25. $C_{20}H_{17}NO_4$. Calculated, %: C 71.63; H 5.11; N 4.18.

Dimethyl 1-methyl-2,2-diphenyl-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate (XIV). A mixture of 0.824 g (4.2 mmol) of *N*-benzhydrylidene-*N*-methylamine (**Ia**), 3.25 g (16.9 mmol) of dibromofluoromethane, 2.029 g (14.1 mmol) of dimethyl maleate, 3.5 g (16.9 mmol) of active lead, and 5.46 g (16.9 mmol) of Bu_4NBr in 40 ml of anhydrous dichloromethane was irradiated for 45 h in an ultrasonic bath. Yield 0.142 g (10%) (*a*). Colorless crystals, mp 162–165°C (Et_2O). IR spectrum ($CHCl_3$), cm^{-1}: 1750 (C=O), 1690 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.61 (3H, CH_3N), 3.07 (3H, CH_3O), 3.70 (3H, CH_3O), 4.79 (1H, C^3-H), 7.20–7.45 m ($11H_{arom}$, H^5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 32.8 (CH_3N), 50.4 (CH_3O), 51.1 (CH_3O), 60.7 (C^3), 79.7 (C^2), 99.0 (C^4), 127.31, 127.34, 127.5, 127.9, 128.1, 128.7, 137.4, 141.4 (C_{arom}), 152.1 (C^5), 165.3 (C=O), 171.1 (C=O). Found, %: C 71.66; H 6.06; N 3.93. $C_{21}H_{21}NO_4$. Calculated, %: C 71.78; H 6.02; N 3.99. Alongside pyrrole **XIV** we isolated 0.377 g of a mixture of benzophenone and aziridine **IIIc** in a ratio 1:1 (^1H NMR data).

Study of the competition between 1,3-cycloaddition and 1,3-cyclization. A mixture of 0.154 g (0.8 mmol) of *N*-benzhydrylidene-*N*-methylamine, 0.70 g (3.6 mmol) of dibromofluoromethane, 0.353 g (2.5 mmol) of dimethyl maleate, 0.6 g (2.9 mmol) of active lead, and 0.936 g (2.9 mmol) of Bu_4NBr in 7 ml of anhydrous dichloromethane was irradiated in an ultrasonic bath for 46 h. The reaction mixture was twice filtered through a fine-porous frit funnel, the solvent was evaporated in a vacuum, the residue was dried in a vacuum (0.1 mm Hg), dissolved in $CDCl_3$, and analyzed by ^1H NMR method. The ratio of products originating from 1,3-cyclization and 1,3-cycloaddition was estimated using signals of *N*-methyl groups of aziridine and pyrroline and the proton signals of the aziridine and pyrroline rings. The ratio of products of 1,3-cyclization and 1,3-cycloaddition was 1:1.

(2*RS*,3*SR*)- and **(2*RS*,3*RS*)-Dimethyl 1-benzyl-2-phenyl-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylates (XVIg).** A mixture of 0.74 g (3.8 mmol) of *N*-benzyl-*N*-benzylideneamine (**Ib**), 3.67 g (19.1 mmol) of dibromofluoromethane, 1.84 g (12.7 mmol) of dimethyl maleate, 3.2 g (15.5 mmol) of active lead, and 4.95 g (15.3 mmol) Bu_4NBr in 45 ml of anhydrous dichloromethane was irradiated 54 h in an ultrasonic bath. Aliquot of the reaction mixture (about 10%) was charged to the top of a chromatographic column packed with silica gel, the products were eluted with ethyl acetate. The solvent was removed. The ratio of *cis*-/*trans*-adducts in the reaction mixture was 1:3.5 (^1H NMR data). The main part of the reaction mixture was worked up by procedure *a* to obtain 0.47 g (35%) of a mixture of *cis*-/*trans*-adducts as a viscous fluid. Crystallization from an ether solution of the isomers mixture with subsequent recrystallization from ether yielded 0.294 g (22%) of compound *trans*-**XVIg** as colorless crystals, mp 83–85°C (Et_2O). IR spectrum ($CHCl_3$), cm^{-1}: 1755 (C=O), 1690 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.67 (3H, CH_3O), 3.73 (3H, CH_3O), 3.93 d (1H, H^2, *J* 7.7 Hz), 3.95 d (1H, CH_2, *J* 14.9 Hz), 4.30 d (1H, CH_2, *J* 14.9 Hz), 4.77 d (1H, H^3, *J* 7.7 Hz), 7.14–7.45 m ($11H_{arom}$, H^5). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 50.3 (CH_3O), 51.3 (CH_3O), 52.0 (CH_2), 55.6 (C^3), 70.5 (C^2), 98.3 (C^4), 126.6, 127.66, 127.69, 128.2, 128.5, 128.7, 135.2, 139.2 (C_{arom}), 151.0 (C^5), 165.3 (C=O), 173.7 (C=O). Found, %: C 71.65; H 6.11; N 3.92. $C_{21}H_{21}NO_4$. Calculated, %: C 71.78; H 6.02; N 3.99. Compound *cis*-**XVI** g was isolated in a mixture with the *trans*-isomer (0.170). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.15 (3H, CH_3O), 3.67 (3H, CH_3O), 3.88 d (1H, CH_2, *J* 14.4 Hz), 4.17 d (1H, C^2-H, *J* 12 Hz), 4.33 d (1H, CH_2, *J* 14.4 Hz), 4.88 d (1H, C^3-H, *J* 12 Hz), 7.14–7.45 m ($11H_{arom}$, C^5-H).

(2*RS*,3*RS*)-Dimethyl 2-phenyl-1-phenethyl-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate (*trans*-XVIh) and dimethyl-(2*RS*,3*SR*)-2-phenyl-1-phenethyl-2,3-dihydro-1*H*-pyrrole-3,4-dicarboxylate (*cis*-XVIh). A mixture of 1.36 g (6.5 mmol) of *N*-benzylidene-*N*-phenethylamine (**Ih**), 7.5 g (39.1 mmol) dibromofluoromethane, 2 g (13.9 mmol) dimethyl maleate, 2.66 g (12.9 mmol) of active lead, and 4.5 g (13.9 mmol) of

Bu_4NBr in 15 ml of anhydrous dichloromethane was irradiated for 5 h in an ultrasonic bath. The separation of the mixture by column chromatography (eluent hexane–ethyl acetate) provided 0.41 g of benzaldehyde, 0.306 g (12.7% with respect to introduced, 32% with respect to reacted imine) of *trans*-**XVIh** as a viscous fluid, and 0.046 g (2% with respect to introduced, 4.8% with respect to reacted imine) of *cis*-**XVIh** as colorless crystals, mp 153–155°C. Characteristics of compound *cis*-**XVIh** are given in the preliminary communication [16].

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