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Regioselectivity of the 1,3-Dipolar Cycloaddition of Fluorinated Fluoren-9-iminium Ylides to Heteroelement-Containing Dipolarophiles: Experimental and Quantum-Chemical Study

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Abstract—N-Substituted 9*H*-fluoren-9-imines react with difluorocarbene to give the corresponding iminium ylides whose further transformations in the absence of active dipolarophiles depend on the substituent at the nitrogen atom and reaction conditions. *N*-Ethyl-, *N*-benzyl-, and *N*-(2-phenylethyl)-9*H*-fluoren-9-imines are thus converted in low yield into the formal cyclodimerization products and/or 9*H*-fluorene-9-carboxamides. *N*-Methyl-substituted fluoreniminium ylide readily adds at the C=N bond of initial *N*-(9*H*-fluoren-9-ylidene)-methanamine with formation of spiro-fused imidazolidine derivative; in the presence of fluorenone, acetaldehyde, or benzaldehyde, addition at the C=O group of the dipolarophile occurs to give the corresponding oxazolidine derivatives. The regioselectivity of the cycloaddition of iminium ylides having a fluorene fragment at a double carbon–heteroelement bond can be described by quantum-chemical calculations in terms of the density functional theory (DFT; local hard and soft acids and bases concept): the cycloaddition leads preferentially to the 2,2-difluoro-substituted adduct.

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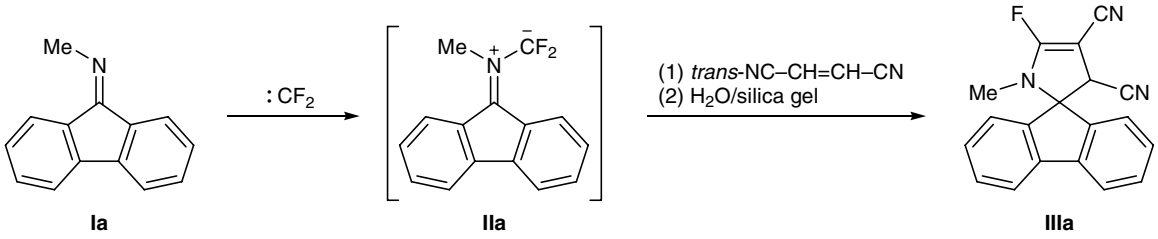
The presence of a fluorene fragment is often responsible for unusual geometric structure of a molecule, its chemical behavior, and unique physical properties. For example, *N*-alkyl-substituted 9*H*-fluoren-9-imines, unlike common *N*-alkyl ketone imines, are characterized by specific polarization of the C=N bond, and they react with butyllithium to give exclusively the corresponding secondary amines (azophilic addition) [1]. Specific structure of poly(9-methylenefluorenes) in solution, crystal, and gas phase and their unusual electrochemical and photoelectron parameters are attributed to π-stacking of the aromatic rings in the fluorene systems [2]. The effect of fluorene system on the chemical behavior of reactive ylide intermediates, in particular nonstabilized azomethine ylides, was not studied.

The possibility for generation of fluoreniminium ylides by prototropic tautomerization and by the carbene technique was demonstrated by the isolation of 1,3-dipolar cycloaddition products of these intermediates and fumaronitrile [3, 4] and *N*-ethylmaleimide [5]. For example, the reaction of *N*-(9*H*-fluoren-9-ylidene)methanamine (**Ia**) with difluorocarbene in the presence of fumaronitrile involves intermediate formation of ylide **IIa** and gives spiro-fused dihydropyrrole **IIIa** in 63% yield [4] (Scheme 1). An analogous reaction of *N*-methyldiphenylmethanimine ylide $Ph_2C{=}N^+(Me){-}C^-F_2$ (**IV**) also leads to the formation of the corresponding 2-fluoro-4,5-dihydropyrrole in a good yield [4].

However, we failed to isolate products derived from ylides like **IV** generated in the system $Ph_2C{=}NAlk{-}CF_2Br_2{-}Pb{-}Bu_4NBr{-}CH_2Cl_2$ in the absence of a dipolarophile. The same applies to difluoro ylides $PhHC{=}N^+(Alk){-}C^-F_2$ generated from difluorocarbene and *N*-benzylidenealkanamines [6]. By contrast, the reaction of fluorenimine **Ia** with difluorocarbene (generated *in situ* by reduction of dibromodifluoromethane with lead powder in the presence of tetrabutylammonium bromide) gave a mixture of three products: imidazolidinone **Va** (32%), bifluorenylidene (**VI**) (32%), and piperazinedione **VIIa** (9%) (Scheme 2). Imidazo-

Scheme 1.



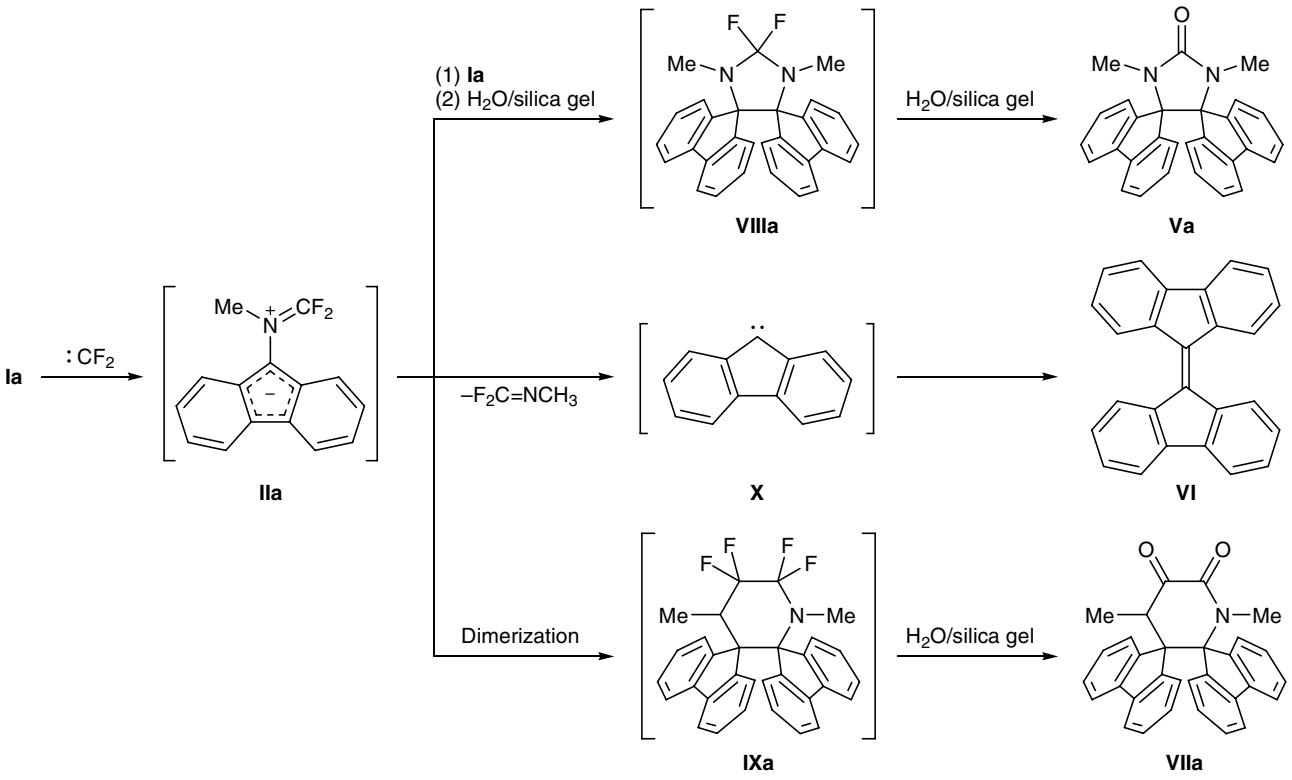
Ia **IIa** **IIIa**

lidinone **Va** is formed as a result of hydrolysis of the primary cycloaddition product, difluoride **VIIIa**, on silica gel during chromatographic treatment of the reaction mixture. Bifluorenylidene (**VI**) is usually formed in reactions involving fluorenylidene intermediate **X** [7]. In our case, compound **X** is likely to result from fragmentation of ylide **IIa**. The third isolated product, compound **VIIa**, may be regarded as a product of formal cyclodimerization of ylide **IIa**, followed by hydrolysis of tetrafluoropiperazine **IXa** on SiO_2.

The structure of compound **Va** was determined on the basis of its ^1H and ^{13}C NMR and IR spectra. The ^{13}C NMR spectrum of **Va** contained a signal at δ_C 163.9 ppm, typical of a carbonyl carbon atom, and a signal at δ_C 78.3 ppm from the C^4 and C^5 atoms of the imidazolidine ring. The spectral data did not allow us to distinguish between structure **VIIa** and regioisomeric piperazine-2,5-dione derivatives. According to the X-ray diffraction data, compound **VIIa** has the structure of piperazine-2,3-dione derivative (see figure); this means that ylide **IIa** undergoes dimerization in the "head-to-head" mode. This is the first example of iminio(dihalo)methanide dimerization, which demonstrates that in some cases stabilization of halogen-containing azomethine ylides in the absence of active dipolarophiles can follow an unusual pathway.

It is known that generation of difluorocarbene in reactions with imines using active lead (Pb*, prepared by reduction of lead tetraacetate with sodium tetrahydridoborate) instead of lead turnings often leads to a different product ratio; in particular, the yield of cycloaddition products derived from intermediate difluoro ylides increases [8]. In fact, by stirring of a mixture of imine **Ia**, active lead, dibromodifluoro-

Scheme 2.



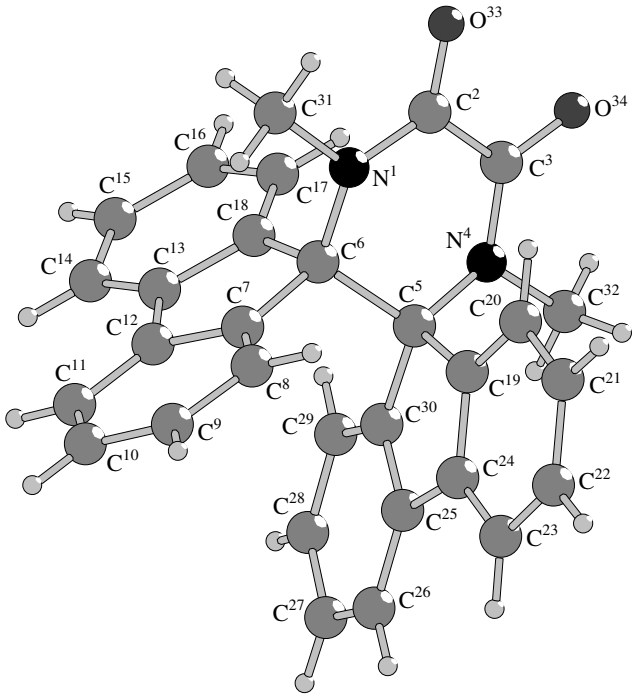


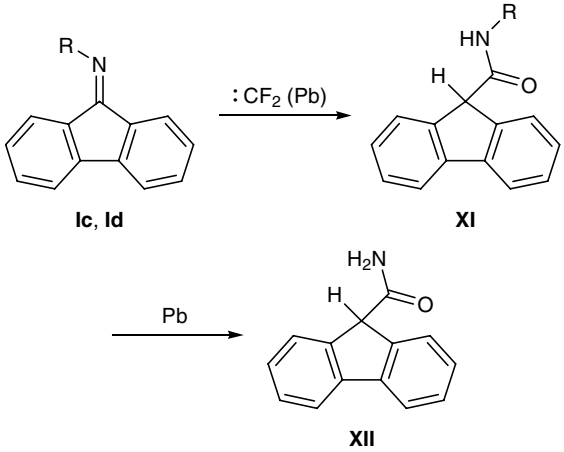
Fig. 1. Structure of the molecule of 1,4-dimethyl-9*H*,9"*H*-dispiro[fluorene-9,5'-piperazine-6',9"-fluorene]-2',3'-dione (**VIIa**) according to the X-ray diffraction data.

methane, and tetrabutylammonium bromide in anhydrous methylene chloride at 40°C we obtained only two products: imidazolidinone **Va** and piperazinedione **VIIa**, which were isolated by column chromatography on silica gel in 82 and 0.3% yield, respectively. No bifluorenylidene (**VI**) was detected in the reaction mixture. Presumably, considerable increase in the yield of cycloaddition product **Va** is favored by the lack of side transformation of ylide **IIa**, i.e., its fragmentation to fluorenylidene.

We performed a detailed study on the reactivity of fluoreniminium ylides toward difluorocarbene generated in the system CF_2Br_2–Pb–Bu_4NBr–CH_2Cl_2; as substrates we used *N*-ethyl- (**Ib**), *N*-benzyl- (**Ic**), *N*-(2-phenylethyl)- (**Id**), *N*-cyclohexyl- (**Ie**), and *N*-phenyl-9*H*-fluoren-9-imines (**If**). The reactions of difluorocarbene with *N*-cyclohexyl and *N*-phenyl derivatives **Ie** and **If** were accompanied by strong tarring so that we failed to isolate any identifiable product. It is known that difluoro-substituted ylides having a bulky group on the nitrogen atom are difficult to involve in cycloaddition reactions. Thus steric factor may be responsible for the absence of cycloaddition products in reactions of Schiff bases **Ie** and **If** with difluorocarbene [6].

It was surprising that analogous reactions of imines **Ib**–**Id**, in which the substituent on the nitrogen atom is only slightly larger than methyl group, gave neither cycloaddition products of intermediate ylide and initial imine nor bifluorenylidene. Among products of the reaction of imine **Id** (R = $PhCH_2CH_2$) with difluorocarbene we detected only amide **XI** which was isolated in 2% yield. Presumably, *N*-benzyl derivative **Ic** loses benzyl group by the action of lead to give 9*H*-fluorene-9-carboxamide (**XII**) (0.4%; Scheme 3).

Scheme 3.



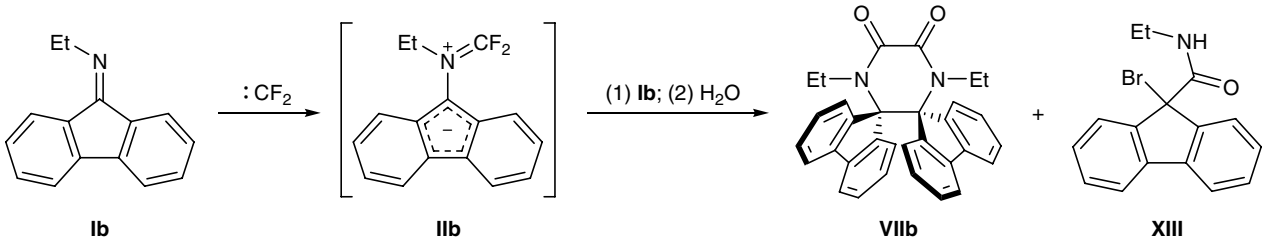
I, R = $PhCH_2$ (**c**), $PhCH_2CH_2$ (**d**).

Amides **XI** and **XII** characteristically showed in the ^{1}H NMR spectra a broadened signal at δ 5.19–5.21 ppm from the NH proton and a signal from 9-H at δ 4.80 and 4.81 ppm, respectively. The structure of **XI** and **XII** was also confirmed by the mass spectra which contained the corresponding molecular ion peaks.

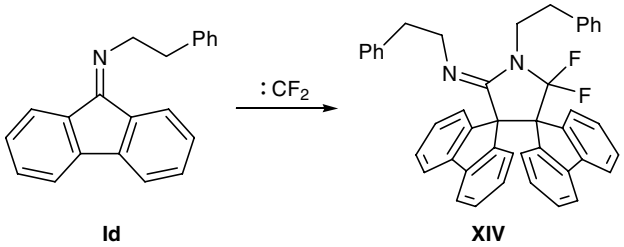
In the reaction of imine **Ib** with difluorocarbene generated by a similar procedure, we isolated only diazine **VIIb** (1.3%) which was formed by hydrolysis of ylide **IIb** dimer over silica gel (Scheme 4). When difluorocarbene was generated with the use of active lead instead of lead powder, we obtained 0.7% of piperazine **VIIb** and 8% of amide **XIII**. The reaction of imine **Id** with difluorocarbene generated using active lead unexpectedly afforded 10% of 2,2-difluoropyrrolidine **XIV** (Scheme 5). The ^{13}C NMR spectrum of **XIV** contained two triplets at δ_C 67.2 ($^2J_{CF}$ = 23 Hz) and 126.3 ppm ($^1J_{CF}$ = 248 Hz) due to C^4 and C^5 in the pyrrolidine ring, and an absorption band at 1700 cm^{-1} (C=N) was present in its IR spectrum.

Scheme 6 shows the most probable transformation sequence leading to amides **XI**–**XIII** and pyrrolidine **XIV**. It includes consecutive formation of ylides **IIb**–**IId**, aziridines **XVb**–**XVd**, imidoyl fluorides **XVIb**–**XVId**, and ketene imines **XVIIb**–**XVIId**. Transforma-

Scheme 4.

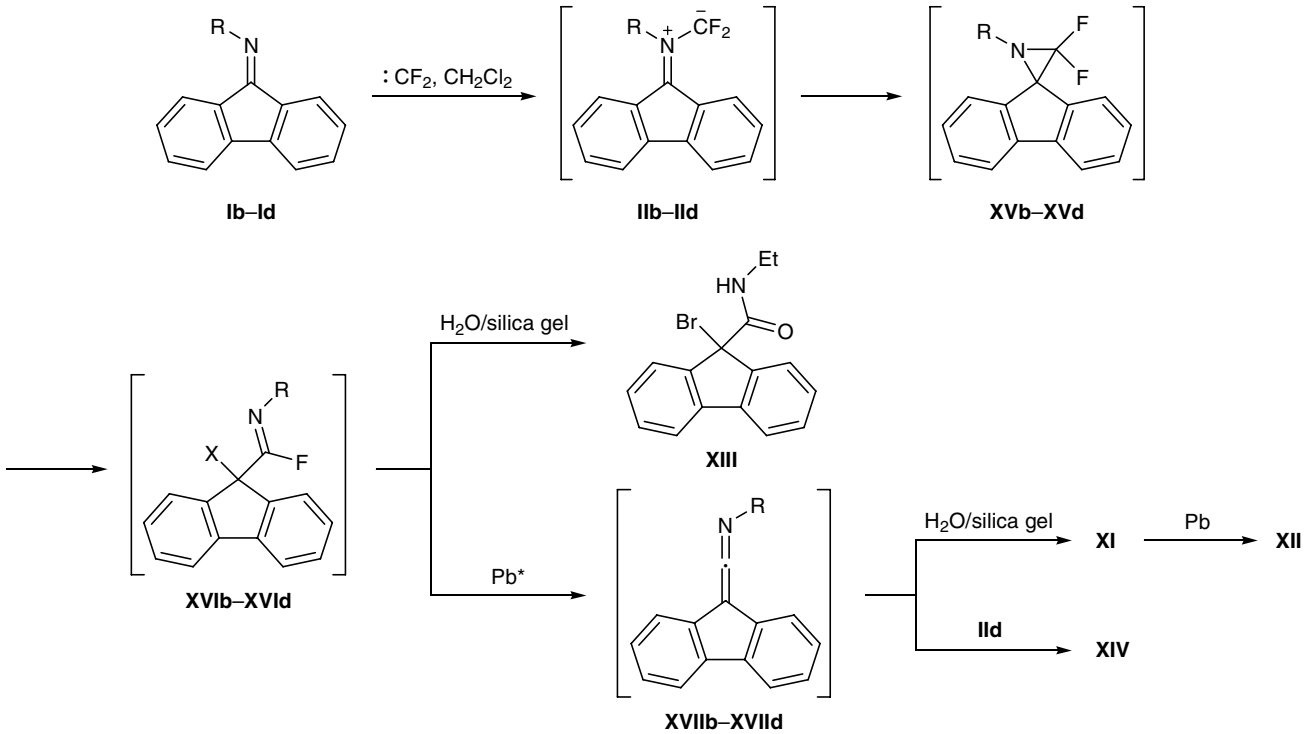


Scheme 5.



tions analogous to **XV**→**XVII** have been reported. For example, reductive cleavage of the aziridine ring in geminal dichloroaziridines by the action of zinc dust is known to give ketene imines in a good yield [9]. Moreover, taking into account our previous data on the stability of 1,2-diaryl-3,3-difluoro- and 1,2-diaryl-3,3-dichloroaziridines [10], aziridine **XV** should be very unstable due to the presence of strong π-donor substituents (benzene rings) and fluorine atoms on C^3. Both these factors favor opening of the three-membered ring at the C–N bond opposite to the CF_2 group. It is also known [11] that *N*-alkyl-substituted ketene imines undergo fast hydrolysis to the corresponding amides [11], which is very consistent with the proposed reaction scheme. *N*-(9*H*-Xanthen-9-ylidene)methanamine behaves similarly in the reaction with difluorocarbene

Scheme 6.



[4]. 9-Bromo-*N*-ethyl-9*H*-fluorene-9-carboxamide (**XIII**) is likely to be formed via opening of the aziridine ring in **XVb**, which is accompanied by insertion of bromine (from tetrabutylammonium bromide) and subsequent hydrolysis of intermediate imidoyl fluoride **XVIb** during chromatography on silica gel.

Insofar as the yields of the products shown in Scheme 6 are very low, the cyclization to aziridines **XVb**–**XVd** contributes little to the stabilization of intermediate fluoreniminium ylides **IIb**–**IId**. Presumably, the main transformation pathway of ylides **IIb**–**IId** is oligomerization. An indirect proof is the formation of small amounts of cyclic dimers **VIIa** and **VIIb**. Thus only N-methyl-substituted ylide **IIa** tends to add at the C=N bond of the initial *N*-alkylfluorenimine. A probable reason for the extremely strong sensitivity of the cycloaddition step in the reaction of imines **Ia**–**Id** with difluorocarbene to the size of the R substituent is that the latter increases in both dipole and dipolarophile in going from compound **Ia** to **Ib**–**Id**.

It is known that the C=N bond in Schiff bases like $R^1N{=}CR^2R^3$ (where R^1 = Alk, Ar; R^2 = R^3 = Ph or R^2 = Ph, R^3 = H) is inactive as dipolarophile toward difluoroazomethine ylides which are formed from those imines via reaction with difluorocarbene. However, such ylides readily add to the more electrophilic C=N bond in *N*-(benzylidene)benzenesulfonamide $PhCH{=}NSO_2Ph$ to give (after hydrolysis) imidazolidin-4-one derivatives [12]. Ylide **IIa** can be regarded as the first halogen-substituted azomethine ylide that is capable of adding to the parent Schiff base. Here, the regioselectivity of the cycloaddition is opposite to that observed in the above noted reactions of phenyl- and diphenylmethaniminium ylides with the C=N bond of *N*-(benzylidene)benzenesulfonamide: the ylide CF_2 group links to the nitrogen rather than carbon atom of the dipolarophile, and the product is imidazolidin-2-one derivative **Va**.

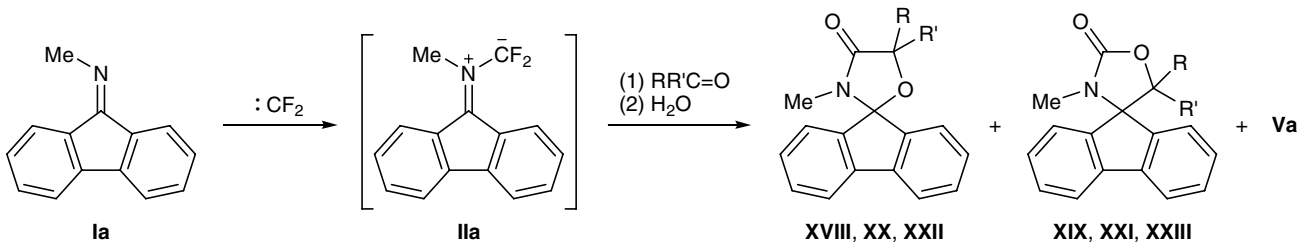
The reasons for the unusual behavior of ylide **IIa** in the above reaction may be the following: (1) specific polarization of the fluoreniminium ylide due to the ability of the fluorene fragment to effectively stabilize the negative charge on C^9; (2) specific electron density distribution in *N*-methylfluorenimine acting as dipolarophile, as compared to Schiff bases derived from benzaldehyde and benzophenone; and (3) attractive interactions (π-stacking) between the aromatic fluorene systems, which are typical of some fluorene derivatives [2] (in our case, such interactions are possible between the dipole and dipolarophile fluorene systems).

We examined cycloaddition reactions of ylide **IIa** with carbonyl-containing dipolarophiles. As the latter we used aromatic carbonyl compounds (benzaldehyde and fluorenone) and acetaldehyde; in the reaction with the latter, no π-stacking with the ylide fluorene system is possible. Imine **Ia** reacted with difluorocarbene generated in the CF_2Br_2–Pb*–Bu_4NBr–CH_2Cl_2 system in the presence of both acetaldehyde and benzaldehyde to give three products: regioisomeric cycloadducts of ylide **IIa** at the aldehyde carbonyl group, oxazolidinones **XVIII/XIX** and **XX/XXI**, respectively, and adduct at the C=N bond of the initial imine, imidazolidinone **Va** (Scheme 7).

The C^2 and C^4 signals in the ^{13}C NMR spectra of regioisomers **XVIII/XIX** and **XX/XXI** were fairly characteristic. The chemical shifts of the carbonyl carbon atom in compounds **XVIII** and **XX** range from δ_C 170 to 173 ppm, and the signal from the spirocarbon atom appears at about δ_C 100 ppm, while the corresponding signals in the spectra of **XIX** and **XXI** are located at δ_C ~158 (C=O) and 79–83 ppm (C^4).

Table 1 contains the yields of the isolated products, their ratios in the reaction mixture before hydrolysis over silica gel (according to the ^1H NMR data), and ratios of the cycloaddition products at the C=O bond of the aldehyde and at the C=N bond of initial imine **Ia**. These data indicate that benzaldehyde is more reactive toward ylide **IIa** than acetaldehyde. In both cases, the cycloaddition is characterized by low regioselectivity, but the results are the opposite: the major product in

Scheme 7.



Ia **IIa** **XVIII**, **XX**, **XXII** **XIX**, **XXI**, **XXIII**

XVIII, **XIX**, R = H, R' = Me; **XX**, **XXI**, R = H, R' = Ph; **XXII**, **XXIII**, RR' = biphenyl-2,2'-diyl.

the reaction with acetaldehyde is imidazolidin-4-one **XVIII**, while in the reaction with benzaldehyde, imidazolidin-2-one **XXI** is mainly formed. Analogous cycloadditions of difluoro ylides **IV** to acetaldehyde and benzaldehyde occur strictly regioselectively, yielding exclusively imidazolidin-4-one derivatives as a result of hydrolysis of initially formed 4,4-difluoroimidazolidines [13]. Thus, incorporation of the ylide carbon atom into the fluorene system changes the regioselectivity in favor of the 2,2-difluoro-substituted cycloaddition product.

Unlike acetaldehyde and benzaldehyde, the cycloaddition of ylide **IIa** to fluorenone was regioselective, and the major product was 2,2-difluoro derivative whose hydrolysis gave oxazolidin-2-one **XXIII**. Apart from compound **XXIII**, we isolated imidazolidinone **Va**, the product of ylide addition at the C=N bond of the initial imine. The lack of published data on analogous reactions of fluorenone with fluorine-containing ylides **IV** having no fluorene fragment does not allow us estimate the effect of the aromatic fluorene system on the regioselectivity of cycloaddition. Therefore, we examined reactions of fluorenone with *C*-phenyl and *C*,*C*-diphenyl ylides **XXIV** and **XXV** derived from Schiff bases **XXVI** and **XXVII**. In the reaction mixtures obtained from compounds **XXVI** and **XXVII**, difluorocarbene (CF_2Br_2–Pb–Bu_4NBr–CH_2Cl_2, ultrasonic activation), and fluorenone we detected by NMR spectroscopy only the corresponding oxazolidin-2-ones **XXVIII** and **XXIX** (Scheme 8). The products were isolated by column chromatography in 24 and 8% yield, respectively.

Thus, phenyl- and diphenylmethylideneammonio(difluoromethanides) add at both aldehyde and fluorenone carbonyl groups to give exclusively the corresponding 4,4-difluorooxazolidinones; this means that the main factor determining the regioselectivity in the addition of ylide **IIa** to fluorenone and *N*-methylfluorenimine is either orbital–charge parameters of the ylide itself or π-stacking of the fluorene systems in the reacting molecules.

Table 1. Preparative yields and product ratios in the reactions of imine **Ia** with difluorocarbene in the presence of acetaldehyde, benzaldehyde, and fluorenone

Comp. no.	Yield, %	Product ratio[a]	C=O-to-C=N-Adduct ratio
Reaction with acetaldehyde			
XVIII	6	**XVIII**:**XIX**:**Va** 1:0.61:1.08	1.5:1
XIX	9		
Va	17		
Reaction with benzaldehyde[b]			
XX	11	**XX**:**XXI**:**Va** 1:2.3:0.67	4.9:1
XXI	13		
Va	18		
Reaction with fluorenone			
XXII	0		
XXIII	39		
Va	21		

[a] According to the ^{1}H NMR data.
[b] Overall yield of isomers **XX** and **XXI** (before separation) 37%.

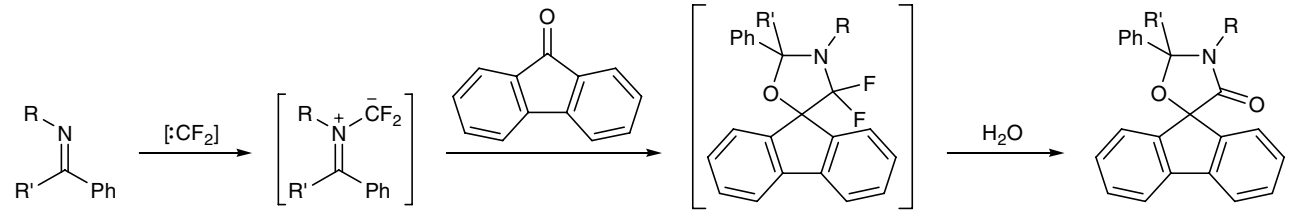
In order to substantiate the above conclusions concerning the effects of steric interactions and π-stacking between the dipole and dipolarophile on the regioselectivity of cycloaddition, we performed quantum-chemical calculations of the charge and orbital parameters of the reactants in terms of the density functional theory (DFT) at the local level of the hard and soft acids and bases (HSAB) principle [14, 15].

According to the DFT method, change in the total energy of a reacting system in going from the initial to transition state is estimated as

$$\partial E = \mu \partial N + \int \rho(r) \delta v(r) \partial r,$$

where μ, ρ(*r*), and ν(*r*) are, respectively, the electronic chemical potential, electron density, and external potential of a system. Electronic chemical potential

Scheme 8.



XXVI, **XXVII** **XXIV**, **XXV** **XXVIII**, **XXIX**

XXIV, **XXVI**, **XXVIII**, R = $PhCH_2$, R' = H; **XXV**, **XXVII**, **XXIX**, R = $PhCH_2CH_2$, R' = Ph.

characterizes the ability of a system to transfer a charge. The first partial derivative of the chemical potential μ with respect to all electrons is the global chemical hardness η, i.e., the resistance of a molecule to charge variation. The global hardness is related to the global softness *S* of a molecule as follows:

$$\eta = 1/2S.$$

The η and *S* values were determined by the finite difference approximation, according to which the quantities η and μ are defined as

$$\eta = \varepsilon_{LUMO} - \varepsilon_{HOMO};$$
$$\mu = (\varepsilon_{LUMO} + \varepsilon_{HOMO})/2.$$

Here, ε_{LUMO} and ε_{HOMO} are the energies of the lowest unoccupied and highest occupied orbitals of the reacting molecules, respectively. In order to pass to local softness of a reaction center, electronic Fukui functions $f(r)$ are used as reaction descriptors which reflect local changes in the electron density upon variation of the number of electrons in the system. According to Yang and Mortier, a local Fukui function for a *k*th atom is defined as

$$f_k^+ = n_k^{N+1} - n_k^N \text{ for nucleophilic attack;}$$
$$f_k^- = n_k^N - n_k^{N-1} \text{ for electrophilic attack;}$$
$$\text{and } f_k^0 = n_k^{N+1} - n_k^{N-1} \text{ for radical attack.}$$

Here, n_k^X is the electron population of a *k*th atom of a molecule containing *X* electrons (it is calculated by the formula $n = N - q$, where *N* is the number of electrons in the given atom, and *q* is its charge). Correspondingly, the local softnesses of a *k*th atom toward nucleophilic (s_k^+), electrophilic (s_k^-), and radical attacks (s_k^0) are calculated by the formulas $s_k^+ = Sf_k^+$, $s_k^- = Sf_k^-$, and $s_k^0 = Sf_k^0$, respectively.

The observed regioselectivity is treated by considering both reagents (ylide and dipolarophile) to be nucleophile and electrophile. According to Chandra and Nguyen [16], the most favorable pathway of cycloaddition of molecule **A** (reaction centers *i* and *j*) to molecule **B** (reaction centers *k* and *l*) may be determined on the basis of the quantity

$$\Delta_{ij}^{kl} = (s_i - s_k)^2 + (s_j - s_l)^2;$$

its lowest value corresponds to the most favorable approach of the reactants. As follows from this equation, the parameter Δ_{ij}^{kl} attains its lowest value when the bond-forming reaction centers are characterized by maximally close local softnesses.

As applied to the reaction of fluoro ylides with C=N-containing dipolarophiles and (taking into account nucleophilic character of the ylide, i.e., using local softnesses toward electrophilic attack s_k^- for the ylide reaction centers and those toward nucleophilic attack s_k^+ for the dipolarophile reaction centers), the following two expressions may be written for the two versions of mutual dipole–imine orientations shown in Scheme 9:

$$\Delta^I = (s_1^- - s_3^+)^2 + (s_2^- - s_4^+)^2;$$
$$\Delta^{II} = (s_1^- - s_4^+)^2 + (s_2^- - s_3^+)^2.$$

The geometric parameters of acetaldehyde, benzaldehyde, fluorenone, Schiff base **Ia**, and ylides **IIa**, **IV** and their orbital energies were calculated by the DFT B3LYP/6-31G* procedure included into GAUSSIAN 03 software package [17]. The atom populations were determined by DFT B3LYP/6-31G* in terms of the Merz–Kollman scheme. Table 2 contains the calculated energies of the highest occupied (ε_{HOMO}) and lowest unocupied (ε_{LUMO}) molecular orbitals, electronic chemical potential (μ), chemical hardnesses (η), global softnesses (*S*), charges on atoms (q, q^{N+1}, q^{N-1}), local Fukui functions (f^+, f^-), and local softnesses of the reaction centers (s^+, s^-) in the above species. The Δ^I and Δ^{II} values for the two reactant approaches in the cycloadditions of ylides **IIa** and **IV** to C=O and C=N-containing dipolarophiles are shown in Scheme 10. The results of calculation of the regioselectivity of the processes under study define orbital and charge requirements to the orientation of reacting molecules with no account taken of steric factors and π-stacking between structural fragments. In this case, the following conclusions can be drawn from the calculated values of Δ (Scheme 10). Fluoreniminium ylide **IIa** should react with all the examined C=O and C=N dipolarophiles (acetaldehyde, benzaldehyde, fluorenone, and *N*-methylfluorenimine) to give 2,2-difluoro-substituted cycloadduct as a result of attack by the hetero-

Scheme 9.

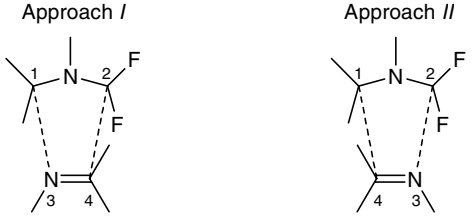
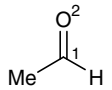
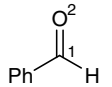
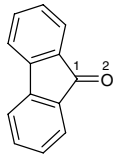
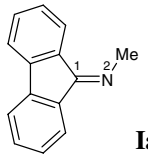
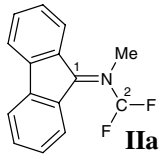
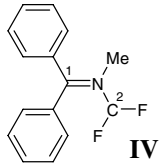


Table 2. Calculated orbital energies, electronic chemical potentials (μ), chemical hardnesses (η), global softnesses (*S*), charges on atoms, local Fukui functions (f^+, f^-) and local softnesses (s^+, s^-) of the reaction centers in acetaldehyde, benzaldehyde, fluorenone, imine **Ia**, and ylides **IIa** and **IV**

Reactant	ε_{HOMO}[a]	ε_{LUMO}[a]	μ	η	*S*	Atom	*q*	q^{N+1}	q^{N-1}	f^+	f^-	s^+	s^-
	–0.2550 (12)	–0.0274 (13)	–0.1412	0.2276	2.19	C^1	0.5337	0.0655		0.4682		1.0253	
						O^2	–0.4432	–0.6552		0.2120		0.4643	
	–0.2552 (28)	–0.0629 (29)	–0.1591	0.1923	2.60	C^1	0.3662	0.1673		0.1989		0.5172	
						O^2	–0.3975	–0.5331		0.1357		0.3527	
	–0.2290 (47)	–0.0823 (48)	–0.1557	0.1467	3.41	C^1	0.4417	0.2885		0.1533		0.5227	
						O^2	–0.4304	–0.5640		0.1336		0.4554	
 **Ia**	–0.2190 (51)	–0.0661 (52)	–0.1426	0.1529	3.27	C^1	0.4440	0.2630		0.1811		0.5921	
						N^2	–0.4510	–0.5537		0.1026		0.3356	
 **IIa**	–0.1698 (63)	–0.0738 (64)	–0.1218	0.0960	5.21	C^1	–0.4037		–0.0509		0.3528		1.8381
						C^2	0.0500		0.3104		0.2605		1.3570
 **IV**	–0.1650 (64)	–0.0661 (65)	–0.1155	0.0989	5.05	C^1	–0.2054		0.0085		0.2139		1.0803
						C^2	–0.0761		0.2418		0.3179		1.6054

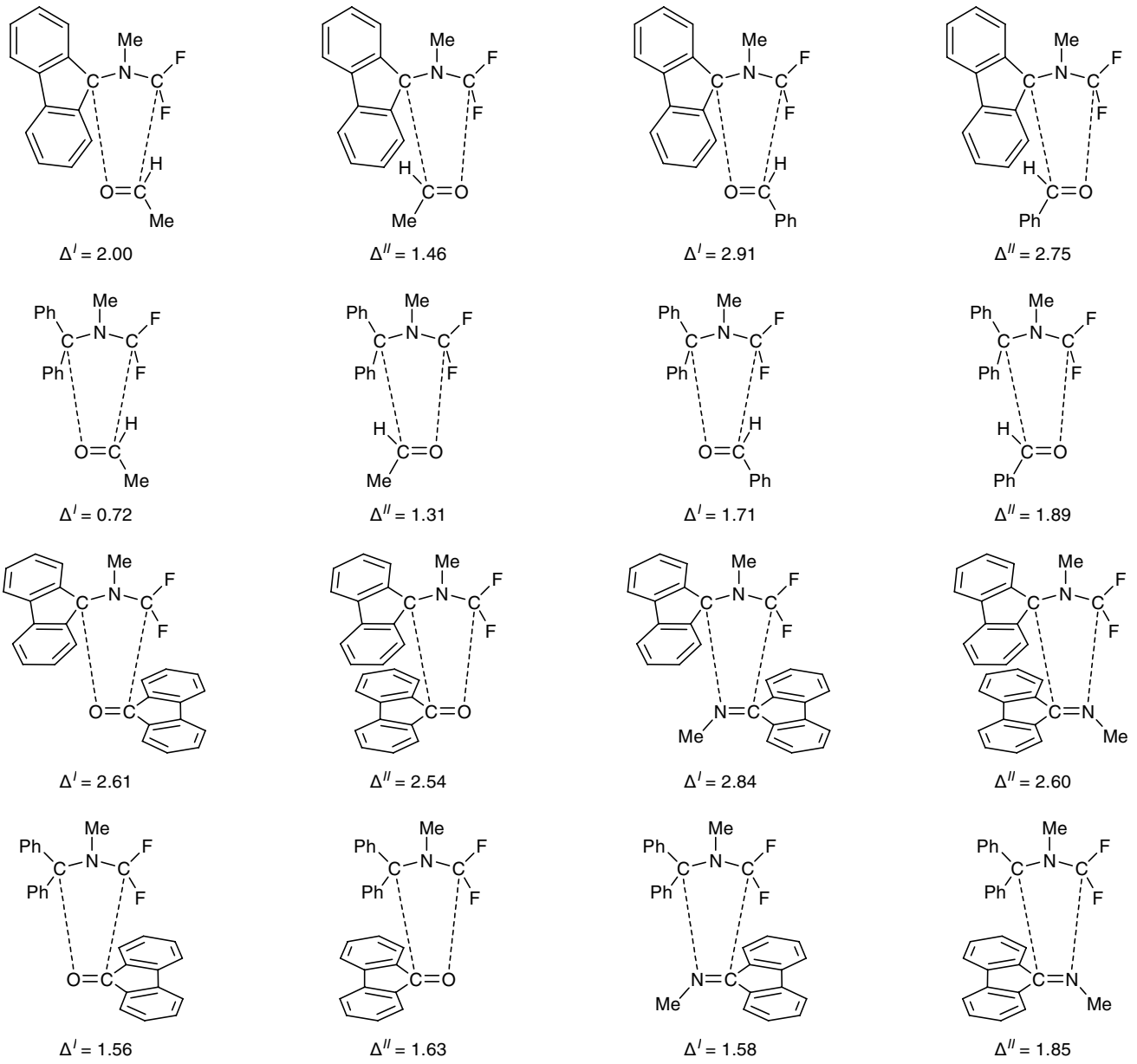
[a] The orbital number is given in parentheses.

atom in the dipolarophile by the CF_2 group of the dipole. Benzophenone imine ylide **IV** in all cases should give rise to cycloadduct resulting from the opposite reactant orientation (4,4-difluoro-substituted derivative). As follows from the data in Table 2, the reason is variation of the relative local softnesses of the carbon reaction centers in the dipole in going from ylide **IIa** to **IV**: the softest reaction center in the former is the fluorene carbon atom, while in the latter, the CF_2 carbon atom. The results of calculations are consistent with the experimental data. All the examined reactions of benzophenone imine ylides lead to the formation of only 4,4-difluoro derivatives [13], whereas cycloadditions of fluoreniminium ylides to fluorenone and *N*-methylfluorenimine give exclusively the corresponding 2,2-difluoro isomers (Table 1).

The reactions of fluorenimine ylide **IIa** with acetaldehyde and benzaldehyde constitute a specific case. The calculations predict preferential formation of the 2,2-difluoro cycloadduct. In keeping with the experimental data, an appreciable amount of the second isomer (which is less favorable from the viewpoint of charge and orbital parameters) is formed in both cases, though it is not the major product in the reaction with benzaldehyde. Nevertheless, these data suggest that steric repulsion between the substituent in the dipolarophile (in our case, methyl or phenyl group) and fluorene system of the ylide should necessarily be taken into account while predicting the result of such reactions (according to the calculations, the fluorene fragment is turned through an angle of 42° with respect to the dipole C–N–CF_2 plane). Therefore, sterically preferred 4,4-difluoro isomer is formed, although it is less favorable from the viewpoint of charge–orbital control.

Thus the chemical behavior of iminium ylides generated by reaction of N-substituted fluorenone imines with difluorocarbene in the absence of active

Scheme 10.



dipolarophiles is determined by the nature of the N-substituent and reaction conditions. *N*-Ethyl, *N*-benzyl, and *N*-(2-phenylethyl) ylides are converted in poor yields into the corresponding cyclodimerization products and/or 9*H*-fluoren-9-carboxamides. N-Methyl-substituted ylide readily adds at the C=N bond of the parent *N*-methylfluorenimine to give imidazolidine derivative, while in the presence of fluorenone, acetaldehyde, or benzaldehyde, oxazolidine derivatives are formed. The regioselectivity in the cycloaddition of fluoreniminium ylides at a double carbon–heteroelement bond corresponds to that predicted on the basis of the local hard and soft acids and bases concept implying preferential formation of the 2,2-difluoro-substituted cycloadduct. In terms of this theoretical model, it is impossible to take into account an additional regiocontrolling factor, π-stacking between the fluorene fragments of the reactants, for it acts in the same direction as orbital–charge requirements to the reaction centers in the reacting molecules.

EXPERIMENTAL

The melting points were determined on a Boetius microscope melting point apparatus; uncorrected values are given. The IR spectra were recorded on

a Carl Zeiss UR-20 instrument using 400-μm cells. The NMR spectra were measured on a Bruker DPX-300 instrument at 300 MHz for ^{1}H and 75 MHz for ^{13}C. The mass spectra (electron impact, 70 eV) were obtained on an MKh-1303 mass spectrometer. The elemental compositions were determined on an HP-185B CHN analyzer. The progress of reactions was monitored by TLC on Silufol-254 plates. The reaction mixtures were separated by column chromatography on silica gel LS (5–40 μm, Chemapol).

Compounds **Ia**–**If** were synthesized by the procedure reported in [18]. Active lead was prepared according to [6].

General procedure for reactions of N-substituted fluorenimines with difluorocarbene. A one-necked flask containing 1.86 g (9.0 mmol) of active lead (method *a*) or freshly prepared lead powder (method *b*) was filled with argon and charged in succession with 25 ml of anhydrous methylene chloride, 3.0 mmol of the corresponding Schiff base, 2–6 equiv of carbonyl compound (if the reaction was carried out in the presence of a carbonyl-containing dipolarophile), and 3.6 g (11.3 mmol) of tetrabutylammonium bromide. The mixture was cooled to 10°C, 1.2 ml (12.6 mmol) of dibromodifluoromethane was added, the flask was tightly capped, the mixture was stirred at 40°C until lead disappeared completely, 7.2 g of silica gel LS (40–100 μm, Chemapol) was added, the mixture was evaporated to dryness under reduced pressure, the residue was applied to the top of a chromatographic column charged with silica gel LS (5–40 μm, Chemapol), and the column was eluted with hexane–ethyl acetate.

1',3'-Dimethyl-9*H*,9''*H*-dispiro[fluorene-9,4'-imidazolidine-5',9''-fluoren]-2'-one (Va) and 1,4-dimethyl-9*H*,9''*H*-dispiro[fluorene-9,5'-piperazine-6',9''-fluoren]-2',3'-dione (VIIa) were obtained together with bifluorenylidene (**VI**) from 0.375 g (1.9 mmol) of compound (**Ia**) (method *b*; reaction time 32 h; eluent hexane–CH_2Cl_2).

Compound **Va**. Yield 0.129 g (32%), mp 307–309°C (from EtOAc–CH_2Cl_2). IR spectrum ($CHCl_3$): ν 1695 cm^{-1} (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 s (6H, CH_3), 7.03–7.36 m (16H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.5 (CH_3); 78.3 (C^4, C^5); 119.9, 125.7, 126.3, 129.2, 141.1, 141.5 (C_{arom}); 163.9 (C=O). Found, %: C 78.00; H 5.33; N 6.77. $C_{29}H_{22}N_2O$. Calculated, %: C 78.03; H 5.35; N 6.76.

Compound **VI**. Yield 0.102 g (32%), red crystals, mp 187–189°C (from CH_2Cl_2–Et_2O); published data [7]: mp 190–192°C [7]). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.24 t (4H, H_{arom}, J = 7.7 Hz), 7.36 t (4H, H_{arom}, J = 7.7 Hz), 7.73 d (4H, H_{arom}, J = 7.7 Hz), 8.42 d (4H, H_{arom}, J = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 119.9, 126.8, 129.1, 138.2, 141.0, 141.3. Mass spectrum, m/z (I_{rel}, %): 329 (28) $[M + 1]^+$, 328 (100) $[M]^+$, 327 (67), 326 (39), 164 (15). Found, %: C 95.02; H 4.89. $C_{26}H_{16}$. Calculated, %: C 95.09; H 4.91.

Compound **VIIa**. Yield 0.04 g (9%), mp 320–322°C (from EtOAc–CH_2Cl_2). IR spectrum ($CHCl_3$): ν 1685 cm^{-1} (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.60 (6H, CH_3), 5.80 d (2H, H_{arom}, J = 7.7 Hz), 6.70 t (2H, H_{arom}, J = 7.7 Hz), 7.09 t (2H, H_{arom}, J = 7.7 Hz), 7.24–7.52 m (8H, H_{arom}), 7.69 d (2H, H_{arom}, J = 7.7 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 31.7 (NCH_3); 75.6 (C^5, C^6); 119.4, 120.1, 125.1, 125.4, 126.4, 128.1, 129.5, 130.3, 138.8, 140.8, 141.8, 143.0 (C_{arom}); 159.1 (C=O). Mass spectrum, m/z (I_{rel}, %): 444 (3) $[M + 2]^+$, 443 (26) $[M + 1]^+$, 442 (72) $[M]^+$, 206 (19), 193 (100), 192 (47), 165 (54). Found, %: C 81.39; H 4.97; N 6.27. $C_{30}H_{22}N_2O_2$. Calculated, %: C 81.43; H 5.01; N 6.33. X-Ray diffraction data: $C_{30}H_{22}N_2O_2$; M 442.50; triclinic crystal system; a = 8.9912(18), b = 15.809(3), c = 16.898(3) Å; α = 112.93 (3), β = 90.06(3), γ = 90.12(3)°; V = 2212.1(8) Å^3; d = 1.329 g/cm^3; space group $P1$; Z = 4; MoK_α irradiation, λ = 0.71073 Å, temperature 133 K; R_{All} = 0.0964, wR_2 = 0.0931; total reflection number 11786, 6830 independent reflections (R_{int} = 0.0763).

Following method *a* (reaction time 18 h), from 0.68 g of compound **Ia** we isolated using hexane–ethyl acetate (3:1 to 1:2) as eluent 0.596 g (82%) of **Va** and 0.002 g (0.3%) of **VIIa**.

1,4-Diethyl-9*H*,9''*H*-dispiro[fluorene-9,5'-piperazine-6',9''-fluorene]-2',3'-dione (VIIb) and 9-bromo-*N*-ethyl-9*H*-fluorene-9-carboxamide (XIII) were obtained from 0.52 g of compound **Ib** (method *b*; reaction time 24 h; eluent hexane–ethyl acetate, 20:1 to 1:3).

Compound **VIIb**. Yield 0.004 g (0.7%), mp 232–236°C (from ethyl acetate). IR spectrum ($CHCl_3$): ν 1700 cm^{-1} (C=O). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.76 t (6H, CH_3, J = 7.3 Hz), 3.03–3.18 m (4H, CH_2), 5.78 d (2H, H_{arom}, J = 8.0 Hz), 6.68 t (2H, H_{arom}, J = 8.0 Hz), 7.08 t (2H, H_{arom}, J = 8.0 Hz), 7.24–7.53 m (8H, H_{arom}), 7.70 d (2H, H_{arom}, J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.8, 41.0, 75.9 (C^5, C^6); 119.0, 120.1, 125.3, 125.4, 126.2, 128.0, 129.5, 130.1, 138.5, 140.9, 141.3, 144.3 (C_{arom}); 158.8

(C^2, C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 472 (3.6) $[M + 2]^+$, 471 (17) $[M + 1]^+$, 470 (47) $[M]^+$, 443 (13), 442 (19) $[M - CO]^+$, 206 (100), 182 (74).

Compound **XIII**. Yield 0.062 g (8%), mp 149–150°C (from Et_2O). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1695 (C=O), 3430 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.09 t (3H, CH_3, J = 7.3 Hz), 3.21–3.31 m (2H, CH_2), 6.11 br.s (1H, NH), 7.36–7.48 m (4H, H_{arom}), 7.69–7.78 m (4H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.4 (CH_3); 35.5 (CH_2); 62.8 (C^9); 120.6, 125.9, 128.7, 129.9, 139.3, 144.9 (C_{arom}); 166.9 (C=O). Found, %: C 60.77; H 4.58; N 4.20. $C_{16}H_{14}BrNO$. Calculated, %: C 60.78; H 4.46; N 4.43.

Following method *a* (reaction time 30 h), from 1 g (4.82 mmol) of Schiff base **Ib** we obtained 0.015 g (1.3%) of piperazine derivative **VIIb**.

9*H*-Fluorene-9-carboxamide (XII) was obtained from 0.7 g (2.60 mmol) of compound **Ic** (method *a*; reaction time 25 h; eluent hexane–EtOAc, 9:1). Yield 0.002 g (0.4%), mp 156–158°C; published data [19]: mp 157–158°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.81 s (1H, 9-H), 5.19 br.s (2H, NH_2), 7.36–7.50 m (4H, H_{arom}), 7.74 d (2H, H_{arom}, J = 7.3 Hz), 7.81 d (2H, H_{arom}, J = 7.3 Hz). Mass spectrum, *m*/*z* (I_{rel}, %): 209 (27) $[M]^+$, 166 (98) $[C_{13}H_{10}]^+$, 165 (100) $[C_{13}H_9]^+$.

***N*-(2-Phenylethyl)-9*H*-fluorene-9-carboxamide (XI)** was obtained from 0.71 g (2.5 mmol) of compound **Id** (method *a*; reaction time 70 h; eluent hexane–EtOAc, 1:1). Yield 0.015 g (2%), mp 188–191°C (from EtOAc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.68 t (2H, PhC**H**$_2$, J = 6.5 Hz), 3.35–3.42 q (2H, NCH_2, J = 6.5 Hz), 4.80 s (1H, 9-H), 5.21 br.s (1H, NH), 6.91–6.92 m (2H, H_{arom}), 7.16–7.18 m (3H, H_{arom}), 7.34 t (2H, H_{arom}), 7.45 t (2H, H_{arom}), 7.62 d (2H, H_{arom}, J = 7.3 Hz), 7.78 d (2H, H_{arom}, J = 7.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 35.2 (Ph**C**H_2); 40.7 (NCH_2); 56.1 (C^9); 120.2, 125.4, 126.3, 127.7, 128.3, 128.5, 128.7, 138.5, 141.3, 141.4 (C_{arom}); 170.5 (C=O). Mass spectrum, *m*/*z* (I_{rel}, %): 313 (14) $[M]^+$, 209 (3), 166 (100) $[C_{13}H_{10}]^+$, 165 (87) $[C_{13}H_9]^+$, 105 (50) $[PhCHCH_3]^+$.

***N*-{5',5'-Difluoro-1'-(2-phenylethyl)-9*H*,9''*H*-dispiro[fluorene-9,3'-pyrrolidine-4',9''-fluoren]-2'-ylidene}-2-phenylethanamine (XIV)** was obtained from 1.14 g (4.02 mmol) of compound **Id** (method *b*; reaction time 9 h; eluent hexane–ethyl acetate, 1:3 to 2:1). Yield 0.130 g (10%), mp 168–169°C (from EtOAc–Et_2O). IR spectrum ($CHCl_3$): ν 1695 cm^{-1} (C=N). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.48 t (2H, PhC**H**$_2$, J = 6.8 Hz), 2.72 t (2H, PhC**H**$_2$, J = 6.8 Hz), 3.34 d.d (2H, NCH_2, J = 7.5, 8.4 Hz), 4.09 d.d (2H, NCH_2, J = 7.5, 8.4 Hz), 6.75–6.76 m (2H, H_{arom}), 6.97–7.43 m (24H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.8 (Ph**C**H_2); 37.6 (Ph**C**H_2); 41.8 (NCH_2); 49.9 (NCH_2); 64.9 ($C^{3'}$); 67.2 t ($C^{4'}$, J_{CF} = 22.9 Hz); 119.5, 119.6, 125.5, 126.0, 126.1 (C_{arom}); 126.3 t ($C^{5'}$, J_{CF} = 248.8 Hz); 126.3, 126.4, 126.6, 127.8, 128.3, 128.5, 128.6, 128.7, 129.0, 139.2, 140.2, 140.4, 140.9, 141.4, 142.7 (C_{arom}); 154.6 (C=N). Mass spectrum, *m*/*z* (I_{rel}, %): 630 (3) $[M + 2]^+$, 629 (12), $[M + 1]^+$, 628 (23) $[M]^+$, 538 (10), 537 (22), 524 (17) $[M - PhCH_2CH_2]^+$, 421 (32), 420 (100) $[M - 2PhCH_2CH_2]^+$, 205 (7), 105 (95) $[PhCHCH_3]^+$. Found, %: C 84.03; H 5.45; N 4.53. $C_{44}H_{34}F_2N_2$. Calculated, %: C 84.05; H 5.45; N 4.46.

3,5-Dimethyl-9'*H*-spiro[oxazolidine-2,9'-fluoren]-4-one (XVIII) and 3,5-dimethyl-9'*H*-spiro[oxazolidine-4,9'-fluoren]-2-one (XIX). The reaction was performed with 0.9 g (4.66 mmol) of compound **Ia** and 1.5 ml (26.8 mmol) of acetaldehyde according to method *a* (rection time 6 h); column chromatography using hexane–ethyl acetate (25:1 to 3:1) as eluent gave 0.204 g (17%) of compound **Va**), 0.072 g (6%) of **XVIII**, and 0.084 g (9%) of **XIX**.

Compound **XVIII**. mp 156–158°C (from Et_2O). IR spectrum ($CHCl_3$): ν 1725 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.66 d (3H, CH_3, J = 6.0 Hz), 2.47 s (3H, NCH_3), 4.90 q (1H, 5-H, J = 6.0 Hz), 7.32–7.66 m (8H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.2 (CH_3); 25.3 (NCH_3); 74.2 (C^5); 99.7 (C^2); 120.3, 120.4, 123.5, 124.2, 128.6, 128.7, 130.8, 131.1, 139.8, 140.4, 141.6, 142.3 (C_{arom}); 172.5 (C=O). Found, %: C 76.68; H 5.63; N 5.38. $C_{17}H_{15}NO_2$. Calculated, %: C 76.96; H 5.70; N 5.28.

Compound **XIX**. IR spectrum ($CHCl_3$): ν 1780 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.98 d (3H, CH_3, J = 6.3 Hz), 2.39 s (3H, CH_3), 4.91 q (1H, 5-H, J = 6.3 Hz), 7.34–7.72 m (8H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.8 (CH_3); 27.0 (NCH_3); 75.2 (C^5); 79.2 (C^4); 120.4, 120.6, 124.0, 125.1, 127.8, 128.3, 129.8, 130.1, 140.3, 140.9, 141.8 (C_{arom}); 158.6 (C=O).

3-Methyl-5-phenyl-9'*H*-spiro[oxazolidine-2,9'-fluoren]-4-on (XX) and 3-methyl-5-phenyl-9'*H*-spiro[oxazolidine-4,9'-fluoren]-2-one (XXI). The reaction was performed with 0.9 g (4.66 mmol) of compound **Ia** and 1 ml (9.84 mmol) of benzaldehyde according to method *a* (reaction time 6 h); column chromatography using hexane–ethyl acetate (50:1 to 3:1) gave 0.217 g (18%) of imidazolidinone **Va** and 0.561 g (37%) of a mixture of compounds **XX** and

XXI, which were separated by fractional crystallization to isolate 0.174 g (11%) of **XX** and 0.204 g (13%) of **XXI**.

Compound **XX**. mp 150–152°C (from Et_2O). IR spectrum (CCl_4): ν 1740 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.53 s (3H, CH_3), 5.81 s (1H, 5-H), 7.31–7.69 m (13H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 25.6 (CH_3); 78.6, 100.0, 120.4, 120.5, 123. 6, 124.8, 126.2, 128.4, 128.5, 128.6, 128.7, 131.0, 131.2, 136.5, 139.9, 140.6, 141.3, 142.2 (C_{arom}); 170.2 (C=O). Found, %: C 80.73; H 5.27; N 4.19. $C_{22}H_{17}NO_2$. Calculated, %: C 80.71; H 5.23; N 4.28.

Compound **XXI**. mp 152–153°C (from Et_2O–CH_2Cl_2). IR spectrum (CCl_4): ν 1780 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.45 s (3H, CH_3), 5.95 s (1H, 5-H), 6.83–7.72 m (13H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 27.1 (CH_3); 75.9, 83.5, 120.0, 120.5, 123.9, 124.6, 125.3, 127.4, 127.8, 127.9, 128.5, 129.4, 130.2, 134.2, 140.0, 141.1, 142.4 (C_{arom}); 158.3 (C=O). Found, %: C 80.68; H 5.27; N 4.33. $C_{22}H_{17}NO_2$. Calculated, %: C 80.71; H 5.23; N 4.28.

The product ratio in the reactions of Schiff base **Ia** with difluorocarbene in the presence of acetaldehyde and benzaldehyde was determined as follows. Silica gel, 5.6 g, was added to the reaction mixture obtained according to method *a* from 0.45 g (2.33 mmol) of compound **Ia** and 0.39 ml (7.0 mmol) of acetaldehyde or 0.71 ml (7.0 mmol) of benzaldehyde, the mixture was evaporated, the residue was held for 5 h on exposure to air and applied to the top of a chromatographic column charged with silica gel, the column was eluted with hexane–ethyl acetate (1:1), the eluate was evaporated under reduced pressure, and the residue was analyzed by ^1H NMR spectroscopy. The isomer ratio was calculated from the intensity of the NCH_3 signals.

1',3'-Dimethyl-9*H*,9''*H*-dispiro[fluorene-9,4'-oxazolidine-5',9''-fluoren]-2'-one (XXII). The reaction was performed with 0.45 g (2.3 mmol) of compound **Ia** and 1.25 g (6.9 mmol) of fluorenone according to method *a* (reaction time 40 h); by column chromatography using hexane–methylene chloride as eluent we isolated 0.36 g (39%) of compound **XXII**, 0.1 g (21%) of imidazolidinone **Va**, and 0.02 g (5%) of bifluorenylidene (**VI**).

Compound **XXII**. mp 269–272°C (from CH_2Cl_2–EtOAc). IR spectrum ($CHCl_3$): ν 1765 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.64 (3H, CH_3), 7.06–7.37 m (16H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 28.1 (CH_3); 79.3 (C^4); 92.2 (C^5); 119.9, 120.3, 125.5, 125.7. 126.8, 129.8, 130.1, 140.1, 140.6, 141.1, 141.3 (C_{arom}); 160.4 (C=O). Found, %: C 83.70; H 4.82; N 3.33. $C_{28}H_{19}NO_2$. Calculated, %: C 83.77; H 4.77; N 3.49.

3-Benzyl-2-phenyl-9'*H*-spiro[oxazolidine-5,9'-fluoren]-2-one (XXIV) was obtained from 0.7 g (3.58 mmol) of *N*-(benzylidene)phenylmethanamine (**XXVI**) according to method *a* (reaction time 20 h; eluent hexane–ethyl acetate). Yield 0.35 g (24%), mp 161–162°C (from Et_2O–CH_2Cl_2). IR spectrum (CCl_4): ν 1725 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.73 d (1H, CH_2, J = 14.5 Hz), 5.28 d (1H, CH_2, J = 14.5 Hz), 6.23 s (1H, 2-H), 7.23–7.57 (18H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 44.7 (CH_2); 88.9 (C^5); 89.7 (C^2); 120.4, 120.6, 123.6, 124.7, 127.8, 128.0, 128.2, 128.3, 128.7, 128.9, 129.1, 130.0, 130.2, 130.5, 135.7, 136.0, 141.0, 141.5, 142.6, 144.4 (C_{arom}); 170.8 (C=O). Found, %: C 83.45; H 5.28; N 3.46. $C_{28}H_{21}NO_2$. Calculated %: C 83.35; H 5.25; N 3.47.

2,2-Diphenyl-3-(2-phenylethyl)-9'*H*-spiro[oxazolidine-5,9'-fluoren]-2-one was obtained from 1.0 g (3.5 mmol) of *N*-(diphenylmethylidene)-2-phenylethanamine (**XXVII**) according to method *a* (reaction time 20 h; eluent hexane–ethyl acetate). Yield 0.14 g (8%), mp 236–237°C (from Et_2O–CH_2Cl_2). IR spectrum (CCl_4): ν 1730 cm^{-1} (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.35–2.41 m (2H, Ph**CH**$_2$), 3.92–3.98 m (2H, NCH_2), 6.93–7.69 m (23H, H_{arom}). ^3C NMR spectrum ($CDCl_3$), δ_C, ppm: 34.2 (Ph**C**H_2); 44.9 (NCH_2); 88.8 (C^5); 97.6 (C^2); 120.2, 124.9, 126.5, 127.8, 128.1, 128.4, 128.5, 128.7, 129.3, 129.8, 137.8, 141.3, 142.6, 143.7 (C_{arom}); 170.6 (C=O). Found, %: C 85.40; H 5.46; N 2.53. $C_{35}H_{27}NO_2$. Calculated, %: C 85.17; H 5.51; N 2.84.

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