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1,3-Dipolar Cycloaddition of Fluorinated Azomethine Ylides at the C=N Bond

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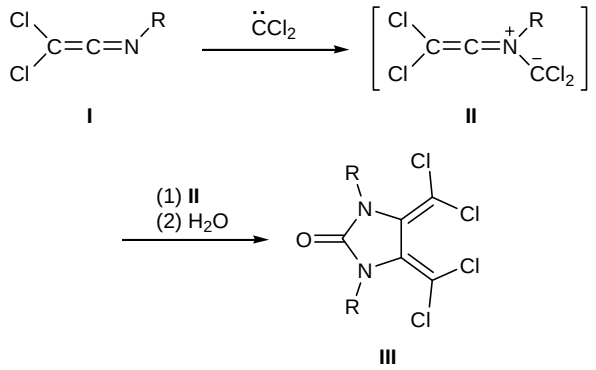
Abstract—Azomethine ylides generated by reaction of difluorocarbene with *N*-alkyl- and *N*-arylimines derived from benzaldehyde and benzophenone react with *N*-benzylidenebenzenesulfonamide in a regioselective fashion, yielding the corresponding imidazolidin-4-ones via 1,3-dipolar cycloaddition at the C=N bond. Ylides generated from benzaldehyde imines give rise to mixtures of stereoisomeric 2,5-diphenyl-1-(phenylsulfonyl)-imidazolidin-4-ones, the *cis* isomer prevailing.

1,3-Dipolar cycloaddition reactions provide a convenient method for the synthesis of nitrogen-containing heterocycles [1]. Compounds of the imidazolidine series are obtained by cycloaddition of azomethine ylides generated by dehydrohalogenation of the corresponding iminium salts at the C=N bond of Schiff bases [2], azirines [2], and 3,4-dihydroisoquinolines [3, 4]. These reactions are convenient for the preparation of imidazolidinecarboxylic acid derivatives, for successful application of the "salt" procedure for generation of ylides requires the presence of a strong π-acceptor substituent at the ylide carbon atom. The only reported example of an alternative "carbene" technique of ylide generation is the synthesis of 1,3-dimethyl-2,4,5-triphenylimidazolidine from phenylcarbene and *N*-benzylidenemethylamine [5]. Functionally substituted imidazolidine derivatives (e.g., oxo and halo) can be prepared via 1,3-dipolar cycloaddition of azomethine ylides generated from dihalocarbenes and Schiff bases. We previously described the only example of addition of a halogen-substituted nitrogen ylide, keteniminiodichloromethanide **I**, at the C=N bond of dichloroketene imine **II**; the final product of this reaction was imidazolidinone **III** (Scheme 1) [6].

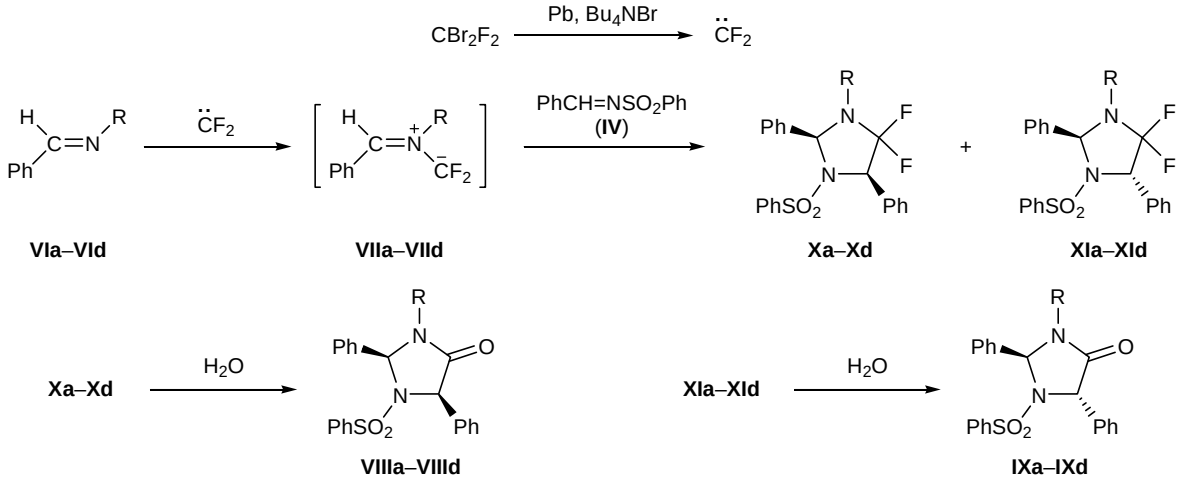
Scheme 1.



R = cyclohexyl.

In the present work we examined reactions of iminiodifluoromethanides, i.e., azomethine ylides generated from Schiff bases and difluorocarbene, with C=N-containing dipolarophiles. It is known that iminiodifluoromethanides prepared *in situ* via addition of difluorocarbene to *N*-alkyl and *N*-arylimines derived from benzaldehyde and benzophenone are readily involved in cycloaddition to electron-deficient alkenes [7, 8], alkynes [9], and aldehydes (at the carbonyl group) [10]. In none of the cases, products of addition of iminiodifluoromethanides at the C=N bond of the initial Schiff base were detected. No such products were formed in analogous reactions performed in the absence of dipolarophiles, which indicates that the C=N bond in Schiff bases $R^1N{=}CR^2R^3$ (where R^1 = alkyl, aryl; $R^2 = R^3$ = aryl or R^2 = aryl, R^3 = H) cannot act as dipolarophile with respect to difluoroazomethine ylides. On the other hand, *N*-alkylimines derived from benzaldehyde are known as fairly efficient traps for some halogen-free azomethine ylides [2, 4]. A probable reason for the inertness of the above imines with respect to difluoro-substituted ylides is low energy of the highest occupied molecular orbital (HOMO) of the

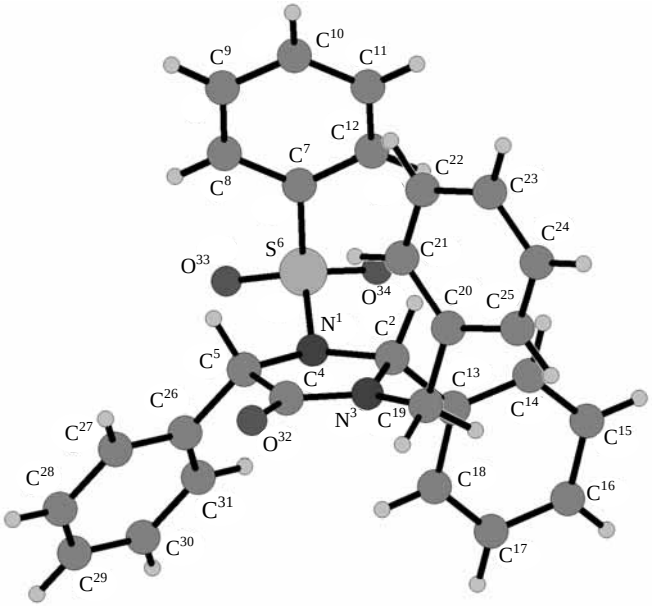
Scheme 2.



R = $PhCH_2$ (**a**), $PhCH_2CH_2$ (**b**), *cyclo*-C_6H_{11} (**c**), Ph (**d**).

dipole due to the presence of two fluorine atoms at one reaction center. Therefore, as potential dipolarophiles we selected electron-deficient Schiff bases PhCH=NSO_2Ph (**IV**) and Ph_2C=NC(O)Ph (**V**) which are characterized by relatively low energies of the lowest unoccupied molecular orbitals (LUMO).

We have found that Schiff bases **IV** and **V** do not react with difluorocarbene generated by reduction of dibromodifluoromethane with lead in the presence of tetrabutylammonium bromide. However, under conditions corresponding to generation of difluorocarbene, a mixture of Schiff bases **IV** and **VIa** gave rise to imidazolidinones **VIIIa** and **IXa** which were isolated by column chromatography in 20 and 18% yield, respectively. Mixtures of diastereoisomeric imidazolidinones **VIIIb**–**VIIId** and **IXb**–**IXd** were also obtained under analogous conditions from Schiff bases **VIb**–**VId**. Isomers **VIIIb**, **VIIIc**, **IXb**, and **IXc** were isolated as individual substances, while compounds **VIIId** and **IXd** were characterized by spectral data for their mixture.



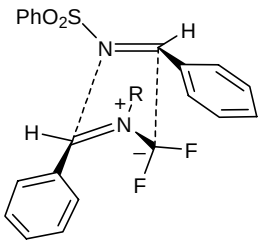
Structure of the molecule of (2*RS*,5*SR*)-3-benzyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**VIIIa**) according to the X-ray diffraction data.

Scheme 2 illustrates the transformation sequence leading to products **VIII** and **IX**. Difluorocarbene adds at the nitrogen atom of the more nucleophilic Schiff base (compound **VI**) to give iminiodifluoromethanide **VII**, and the latter adds in a regioselective fashion to electrophilic Schiff base **IV**. The primary addition products, difluoroimidazolidines **X** and **XI** could not be isolated, for they undergo fast hydrolysis to the corresponding imidazolidinones during chromatographic separation.

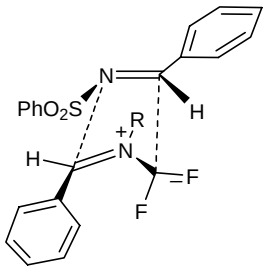
The structure of the products was determined on the basis of their ^{1}H and ^{13}C NMR and IR spectra and elemental analyses. In the ^{1}H NMR spectra of **VIII** and **IX**, signals from the 2-H and 5-H protons in the imidazole ring appeared at δ 5.19–5.50 and 5.83–6.77 ppm, respectively, as singlets for the *cis* isomers and doublets ($^4J_{2,5}$ = 2.0–2.4 Hz) for the *trans* isomers. This is consistent with the difference in the J_{cis} and J_{trans} values observed for *cis*- and *trans*-2,3-diaryl-3-alkyloxazolidin-4-ones: the *trans* coupling constants are larger than the *cis* coupling constants [10]. In the

^{13}C NMR spectra, the C^2 and C^5 signals of the *cis* isomers are displaced by 1 ppm upfield relative to the corresponding signals of the *trans* isomer. The structure of compound **VIIIa** was rigorously proved by the X-ray diffraction data, according to which the benzene rings in positions *2* and *5* of the imidazolidine ring are arranged *cis* (see figure; Tables 1, 2).

Poor preparative yields of imidazolidinones **VIII** and **IX** (Table 3) resulted from difficulties in their chromatographic separation; the isomeric products are poorly soluble and are characterized by similar R_f values. In order to estimate the product ratio and hence the stereoselectivity in the cycloaddition of azomethine ylides **VII** at the C=N bond, the reaction mixtures were subjected to hydrolysis on silica gel and were analyzed by ^1H NMR spectroscopy. We found that neither the reaction time nor the mode of treatment of the reaction mixture affects the ratio of stereoisomers **VIIIa**–**VIIId** and **IXa**–**IXd** (Table 3). In all cases, the major product is the corresponding *cis* isomer **VIII**. Taking into account that *E* isomers of Schiff bases derived from benzaldehyde are more stable, the azomethine ylide generated therefrom should have *Z* configuration. The observed *cis* stereoselectivity may be rationalized in terms of formation of more favorable transition state **A** which, in contrast to structure **B**, lacks steric interactions between the benzene ring of the dipole and the bulky phenylsulfonyl group in the dipolarophile.



A



B

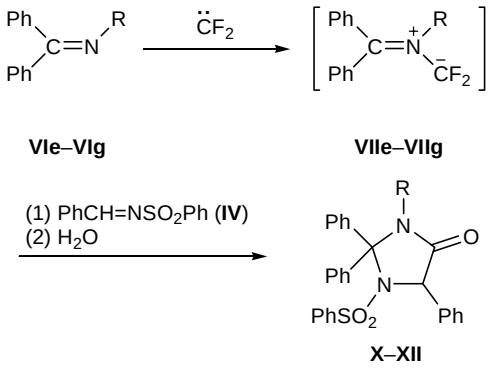
On the other hand, steric loading of the ylide via introduction of a second phenyl substituent to the C=N carbon atom does not hamper cycloaddition at the C=N bond of Schiff base **IV** derived from benzophenone. Iminiodifluoromethanides **VIIe**–**VIIg** generated from benzophenone imines **VIe**–**VIg** are also capable of reacting with Schiff base **IV** to afford imidazolidinones **X**–**XII** as final products (Scheme 3).

We also made an attempt to estimate the reactivity of the C=N bond in *N*-arylidenebenzenesulfonamides as dipolarophiles with respect to iminiodifluoromethanides. For this purpose, we performed a competing reaction of Schiff base **VIe** with difluorocarbene in the presence of equimolar amounts of *N*-benzylidenebenzenesulfonamide (**IV**) and fumarodinitrile (Scheme 4). We recently showed that fumarodinitrile acts as an efficient trap for difluoro ylides generated from difluorocarbene and N-alkyl-substituted aromatic ketone imines; the final products of these reactions were substituted 2-fluoro-4,5-dihydropyrrole-3,4-dicarbonitriles which were obtained in up to 84% yield [11]. Analysis of the reaction mixture (after filtration through a thin layer of silica gel to complete hydrolysis of the primary cycloaddition products) showed that compounds **X** and **XIII** were formed at a ratio of 2:3. This means that *N*-benzylidenebenzenesulfonamide (**IV**) is a less efficient dipole trap

Table 1. Principal bond lengths *d* in the molecule of (2*RS*,5*SR*)-3-benzyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**VIIIa**)

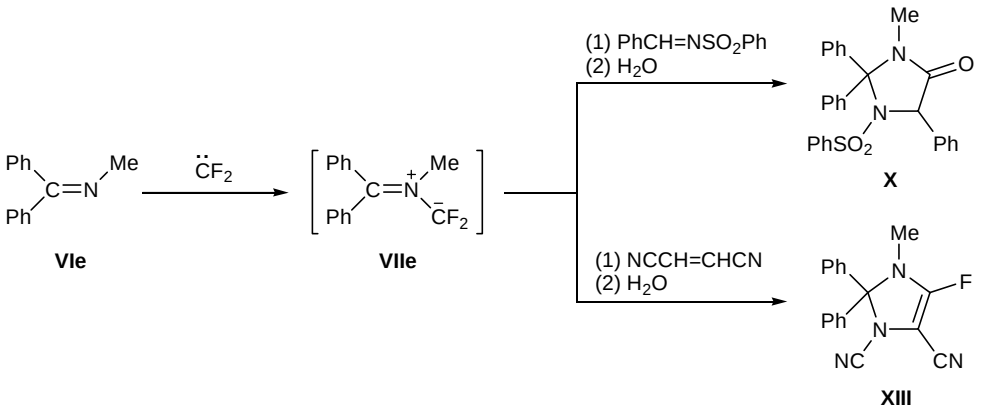
Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
S^6–O^{33}	1.427(1)	C^7–C^8	1.391(2)	C^{20}–C^{21}	1.387(2)
S^6–O^{34}	1.428(1)	C^7–C^{12}	1.394(2)	C^{20}–C^{25}	1.399(2)
S^6–N^1	1.653(1)	C^8–C^9	1.386(2)	C^{21}–C^{22}	1.390(2)
S^6–C^7	1.758(1)	C^9–C^{10}	1.385(2)	C^{22}–C^{23}	1.388(2)
O^{32}–C^4	1.217(1)	C^{10}–C^{11}	1.380(2)	C^{23}–C^{24}	1.386(2)
N^1–C^5	1.472(1)	C^{11}–C^{12}	1.389(2)	C^{24}–C^{25}	1.382(2)
N^1–C^2	1.492(1)	C^{13}–C^{18}	1.387(2)	C^{26}–C^{27}	1.395(2)
N^3–C^4	1.350(1)	C^{13}–C^{14}	1.389(2)	C^{26}–C^{31}	1.386(2)
N^3–C^{19}	1.454(2)	C^{14}–C^{15}	1.393(2)	C^{27}–C^{28}	1.386(2)
N^3–C^2	1.455(1)	C^{15}–C^{16}	1.383(2)	C^{28}–C^{29}	1.385(2)
C^2–C^{13}	1.512(1)	C^{16}–C^{17}	1.387(2)	C^{29}–C^{30}	1.381(2)
C^4–C^5	1.530(2)	C^{17}–C^{18}	1.388(2)	C^{30}–C^{31}	1.392(2)
C^5–C^{26}	1.517(2)	C^{19}–C^{20}	1.516(2)		

Scheme 3.



VIe, **VIIe**, **X**, R = Me; **VIf**, **VIIf**, **XI**, R = $PhCH_2$; **VIg**, **VIIg**, **XII**, R = $PhCH_2CH_2$.

Scheme 4.



for iminiodifluoromethanides than fumarodinitrile; therefore, it occupies an intermediate place in the reactivity series between maleic and fumaric acid derivatives having two activating groups at the double C=C bond and derivatives of acrylic acid which possess only one activating group.

Unlike *N*-benzylidenebenzenesulfonamide (**IV**), *N*-(diphenylmethylene)benzamide (**V**) showed no activity as dipolarophile toward ylides **VIIa**–**VIIg**.

Thus cycloaddition of iminiodifluoromethanides, generated from difluorocarbene and *N*-alkyl and *N*-aryl benzaldehyde and benzophenone imines, at the C=N bond of *N*-benzylidenebenzenesulfonamide occurs in a regioselective fashion, yielding the corresponding imidazolidine derivatives. Ylides generated from benzaldehyde imines give rise to formation of two possible stereoisomers, the *cis* isomer prevailing.

EXPERIMENTAL

The IR spectra were recorded from solutions in chloroform on a UR-20 spectrometer using 400-μm cells. The NMR spectra were measured on a Bruker

Table 2. Principal bond angles ω in the molecule of (2*RS*,5*SR*)-3-benzyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**VIIIa**)

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
$O^{32}C^{4}N^{3}$	126.59(10)	$S^{6}C^{7}C^{12}$	119.17(8)	$C^{14}C^{15}C^{16}$	119.84(13)
$O^{32}C^{4}C^{5}$	125.36(10)	$C^{2}N^{1}C^{5}$	111.45(8)	$C^{14}C^{13}C^{18}$	119.41(11)
$O^{33}S^{6}O^{34}$	121.55(4)	$C^{2}N^{3}C^{4}$	115.17(9)	$C^{15}C^{16}C^{17}$	120.01(12)
$O^{33}S^{6}N^{1}$	105.78(5)	$C^{2}N^{3}C^{19}$	121.04(8)	$C^{16}C^{17}C^{18}$	120.04(11)
$O^{33}S^{6}C^{7}$	108.72(5)	$C^{2}C^{13}C^{14}$	119.36(9)	$C^{19}C^{20}C^{21}$	123.3(1)
$O^{34}S^{6}N^{1}$	105.29(5)	$C^{2}C^{13}C^{18}$	121.22(10)	$C^{19}C^{20}C^{25}$	118.22(10)
$O^{34}S^{6}C^{7}$	108.35(5)	$C^{4}N^{3}C^{19}$	122.30(9)	$C^{20}C^{21}C^{22}$	120.98(11)
$N^{1}C^{2}N^{3}$	101.63(8)	$C^{4}C^{5}C^{26}$	111.22(8)	$C^{20}C^{25}C^{24}$	120.75(11)
$N^{1}S^{6}C^{7}$	106.12(5)	$C^{5}C^{26}C^{27}$	117.89(9)	$C^{21}C^{20}C^{25}$	118.4(1)
$N^{1}C^{2}C^{13}$	113.00(8)	$C^{5}C^{26}C^{31}$	122.68(10)	$C^{21}C^{22}C^{23}$	119.94(11)
$N^{1}C^{5}C^{4}$	103.00(8)	$C^{7}C^{8}C^{9}$	118.87(11)	$C^{22}C^{23}C^{24}$	119.55(12)
$N^{1}C^{5}C^{26}$	115.60(8)	$C^{7}C^{12}C^{11}$	118.71(11)	$C^{23}C^{24}C^{25}$	120.32(12)
$N^{3}C^{2}C^{13}$	113.94(8)	$C^{8}C^{7}C^{12}$	121.16(10)	$C^{26}C^{27}C^{28}$	120.3(1)
$N^{3}C^{4}C^{5}$	108.04(9)	$C^{10}C^{9}C^{8}$	120.44(12)	$C^{26}C^{31}C^{30}$	119.98(11)
$N^{3}C^{19}C^{20}$	113.72(9)	$C^{9}C^{10}C^{11}$	120.22(13)	$C^{27}C^{26}C^{31}$	119.4(1)
$S^{6}N^{1}C^{2}$	115.87(7)	$C^{10}C^{11}C^{12}$	120.51(12)	$C^{27}C^{28}C^{29}$	120.03(11)
$S^{6}N^{1}C^{5}$	117.81(7)	$C^{13}C^{14}C^{15}$	120.36(10)	$C^{28}C^{29}C^{30}$	119.86(12)
$S^{6}C^{7}C^{8}$	119.65(8)	$C^{13}C^{18}C^{17}$	120.34(11)	$C^{29}C^{30}C^{31}$	120.41(11)

Table 3. Reactions of difluorocarbene with Schiff bases **VIa**–**VId** in the presence of *N*-benzylidenebenzenesulfonamide (**IV**)

Schiff base	R	Reaction conditions[a]	Yield of **VIII**, %	Yield of **IX**, %	Ratio **VIII**–**IX** (^{1}H NMR data)
VIa	$PhCH_2$	*a*	20	18	3:2
VIb	$PhCH_2CH_2$	*b*	8	11	3:2
VIc	*cyclo*-C_6H_{11}	*a*	2	17	4:3
VId	Ph	*a*	17 (**VIIId** + **IXd**)		2:1
VId	Ph	*b*	24 (**VIIId** + **IXd**)		2:1

[a] *a*: Activated Pb/CF_2Br_2/Bu_4NBr/CH_2Cl_2; *b*: nonactivated Pb/CF_2Br_2/Bu_4NBr/CH_2Cl_2.

DPX 300 instrument at 300 MHz for ^{1}H and 75 MHz for ^{13}C. The elemental compositions were determined on an HP-185B CHN analyzer.

Methylene chloride was dried by distillation over P_2O_5. Tetrabutylammonium bromide (Merck) was kept for a week in a desiccator over P_2O_5. The progress of reactions was monitored by TLC on Silufol plates. The reaction mixtures were separated by column chromatography on silica gel LS 5/40 μm (Chemapol).

N-Benzylidenebenzenesulfonamide was prepared by the procedure reported in [12]; *N*-(diphenylmethylene)benzamide was synthesized as described in [13]; and activated lead was prepared according to [9].

Reactions of Schiff bases with difluorocarbene in the presence of *N*-benzylidenebenzenesulfonamide. *a*. A 50-ml round-bottom flask was charged under argon in succession with 1.06 g (5.12 mmol) of activated lead, 20 ml of dry methylene chloride, 1.65 g (5.12 mmol) of tetrabutylammonium bromide, 0.50 g (2.56 mmol) of Schiff base **VIa**, and 0.75 g (3.06 mol) of Schiff base **IV**. The mixture was cooled with water to 10–15°C, 1.35 g (6.43 mmol) of dibromodifluoromethane was added, and the flask was tightly capped, placed in an ultrasonic bath (160 W), and irradiated at 45°C until lead disappeared completely (35 h). When the reaction was over, 3.5 g of silica gel (LS 40/100 μm, Chemapol) was added, the mixture was evaporated to dryness under reduced pressure, and the residue was applied to a column charged with silica gel. The column was eluted with a 1:2 hexane–chloroform mixture. Recrystallization from diethyl ether gave 0.245 g (20%) of (2*RS*,5*SR*)-3-benzyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**VIIIa**) and 0.217 g (18%) of (2*RS*,5*RS*)-3-benzyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**IXa**).

Compound **VIIIa**. mp 125–127°C (from diethyl ether). IR spectrum: ν(C=O) 1710 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.40 d (1H, CH_2, $^2J_{HH}$ = 14.5 Hz), 5.03 d (1H, CH_2, $^2J_{HH}$ = 14.5 Hz), 5.31 s (1H, 5-H), 5.86 s (1H, 2-H), 6.91–7.51 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 43.9 (CH_2); 63.3 (C^5); 74.7 (C^2); 127.0, 127.1, 127.8, 127.9, 128.0, 128.05, 128.1, 128.59, 128.6, 128.7, 129.6, 132.8, 134.1, 134.8, 135.5, 137.1 (C_{arom}); 167.2 (C=O). Found, %: C 71.70; H 5.15; N 5.75. $C_{28}H_{24}N_2O_3S$. Calculated, %: C 71.77; H 5.16; N 5.98.

X-Ray diffraction data: *M* 468.55. Crystal habit 0.55×0.48×0.38 mm. Monoclinic crystals with the following unit cell parameters: *a* = 12.4706(4), *b* = 9.9578(3), *c* = 18.1974(6) Å; β = 94.3150(10)°; *V* = 2253.34(12) Å^3; *d* = 1.381 g/cm^3; space group $P2_1/c$. The data were acquired on a CCD Apex Area Detector diffractometer (MoK_α irradiation, λ = 0.71073 Å, graphite monochromator, θ_{max} = 30.00°; –120°C).

Compound **IXa**. mp 236–240°C (from diethyl ether). IR spectrum: ν(C=O) 1710 cm^{-1}. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.29 d (1H, CH_2, $^2J_{HH}$ = 14.5 Hz), 5.09 d (1H, CH_2, $^2J_{HH}$ = 14.5 Hz), 5.26 d (1H, 5-H, $^4J_{HH}$ = 2.0 Hz), 5.93 d (1H, 2-H, $^4J_{HH}$ = 2.0 Hz), 7.00–7.39 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 43.4 (CH_2); 64.6 (C^5); 75.8 (C^2); 126.3, 127.1, 127.9, 128.0, 128.1, 128.4, 128.5, 128.6, 129.6, 131.8, 134.3, 137.0, 139.0 (C_{arom}); 167.5 (C=O). Found, %: C 71.89; H 5.16; N 5.88. $C_{28}H_{24}N_2O_3S$. Calculated, %: C 71.77; H 5.16; N 5.98.

b. A 50-ml round-bottom flask was charged under argon in succession with 40 ml of methylene chloride, 1.92 g (9.3 mmol) of freshly prepared lead filings, 3.0 g (9.3 mmol) of tetrabutylammonium bromide, 1.0 g (4.8 mmol) of *N*-benzylidenephenethylamine (**VIb**), 1.40 g (5.7 mmol) of Schiff base **IV**, and 2.5 g (11.9 mmol) of dibromodifluoromethane. The mixture was cooled with water to 10–15°C, 1.35 g (6.43 mmol) of dibromodifluoromethane was added, and the flask was tightly capped, placed in an ultrasonic bath (160 W), and irradiated at 45°C until lead disappeared

completely (28 h). Silica gel, 6 g, was added, the mixture was evaporated to dryness under reduced pressure, and the residue was applied to a column charged with silica gel (LS 5/40 μm, Chemapol). The column was eluted with a 1:2 hexane–chloroform mixture. Recrystallization from diethyl ether gave 0.192 g (8.3%) of (2*RS*,5*SR*)-2,5-diphenyl-1-phenylsulfonyl-3-phenethylimidazolidin-4-one (**VIIIb**) and 0.243 g (10.5%) of (2*RS*,5*RS*)-2,5-diphenyl-1-phenylsulfonyl-3-phenethylimidazolidin-4-one (**IXb**).

Compound **VIIIb**. mp 104–106°C (from diethyl ether). IR spectrum: ν(C=O) 1710 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.59–2.69 m (1H, CH_2), 2.72–2.89 m (2H, CH_2), 3.78–3.88 m (1H, CH_2), 5.29 s (1H, 5-H), 5.93 s (1H, 2-H), 7.04–7.45 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 33.0 (Ph**C**H_2); 41.9 (NCH_2); 63.3 (C^5); 75.5 (C^2); 126.5, 127.06, 127.2, 127.9, 127.96, 128.0, 128.2, 128.4, 128.46, 128.5, 129.6, 132.7, 135.0, 135.8, 137.5, 137.7 (C_{arom}); 167.2 (C=O). Found, %: C 72.19; H 5.47; N 5.69. $C_{29}H_{26}N_2O_3S$. Calculated, %: C 72.18; H 5.43; N 5.80.

Compound (**IXb**). mp 209–211°C (from diethyl ether). IR spectrum: ν(C=O) 1705 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.63–2.80 m (2H, CH_2), 2.86–2.92 m (1H, CH_2), 3.99–4.06 m (1H, CH_2), 5.19 d (1H, 5-H, $^4J_{HH}$ = 2.4 Hz), 5.83 d (1H, 2-H, $^4J_{HH}$ = 2.4 Hz), 6.98–7.39 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 32.8 (Ph**C**H_2); 40.7 (NCH_2); 64.3 (C^5); 76.7 (C^2); 126.2, 126.6, 127.4, 127.8, 128.0, 128.2, 128.23, 128.4, 128.5, 129.6, 131.7, 135.0, 136.1, 137.3, 139.2 (C_{arom}); 167.7 (C=O). Found, %: C 72.13; H 5.58; N 5.79. $C_{29}H_{26}N_2O_3S$. Calculated, %: C 72.18; H 5.43; N 5.80.

Reaction of *N*-benzylidenecyclohexylamine (VIc) with difluorocarbene in the presence of *N*-benzylidenebenzenesulfonamide (IV). Following the above procedure (method *a*), from 0.36 g of Schiff base **VIc** and 0.57 g of Schiff base **IV** (reaction time 20 h), we isolated by column chromatography (eluent hexane–ethyl acetate, 2:1) 0.023 g (2%) of (2*RS*,5*SR*)-3-cyclohexyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**VIIIc**) and 0.147 g (17%) of (2*RS*,5*RS*)-3-cyclohexyl-2,5-diphenyl-1-phenylsulfonylimidazolidin-4-one (**IXc**).

Compound **VIIIc**. mp 154–156°C (from diethyl ether). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.88–1.71 m (10H, CH_2, cyclohexyl), 3.52 m (1H, CH, cyclohexyl), 5.29 s (1H, 5-H), 6.11 s (1H, 2-H), 7.28–7.55 m (15H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 24.7, 25.3, 25.4, 29.3, 30.3, 53.6 (cyclohexyl); 63.4 (C^5); 75.0 (C^2); 126.9, 127.1, 127.13, 127.2, 127.8, 127.9, 128.2, 128.6, 128.7, 129.3, 132.9, 137.6, 137.9 (C_{arom}); 167.3 (C=O). Found, %: C 69.63; H 6.26; N 5.90. $C_{27}H_{28}N_2O_3S$. Calculated, %: C 70.41; H 6.13; N 6.08.

Compound **IXc**. mp 260–263°C (decomp., from ethyl acetate). The product is insoluble in chloroform and poorly soluble in DMSO. IR spectrum (KBr), ν, cm^{-1}: 1700 (C=O). ^1H NMR spectrum (DMSO-d_6), δ, ppm: 0.80–1.58 m (10H, CH_2, cyclohexyl), 3.69 m (1H, CH, cyclohexyl), 5.44 d (1H, 5-H, $^4J_{HH}$ = 2.2 Hz), 6.36 d (1H, 2-H, $^4J_{HH}$ = 2.2 Hz), 7.06–7.48 m (15H, H_{arom}). Found, %: C 70.39; H 6.16; N 6.01. $C_{27}H_{28}N_2O_3S$. Calculated, %: C 70.41; H 6.13; N 6.08.

Reaction of *N*-benzylideneaniline (VId) with difluorocarbene in the presence of *N*-benzylidenebenzenesulfonamide (IV). Following the above procedure (method *a*), from 0.42 g of Schiff base **VId** and 0.68 g of Schiff base **IV** (reaction time 15 h), we isolated by column chromatography (eluent hexane–ethyl acetate, 1:1) with subsequent recrystallization from diethyl ether a mixture of (2*RS*,5*SR*)-2,3,5-triphenyl-1-phenylsulfonylimidazolidin-4-one (**VIIId**) and (2*RS*,5*RS*)-2,3,5-triphenyl-1-phenylsulfonylimidazolidin-4-one (**IXd**) at a ratio of 3:1; overall yield 0.179 g (17%).

Compound **VIIId**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.50 s (1H, 5-H), 6.77 s (1H, 2-H), 7.07–7.39 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 63.7 (C^5), 76.4 (C^2), 122.7–137.4 (C_{arom}), 167.0 (C=O).

Compound **IXd**. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 5.35 d (1H, 5-H, $^4J_{HH}$ = 2.2 Hz), 6.74 d (1H, 2-H, $^4J_{HH}$ = 2.2 Hz), 7.07–7.39 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 64.8 (C^5), 78.1 (C^2), 124.0–137.0 (C_{arom}), 167.0 (C=O).

An analogous reaction with the use of nonactivated lead (method *b*, reaction time 70 h) afforded a mixture of diastereoisomers **VIIId** and **IXd** at a ratio of 3:1, yield 24%.

Reaction of *N*-(diphenylmethylene)methylamine (VIe) with difluorocarbene in the presence of *N*-benzylidenebenzenesulfonamide (IV). Following the above procedure (method *b*), from 0.65 g of Schiff base **VIe** and 1.0 g of Schiff base **IV** (reaction time 34 h), we isolated by column chromatography (eluent hexane–ethyl acetate, 4:1) 0.5 g (33%) of 3-methyl-2,2,5-triphenyl-1-phenylsulfonylimidazolidin-4-one (**X**). mp 219–221°C (from ethyl acetate–diethyl ether). IR spectrum: ν(C=O) 1705 cm^{-1}. ^1H NMR spectrum

($CDCl_3$), δ, ppm: 2.66 s (3H, CH_3), 5.48 s (1H, 5-H), 6.32–7.82 m (20H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 26.4 (CH_3); 65.6 (C^5); 88.3 (C^2); 126.4, 127.4, 127.5, 127.9, 128.0, 128.1, 128.2, 128.3, 128.6, 128.9, 129.0, 130.3, 131.4, 134.4, 136.4, 137.6, 140.0 (C_{arom}); 167.7 (C=O). Found, %: C 71.59; H 5.26; N 5.82. $C_{28}H_{24}N_2O_3S$. Calculated, %: C 71.77; H 5.16; N 5.98.

Reaction of *N*-(diphenylmethylene)benzylamine (VIf) with difluorocarbene in the presence of *N*-benzylidenebenzenesulfonamide (IV). Following the above procedure (method *b*), from 0.7 g of Schiff base **VIf** and 0.78 g of Schiff base **IV** (reaction time 48 h), we isolated by column chromatography (eluent hexane–ethyl acetate, 4:1) 0.46 g (30%) of 3-benzyl-2,2,5-triphenyl-1-phenylsulfonylimidazolidin-4-one (**XI**). mp 193–195°C (from ethyl acetate–diethyl ether). IR spectrum: ν(C=O) 1710 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.34 d and 4.50 d (2H, CH_2, *AB* system, *J* = 16.0 Hz), 5.38 s (1H, 5-H), 6.50–7.84 m (25H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 45.1 (CH_2); 64.9 (C^5); 88.7 (C^2); 126.4, 126.7, 127.0, 127.5, 127.8, 128.1, 128.2, 128.3, 128.8, 128.9, 129.0, 130.0, 131.6, 134.8, 135.4, 137.0, 137.7, 139.3 (C_{arom}); 168.6 (C=O). Found, %: C 74.70; H 5.32; N 5.23. $C_{34}H_{28}N_2O_3S$. Calculated, %: C 74.98; H 5.18; N 5.14.

Reaction of *N*-(diphenylmethylene)phenethylamine (VIg) with difluorocarbene in the presence of *N*-benzylidenebenzenesulfonamide (IV). Following the above procedure (method *b*), from 1.0 g of Schiff base **VIg** and 1.03 g of Schiff base **IV** (reaction time 26 h), we isolated by column chromatography (eluent hexane–ethyl acetate, 4:1) 0.377 g (19%) of 3-phenethyl-2,2,5-triphenyl-1-phenylsulfonylimidazolidin-4-one (**XII**). mp 184–186°C (from ethyl acetate). IR spectrum: ν(C=O) 1700 cm^{-1}. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.74 d.d.d (1H, PhC**H**$_2$, *J* = 12.3, 4.3 Hz), 2.48 d.d.d (1H, PhC**H**$_2$, *J* = 12.1, 4.3 Hz), 3.19 d.d.d (1H, NCH_2, *J* = 12.3, 4.3 Hz), 3.41 d.d.d (1H, NCH_2, *J* = 12.4, 4.3 Hz), 5.42 s (1H, 5-H), 6.48–7.88 m (25H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 32.3 (Ph**C**H_2); 44.0 (NCH_2); 65.3 (C^5); 88.4 (C^2); 126.1, 126.6, 127.5, 128.06, 128.1, 128.2, 128.3, 128.4, 128.5, 128.7, 128.9, 129.1, 129.8, 131.5, 134.6, 137.5, 138.0, 138.8, 139.6 (C_{arom}); 167.7 (C=O). Found, %: C 75.02; H 5.87; N 4.79. $C_{35}H_{30}N_2O_3S$. Calculated, %: C 75.24; H 5.41; N 5.01.

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