Synthesis of Alkoxy- and Phenylsulfanyl-Substituted 1,1-Dihalospiro[2.2]pentanes and Their Reactivity toward Methyllithium

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Abstract—A number of new alkoxy- and phenylsulfanyl-substituted 1,1-dihalospiro[2.2]pentanes having different halogen atoms were synthesized. 1,1-Dihalo-4-*tert*-butoxyspiro[2.2]pentanes reacted with methyllithium at −55 to −10°C to give exclusively 1-*tert*-butoxy-2-vinylidenecyclopropane. The reaction of 1-bromo-1-fluoro-4-phenylsulfanylspiro[2,2]pentane with methyllithium resulted in replacement of the fluorine atom by methyl group.

Reactions of geminal dihalocyclopropanes with alkyllithiums underlie a classical procedure for the preparation of substituted allenes [1]. However, while studying chemical properties of polyspirocyclo-propanes (triangulanes) we found that *gem*-dihalo-spiropentanes reacted with methyllithium in an unexpected fashion. Only a small amount of allene was formed at −55°C, whereas the major products were those resulting from unusual skeletal rearrangement (Scheme 1) [2]. The product structure depended on the nature of halogen atoms and other substituents in the initial spiropentane. Reactions of diiodo-, dibromo-, and bromochlorospiropentanes with MeLi afforded monomeric or dimeric halocyclobutenes [3, 4], and the main reaction pathway of *gem*-bromofluorospiro-pentanes was formal replacement of the fluorine atom

Scheme 1.
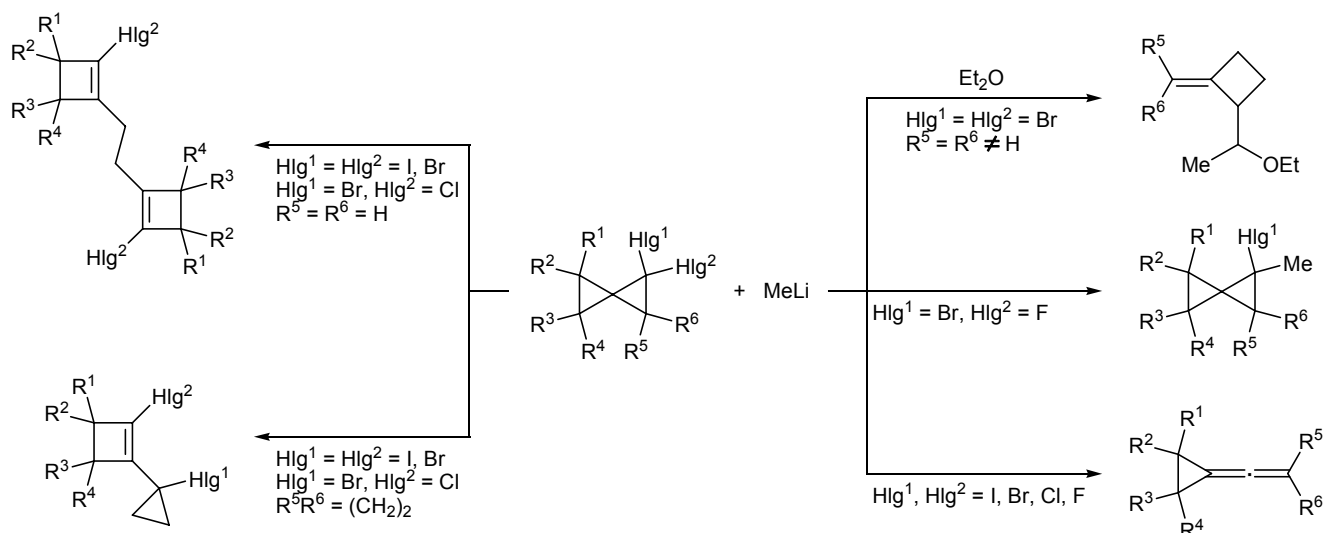
by methyl group with formation of 1-halo-1-methyl-spiropentanes [5] (Scheme 1).

We previously studied reactions of methyllithium with a large series of *gem*-dihalospiropentanes having various alkyl, cycloalkyl, and aryl substituents in the spiropentane fragment. The obtained results allowed us to propose a general scheme for the dihalotriangulane rearrangement [3, 6]. In continuation of these studies, in the present work we tried to involve in reaction with methyllithium a number of new *gem*-dihalospiropentanes having electron-donor heteroatom substituents.

Hlg = Br, Cl, F; X = O, S.
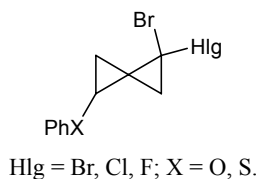
A conventional method for the preparation of such dihalospiropentanes is based on [1+2]-cycloaddition of dihalocarbenes to 2-phenoxy- and 2-phenylsulfanyl-cyclopropanes **I** and **II**. Various methylidenecyclopropanes were previously synthesized in two steps including addition of chloro(methyl)carbene at the double bond of the corresponding alkene and subsequent dehydrohalogenation of the adduct [7]. We made an attempt to obtain methylidenecyclopropane **I** in such a way and found that the first step smoothly afforded 1-chloro-1-methyl-2-phenoxycyclopropane (**IV**) in a high yield (Scheme 2). However, the subsequent dehydrohalogenation of **IV** with potassium *tert*-butoxide in DMSO unexpectedly produced *tert*-butoxy-substituted methylidenecyclopropane **V** as the only product, i.e., formal nucleophilic replacement of the phenoxy group by *tert*-butoxy occurred. We failed to change the reaction direction toward formation of target compound **I** by varying the conditions (temperature, solvent, reactant ratio, and order of their addition) or using other bases instead of potassium *tert*-butoxide [KOH, NaOEt, (Me$_3$Si)$_2$NNa].

It is known that classical nucleophilic substitution reactions are not typical of strained carbocycles [8]. Products of formal nucleophilic substitution in three-membered rings were described mainly for bromo-cyclopropanes; they are usually formed as a result of 1,2-elimination of HBr and subsequent addition of nucleophile at the strained double bond in cyclo-propene intermediate [9]. Such two-step sequence was proposed for the first time for the reaction of methyl bromocyclopropanecarboxylate with *t*-BuOK in *t*-BuOH [10]. In our case the reaction of phenoxy-substituted cyclopropane **IV** with potassium *tert*-butoxide is likely to involve elimination of phenol molecule with formation of highly reactive chloro(methyl)cyclo-propene **A** which takes up *t*-BuOH molecule generated during the process to give intermediate **B**, and dehy-drochlorination of the latter leads to methylidene-cyclopropane **V**. Thus we have revealed previously unknown formal nucleophilic substitution of phenoxy group in cyclopropane ring by the action of potassium *tert*-butoxide.

Sulfanyl derivative **II** was prepared as described in [11] from lithiated methylidenecyclopropane and diphenyl disulfide (Scheme 3). Substituted methylidene-cyclopropanes **II** and **V** were brought into [1+2]-cycloaddition reactions with various dihalocarbenes. The addition of dibromocarbene to methylidenecyclo-propane **V** was carried out under the Doering–Hoffmann reaction conditions [12], while mixed di-halocarbenes, i.e., those having two different halogen atoms, reacted with **V** according to Makosza [13] (see table). *tert*-Butoxy-substituted dihalospiropentanes **VIa**–**VIc** were isolated in good or satisfactory yields and were characterized by ^{1}H and ^{13}C NMR spectra and elemental analyses (Scheme 4).

Phenylsulfanyl derivative **II** turned out to be low reactive toward dihalocarbenes. The reaction of **II** with dibromocarbene under different conditions gave no target dibromospiropentane. Moreover, the major product formed in the Makosza reaction was tetrabromide
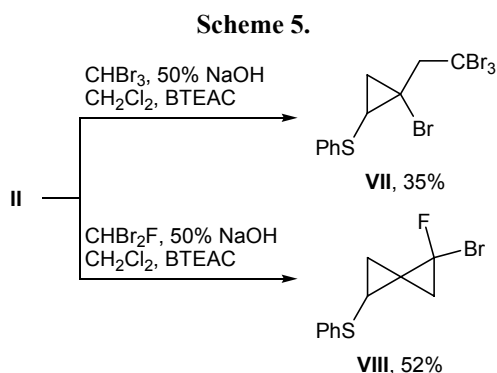
Scheme 2.

Scheme 3.

II, 17%

Scheme 4.

**VIa–VIc**
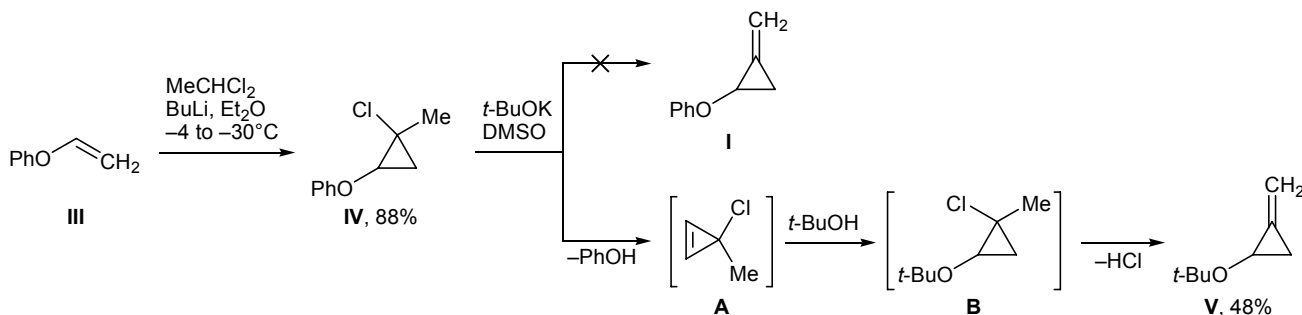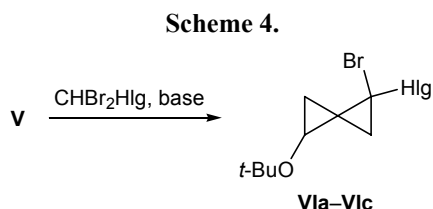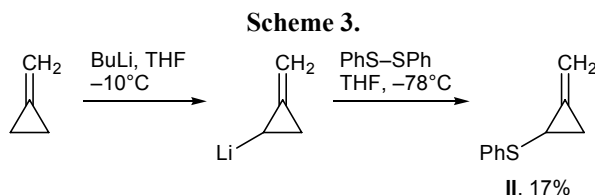
Hlg = Br (**a**), Cl (**b**), F (**c**).

VII which may be regarded as formal addition product of carbon tetrabromide at the double bond of alkene **II** (Scheme 5). The structure of **VII** was unambiguously determined by X-ray analysis (see figure).

**Scheme 5.**

VII, 35%

VIII, 52%

In keeping with published data, analogous tetrabromides were formed in reactions of sterically hindered or electrophilic alkenes with bromoform under phase transfer catalysis [14]. It was presumed that generation of dibromocarbene is accompanied by formation of carbon tetrabromide which then adds at the double bond of alkene according to the radical mechanism [15]. We never observed formation of tetrabromo-substituted adducts while preparing various *gem*-dibromospiropentanes from substituted methylidenecyclopropanes [3]; therefore, the presence of a bulky phenylsulfanyl substituent in molecule **II** considerably reduces its reactivity in [1+2]-cycloaddition processes. We succeeded in obtaining the desired spiropentane adduct **VIII** only by reaction of alkene **II** with less bulky bromofluorocarbene (Scheme 5).

New *gem*-dihalospiropentanes **VIa–VIc** and **VIII** were brought into reaction with methyllithium under the conditions described previously, which were varied depending on the halogen nature [3–5]. No rearrange-

Reaction conditions and yields of 1-bromo-1-halo-4-*tert*-butoxyspiro[2.2]pentanes **VIa–VIc**

Compound no.	Reaction conditions	Yield,[a] %
VIa	*t*-BuOK, petroleum ether	56
VIb	50% NaOH, CH$_2$Cl$_2$, dibenzo-18-crown-6	67
VIc	50% NaOH, CH$_2$Cl$_2$, Et$_3$BzlNCl	40

[a] After chromatographic isolation.

ment products of the cyclobutane series were formed in reactions of *tert*-butoxy-substituted dihalospiropentanes **VIa–VIc**, while the only reaction pathway was that leading to allene **IX** (Scheme 6).

Scheme 6.

IX
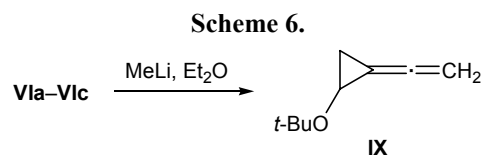
The reaction of phenylsulfanyl derivative **VIII** with methyllithium afforded exclusively bromo(methyl)-spiropentane **X** as formal product of replacement of the fluorine atom by methyl group (Scheme 7).

Scheme 7.

X, 40%
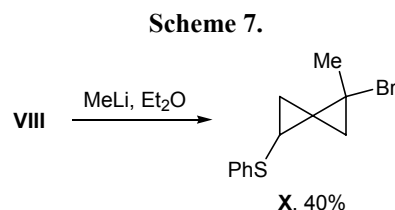
To conclude, we have studied the reactivity of a number of *gem*-dihalospiropentanes having various halogen atoms and heteroatom substituents toward
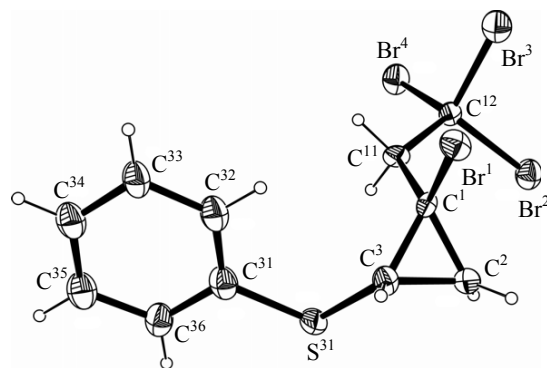
Structure of the molecule of 1-bromo-1-(2,2,2-tribromoethyl)-2-phenylsulfanylcyclopropane (**VII**) according to the X-ray diffraction data.

methyllithium at low temperature and found that the presence of a bulky alkoxy substituent in the spiro-pentane fragment hampers carbenoid skeletal rear-rangement and forces the reaction to follow exclu-sively the carbene path with formation of allenes. 1-Bromo-1-fluoro-4-phenylsulfanylspiro[2.2]pentane reacts with methyllithium to give only product of formal replacement of the fluorine atom by methyl group without rearrangement. Thus the examined dihalospiropentanes do not tend to undergo carbenoid skeletal rearrangement.

<div align="center">EXPERIMENTAL</div>

The ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 instrument at 400 and 100 MHz, respectively, from solutions in $CDCl_3$ using the solvent signals as reference (δ 7.24 ppm, δ_C 77.10 ppm). The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT ITD-700 mass spectrometer. The high-resolution mass spectra (positive ion detection) were run on Bruker micrOTOF II (ESI) and JEOL GCmate instruments (70 eV). The X-ray analysis of a single crystal of compound **VII** was performed at room temperature on an Enraf–Nonius CAD-4 auto-matic diffractometer (λAgK_α irradiation, graphite monochromator, ω-scanning). The progress of reac-tions and the purity of products were monitored by TLC on Silufol UV-254 plates. Silica gel Merck (40–60 μm) was used for preparative column chroma-tography.

[(2-Methylidenecyclopropyl)sulfanyl]benzene (II). A solution of 0.021 mol of butyllithium (8.75 ml of a 1.6 M solution in hexane) in 20 ml of anhydrous THF was cooled to –10°C, a solution of 1.08 g (0.020 mol) of methylidenecyclopropane in 4 ml of anhydrous THF was added dropwise, the mixture was stirred for 1 h at 0°C and cooled to –78°C, and a solu-tion of 2.89 g (0.020 mol) of benzenesulfenyl chloride in 6 ml of anhydrous THF was added. The mixture was allowed to warm up to 0°C and treated with an equal volume of ice water, the organic phase was separated, the aqueous phase was extracted with diethyl ether (3×20 ml), the extracts were combined with the or-ganic phase, washed with water (3×20 ml), and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the product was isolated by column chromatography. Yield 0.55 g (17%), colorless liquid, R_f 0.2 (petroleum ether). ^1H NMR spectrum, δ, ppm (J, Hz): 1.42 d.d.d.d (1H, CH_2, $^2J = 9.3$, $^3J = 4.2$, $^4J = 2.1, 2.7$), 1.88 d.d.d.d (1H, CH_2, $^2J = 9.3$, $^3J = 7.7$,

$^4J = 2.0, 2.6$), 2.93 d.d.d.d (1H, CH, $^3J = 7.7, 4.2$, $^4J = 2.1, 2.3$), 5.58–5.61 m and 5.66–5.68 m (1H each, =CH_2), 7.20 t.t (1H, H_{arom}, $^3J = 7.4$, $^4J = 1.2$), 7.31–7.36 m (2H, H_{arom}), 7.42–7.46 m (2H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm (J, Hz): 14.32 (CH_2, $^1J = 164.6$, $^2J = 9.6, 3.8$), 15.66 (CH, $^1J = 180.1$), 106.49 (=CH_2, $^1J = 162.8$, $^2J = 2.8, 5.2$), 125.70 (CH_{arom}), 127.37 (2C, CH_{arom}), 129.07 (2C, CH_{arom}), 132.09 (C=), 138.22 (C_{arom}). Found: m/z 163.0576 $[M + H]^+$. $C_{10}H_{10}S$. Cal-culated: $[M + H]$ 163.0581.

1-Chloro-1-methyl-2-phenoxycyclopropane (IV). A solution of 9.70 g (0.081 mol) of vinyloxybenzene and 12.02 g (0.122 mol) of 1,1-dichloroethane in 45 ml of anhydrous diethyl ether was cooled to –40°C, a so-lution of 0.130 mol of butyllithium (81.0 ml of a 1.6 M solution in hexane) was added over a period of 1.5 h under argon. The mixture was stirred for 4 h at room temperature and treated with 80 ml of water, the organic layer was separated, and the aqueous phase was extracted with diethyl ether (3×50 ml). The ex-tracts were combined with the organic phase, washed with a saturated solution of sodium chloride, and dried over $MgSO_4$. The solvent was distilled off under reduced pressure, and the residue was distilled in a vacuum. Yield 13.0 g (88%), mixture of stereo-isomers **A** and **B** (2:1). Colorless liquid, bp 127°C (2 mm), R_f 0.75 (petroleum ether–ethyl acetate, 5:1). ^1H NMR spectrum, δ, ppm (J, Hz), isomer **A**: 1.17 d.d (1H, CH_2, $^2J = 7.8$, $^3J = 4.2$), 1.51 d.d (1H, CH_2, $^2J = 7.8$, $^3J = 8.0$), 1.61 s (3H, CH_3), 3.96 d.d (1H, CH, $^3J = 4.2, 8.0$), 7.02–7.07 m (3H, Ph), 7.33–7.38 m (2H, Ph); isomer **B**: 1.25–1.30 m (1H, CH_2), 1.36 d.d (1H, CH_2, $^2J = 7.7$, $^3J = 4.4$), 1.74 s (3H, CH_3), 3.96 d.d (1H, CH, $^3J = 4.4, 7.4$), 7.02–7.07 m (3H, Ph), 7.33–7.38 m (2H, Ph). ^{13}C NMR spectrum, δ_C, ppm (J, Hz), isomer **A**: 20.92 (CH_3, $^1J = 129$), 22.81 (CH_2, $^1J = 162$), 41.81 (C^1), 60.92 (CH, $^1J = 189$), 114.76 (2C, CH_{arom}, $^1J = 159$), 121.65 (CH_{arom}, $^1J = 160$), 129.63 (2C, CH_{arom}, $^1J = 159$), 158.19 (C_{arom}); isomer **B**: 22.42 (CH_2, $^1J = 164$), 26.05 (CH_3, $^1J = 128$), 42.36 (C^1), 58.48 (CH, $^1J = 184$), 114.90 (2C, CH_{arom}, $^1J = 159$), 121.65 (CH_{arom}, $^1J = 160$), 129.48 (CH_{arom}, $^1J = 159$), 158.23 (C_{arom}). Found, %: C 65.71; H 5.89. $C_{10}H_{11}ClO$. Cal-culated, %: C 65.76; H 6.07.

1-*tert*-Butoxy-2-methylidenecyclopropane (V). A solution of 5.61 g (50 mmol) of potassium *tert*-butoxide in 20 ml of DMSO was heated to 40°C, 6.02 g (33 mmol) of chloro(methyl)cyclopropane **IV** was added under argon over a period of 1 h, and the mixture was stirred for 4 h at room temperature and treated with an equal volume of ice water. The organic

phase was separated, the aqueous phase was extracted with diethyl ether (3×20 ml), the extracts were combined with the organic phase, washed with water (3×20 ml), and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the residue was distilled in a vacuum. Yield 1.99 g (48%), colorless liquid, bp 58–60°C (60 mm). ^1H NMR spectrum, δ, ppm: 1.21–1.27 m (1H, CH_2), 1.30 s (9H, t-Bu), 1.39–1.46 m (1H, CH_2), 3.65–3.70 m (1H, CH), 5.52 br.s and 5.67 br.s (1H each, CH_2=). ^{13}C NMR spectrum, $δ_C$, ppm (J, Hz): 12.91 (CH_2, $^1J = 161$), 28.23 (CH_3, $^1J = 126$), 46.25 (C^1, $^1J = 181$), 75.03 (CMe_3), 106.68 (CH_2=, $^1J = 161$), 133.80 (C^2). Found, %: C 76.07; H 11.37. $C_8H_{14}O$. Calculated, %: C 76.14; H 11.18.

1,1-Dibromo-4-*tert*-butoxyspiro[2.2]pentane (VIa). A mixture of 1.39 g (11 mmol) of alkene **V** and 2.9 g (26 mmol) of potassium *tert*-butoxide in 10 ml of petroleum ether was cooled to 0°C, 3.34 g (1.2 ml, 13 mmol) of bromoform was added dropwise under stirring. The mixture was allowed to warm up to room temperature, stirred for 72 h, and treated with an equal volume of ice water. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×10 ml), the extracts were combined with the organic phase, washed with water (3×10 ml), and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography. Yield 1.84 g (56%), colorless oily substance, R_f 0.2 (petroleum ether). ^1H NMR spectrum, δ, ppm (J, Hz): 1.27 s (9H, t-Bu), 1.35 d.d.d (1H, CH_2, $^2J = 4.0$, $^3J = 6.1$, $^4J = 0.5$), 1.39–1.42 m (1H, CH_2), 2.06 d.d (1H, CH_2, $^2J = 6.7$, $^4J = 1.4$), 2.11 br.d (1H, CH_2, $^2J = 6.7$), 3.77 d.d.d (1H, CH, $^3J = 4.0, 6.7$, $^4J = 1.4$). ^{13}C NMR spectrum, $δ_C$, ppm (J, Hz): 18.78 (CH_2, $^1J = 163$), 28.14 (CH_2, $^1J = 166$), 28.31 (CH_3, $^1J = 126$), 30.41 (C_{spiro}), 31.33 (C_{spiro}), 55.56 (CH, $^1J = 182$), 75.21 (CMe_3). Found, %: C 36.26; H 4.75. $C_9H_{14}Br_2O$. Calculated, %: C 36.27; H 4.74.

1-Bromo-1-chloro-4-*tert*-butoxyspiro[2.2]pentane (VIb). A mixture of 1.39 g (11 mmol) of alkene **V**, 2.74 g (13 mmol) of dibromochloromethane, and 0.1 g (0.3 mmol) of dibenzo-18-crown-6 in 22 ml of methylene chloride was cooled to 0°C, 22 ml of 50% aqueous sodium hydroxide was added dropwise under stirring, and the mixture was stirred for 24 h at room temperature and poured onto ice (20 g). The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×10 ml), the extracts were combined with the organic phase, washed with water (3×10 ml), and dried over $MgSO_4$, the

solvent was distilled off under reduced pressure, and the residue was purified by column chromatography. The product was a mixture of stereoisomers A and B at a ratio of 1:1. Yield 1.87 g (67%), colorless liquid, R_f 0.5 (petroleum ether–ethyl acetate, 1:1). ^1H NMR spectrum, δ, ppm (J, Hz): 1.26 s and 1.27 s (9H each, t-Bu), 1.29–1.33 m (2H), 1.34–1.37 m (1H), 1.49–1.52 m (1H), 1.96–2.03 m (4H), 3.72 d.d.d (1H, CH, $^2J = 3.9$, $^3J = 6.8$, $^4J = 1.4$), 3.85 d.d.d (1H, CH, $^2J = 3.9$, $^3J = 6.7$, $^4J = 1.3$). ^{13}C NMR spectrum, $δ_C$, ppm (J, Hz): 16.85 (CH_2, $^1J = 163$), 18.15 (CH_2, $^1J = 163$), 27.27 (CH_2, $^1J = 165$), 27.31 (CH_2, $^1J = 165$), 28.23 and 28.28 (CH_3, $^1J = 125$), 30.75 and 30.81 (C_{spiro}), 47.23 and 47.84 (CBrCl), 53.77 (CH, $^1J = 183$), 54.90 (CH, $^1J = 184$), 75.12 and 75.17 (CMe_3). Found, %: C 42.47; H 5.63. $C_9H_{14}BrClO$. Calculated, %: C 42.63; H 5.57.

Bromofluorospiropentanes VIc and VIII (*general procedure*). A mixture of 16 mmol of alkene **II** or **V**, 9.22 g (48 mmol) of dibromofluoromethane, and 0.73 g (2.6 mmol) of benzyl(triethyl)ammonium chloride in 10 ml of methylene chloride was cooled to 0°C, 10 ml of 50% aqueous sodium hydroxide was added dropwise under stirring, and a drop of ethanol was then added. The mixture was stirred for 48 h at room temperature and treated with an equal volume of ice water. The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×20 ml), the extracts were combined with the organic phase, washed with water (3×20 ml), and dried over $MgSO_4$, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography.
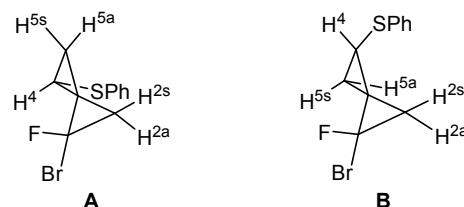
1-Bromo-1-fluoro-4-phenylsulfanylspiro[2.2]-pentane (VIc) was obtained from 2.59 g of alkene **II**. The product was a mixture of two stereoisomers **A** and **B** at a ratio of 1:0.8. Yield 2.17 g (52%), colorless oily substance, R_f 0.1 (petroleum ether). ^1H NMR spectrum,* δ, ppm (J, Hz): isomer **A**: 1.10 br.d.d.d (1H, 5-H_a, $^2J = 5.3$, $^3J_{5a,4} = 4.8$, $^4J_{HF} = 8.6$), 1.42–1.47 m

* The NMR spectra were recorded in $CDCl_3$–C_6D_6 (1:2) to avoid overlap of signals from protons in the cyclopropane fragment of the two isomers.

(2H, 5-H$_s$, 2-H$_a$), 1.77 br.d.d (1H, 2-H$_s$, ^2J = 7.8, $^3J_{HF}$ = 12.8), 2.82 d.d (1H, 4-H, $^3J_{5a,4}$ = 4.8, $^3J_{5s,4}$ = 8.1), 7.17–7.23 m (1H, H$_{arom}$), 7.27–7.34 m (2H, H$_{arom}$), 7.36–7.41 m (2H, H$_{arom}$); isomer **B**: 1.25 d.d (1H, 5-H$_a$, ^2J = 5.2, $^3J_{5a,4}$ = 5.1), 1.51 d.d (1H, 2-H$_a$, ^2J = 7.9, $^3J_{HF}$ = 4.2), 1.65 d.d (1H, 5-H$_s$, ^2J = 5.2, $^3J_{5s,4}$ = 8.0), 1.68 br.d.d (1H, 2-H$_s$, ^2J = 7.9, $^3J_{HF}$ = 12.1), 2.66 d.d.d (1H, 4-H, $^3J_{5a,4}$ = 5.1, $^3J_{5s,4}$ = 8.0, $^4J_{HF}$ = 1.3), 7.17–7.23 m (1H, H$_{arom}$), 7.27–7.34 m (2H, H$_{arom}$), 7.36–7.41 m (2H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm (J, Hz): isomer **A**: 17.78 (C^5), 21.02 (C^4, $^3J_{CF}$ = 2.2), 22.14 (C^2, $^2J_{CF}$ 11.8), 29.80 (C$_{spiro}$, $^2J_{CF}$ = 10.4), 83.45 (C^1, $^1J_{CF}$ = 305), 125.65 (CH$_{arom}$), 126.73 (2C, CH$_{arom}$), 129.03 (2C, CH$_{arom}$), 136.34 (C$_{arom}$); isomer **B**: 16.64 (C^5, $^3J_{CF}$ = 2.2), 21.84 (C^2, $^2J_{CF}$ = 11.2), 22.81 (C^4), 29.58 (C$_{spiro}$, $^2J_{CF}$ = 10.0), 83.17 (C^1, $^1J_{CF}$ = 306), 125.88 (CH$_{arom}$), 127.56 (2C, CH$_{arom}$), 128.91 (2C, CH$_{arom}$), 136.09 (C$_{arom}$). Found: m/z 271.9676 [M]$^+$. C$_{11}$H$_{10}$BrFS. Calculated: M 271.9671.

1-Bromo-4-*tert*-butoxy-1-fluorospiro[2.2]pentane (VIII) was obtained from 2.02 g of alkene **V**. The product was a mixture of two stereoisomers **A** and **B** at a ratio of 1:0.7. Yield 1.52 g (40%), colorless liquid, R_f 0.5 (petroleum ether). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.13–1.19 m (2H, CH$_2$), 1.25 s (9H, t-Bu, **B**), 1.26 s (9H, t-Bu, **A**), 1.33–1.37 m (1H, CH$_2$), 1.47–1.53 m (1H, CH$_2$), 1.71–1.76 m (2H, CH$_2$), 1.93–2.03 m (2H, CH$_2$), 3.63 d.d.d (1H, CH, ^2J = 3.9, ^3J = 6.7, ^4J = 1.5, **B**), 3.83–3.87 m (1H, CH, **A**). ^{13}C NMR spectrum, δ_C, ppm (J, Hz): 15.02 (CH$_2$, $^1J_{CH}$ = 164, **B**), 16.63 (CH$_2$, $^1J_{CH}$ = 163, **A**), 22.15 (CH$_2$, $^2J_{CF}$ = 11.8, $^1J_{CH}$ = 165, **B**), 22.37 (CH$_2$, $^2J_{CF}$ = 11.8, $^1J_{CH}$ = 165, **A**), 28.07 (CH$_3$, $^1J_{CH}$ = 123, **A**), 28.19 (CH$_3$, $^1J_{CH}$ = 123, **B**), 29.70 (C$_{spiro}$, **A**, **B**), 51.85 (CH, $^1J_{CH}$ = 166, **A**), 53.50 (CH, $^1J_{CH}$ = 166, **B**), 74.97 (C Me$_3$, B), 75.16 (C Me$_3$, **A**), 84.03 (CBrF, $^1J_{CF}$ = 305), 85.11 (CBrF, $^1J_{CF}$ = 303). Found, %: C 45.77; H 5.94. C$_9$H$_{14}$BrFO. Calculated, %: C 45.59; H 5.95.

1-Bromo-1-(2,2,2-tribromoethyl)-2-phenylsul-fanylcyclopropane (VII). A mixture of 0.10 g (0.62 mmol) of alkene **II**, 0.78 g (3.1 mmol) of CHBr$_3$, and 0.02 g (0.01 mmol) of BTEAC in 3 ml of methylene chloride was cooled to 0°C, 2.5 ml of 50% aqueous sodium hydroxide was added dropwise under stirring, and a drop of ethanol was then added. The mixture was allowed to warm up to room temperature, stirred for 10 days, and treated with an equal volume

of ice water. The organic phase was separated, the aqueous phase was extracted with methylene chloride (3×4 ml), the extracts were combined with the organic phase, washed with water (3×4 ml), and dried over MgSO$_4$, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography. Yield 0.11 g (35%), colorless crystals, mp 51°C, R_f 0.1 (petroleum ether). ^{1}H NMR spectrum, δ, ppm (J, Hz): 1.95 d.d.d (1H, 3-H, ^2J = 7.9, ^3J = 9.7, ^4J = 1.4), 2.04 d.d (1H, 3-H, ^2J = 7.9, ^3J = 6.6), 2.91 d.d (1H, 2-H, ^3J = 9.7, 6.6), 3.68 d (1H, 1-CH$_2$, ^2J = 16.7), 3.90 d.d (1H, 1-CH$_2$, ^2J = 16.7, ^4J = 1.4), 7.23 t.t (1H, H$_{arom}$, ^3J = 7.1, ^4J = 1.4), 7.30–7.40 m (4H, H$_{arom}$). ^{13}C NMR spectrum, δ_C, ppm (J, Hz): 22.30 (C^3, $^1J_{CH}$ = 167), 30.29 (1-CH$_2$, $^1J_{CH}$ = 184), 34.67 (CBr$_3$), 35.81 (C^1), 60.89 (C^2, $^1J_{CH}$ = 135), 125.82 (CH$_{arom}$, $^1J_{CH}$ = 165), 126.39 (2C, CH$_{arom}$, $^1J_{CH}$ = 161), 129.38 (2C, CH$_{arom}$, $^1J_{CH}$ = 162), 136.13 (C$_{arom}$). Mass spectrum (EI), m/z (I_{rel}, %): 498 (2), 496 (7), 494 (10), 492 (7), 491 (2) [M + H]$^+$, 417 (23), 415 (69), 413 (69), 411 (23) [M + H – Br]$^+$, 335 (6), 333 (12), 331 (6) [M + H – 2Br] $^+$, 305 (10), 303 (10) , 255 (40), 253 (52), 251 (27), 229 (27), 227 (28), 222 (34), 218 (19), 201 (15), 199 (15), 173 (63), 147 (100), 109 (86), 91 (45), 65 (75), 50 (51), 45 (57), 39 (41). C$_{11}$H$_{10}$Br$_4$S. M 493.88.

Reaction of dihalospiropentanes VIa–VIc and VIII with methyllithium (*general procedure*). A solution of 5.0 mmol of compound **VIa**, **VIb**, **VIc**, or **VIII** in 10 ml of diethyl ether was cooled to –55 (**VIa**, **VIb**) or –10°C (**VIc**, **VIII**), 5.0 ml (7.5 mmol) of a 1.5 N solution of methyllithium in diethyl ether was added dropwise, and the mixture was stirred for 1 h at the same temperature. The mixture was then allowed to warm up to 0°C and treated with an equal volume of ice water. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×5 ml), the extracts were combined with the organic phase, washed with 10 ml of water, and dried over MgSO$_4$, the solvent was distilled off under reduced pressure, and the residue was purified by column chromatography.

1-*tert*-Butoxy-2-vinylidenecyclopropane (IX) was obtained from 1.03 g of **VIa** (yield 0.48 g, 69%), 0.87 g of **VIb** (0.33 g, 48%), or 0.81 g of **VIc** (0.39 g, 57%). Colorless oily substance, R_f 0.7 (petroleum ether). ^{1}H NMR spectrum, δ, ppm: 1.28 s (9H, t-Bu), 1.70–1.78 m and 1.80–1.87 m (1H each, CH$_2$), 3.94–3.98 m (1H, CH), 4.78–4.84 m and 4.85–4.91 m (1H each, CH$_2$=). ^{13}C NMR spectrum, δ_C, ppm (J, Hz): 16.28 (CH$_2$, $^1J_{CH}$ = 165), 28.14 (CH$_3$, $^1J_{CH}$ = 125),

51.03 (CH, $^1J_{CH}$ = 184), 75.81 (**C**Me$_3$), 76.38 (**C**H$_2$=, $^1J_{CH}$ 167), 79.24 (C^2), 194.54 (=C=). Found: m/z 138.1045 $[M]^+$. C$_9$H$_{14}$O. Calculated: M 138.1045.

1-Bromo-1-methyl-4-phenylsulfanylspiro[2.2]-pentane (X) was obtained from 1.37 g of bromo-fluorospiropentane **VIII**. The product was a mixture of two stereoisomers **A** and **B** at a ratio of 1:0.5. Yield 0.54 g (40%), colorless oily substance, R_f 0.1 (petroleum ether). ^{1}H NMR spectrum, δ, ppm (J, Hz): isomer **A**: 1.32–1.39 m (2H, CH$_2$), 1.40 d and 1.62 d (1H each, CH$_2$, ^2J = 6.1), 1.77 s (3H, CH$_3$), 2.77 d.d.d (1H, CH, ^3J = 7.3, 4.2, ^4J = 1.3), 7.08–7.45 m (5H, Ph); isomer **B**: 1.32–1.39 m (2H, CH$_2$), 1.34 d and 1.57 d (1H each, CH$_2$, ^2J = 6.0), 1.74 s (3H, CH$_3$), 2.83 d.d (1H, CH, ^3J = 7.3, 4.2), 7.08–7.45 m (5H, Ph). ^{13}C NMR spectrum, δ$_C$, ppm (J, Hz): isomer **A**: 16.89 (C^5, ^1J = 166), 22.09 (C^2, $^1J_{CH}$ = 158), 22.64 (C^4, ^1J = 164), 27.77 (CH$_3$, ^1J = 130), 29.82 (C$_{spiro}$), 126.21 (CH$_{arom}$), 128.04 (2C, CH$_{arom}$), 128.86 (2C, CH$_{arom}$), 137.09 (C$_{arom}$); isomer B: 19.05 (C^5, ^1J = 160), 21.27 (C^4, ^1J = 163), 22.01 (C^2, ^1J = 163), 27.56 (CH$_3$, ^1J = 127), 29.49 (C$_{spiro}$), 126.01 (CH$_{arom}$), 127.87 (2C, CH$_{arom}$), 128.80 (2C, CH$_{arom}$), 137.09 (C$_{arom}$). Found: m/z 271.9676 $[M]^+$. C$_{12}$H$_{13}$BrS. Calculated: M 271.9671.

REFERENCES

1. Lee-Ruff, E., *Meth. Org. Chem. (Houben–Weyl)*, 1997, vol. E17a, p. 2388; Fedoryński, M., *Chem. Rev.*, 2003, vol. 103, p. 1099.

2. Lukin, K.A., Zefirov, N.S., Yufit, D.S., and Struchkov, Y.T., *Tetrahedron*, 1992, vol. 48, p. 9977.

3. Averina, E.B., Karimov, R.R., Sedenkova, K.N., Grishin, Yu.K., Kuznetzova, T.S., and Zefirov, N.S., *Tetrahedron*, 2006, vol. 62, p. 8814; Sedenkova, K.N., Averina, E.B., Grishin, Yu.K., Kuznetsova, T.S., and Zefirov, N.S., *Russ. J. Org. Chem.*, 2008, vol. 44, p. 958; Averina, E.B., Sedenkova, K.N., Grishin, Yu.K., Kuznetzova, T.S., and Zefirov, N.S., *Arkivoc*, 2008, part (iv), p. 71.

4. Sedenkova, K.N., Averina, E.B., Grishin, Yu.K., Kuznetsova, T.S., and Zefirov, N.S., *Tetrahedron*, 2010, vol. 66, p. 8089.

5. Averina, E.B., Sedenkova, K.N., Borisov, I.S., Grishin, Yu.K., Kuznetsova, T.S., and Zefirov, N.S., *Tetrahedron*, 2009, vol. 65, p. 5693.

6. Zefirov, N.S. and Kuznetsova, T.S., *Synlett*, 2011, p. 2299; Sedenkova, K.N., Averina, E.B., Grishin, Yu.K., Rybakov, V.B., Kuznetzova, T.S., and Zefirov, N.S., *Eur. J. Org. Chem.*, 2010, p. 2145.

7. Zefirov, N.S., Kozhushkov, S.I., Kuznetsova, T.S., Kokoreva, O.V., Lukin, K.A., and Tratch, S.S., *J. Am. Chem. Soc.*, 1990, vol. 112, p. 7702.

8. Turkenburg, L.A.M., de Wolf, W.H., Bickelhaupt, F., Stam, C.H., and Konijn, M., *J. Am. Chem. Soc.*, 1982, vol. 104, p. 3471.

9. Banning, J.E., Prosser, A.R., Alnasleh, B.K., Smarker, J., Rubina, M., and Rubin, M., *J. Org. Chem.*, 2011, vol. 76, p. 3968.

10. Wiberg, K.B., Barnes, R.K., and Albin, J., *J. Am. Chem. Soc.*, 1957, vol. 79, p. 4994.

11. De Meijere, A., Kozhushkov, S.I., and Zefirov, N.S., *Synthesis*, 1993, p. 681.

12. Doering, W.v.E. and Hoffmann, A.K., *J. Am. Chem. Soc.*, 1954, vol. 76, p. 6162.

13. Mąkosza, M. and Wawrzyniewicz, M., *Tetrahedron Lett.*, 1969, vol. 10, p. 4659.

14. Dehmlow, E.V. and Lissel, M., *Chem. Ber.*, 1978, vol. 111, p. 3873.

15. Kharasche, M.S., Jensen, E.V., and Urry, W.H., *J. Am. Chem. Soc.*, 1947, vol. 69, p. 1100.