Reactions of diazoalkanes with unsaturated compounds
14.* Reactions of diazomethane, diazocyclopropane, and methyl diazoacetate with 1,1,2,2-tetrafluoro-3-vinylcyclobutane and 2,3,3-trifluoro-1-vinylcyclobutene to form [3+2] and [1+2] cycloadducts**

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The reactions of diazomethane and diazocyclopropane generated *in situ* with 1,1,2,2-tetrafluoro-3-vinylcyclobutane (**1**) and 2,3,3-trifluoro-1-vinylcyclobutene (**2**) proceeded at the double bond of the substituent as the 1,3-dipolar cycloaddition to form the corresponding 1-pyrazolines. Under the conditions of thermolysis (340—400 °C), the resulting cyclobutylpyrazolines **4** and **5** selectively lost the dinitrogen molecule to generate 3-cyclopropyl-1,1,2,2-tetrafluorocyclobutane (**6**) or 1,1,2,2-tetrafluoro-3-spiropentylcyclobutane (**7**), respectively, in high yields. In the presence of $Pd(acac)_2$, the reactions of these fluorine-containing unsaturated compounds and 2-chloro-1,1,2-trifluoro-3-vinylcyclobutane (**3**) with diazomethane gave rise directly to cyclopropane derivatives **6**, **11**, and **12**, respectively. The reactions of compounds **1** and **2** with methyl diazoacetate in the presence of $Rh_2(OAc)_4$ proceeded analogously to yield *cis*- and *trans*-disubstituted cyclopropanes.

Key words: fluorinated vinyl- and cyclopropylcyclobutanes and -cyclobutenes, tetrafluorocyclobutyl- and trifluorocyclobutenyl-1-pyrazolines, diazo compounds, catalytic cyclopropanation, 1,3-dipolar cycloaddition, thermal dinitrogen elimination.

The 1,3-dipolar addition to various unsaturated compounds giving rise to nitrogen heterocycles and the [1+2] cycloaddition of the carbenes, which are derived from the latter compounds, to form three-membered rings are typical chemical transformations of diazoalkanes producing new C—C bonds. The [1+2] cycloaddition reactions take place due to energetically favorable elimination of the nitrogen molecule from diazo compounds, which generally proceeds in the presence of transition metal complexes. These transformations were examined for a rich variety of alkenes, cycloalkenes, polyenes, and acetylenes as unsaturated substrates. However, the reactions of aliphatic diazo compounds with fluorine-containing unsaturated compounds remain poorly studied. For the most part, studies were devoted to the 1,3-dipolar cycloaddition involving unsaturated compounds containing fluorine atoms, which are either directly bound to the double bond[3—6] or are remote from this bond,[7—13] whereas examples of catalytic cyclopropanation of double bonds are few in number.[14,15] However, fluorine-containing cyclopropanes and pyrazolines obtained in these reactions are of interest as new synthons for preparing biologically active compounds.

In the present study, we examined the reactions of 1,1,2,2-tetrafluoro-3-vinylcyclobutane (**1**)[16] and 2,3,3-trifluoro-1-vinylcyclobutene (**2**)[17,18] with diazomethane and methyl diazoacetate (both in the presence and in the absence of catalysts) as well as with diazocyclopropane generated *in situ*. Vinylcyclobutene **2** was synthesized from readily accessible 2-chloro-1,1,2-trifluoro-3-vinylcyclobutane (**3**). However, contrary to procedures described previously,[17,18] dehydrochlorination of the latter compound was carried out under the action of a 45% aqueous solution (instead of alcoholic solution) of KOH in the presence of $PhCH_2Et_3N^+Cl^-$, which simplified isolation of the target product. In addition, we measured the ^{13}C and ^{19}F NMR spectra of diene **2**, which have not been described previously. The ^1H NMR spectra, which were recorded on instruments operating at different frequencies, revealed the equivalence of the methylene protons of the cyclobutene ring manifested as a doublet of triplets with the spin-spin coupling constants J = 12.0 and 3.0 Hz. The chemical shifts of these protons at δ 2.54 and 2.74 (60 MHz), which have been reported earlier,[17] are wrong and are in reality the manifestation of the spin-spin coupling constant J_{HF} = 12.0 Hz.

The direct reaction of tetrafluorovinylcyclobutane (**1**) with diazomethane in an ethereal solution proceeded rather slowly (20 °C, 3 days) to give a mixture of diastereomeric 3-(2,2,3,3-tetrafluorocyclobutyl)-1-pyrazolines (**4**) in a ratio of ~1.8 : 1 in a total yield of ~85%. Both isomers were isolated in the individual form

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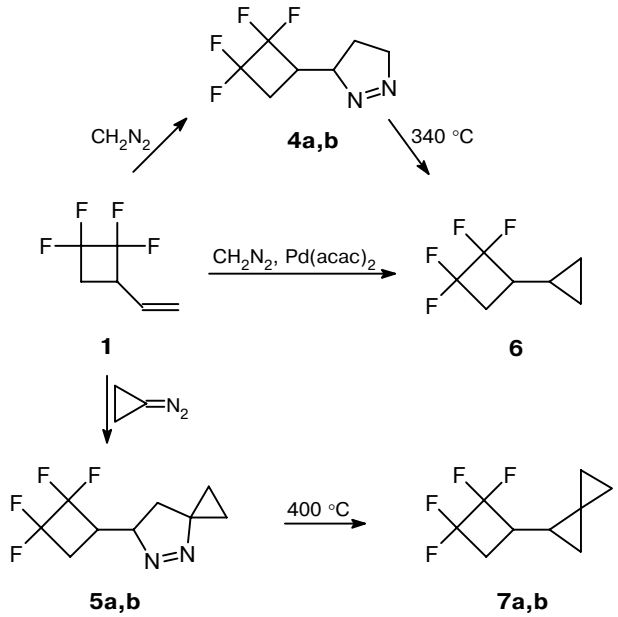
by preparative TLC and were characterized by the ^1H, ^{13}C, and ^{19}F NMR spectra. The spectra of both isomers are similar, each being characterized by the presence of the CH_2CH_2 fragment in the five-membered heterocycle. This is indicative of the regioselective addition of diazomethane to the unsymmetrically substituted double bond in **1**, the terminal nitrogen atom of the diazo compound forming a bond with the substituted C atom of the vinyl group.

Like the reaction of **1** with diazomethane, the reaction with diazocyclopropane, which was generated *in situ* by decomposition of *N*-cyclopropyl-*N*-nitrosourea under the action of MeONa at −20 °C or under the action of an equimolar mixture of KOH and K_2CO_3 at −10 °C, also afforded the corresponding 1,3-dipolar cycloaddition products, *viz.*, isomeric 5-cyclobutylspiro[1-pyrazoline-3,1′-cyclopropanes] (**5**) (Scheme 1). In the former case, isomeric pyrazolines **5** were obtained in a total yield of up to 48% (the isomer ratio was *ca.* 2.3 : 1), whereas the latter reaction gave rise to isomers of **5** in ~35% yield in a ratio of *ca.* 1.4 : 1. However, the target products obtained in the reaction with the use of a mixture of KOH and K_2CO_3 were more pure because the presence of MeONa led, apparently, to the partial replacement of the fluorine atoms by the methoxy groups to form the corresponding impurities. The isomers of **5** were separated by preparative TLC. The major isomer (**5a**) was isolated in the individual form, whereas isomer **5b** was enriched to ~85%. The ^1H NMR spectra of both spiro(pyrazolinecyclopropanes) **5** have two characteristic groups of signals at δ ~1.1 and 1.7−1.8 for the protons of the cyclopropane ring, which are in the *anti* and *syn* orientations, respectively, relative to the nitrogen atoms, and signals of the methylene fragment of the pyrazoline ring with the geminal spin-spin coupling constant of 12.8 Hz.

Scheme 1



Tetrafluorocyclopropylcyclobutane (**6**), which was obtained in 82—85% yield by passing a mixture of pyrazolines **4a,b** under a stream of argon through a quartz tube at 340 °C, was virtually free from impurities of isomerization and dehydrofluorination products, which indicates that this process is highly selective, unlike, for example, thermolysis of the products of the 1,3-dipolar cycloaddition of diazomethane to the strained endocyclic bond in 3,3-difluoro- and 3,3,4,4-tetrafluorocyclobutenes.[8]

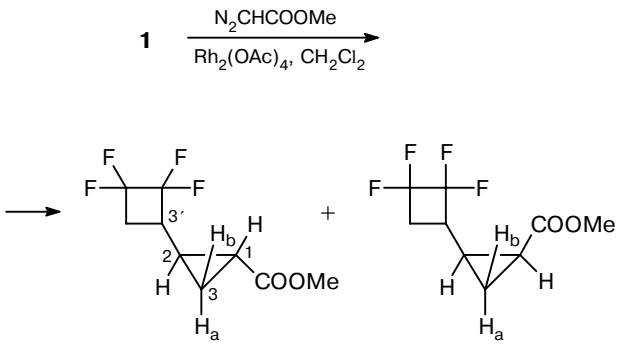
Compound **6** can also be prepared in one step by direct cyclopropanation of unsaturated compound **1** with diazomethane. The use of palladium compounds, in particular $Pd(acac)_2$, as catalysts for decomposition of CH_2N_2 made it possible to perform the reaction according to a one-pot procedure involving simultaneous generation of CH_2N_2 (from *N*-methyl-*N*-nitrosourea under the action of KOH) and its catalytic decomposition (see Ref. 19). The reaction with the use of a threefold molar excess (with respect to the initial **1**) of methylnitrosourea afforded cyclopropylcyclobutane **6** in ~90% yield.

Thermolysis of spiro(pyrazolinecyclopropane) **5** proceeded at higher temperature (400—410 °C) compared to that of pyrazoline **4** to give (tetrafluorocyclobutyl)spiropentane (**7**) as a mixture of two diastereomers in 70—75% yield. According to the ^{13}C and ^{19}F NMR spectra, spiropentanes **7a,b** were generated from pyrazoline **5a** in a ratio of 2.1 : 1, whereas the reaction of pyrazoline, which was enriched with isomer **5b** to 85%, gave rise to spiropentanes **7a,b** in a ratio of 1 : 1.2.

Unlike diazomethane, methyl diazoacetate virtually did not react with tetrafluorovinylcyclobutane **1** in the absence of catalysts at 20—25 °C; however, methyl diazoacetate eliminated the dinitrogen molecule in the presence of $Rh_2(OAc)_4$ (~1 mol.%) in CH_2Cl_2 accompanied by the addition of the carbene fragment at the double bond of **1**. The latter reaction afforded dimethyl fumarate and dimethyl maleate along with a mixture of isomeric methyl 2-(2,2,3,3-tetrafluorocyclobutyl)cyclopropanecarboxylates (**8**) (Scheme 2). These isomers were isolated by vacuum distillation in a total yield of ~50%. The ^1H NMR spectrum of the resulting product has four singlet signals of the methoxy groups at δ 3.69−3.72 with the integral intensity ratio of ~1.1 : 1 : 1.6 : 1.5, which is indicative of low selectivity of the addition of methoxycarbonylcarbene to the double bond of olefin **1**. Preparative TLC of the mixture of isomeric esters **8** on neutral Al_2O_3 yielded chromatographic zones enriched with the *trans* (R_f 0.57±0.04) and *cis* isomers (R_f 0.65±0.04) to approximately 92 and 80%, respectively. The ^1H NMR spectra of compounds from these zones have two sets of signals each and differ noticeably from one another in the multiplicities of the signals for the protons at the C(1) and C(3) atoms of the cyclopropane ring, which corresponds to the different vici-

nal spin-spin coupling constants (J_{cis} ~ 8.5 and J_{trans} ~ 5.0 Hz). Thus, two cisoid spin-spin coupling constants can appear only for the H(1) and H(3a) protons in the spectra of the *cis* isomers; on the contrary, two transoid constants should appear in the case of the H(3b) proton. Actually, the latter constants were observed in the ^{1}H NMR spectrum of the compounds from the upper zone (see the Experimental section). The NMR spectra of both specimens have two sets of signals each with the integral intensity ratio of ~1.5 : 1, which is attributable to the presence of diastereomers with respect to the asymmetrical C(2) and C(3′) atoms, respectively. However, the complexity of the signals for the corresponding methine protons involved in additional interactions with the F atoms did not allow us to assign them to the *parf* and *pref* series.

Scheme 2

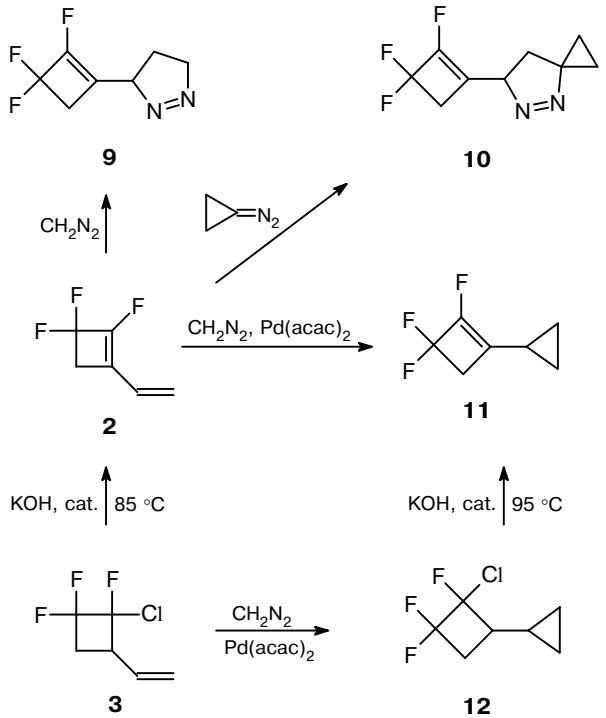


trans-**8a,b** *cis*-**8a,b**

Unlike the reaction of diazomethane with vinylcyclobutane **1**, the reaction with trifluorovinylcyclobutene **2** proceeded much more rapidly (during 0.5 h at 20 °C) and, in spite of the presence of the strained endocyclic double bond and the use of an excess of CH_2N_2, gave rise to the product of the 1,3-dipolar cycloaddition at the vinyl group, *viz.*, to 1-pyrazoline **9**, in ≥90% yield (Scheme 3). The fact that the reaction proceeded selectively at the vinyl group seems to be reasonable because it is known[3,7] that the presence of the fluorine atoms at the double bond leads to weakening of its dipolarophilic properties. The ^{1}H NMR spectrum of the resulting compound has one set of signals corresponding to the five-spin system of the α-substituted pyrazoline ring, the spin-spin coupling constants of the CH_2CH_2 fragment being in good agreement with those for isomeric pyrazolines **4a,b**. However, 1-pyrazoline **9** is unstable. Thus, it turned red and underwent rapid resinification even in attempting to concentrate its solutions at 5—10 °C. Interestingly, related spirocyclopropane-containing 1-pyrazoline **10** is more stable. The latter compound was obtained in 40—45% yield (according to the ^{1}H NMR spectroscopic data) by the addition of diazocyclopropane, which was generated by decomposition of *N*-cyclopropyl-*N*-nitrosourea with K_2CO_3 at *ca.* 0 °C, to olefin **1**. Vacuum microdistillation (0.1 Torr) of the reaction mixture afforded 5-(trifluorocyclobutenyl)spiro[1-pyrazoline-3,1′-cyclopropane] (**10**) with a purity of *ca.* 92%, which remained unchanged upon storage in a $CDCl_3$ solution for several days. In the earlier studies of other spiro[1-pyrazoline-3,1′-cyclopropanes],[20,21] we have observed the enhancement of stability of 1-pyrazolines upon the introduction of the spirocyclopropane fragment.

The catalytic (in the presence of $Pd(acac)_2$) reaction of diazomethane with unsaturated compound **2** also proceeded selectively at the vinyl group. However, the latter reaction, unlike the reaction with **1**, afforded 1-cyclopropyl-2,3,3-trifluorocyclobutene (**11**) in a yield of at most 40% even with the use of a fivefold excess of CH_2N_2. To estimate the reactivities of unsaturated acceptors **1** and **2**, we examined their cyclopropanation in the competitive reactions with styrene (the molar ratio CH_2N_2 : olefin **1** (or diene **2**) : styrene = 0.2 : 1 : 1); the formation of cyclopropylbenzene and cyclopropanes **6** or **11** was judged from the GLC data and the ^{1}H NMR spectra. All three unsaturated compounds showed approximately equal reactivities, the relative reactivity of vinylcyclobutene **2** being even slightly higher ($k_{rel} \approx 1.1$) than that of vinylcyclobutane **1** ($k_{rel} \approx 0.9$).

Scheme 3



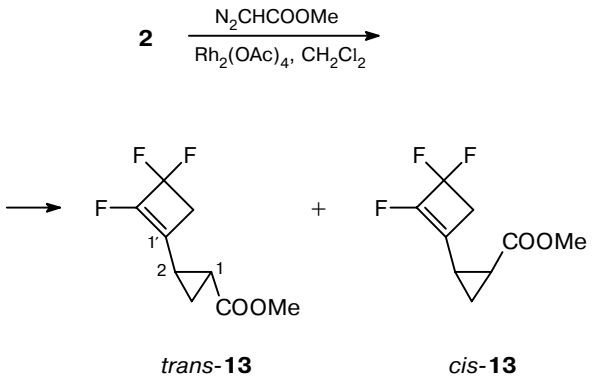
The relatively low yield of cyclopropylcyclobutene **11** (<40%) observed in catalytic cyclopropanation of diene **2** with diazomethane is, apparently, associated with a decrease in the catalytic activity of the Pd catalyst due to its transformation into an inactive complex with

pyrazoline **9**, which was concurrently formed through the 1,3-dipolar cycloaddition of CH_2N_2 to unsaturated compound **2** (see above).

Yet another procedure for the synthesis of compound **11** involves cyclopropanation by chlorotrifluorovinylcyclobutane (**3**) instead of rather labile trifluorovinylcyclobutene (**2**) followed by dehydrochlorination of the cyclopropanation product. The reaction of compound **3** (a mixture of two isomers) with diazomethane catalyzed by Pd compounds proceeded readily under the conditions of the simultaneous generation and catalytic decomposition of the latter[19] to form a mixture of isomeric 2-chloro-3-cyclopropyl-1,1,2-trifluorocyclobutanes (**12**) in a total yield of *ca.* 90%. These compounds are much more stable compared with **2**. Subsequent dehydrochlorination of a mixture of two isomers **12** with a 45% solution of KOH in the presence of $PhCH_2Et_3N^+Cl^-$ afforded cyclopropylcyclobutene **11** in 92% yield.

Cyclopropanation of diene **2** under the action of methyl diazoacetate in the presence of $Rh_2(OAc)_4$ also proceeded at the exocyclic double bond. The reaction with the use of the diene and methyl diazoacetate taken in a molar ratio of 2.2 : 1 gave rise to isomeric methyl 2-(trifluorocyclobutenyl)cyclopropanecarboxylates (**13**) in 58% yield in the ratio *trans*-**13** : *cis*-**13** of approximately 1.4 : 1.

Scheme 4



trans-**13** *cis*-**13**

The structures of the resulting compounds were established by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. Unlike the ^1H NMR spectra of vinyl- and cyclopropyl-substituted cyclobutenes **2** and **11**, the NMR spectra of isomeric esters **13** reveal the nonequivalence of the methylene protons of the four-membered ring due to the presence of the additional substituent in the cyclopropane fragment, this effect being more pronounced for the *cis* isomer ($\Delta\delta \approx 0.13$) than for the *trans* isomer ($\Delta\delta \approx 0.02$). Analogously, the ^{19}F NMR spectrum has a signal of the CF_2 group of the *trans* isomer as a multiplet with small spin-spin coupling constants ($J < 10$ Hz) resulting from coupling with the adjacent H and F atoms, whereas the signals for the fluorine atoms of the CF_2 group in the *cis* isomer have different chemical shifts ($\Delta\delta \approx 2.5$) and are split into a doublet with the spin-spin coupling constants $^2J_{FF} = 203$—205 Hz. An analogous situation was observed in the ^{19}F NMR spectra of pyrazolines **9** and **10** containing the asymmetrical C atom adjacent to the cyclobutene fragment; however, the difference between the chemical shifts of the geminal fluorine atoms in these cases is only 0.4—0.5 ppm (see the Experimental section).

To summarize, the 1,3-dipolar cycloaddition of diazomethane and diazocyclopropane generated *in situ* can proceed regioselectively at the vinyl group of compounds **1** and **2** and elimination of the dinitrogen molecule from 1-pyrazolines derived from vinylcyclobutane **1** can proceed selectively as exemplified by the reactions of 1,1,2,2-tetrafluoro-3-vinylcyclobutane (**1**) and 2,3,3-trifluoro-1-vinylcyclobutene (**2**) with diazo compounds. Catalytic cyclopropanation of the above-mentioned olefins with diazomethane in the presence of $Pd(acac)_2$ or with methyl diazoacetate in the presence of $Rh_2(OAc)_4$ made it possible to obtain the corresponding cyclopropylcyclobutanes or -cyclobutenes in rather high yields. The most convenient procedure for the preparative synthesis of 1-cyclopropyl-2,3,3-trifluorocyclobutene (**11**) involves cyclopropanation of 2-chloro-1,1,2-trifluoro-3-vinylcyclobutane (**3**) with diazomethane in the presence of $Pd(acac)_2$ followed by dehydrochlorination of the resulting 2-chloro-3-cyclopropyl-1,1,2-trifluorocyclobutane (**12**). The ^1H, ^{13}C, and ^{19}F NMR spectra of all the compounds synthesized were interpreted in detail.

Experimental

The ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200.13 and 50.3 MHz), Bruker AM-300 (300.13 and 75.5 MHz), and Bruker DRX-500 (500.13 MHz) spectrometers for solutions in $CDCl_3$ containing 0.05% of Me_4Si as the internal standard. The ^{19}F NMR spectra were measured on Bruker AC-200 (188.3 MHz) and Bruker DRX-500 (470.8 MHz) spectrometers; the chemical shifts are given relative to CCl_3F. The mass spectra were obtained on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, a 30-m RSL-200 capillary column or a direct inlet system). 1,1,2,2-Tetrafluoro-3-vinylcyclobutane (**1**), 2-chloro-1,1,2-trifluoro-3-vinylcyclobutane (**3**),[16—18] *N*-cyclopropyl-*N*-nitrosourea,[22] palladium acetylacetonate,[23] and dirhodium tetraacetate[24] were prepared according to known procedures. The solvents were distilled before use. Preparative TLC was carried out on plates (20×20 cm) with a nonfixed layer of an adsorbent (silica gel L 40/100 (Chemapol), unless otherwise indicated); the thickness of the layer was 2 mm. The competitive reactions of diazomethane with the unsaturated compounds (olefin **1**—styrene and diene **2**—styrene) were carried out according to a procedure described previously.[25]

2,3,3-Trifluoro-1-vinylcyclobutene (2). 2-Chloro-2,3,3-trifluoro-1-vinylcyclobutane (**3**) (34.2 g, 0.2 mol) and benzyltriethylammonium chloride (0.8 g, 3.5 mmol) were placed in a flask equipped with a stirrer, a dropping funnel, and a system for purging with argon. Then a 45% aqueous solution of KOH (20 mL) was added dropwise with intense stirring at 85 °C for 30 min, the product that formed with a small amount of water being collected (argon was fed at a rate of ~3 mL · min^{-1}) in a

trap cooled to −20 °C. The liquid phase was decanted from ice, dried with anhydrous Na_2SO_4, and distilled under reduced pressure. Trifluorovinylcyclobutene **2** was obtained as a colorless liquid in a yield of 22.8 g (83%), b.p. 49—50 °C (200 Torr) (*cf.* lit.[17,18]). ^{1}H NMR ($CDCl_3$), δ: 2.70 (dt, 2 H, CH_2, J_{HF} = 12.0 and 3.0 Hz); 5.40 (d, 1 H, =CH_2, J_{trans} = 17.2 Hz); 5.51 (d, 1 H, =CH_2, J_{cis} = 10.6 Hz); 6.54 (dd, 1 H, =CH, J_{trans} = 17.2 Hz, J_{cis} = 10.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 36.2 (dt, C(4), J_{CF} ≈ 19 and 22 Hz); 118.3 (td, CF_2, $^1J_{CF}$ = 272 Hz, $^2J_{CF}$ = 25 Hz); 122.9 (d, =CH_2, $^4J_{CF}$ = 7 Hz); 123.4 (td, C(1), $^3J_{CF}$ = 17 Hz, $^2J_{CF}$ = 5 Hz); 124.1 (br.d, =CH, J_{CF} = 3 Hz); 138.2 (dt, =CF, $^1J_{CF}$ = 350 Hz, $^2J_{CF}$ = 26 Hz). ^{19}F NMR ($CDCl_3$), δ: −110.3 (br.s, CF_2), −112.2 (br.t, =CF, $^4J_{HF}$ = 12.0 Hz).

3-(2,2,3,3-Tetrafluorocyclobutyl)-1-pyrazolines (4). A solution of 1,1,2,2-tetrafluoro-3-vinylcyclobutane (**1**) (6.94 g, 0.045 mol) and an ethereal solution (200 mL) of diazomethane (~7.6 g, 0.18 mol) were kept at 20 °C for 3 days and then passed through a layer of Al_2O_3 (1 cm). The solvent and the unconsumed starting compounds were removed at 20 Torr. A yellowish liquid was obtained in a yield 7.52 g (85%). According to the ^{1}H and ^{13}C NMR spectra, the liquid was a mixture of *parf*- and *pref*-cyclobutylpyrazolines **4** (the isomer ratio **4a** : **4b** ≈ 1.8 : 1). Found (%): C, 42.89; H, 4.20; N, 14.34. $C_7H_8F_4N_2$. Calculated (%): C, 42.86; H, 4.11; N, 14.28. The isomers were separated by preparative TLC (Al_2O_3; ether—heptane—methanol as the eluent, 1 : 6 : 1) and characterized by NMR spectroscopy.

Isomer 4a. R_f = 0.50. ^{1}H NMR ($CDCl_3$), δ: 1.25 (ddt, 1 H, H(4a), $^2J_{ab}$ = 13.0 Hz, ^3J = 9.5 Hz, ^3J ≈ 8.3 Hz); 2.00 (ddt, 1 H, H(4b), $^2J_{ab}$ = 13.0 Hz, ^3J ≈ 9.0 Hz, ^3J = 4.4 Hz); 2.57 (m, 1 H, H(3′)); 2.93 (m, 2 H, H(4′)); 4.34 (dddd, 1 H, H(5b), $^2J_{ab}$ = 17.2 Hz, ^3J = 9.3 Hz, ^3J = 8.2 Hz, ^4J = 2.4 Hz); 4.45 (m, 1 H, H(3)); 4.76 (dddd, 1 H, H(5a), $^2J_{ab}$ = 17.2 Hz, ^3J = 9.5 Hz, ^3J = 4.4 Hz, ^4J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 22.2 (s, C(4)); 34.0 (tdd, C(4′), $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 9.1 and 3.6 Hz); 43.1 (tdd, C(3′), $^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 10.1 and 3.5 Hz); 76.9 (s, C(5)); 85.2 (s, C(3)); 117.7 (ddt, CF_2, $^1J_{CF}$ = 295 and 282 Hz, $^2J_{CF}$ = 27 Hz); 118.1 (ddt, CF_2, $^1J_{CF}$ = 300 and 286 Hz, $^2J_{CF}$ = 25 Hz). ^{19}F NMR ($CDCl_3$), δ: −108.8 and −127.6 (both d, CF_2, J_{FF} = 209 Hz), −109.6 and −116.7 (both d, CF_2, J_{FF} = 208 Hz). The partial mass spectrum, m/z (I_{rel} (%)): 196 (1.5) $[M]^+$, 114 (7), 104 (100), 103 (46), 77 (40), 68 (97), 67 (68).

Isomer 4b. R_f = 0.34. ^{1}H NMR ($CDCl_3$), δ: 1.22 and 1.92 (both m, 1+1 H, C(4)H_2, $^2J_{ab}$ ≈ 13.0 Hz); 2.53 and 2.65 (both m, 1+1 H, C(4′)H_2); 3.08 (m, 1 H, H(3′)); 4.28 (dtd, 1 H, H(5b), ^2J = 17.5 Hz, ^3J ≈ 8.7 Hz, ^4J = 2.5 Hz); 4.56 (br.qt, 1 H, H(3), ^3J ≈ 8.5 Hz, ^4J ≈ 2.5 Hz); 4.76 (dddd, 1 H, H(5a), $^2J_{ab}$ = 17.5 Hz, ^3J = 9.7 Hz, ^3J = 4.0 Hz, ^4J = 2.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 20.7 (s, C(4)); 31.7 (td, C(4′), $^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 9.5 Hz); 41.9 (tdd, C(3′), $^2J_{CF}$ = 23 Hz, $^3J_{CF}$ = 9.9 and 3.3 Hz); 76.1 (s, C(5)); 83.9 (s, C(3)); 117.1 (ddt, CF_2, $^1J_{CF}$ = 296 and 284 Hz, $^2J_{CF}$ = 26 Hz); 118.2 (ddt, CF_2, $^1J_{CF}$ = 299 and 288 Hz, $^2J_{CF}$ = 26 Hz). The partial mass spectrum, m/z (I_{rel} (%)):196 (9) $[M]^+$, 114 (10), 104 (100), 103 (53), 77 (45), 68 (99), 67 (70).

5-(2,2,3,3-Tetrafluorocyclobutyl)spiro(1-pyrazoline-3,1′-cyclopropanes) (5). ***Method A.*** A solution of MeONa (0.22 g, 4 mmol) in methanol (1 mL) was added with intense stirring to a solution of tetrafluorovinylcyclobutane (**1**) (5.0 g, 32 mmol) and *N*-cyclopropyl-*N*-nitrosourea (0.39 g, 3 mmol) in CH_2Cl_2 (15 mL) at −20 °C for 15 min. Then the reaction mixture was stirred for 10 min and the temperature was raised to 20 °C during 30 min. The resulting straw-yellow turbid solution was passed through a layer of Al_2O_3 (~1 cm) and washed with CH_2Cl_2 (4 mL). The solvent and an excess of the olefin were distilled off on a rotary evaporator. A yellowish oil was obtained in a yield of 0.32 g (48%). According to the ^{1}H and ^{13}C NMR spectra, the liquid was a mixture of two isomeric pyrazolines **5** in the ratio **5a** : **5b** = 2.3 : 1. Found (%): C, 49.18; H, 4.95. $C_9H_{10}F_4N_2$. Calculated (%): C, 48.65; H, 4.54. The isomers were separated by preparative TLC (Al_2O_3; ether—heptane as the eluent, 5 : 4). Isomer **5a** was isolated in the individual form, whereas isomer **5b** was isolated with an impurity of isomer **5a** (~6 : 1).

Method B. A powdered mixture of K_2CO_3 (0.66 g, 4.8 mmol) and KOH (0.27 g, 4.8 mmol) was added with intense stirring to a solution of 1,1,2,2-tetrafluoro-3-vinylcyclobutane (**1**) (3.70 g, 24 mmol) and *N*-cyclopropyl-*N*-nitrosourea (0.48 g, 3.7 mmol) in CH_2Cl_2 (10 mL) at −10 °C. Then the reaction mixture was stirred for 30 min and the temperature was raised to 20 °C during 30 min. Subsequent treatment was carried analogously to the method A. A yellowish oil was obtained in a yield of 0.29 g (35%). According to the ^{1}H and ^{13}C NMR spectra, the liquid was a mixture of two isomeric pyrazolines **5a,b** in a ratio of 1.4 : 1.

Isomer 5a, R_f = 0.50, m.p. 39—41 °C. ^{1}H NMR ($CDCl_3$), δ: 1.12 (m, 2 H, H(1′) and H(2′), directed away from the N atom of the heterocycle); 1.55 (dd, 1 H, H(4b), ^2J = 12.8 Hz, $J_{4b,5}$ = 7.0 Hz); 1.68 and 1.81 (both m, 1 H each, H(1′) and H(2′), directed toward the N atom of the heterocycle); 2.06 (dd, 1 H, H(4a), ^2J = 12.8 Hz, $J_{4a,5}$ = 9.4 Hz); 2.63 (m, 1 H, C(3″)H); 2.91 (m, 2 H, C(4″)H_2); 4.70 (ddd, 1 H, H(5), $J_{5,3''}$ = 10.2 Hz, $J_{4a,5}$ = 9.4 Hz, $J_{4b,5}$ = 7.0 Hz). ^{13}C NMR (CD_2Cl_2), δ: 14.1 (s, CH_2CH_2); 30.0 (s, C(4)); 34.0 (tdd, C(4″)H_2, $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 9.9 and 3.0 Hz); 43.8 (tdd, C(3″)H, $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 9.8 and 4.2 Hz); 70.1 (s, C(5)); 84.1 (s, C(3)); 118.1 (ddt, CF_2, $^1J_{CF}$ = 290 and 268 Hz, $^2J_{CF}$ = 28 Hz); 118.5 (ddt, CF_2, $^1J_{CF}$ = 287 and 272 Hz, $^2J_{CF}$ = 27 Hz). ^{19}F NMR ($CDCl_3$), δ: −109.4 and −127.9 (both d, CF_2, J_{FF} = 209 Hz), −110.3 and −117.1 (both d, CF_2, J_{FF} = 208 Hz).

Isomer 5b, R_f = 0.38. ^{1}H NMR ($CDCl_3$), δ: 1.11 (m, 2 H, H(1′) and H(2′), directed away from the N atom of the heterocycle); 1.54 (dd, 1 H, H(4b), ^2J = 12.8 Hz, $J_{4b,5}$ = 7.4 Hz); 1.69 and 1.82 (both m, 1 H each, H(1′) and H(2′), directed toward the N atom of the heterocycle); 1.96 (dd, 1 H, H(4a), ^2J = 12.8 Hz, $J_{4a,5}$ = 9.4 Hz); 2.46 and 3.20 (both m, 1 H each, C(4″)H_2); 2.62 (m, 1 H, C(3″)H); 4.87 (br.dt, 1 H, H(5), $J_{4a,5}$ = 9.4 Hz, $J_{5,3''}$ ≈ $J_{4b,5}$ ≈ 7.4 Hz). ^{13}C NMR (CD_2Cl_2), δ: 14.2 (s, CH_2CH_2); 28.3 (s, C(4)); 32.1 (tdd, C(4″)H_2, $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 11 and 2.5 Hz); 42.6 (tdd, C(3″)H, $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 9.9 and 3.1 Hz); 69.5 (s, C(5)); 83.1 (s, C(3)); 117.6 (ddt, CF_2, $^1J_{CF}$ = 289 and 267 Hz, $^2J_{CF}$ = 28 Hz); 118.0 (ddt, CF_2, $^1J_{CF}$ = 286 and 272 Hz, $^2J_{CF}$ = 26 Hz). ^{19}F NMR ($CDCl_3$), δ: −107.6 and −129.3 (both d, CF_2, J_{FF} = 210 Hz), −110.4 and −118.5 (both d, CF_2, J_{FF} = 209 Hz).

3-Cyclopropyl-1,1,2,2-tetrafluorocyclobutane (6). *Cyclopropanation of olefin **1** with diazomethane.* The reaction was carried out under the conditions of the simultaneous generation and catalytic decomposition of CH_2N_2.[19] A solution of $Pd(acac)_2$ (0.015 g, 0.05 mmol) in CH_2Cl_2 (1 mL) was added to a stirred mixture of tetrafluorovinylcyclobutane **1** (0.77 g, 5 mmol) in CH_2Cl_2 (6 mL) and a 45% aqueous solution of KOH (5 mL) at 5 °C and then *N*-methyl-*N*-nitrosourea (1.54 g, 15 mmol) was added portionwise. The reaction mixture was stirred at 5—8 °C until liberation of nitrogen ceased. Then the organic layer was separated, passed through a thin layer of Al_2O_3, and fractionated under atmospheric pressure. Compound **6** was obtained as a colorless liquid in a yield of

0.75 g (89%), b.p. 113—115 °C. ^{1}H NMR ($CDCl_3$), δ: 0.25 and 0.61 (both m, 2 H each, CH_2CH_2); 0.82 (m, 1 H, CH in *cyclo*-C_3H_5); 2.13 (m, 2 H, H(4)); 2.55 (m, 1 H, H(3)). ^{13}C NMR ($CDCl_3$), δ: 2.5 and 3.5 (both s, CH_2CH_2); 7.6 (dd, CH in *cyclo*-C_3H_5, $^3J_{CF}$ = 6.3 and 3.2 Hz); 34.1 (tdd, C(4), $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 12 and 2.2 Hz); 45.0 (tdd, C(3), $^2J_{CF}$ = 21 Hz, $^3J_{CF}$ = 9.4 and 3.4 Hz); 117.7 (ddt, CF_2, $^1J_{CF}$ = 295 and 283 Hz, $^2J_{CF}$ = 27 Hz); 118.7 (ddt, CF_2, $^1J_{CF}$ = 299 and 288 Hz, $^2J_{CF}$ = 25 Hz). ^{19}F NMR ($CDCl_3$), δ: −111.2 and −130.3 (both d, CF_2, J_{FF} = 207 Hz), −111.4 and −118.6 (both d, CF_2, J_{FF} = 210 Hz). The partial mass spectrum, *m*/*z* (I_{rel} (%)): 168 (1) $[M]^+$, 153 (6), 117 (7), 104 (100), 103 (42), 99 (12), 84 (25), 77 (35), 68 (27), 67 (66). Found (%): C, 50.18; H, 5.00. $C_7H_8F_4$. Calculated (%): C, 50.01; H, 4.80.

Thermolysis of pyrazoline ***4***. Pyrazoline **4** (2.4 g, 12 mmol) as a mixture of isomers (1.8 : 1) was passed through a quartz tube (the inner diameter was 0.6 cm and the length was 18 cm), which was filled with small-sized quartz grains (by 2/3 of the volume) and purged with argon (4—5 mL · min^{-1}) at 340 °C for 1 h, the reaction products being collected in a trap cooled to −60 °C. The pyrolyzate was distilled and a colorless liquid was obtained in a yield of 1.66 g (82%), b.p. 113−114 °C. According to the GLC data and the ^{1}H and ^{13}C NMR spectra, the liquid was identical with compound **6** prepared as described above.

(2,2,3,3-Tetrafluorocyclobutyl)spiropentane (7) (a mixture of isomers). Pyrazoline **5a** (0.10 g, 0.45 mmol) was added microportionwise into a vertical pyrolyzer at 400 °C, the pyrolyzate was recondensed at 50 Torr into a cooled microtrap, and a mixture of diastereomeric spiropentanes **7** was obtained in a yield of 0.062 g (71%) (according to the ^{13}C NMR spectral data, **7a** : **7b** ≈ 2.1 : 1). ^{1}H NMR ($CDCl_3$), δ: 0.79 (m, CH_2CH_2 in both isomers); 0.67 and 1.10 (both m, 2 H(2) in both isomers); 1.31 (m, H(1) in both isomers); 2.11 and 2.50 (both m, C(4′)H_2 in isomer **b**); 2.23 and 2.59 (both m, C(4′)H_2 in isomer **a**); 2.30 and 2.47 (both m, C(3′)H in isomers **a** and **b**, respectively). ^{13}C NMR ($CDCl_3$), δ: 4.1 and 5.7 (both s, C(4,5) in isomer **a**); 4.3 and 5.5 (both s, C(4,5) in isomer **b**); 11.0 and 11.2 (both s, C(2) in isomers **a** and **b**, respectively); 12.7 and 13.6 (both s, C(3) in isomers **a** and **b**, respectively); 14.2 and 14.9 (both br.d, $^3J_{CF}$ ≈ 6, C(1) in isomers **a** and **b**, respectively); 33.1 and 33.8 (both m, C(4′)H_2 in isomers **b** and **a**, respectively); 43.3 (m, C(3′)H in both isomers); 118.0−118.9 (m, CF_2CF_2 in both isomers, $^1J_{CF}$ = 290−299 Hz, $^2J_{CF}$ ≈ 27 Hz). ^{19}F NMR ($CDCl_3$), δ: −109.2 and −129.7 (both d, CF_2 in isomer **a**, J_{FF} = 206 Hz); −109.3 and −118.1 (both d, CF_2 in isomer **a**, J_{FF} = 207 Hz); −109.7 and −128.3 (both d, CF_2 in isomer **b**, J_{FF} = 206 Hz); −110.7 and −117.3 (both d, CF_2 in isomer **b**, J_{FF} = 208 Hz).

Methyl 2-(2,2,3,3-tetrafluorocyclobutyl)cyclopropanecarboxylate (8). A solution of methyl diazoacetate (0.75 g, 7.5 mmol) in CH_2Cl_2 (2 mL) was added to a stirred solution of tetrafluorovinylcyclobutane (**1**) (3.08 g, 20 mmol) and $Rh_2(OAc)_4$ (0.031 g, 0.07 mmol) in CH_2Cl_2 (7 mL) at 20 °C for 4 h. After completion of the reaction, an excess of the olefin and the solvent were distilled off *in vacuo*. The residue (~1.2 g) was dissolved in ether (20 mL) and passed through a layer of Al_2O_3 (~1.5 cm) to remove the catalyst and the major portion of dimethyl fumarate and dimethyl maleate. After removal of the solvent and vacuum distillation, a colorless liquid with the b.p. 91—95 °C (24 Torr) was obtained in a yield of 0.84 g (49%), which contained no less than 95% (GLC, ^{1}H NMR spectrum) of the target product **8** as a mixture of four isomers (the ratio of the *trans*- and *cis*-esters was ~1.1 : 1, the ratio of the epimers in each ester **a** : **b** ≈ 1.6 : 1). Elemental analysis was carried out for a specimen, which was obtained by purification of the reaction product by TLC (Al_2O_3 5−40μ, heptane—ether, 1 : 1) and vacuum microdistillation of the chromatographic zone with R_f 0.60±0.05. Found (%): C, 47.95; H, 4.91. $C_9H_{10}F_4O_2$. Calculated (%): C, 47.80; H, 4.46. The partial mass spectrum of the major isomer, *m*/*z* (I_{rel} (%)): 226 (28) $[M]^+$, 195 (52), 127 (35), 111 (20), 103 (32), 59 (100). The mass spectra of the other isomers are characterized by very similar fragmentations and intensities of the peaks. To make the assignment of the signals in the ^{1}H NMR spectra, two chromatographic zones, which were enriched with the diastereomeric *trans* (R_f 0.57±0.04) and *cis* isomers (R_f 0.65±0.04) to ~92 and 80%, respectively, were isolated by preparative TLC under the same conditions. ^{1}H NMR ($CDCl_3$), δ: for *trans*-**8**, 0.84 (ddd, H(3a) in isomer **a**, ^2J = 4.7 Hz, J_{cis} = 8.3 Hz, J_{trans} = 6.5 Hz); 0.90 (ddd, H(3a) in isomer **b**, ^2J = 4.8 Hz, J_{cis} = 8.5 Hz, J_{trans} = 6.3 Hz); 1.29 (ddd, H(3b) in isomer **a**, ^2J = 4.7 Hz, J_{cis} = 8.4 Hz, J_{trans} = 6.0 Hz); 1.33 (dt, H(3b) in isomer **b**, $^2J \approx J_{trans}$ = 4.7 Hz, J_{cis} = 8.5 Hz); 1.55 (dt, H(1) in isomer **b**, J_{cis} = 8.5 Hz, J_{trans} ≈ 4.7 Hz); 1.60 (m, H(1) in isomer **a** and H(2) in both isomers); 2.22 (m, CH_2CF_2); 2.61 (m, $CHCF_2$); for *cis*-**8**, 1.03 (dt, H(3a) in isomer **a**, $^2J \approx J_{1,2}$ = 5.1 Hz, $J_{2,3}$ = 6.8 Hz); 1.12 (dt, H(3a) in isomer **b**, $^2J \approx J_{1,2}$ = 5.1 Hz, $J_{2,3}$ = 6.7 Hz); 1.16 (dt, H(3b) in isomer **a**, ^2J = 4.8 Hz, J_{cis} = 8.4 Hz); 1.26 (dt, H(3b) in isomer **b**, ^2J = 4.8 Hz, J_{cis} = 8.4 Hz); 1.43 (m, H(2) in both isomers); 1.81 (dt, H(1) in isomer **b**, J_{trans} = 5.5 Hz, J_{cis} = 8.4 Hz); 1.91 (dt, H(1) in isomer **a**, J_{trans} = 5.5 Hz, J_{cis} = 8.4 Hz); 2.16, 2.51 and 2.90 (all m, $CHCH_2CF_2$ in isomer **b**), 2.19, 2.69 and 2.91 (all m, $CHCH_2CF_2$ in isomer **a**). ^{19}F NMR ($CDCl_3$), δ: from −110.2 to −111.6 (overlapping doublets of the C(1)F_2 group of all four isomers); −118.0 and −129.4 (both d, C(2)F_2 in isomer *trans*-**8a**, J_{FF} = 207 Hz); −118.2 and −129.6 (both d, C(2)F_2 in isomer *trans*-**8b**, J_{FF} = 207 Hz); −118.3 and −130.2 (both d, C(2)F_2 in isomer *cis*-**8a**, J_{FF} = 207 Hz); −118.4 and −130.5 (both d, C(2)F_2 in isomer *cis*-**8b**, J_{FF} = 207 Hz).

3-(2,3,3-Trifluorocyclobuten-1-yl)-1-pyrazoline (9). Trifluorovinylcyclobutene (**2**) (0.11 g, 0.8 mmol) was added to an ethereal solution (5 mL) of diazomethane (~3 mmol) at 20 °C and the reaction mixture was kept for 0.5 h. Then a portion (1/10) of the reaction solution was withdrawn, $CDCl_3$ (0.5 mL) was added at −10 °C, and the ether was distilled off *in vacuo*. Then $CDCl_3$ (0.3 mL) was added and the reaction mixture was concentrated *in vacuo* to 0.4 mL. According to the ^{1}H NMR spectrum, the resulting compound was pyrazoline **9** with the purity of 93−95%. ^{1}H NMR ($CDCl_3$), δ: 1.59 (ddt, 1 H, H(4a), $^2J_{ab}$ = 12.5 Hz, ^3J = 9.5 Hz, ^3J ≈ 8.0 Hz); 2.02 (dtd, 1 H, H(4b), $^2J_{ab}$ = 12.5 Hz, ^3J ≈ 9.3 Hz, ^3J = 4.7 Hz); 2.78 (m, 2 H, C(4′)H_2, $^4J_{HF}$ = 12.1 Hz); 4.42 (dddd, 1 H, H(5b), $^2J_{ab}$ = 17.5 Hz, ^3J = 9.3 Hz, ^3J = 8.0 Hz, ^4J = 2.2 Hz); 4.79 (dddd, 1 H, H(5a), $^2J_{ab}$ = 17.5 Hz, ^3J = 9.5 Hz, ^3J = 4.7 Hz, ^4J = 2.3 Hz); 5.09 (m, 1 H, H(3)). ^{19}F NMR ($CDCl_3$), δ: −111.3 (ttd, =CF, $^4J_{FH}$ = 12.1 Hz, $^3J_{FF} \approx {}^4J_{FH}$ = 4.0 Hz); −112.2 and −112.7 (both br.d, CF_2, $^2J_{FF}$ ≈ 202 Hz). The remaining portion of the reaction mixture was concentrated *in vacuo* and a reddish liquid, which underwent rapid resinification at room temperature, was obtained in a yield of 0.13 g.

5-(2,3,3-Trifluorocyclobuten-1-yl)spiro[1-pyrazoline-3,1′-cyclopropane] (10). A powdered mixture of K_2CO_3 (0.66 g, 4.8 mmol) and KOH (0.30 g, 4.8 mmol) was added with intense stirring to a solution of trifluorovinylcyclobutene (**2**) (1.34 g, 10 mmol) and *N*-cyclopropyl-*N*-nitrosourea (0.48 g, 3.7 mmol) in CH_2Cl_2 (5 mL) at −5 °C. The reaction mixture was stirred for 30 min, filtered through a dense filter, and washed with CH_2Cl_2. The filtrate was concentrated *in vacuo* without heating. Then the residue was treated with ether

(3 mL) and passed through a thin layer of neutral Al_2O_3. After removal of the solvents, a viscous liquid was obtained in a yield of 0.43 g. The major signals in the ^1H NMR spectrum of this liquid corresponded to compound **10**. Taking into account the integral intensity of the signals and the amount of the compound obtained, the yield of the target product was 40—45%. Microdistillation of the residue *in vacuo* (0.1 Torr) afforded pyrazoline **10** in a yield of 0.19 g (24%) with the purity of ~90% (T_{bath} 90—95 °C). ^1H NMR ($CDCl_3$), δ: 1.16 (m, 2 H, H(1′) and H(2′), directed away from the N atom of the heterocycle); 1.79 (m, 2 H, H(1′) and H(2′), oriented toward the N atom of the heterocycle); 1.82 (dd, 1 H, H(4b), ^2J = 12.6 Hz, $J_{4b,5}$ = 7.2 Hz); 2.09 (dd, 1 H, H(4a), ^2J = 12.6 Hz, $J_{4a,5}$ = 9.7 Hz); 2.73 (m, 2 H, C(4″)H_2); 5.32 (m, 1 H, H(5)). ^{19}F NMR ($CDCl_3$), δ: −111.7 (=CF); −112.4 and −112.8 (AB spectrum, CF_2, $^2J_{FF}$ ≈ 203 Hz). Attempts to purify the resulting pyrazoline by TLC (on SiO_2 or Al_2O_3) led to its transformation into unidentified compounds.

1-Cyclopropyl-2,3,3-trifluorocyclobut-1-ene (11). ***Method A.*** An excess of diazomethane, which was generated in an individual reactor by decomposition of *N*-methyl-*N*-nitrosourea (8.2 g, 0.08 mol) and then was blew off with a stream of argon, was passed through a solution of trifluorovinylcyclobutene **2** (2.15 g, 0.016 mol) and $Pd(acac)_2$ (0.05 g, 0.16 mmol) in a mixture of pentane (2 mL) and CH_2Cl_2 (3 mL) at 0—5 °C for ~2 h (see Refs. 26 and 27). After completion of the reaction, the mixture was filtered through a layer of Al_2O_3 (~1 cm) and fractionated in the presence of hydroquinone. The fractions contained the initial diene **2** and cyclopropylcyclobutene **11** in different ratios. According to the GLC data and the ^1H NMR spectrum, the last fraction (0.42 g) with the b.p. 72—73 °C (200 Torr) contained 95—96% of compound **11**. The total yield of cyclopropyltrifluorocyclobutene (taking into account all fractions) was 38—40%. ^1H NMR ($CDCl_3$), δ: 0.71 and 0.89 (both m, 2 H each, CH_2CH_2); 1.62 (m, 1 H, CH), 2.36 (dt, 2 H, CH_2, J_{HF} = 12.0 and 2.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 5.5 (s, CH_2CH_2); 6.9 (q, CH, J_{CF} ≈ 4 Hz); 36.3 (dt, C(4), J_{CF} ≈ 19 and 22 Hz); 118.0 (td, CF_2, $^1J_{CF}$ = 275 Hz, $^2J_{CF}$ = 26 Hz); 129.5 (td, C(1), J_{CF} ≈ 17 and 6 Hz); 138.4 (dt, CF, $^1J_{CF}$ = 336 Hz, $^2J_{CF}$ = 26 Hz). ^{19}F NMR ($CDCl_3$), δ: −111.6 (br.s, CF_2), −120.6 (br.t, =CF, $^4J_{HF}$ = 12 Hz). The partial mass spectrum, *m/z* (I_{rel} (%)): 148 (61) $[M]^+$, 147 (16), 133 (100), 127 (38).

Method B. *Step 1.* **2-Chloro-3-cyclopropyl-1,1,2-trifluorocyclobutanes (12).** The reaction was carried out analogously to the synthesis of compound **6** under the conditions of the simultaneous generation and catalytic decomposition of CH_2N_2.[19] A solution of 2-chloro-1,1,2-trifluoro-3-vinylcyclobutane (**3**) (12.0 g, 0.07 mol) in a mixture of pentane (30 mL) and CH_2Cl_2 (20 mL) was added to a 45% aqueos solution of KOH (50 mL) at 5 °C. Then a solution of $Pd(acac)_2$ (0.15 g, 0.5 mmol) in CH_2Cl_2 (2 mL) was added and *N*-methyl-*N*-nitrosourea (12.4 g, 0.12 mol) was added portionwise (0.5—0.8 g per portion, during 12—15 min) with stirring, the temperature being maintained at 5—8 °C. After completion of gas evolution, the organic layer was separated and passed through a thin layer of Al_2O_3. The adsorbent was washed with pentane (3 mL) and the solution was dried with anhydrous $CaCl_2$ and fractionated under atmospheric pressure. Chlorocyclopropyltrifluorocyclobutane **12** was obtained as a mixture of two isomers in a ratio of ~1 : 1 in a yield of 11.5 g (89%); colorless liquid, b.p. 137—140 °C. ^1H NMR (200 MHz, $CDCl_3$), δ: 0.12—0.45 and 0.53—0.79 (both m, 2 H each, CH_2CH_2); 0.87—1.10 (m, 1 H, CH); 1.95—2.80 (m, 3 H, $CHCH_2$). ^{19}F NMR ($CDCl_3$), δ; for isomer **12a**: −98.2 and −117.6 (both br.d, CF_2, $^2J_{FF}$ = 197 Hz), −135.5 (br.s, CClF), for isomer **12b**: −105.9 and −108.4 (both br.d, CF_2, $^2J_{FF}$ = 198 Hz); −111.2 (br.s, CClF). The partial mass spectrum, *m/z* (I_{rel} (%)): 169 and 171 (2 and 0.7) $[M-Me]^+$, 149 (21) $[M-Cl]^+$, 120 and 122 (37 and 13) $[M-(CF_2=CH_2)]^+$, 85 (80) $[C_5H_6F]^+$, 67 (100) $[C_5H_7]^+$.

Step 2. A 45% aqueous solution of KOH (7 mL, 0.09 mmol) was added dropwise with intense stirring to a mixture of isomers of chlorocyclopropyltrifluorocyclobutane **12** (8.3 g, 0.045 mol) and $PhCH_2Et_3N^+Cl^-$ (0.2 g) under an atmosphere of argon at 95 °C during 0.5 h. Cyclopropyltrifluorocyclobutene **11** that formed was blew off with a stream of argon (3—4 mL · min^{-1}) into a trap cooled to −20 °C. The product was dried with anhydrous Na_2SO_4 and distilled under atmospheric pressure. 1-Cyclopropyl-2,3,3-trifluorocyclobutene (**11**) was obtained in a yield of 6.1 g (92%) with the purity of *ca.* 98%, b.p. 110—111 °C. The spectral characteristics corresponded to the compound obtained according to the method A. Found (%): C, 56.48; H, 4.51. $C_7H_7F_3$. Calculated (%): C, 56.76; H, 4.76.

Methyl *cis*-/*trans*-2-(2,3,3-trifluorocyclobuten-1-yl)cyclopropanecarboxylate (13). Dirhodium tetraacetate $Rh_2(OAc)_4$ (0.057 g, 0.15 mmol) was added to a stirred solution of trifluorovinylcyclobutene (**2**) (5.36 g, 0.04 mol) in CH_2Cl_2 (10 mL) and then a solution of methyl diazoacetate (1.80 g, 0.018 mol) in CH_2Cl_2 (2 mL) was added at 20 °C for 4 h. The reaction mixture was concentrated and the residue was dissolved in ether and passed through a layer of Al_2O_3. After removal of the solvents and vacuum distillation, ether **13** was obtained as a mixture of *trans* and *cis* isomers in a yield of 2.15 g (58%) in a ratio of 1.4 : 1, b.p. 60—62 °C (10 Torr). ^1H NMR ($CDCl_3$), δ: for *trans*-**13**: 1.20 (ddd, H(3a), ^2J = 4.8 Hz, J_{cis} = 8.5, J_{trans} = 6.1 Hz); 1.50 (m, H(3b)); 1.94 (ddd, H(1), J_{cis} = 8.6 Hz, J_{trans} = 4.5 and 5.6 Hz); 2.19 (m, H(2)); 2.45 (m, CH_2CF_2); 3.72 (s, OMe), for *cis*-**13**: 1.34 (dt, H(3b), ^2J = 5.0 Hz, J_{cis} = 8.5 Hz); 1.50 (m, H(3a)); 1.98 (m, H(2)); 2.55 (dt, H(1), J_{trans} = 6.0 Hz, J_{cis} = 8.4 Hz); 2.53 and 2.66 (both m, CH_2CF_2); 3.70 (s, OMe). ^{13}C NMR ($CDCl_3$), δ: for *trans*-**13**: 13.9 (s, C(3)); 17.0 (q, C(2), J_{CF} ≈ 4 Hz); 20.2 (s, C(1)); 36.8 (dt, C(4′), J_{CF} ≈ 18 and 23 Hz); 52.3 (s, OMe); 117.6 (td, CF_2, $^1J_{CF}$ = 275 Hz, $^2J_{CF}$ = 26 Hz); 125.5 (C(1′)); 139.6 (dt, CF, $^1J_{CF}$ = 340 Hz, $^2J_{CF}$ = 25 Hz); 172.5 (C=O), for *cis*-**13**: 12.4 (s, C(3)); 15.5 (q, C(2), J_{CF} ≈ 4 Hz); 20.8 (s, C(1)); 38.8 (dt, C(4′), J_{CF} ≈ 18 and 23 Hz); 52.1 (s, OMe); 117.7 (td, CF_2, $^1J_{CF}$ = 275 Hz, $^2J_{CF}$ = 26 Hz); 125.3 (C(1′)); 140.0 (dt, CF, $^1J_{CF}$ = 340 Hz, $^2J_{CF}$ = 25 Hz); 171.4 (C=O). ^{19}F NMR ($CDCl_3$), δ: for *trans*-**13**: −112.1 (CF_2); −116.0 (=CF); for *cis*-**13**: −111.6 and −114.1 (both br.d, CF_2, $^2J_{FF}$ ≈ 204 Hz); −113.6 (=CF). The partial mass spectrum, *m/z* (I_{rel} (%)): 206 (26) $[M]^+$, 186 (9), 175 (20), 127 (75), 59 (100). Found (%): C, 52.16; H, 4.49. $C_9H_9F_3O_2$. Calculated (%): C, 52.43; H, 4.40.

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