1,3-Dipolar cycloaddition of diazomethane and diazocyclopropane to 2-fluoro-3-methylbutadiene and thermal transformations of fluorine-containing vinylpyrazolines and vinylcyclopropanes ✽

E. V. Guseva, N. V. Volchkov, E. V. Shulishov, Yu. V. Tomilov, and O. M. Nefedov*

N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 6390. E-mail: tom@ioc.ac.ru

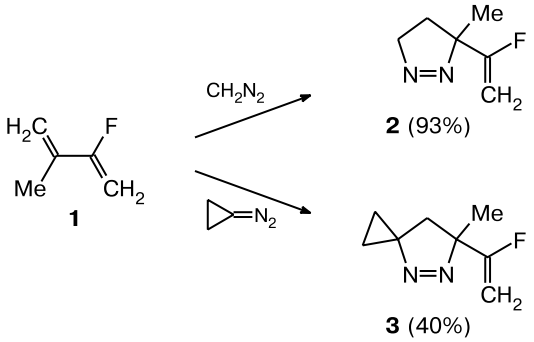
Reactions of 2-fluoro-3-methylbuta-1,3-diene with diazomethane in ether at 15 °C and with diazocyclopropane generated *in situ* by decomposition of *N*-cyclopropyl-*N*-nitrosourea in the presence of K_2CO_3 in CH_2Cl_2 at −10 °C selectively involve the double bond at the methyl group to give 3-(1-fluorovinyl)-3-methylpyrazolines. Thermal dediazotization of the latter at 250 °C yields 1-(1-fluorovinyl)-1-methylcyclopropane and -spiropentane **5**, which are capable of isomerizing, under more severe conditions (400—600 °C), into 1-fluoro-2-methylcyclopent-1-ene and 5-fluoro-4-methylspiro[2.4]hept-4-ene (**7**), respectively. Spiropentane derivative **5** partially isomerizes into 1-fluoro-2-methyl-3-methylidenecyclohex-1-ene. In a similar way, thermolysis of 6-(2,3,3-trifluorocyclobut-1-enyl)-4,5-diazaspiro[2.4]hept-4-ene at 400 °C gives a mixture of 1-(spiropentyl)-2,3,3-trifluorocyclobut-1-ene and 2,3,3-trifluoro-1-(2-methylidenecyclobutyl)cyclobut-1-ene. Thermolysis of 1-cyclopropyl-2,3,3-trifluorocyclobut-1-ene at 550—620 °C affords a mixture of 1-(trifluorovinyl)cyclopentene and 2,3-difluorotoluene.

Key words: fluorovinylcyclopropanes, fluorovinylpyrazolines, trifluorocyclobutenes, fluorocycloalkenes, spiropentanes, dediazotization, thermolysis, rearrangements; ^1H, ^{13}C, and ^{19}F NMR spectra.

Fluorinated vinylcyclopropanes,[1—4] which can isomerize into fluorine-containing cyclopentenes, are of certain interest as fluorine-containing starting material. The presence of fluorine atoms in the cyclopropane fragment can reduce the energy of activation of the vinylcyclopropane→cyclopentene rearrangement (thus facilitating it)[2—4] or even change the direction of the reaction compared to analogous nonfluorinated structures.[4] The effect of F atoms in the vinyl group of vinylcyclopropanes on their thermal transformations has not been discussed to date.

In the present work, we studied 1,3-dipolar cycloaddition of diazomethane and diazocyclopropane to 2-fluoro-3-methylbuta-1,3-diene, which affords the corresponding pyrazolines, and thermal dediazotization of the pyrazolines obtained and previously synthesized 6-(2,3,3-trifluorocyclobut-1-enyl)-4,5-diazaspiro[2.4]hept-4-ene.[5] Deeper thermolysis of (fluorovinyl)cyclopropanes, spiropentanes, and 1-cyclopropyl-2,3,3-trifluorocyclobut-1-ene[5] were also investigated.

The reaction of 2-fluoro-3-methylbuta-1,3-diene (**1**) with diazomethane in ether (15 °C, 3 days) selectively involves the methylated double bond to give 3-(1-fluorovinyl)-3-methylpyrazoline (**2**) in ~95% yield. In the olefin range, its ^1H NMR spectrum contains no signals other than for protons of a fluorovinyl group with characteristic spin-spin coupling constants ($J_{H,F\text{-}cis}$ = 17.7 and $J_{H,F\text{-}trans}$ = 49.9 Hz). The N atom is attached to the methylated carbon atom, which follows from the ^1H NMR signals for the CH_2—CH_2 fragment included in the five-membered ring of the resulting pyrazoline (^3J = 7.7 Hz). According to the data on the highest reactivity of electron-deficient double bonds in 1,3-dipolar cycloaddition,[6] the observed regioselective addition of diazoalkanes suggests that the α-fluorovinyl group in diene **1** exhibit electron-withdrawing properties relative to the isopropenyl fragment.



The reaction of fluorobutadiene **1** with diazocyclopropane (generated *in situ* by decomposition of *N*-cyclo-

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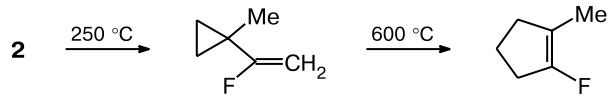
propyl-*N*-nitrosourea in the presence of an equimolar mixture of KOH and K_2CO_3 in CH_2Cl_2 at −5 °C) also involves the methylated double bond to highly regioselectively give 6-(1-fluorovinyl)-6-methyl-4,5-diazaspiro[2.4]hept-4-ene (**3**) in ~40% yield. The presence of the quaternary C atoms at the endocyclic azo group makes this compound very stable and capable of being distilled *in vacuo* (0.1 Torr). It should be noted that the reactions of 2-methylbutadiene with both diazomethane[7] and diazocyclopropane[8] involve the nonsubstituted double bond; in the latter case, the resulting 1-pyrazoline is very labile.

Because 1-pyrazolines are known to easily undergo thermal decomposition to give cyclopropanes and/or corresponding isomeric olefins,[9] we studied the thermolysis of pyrazolines **2** and **3** with the aim of obtaining fluorovinylcyclopropanes. Pyrolysis was carried out by passing the vapor of pyrazoline with argon through a quartz tube packed with quartz (atmospheric pressure, $T > 250$ °C).

It turned out that the thermolysis of pyrazoline **2** proceeds smoothly at 250—260 °C to give 1-(1-fluorovinyl)-1-methylcyclopropane (**4**) in up to 85% yield, its isomeric compounds being virtually absent. The spectroscopic characteristics of compound **4** fully agree with the sample prepared by catalytic cyclopropanation of fluorobutadiene **1** with diazomethane in the presence of $Pd(acac)_2$.[10]

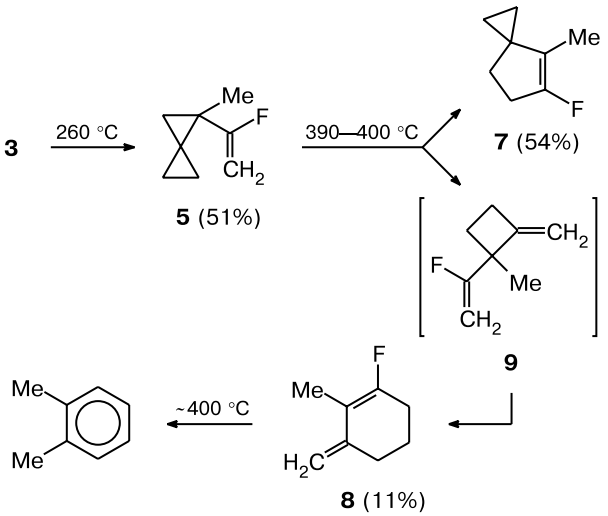


4 (85%) **6** (22%)

Under analogous thermolysis conditions, the conversion of spirocyclopropane-containing pyrazoline **3** is also fairly high; however, considerable resinification arises, in contrast to pyrazoline **2**. Nevertheless, the major volatile product is 1-(1-fluorovinyl)-1-methylspiropentane (**5**) (yield up to 51%), which was structurally identified by ^1H and ^{13}C NMR spectroscopy (see Experimental).

Subsequent transformations of vinylcyclopropanes **4** and **5** require very drastic conditions, especially for compound **4** (its high conversion was reached only at 580—600 °C). Under these conditions, the isomerization of compound **4** mainly gives the expected volatile 1-fluoro-2-methylcyclopentene (**6**); however, its yield is only 22%.

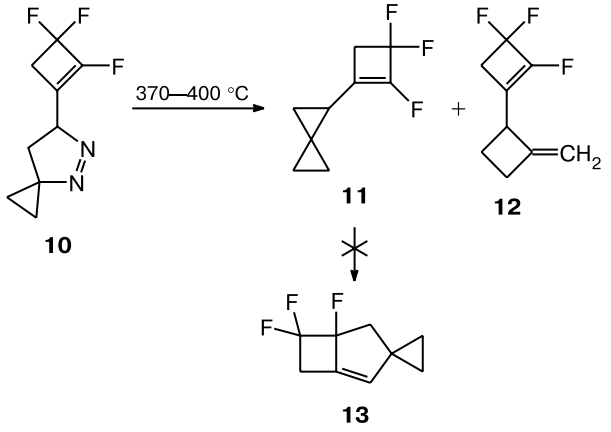
The isomerization of vinylspiropentane **5** proceeds virtually completely at 390—400 °C; the major volatile products are 5-fluoro-4-methylspiro[2.4]hept-4-ene (**7**) and 1-fluoro-2-methyl-3-methylidenecyclohex-1-ene (**8**) (total yield was 65—68%; **7** : **8** ≈ 5 : 1). Compound **7** was isolated by preparative GLC (98% purity); compound **8** was enriched to ~85%. The structures of the fluorocycloalkenes obtained were determined from ^1H, ^{13}C, and ^{19}F NMR spectra. Both compounds contain the FC=CMe fragment; the spectra of compound **7** show characteristic high-field signals for the spirocyclopropane fragment, while the spectra of compound **8** show signals for the methylidene fragment and three alicyclic CH_2-group. The thermolysis of vinylspiropentane **5** at 430—440 °C gives a more complex mixture containing *o*-xylene (~10%) and a number of unidentified compounds. The total yield of compounds **7** and **8** decreases to ~50% and the ratio of **7** : **8** is ~2.6 : 1).



The formation of spiroheptene **7** is due to a vinylcyclopropane→cyclopentene rearrangement, which is analogous to the isomerization of isopropenylspiropentane into 5-methylspiro[2.4]hept-4-ene at 235—275 °C.[11] The minor product **8** (~11%) seems to form as a result of the rearrangement of the spiropentane fragment in compound **5** to the corresponding methylidenecyclobutane **9**, which is probably unstable at 380—400 °C and isomerizes into the more stable cyclohexene **8**. The thermolysis of the latter at a higher temperature affords *o*-xylene *via* dehydrofluorination. Indeed, thermal isomerization of spiropentanes usually leads to the corresponding methylidenecyclobutanes, most probably through the initial cleavage of the C(1)—C(2) bond rather than the C(1)—C(3) bond.[11] Thus, the presence of fluorine in the vinyl fragment of vinylspiropentanes radically does not affect the direction of their isomerization.

In addition, we studied the thermolysis of 4,5-diazaspiro[2.4]hept-4-ene **10** obtained earlier from 2,3,3-trifluoro-1-vinylcyclobut-1-ene and the *in situ* generated diazocyclopropane.[5] Compound **10** (~92% purity) is very labile;[5,12] however, its noticeable dediazotization occurs only at $T > 320$ °C and is accompanied by intense resinification. At 370 °C, the conversion of pyrazoline **10** is no higher than 60% and the volatile fraction of pyrolyzates mainly contains the expected 2,3,3-trifluoro-1-(spiropent-1-yl)cyclobutene (**11**); the yield of compound **11** from the starting pyrazoline is ~22%. At 400 °C, compound **10** converts virtually completely to give spiro-

pentane **11** and its isomer, namely, 2,3,3-trifluoro-1-(2-methylidenecyclobutyl)cyclobut-1-ene (**12**) in a total yield of ~27% (**11** : **12** ≈ 2.5 : 1). The structures of products **11** and **12** containing the 2,3,3-trifluorocyclobutenyl fragment were proved by ^{1}H, ^{13}C, and ^{19}F NMR spectra. The pyrolysis of pyrazoline **10** at 400 °C gives a number of minor products; however, isomer **13** was not detected.



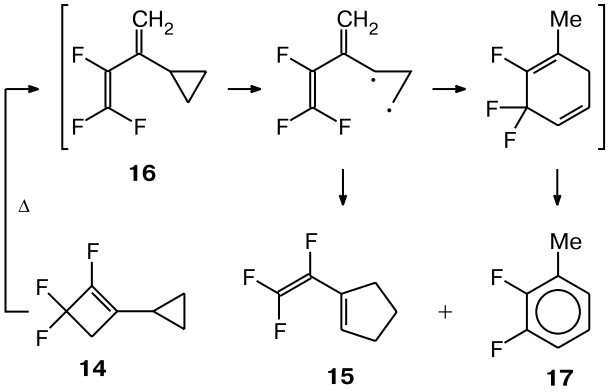
Unlike spiropentane **11**, 1-cyclopropyl-2,3,3-trifluorocyclobut-1-ene (**14**) is resistant to pyrolysis up to 530 °C. Its conversion at 550 °C was ~20%, mainly giving 1-(trifluorovinyl)cyclopent-1-ene (**15**) (Table 1). Apparently, the cyclobutene ring of compound **14** undergoes opening to give diene **16**, which then isomerizes into vinylcyclopentene **15**. It should be noted that the nonfluorinated hydrocarbon analog of compound **14**, namely, 1-cyclopropylcyclobut-1-ene, is capable of selectively isomerizing into 2-cyclopropylbuta-1,3-diene[13a] during low-temperature pyrolysis (143—193 °C, static conditions) and photolysis.[13b] The observed enhanced thermal stability and high isomerization temperature of cyclopropylcyclobutene **14** compared to its nonfluorinated analog correlates with the known fact[13c] that introduction of fluorine atoms into a cyclobutene ring significantly increases the energy of activation of thermal cyclobutene→butadiene isomerization.

The thermolytic conversion of cyclobutene **14** substantially increases at 600—620 °C; however, the process is complicated by intense resinification and the formation of 2,3-difluorotoluene (**17**) (see Table 1), probably, as the result of the opening of the cyclopropane ring in diene **16** followed by closing of a six-membered ring and its partial dehydrofluorination.

Table 1. Conversion of 1-cyclopropyl-2,3,3-trifluorocyclobut-1-ene (**14**) and the yields of the products of its thermolysis at different temperatures*

T/°C	Conversion (%)	Yield (%)		Ratio of
		15	**17**	**15** : **17**
550	19	18	—	—
600	95	32	17	1.9 : 1
620	100	6	38	1 : 6.4

* For the thermolysis conditions, see Experimental.



The structure of (trifluorovinyl)cyclopentene **15** was confirmed by ^{1}H, ^{13}C, and ^{19}F NMR spectra. In particular, the trifluorovinyl fragment is manifested in the ^{19}F NMR spectrum by signals with characteristic spin-spin coupling constants ($^2J_{F,F}$ = 71.0 Hz, $^3J_{F,F\text{-}trans}$ = 102.5 Hz, and $^3J_{F,F\text{-}cis}$ = 27.5 Hz). The ^{13}C NMR data for 2,3-difluorotoluene **17** agree with those for an authentic sample prepared according to a known procedure.[14]

Hence, the α-fluorovinyl fragment in vinylcyclopropanes and vinylspiropentanes does not impede the vinylcyclopropane→cyclopentene rearrangement; however, this process requires sufficiently drastic conditions (490—600 °C). Spiropentane derivatives undergo parallel isomerization into methylidenecyclobutanes, while for trifluorocyclobutenylcyclopropanes, which contain the "vinylic" fragment in the four-membered carbocycle, the primary reaction is cyclobutene→butadiene isomerization.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200 and 50.3 MHz), Bruker AM-300 (300 and 75.5 MHz), and Bruker DRX-500 spectrometers (500 MHz) in $CDCl_3$ with 0.05% Me_4Si as the internal standard. ^{19}F NMR spectra were recorded on a Bruker AC-200 spectrometer (188.3 MHz); chemical shifts were referenced to CCl_3F as the external standard. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, RSL-200 capillary column (30 m) or direct inlet probe). Preparative separation was carried out in a column (180×0.6 cm) with 5% SE-30 on Chromaton N-AW-HMDS (argon as a carrier gas, 80 mL min^{-1}, column temperature 45—90 °C). The starting 2-fluoro-3-methylbuta-1,3-diene (**1**),[10] 6-(2,3,3-trifluorocyclobut-1-enyl)-4,5-diazaspiro[2.4]hept-4-ene (**10**),[5] and 1-cyclopropyl-2,3,3-trifluorocyclobut-1-ene (**14**)[5] were prepared according to known procedures.

3-(1-Fluorovinyl)-3-methyl-4,5-dihydro-3*H*-pyrazole (2). A solution of 2-fluoro-3-methylbuta-1,3-diene (**1**) (0.52 g,

6 mmol) and diazomethane (~23 mmol) in 10 mL of ether was kept at 15 °C for 3 days and then passed through a layer of Al_2O_3 (0.5 cm). The solvent and the unconsumed reagents were removed at 20 Torr to give pyrazoline **2** (0.71 g, ~93%) as a yellowish liquid. Found (%): C, 56.17; H, 7.04; N, 21.86. $C_6H_9FN_2$. Calculated (%): C, 56.35; H, 7.13; N, 21.67. ^{1}H NMR ($CDCl_3$), δ: 1.47, 1.91 (both br.dt, 1 H each, CH_2, ^2J = 12.6 Hz, ^3J = 7.7 Hz); 1.52 (s, Me); 4.62 (t, 2 H, NCH_2, $J \approx 7.7$ Hz); 4.67 (dd, 1 H, =CH(*trans*), $J_{H,F\text{-}trans}$ = 49.8 Hz, ^2J = 3.5 Hz); 4.76 (dd, 1 H, =CH(*cis*), $J_{H,F\text{-}cis}$ = 17.9 Hz, ^2J = 3.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.2 (d, Me, $^3J_{C,F} \approx 3.0$ Hz); 27.3 (s, C(4)); 77.0 (s, C(5)); 90.4 (d, $=CH_2$, $^2J_{C,F}$ = 19.4 Hz); 91.4 (d, C(3); $^2J_{C,F}$ = 25.6 Hz); 164.9 (d, CF, $^1J_{C,F} \approx 258$ Hz). ^{19}F NMR ($CDCl_3$), δ: −106.5 (dd, $J_{H,F\text{-}trans}$ = 49.8 Hz, $J_{H,F\text{-}cis}$ = 17.9 Hz). MS, *m/z* (I_{rel} (%)): 127 $[M - H]^+$ (5), 113 $[M - Me]^+$ (7), 99 (30), 85 (63), 79 (39), 65 (30), 58 (57), 39 (100).

6-(1-Fluorovinyl)-6-methyl-4,5-diazaspiro[2.4]hept-4-ene (3). *N*-Cyclopropyl-*N*-nitrosourea (2.71 g, 21 mmol) was added at −10 °C for 30 min to a vigorously stirred solution of 2-fluoro-3-methylbuta-1,3-diene (**1**) (3.60 g, 42 mmol), K_2CO_3 (3.48 g, 25 mmol), and KOH (1.41 g, 25 mmol) in 15 mL of CH_2Cl_2. Then, the reaction mixture was stirred at 0 °C for 1 h and filtered. The filtrate was concentrated and distilled *in vacuo* (T_{bath} 70—75 °C, 0.1 Torr) to give pyrazoline **3** (1.30 g, 40%) as a slightly yellow oily liquid. Found (%): C, 62.23; H, 7.13; N, 18.20. $C_8H_{11}FN_2$. Calculated (%): C, 62.38; H, 7.24; N, 18.08. ^{1}H NMR ($CDCl_3$), δ: 1.11 (m, 2 H, H(1) and H(2) oriented from the N atom of the heterocycle); 1.55 (s, 3 H, Me); 1.62 (dd, 1 H, H_a(7), ^2J = 12.5 Hz, $J_{H,F} \approx 1.0$ Hz); 1.75 (m, 2 H, H(1) and H(2) oriented toward the N atom of the heterocycle); 2.10 (d, 1 H, H_b(7), ^2J = 12.5 Hz); 4.66 (dd, 1 H, =CH(*trans*), $J_{H,F\text{-}trans}$ = 49.1 Hz, ^2J = 3.4 Hz); 4.76 (dd, 1 H, =CH(*cis*), $J_{H,F\text{-}cis}$ = 17.8 Hz, ^2J = 3.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 13.6, 14.2 (both s, CH_2CH_2); 22.2 (d, Me, $^3J_{C,F} \approx 3.0$ Hz); 35.3 (s, C(7)); 69.3 (s, C(3)); 90.1 (d, C(6), $^2J_{C,F}$ = 25.8 Hz); 90.5 (d, $=CH_2$, $^2J_{C,F}$ = 19.0 Hz); 165.1 (d, CF, $^1J_{C,F} \approx 259$ Hz). ^{19}F NMR ($CDCl_3$), δ: −105.8 (dd, $J_{H,F\text{-}trans}$ = 49.1 Hz, $J_{H,F\text{-}cis}$ = 17.8 Hz). MS, *m/z* (I_{rel} (%)): 125 $[M - H - N_2]^+$ (4), 111 (33), 97 (15), 85 (22), 77 (15), 66 (12), 59 (11), 51 (27), 39 (100).

Thermal transformations of pyrazolines and vinylcyclopropanes (general procedure). A quartz tube (inner diameter 0.6 cm, length 18 cm, two-thirds full of small quartz) purged with argon (~4 mL min^{-1}) was heated in a tube microfurnace (heating zone range ~12 cm). The heating temperature was set and measured with an electronic thermometer, its sensor being fixed in the central zone of the microfurnace. Test compounds were injected with a syringe into the initial heating zone in microportions (~1 g h^{-1}) and thermolysis products were collected in a trap cooled to −40 °C. The compositions of the reaction mixtures were determined from GC-MS and ^{1}H NMR data. Then the reaction mixtures were distilled or separated by preparative GLC and identified by conventional methods.

1-(1-Fluorovinyl)-1-methylcyclopropane (4) was obtained from pyrazoline **2** (0.51 g, 4 mmol) at 250 °C. The yield of compound **4** was 0.34 g (85%). The product is identical in GLC and ^{1}H NMR data with a sample prepared earlier by catalytic cyclopropanation of 2-fluoro-3-methylbuta-1,3-diene (**1**).[10]

1-(1-Fluorovinyl)-1-methylspiro[2.2]pentane (5). A pyrolyzate (0.66 g) obtained from pyrazoline **3** (1.31 g, 8.5 mmol) at 260 °C was distilled at an atmospheric pressure to give vinylspiropentane **5** (0.54 g, 51%) as a colorless liquid, b.p. 110—112 °C. Found (%): C, 76.01; H, 8.74. $C_8H_{11}F$. Calculated (%): C, 75.85; H, 8.52. ^{1}H NMR ($CDCl_3$), δ: 0.71 (ddd, 1 H, H(4), ^2J = 4.1 Hz, J_{trans} = 5.3 Hz, J_{cis} = 8.8 Hz); 0.78 (m, 1 H, H(5)); 0.89 (m, 3 H, H(4), H(5) and H_a(2)); 1.23 (s, 3 H, Me); 1.40 (d, 1 H, H_b(2), ^2J = 4.2 Hz); 4.23 (dd, 1 H, FC=CH(*trans*), $^3J_{H,F\text{-}trans}$ = 50.0 Hz, ^2J = 3.0 Hz); 4.52 (dd, 1 H, FC=CH(*cis*), $^3J_{H,F\text{-}cis}$ = 17.3 Hz, ^2J = 3.0 Hz). ^{13}C NMR ($CDCl_3$), δ: 4.1, 5.8 (both s, C(4), C(5)); 19.2 (d, C(2), $^3J_{C,F}$ = 3.7 Hz); 19.3 (d, Me, $^3J_{C,F}$ = 4.2 Hz); 21.3 (d, C(1), $^2J_{C,F}$ = 27.2 Hz); 29.1 (s, C(3)); 87.2 (d, $=CH_2$, $^2J_{C,F}$ = 22.8 Hz); 168.8 (d, =CF, $^1J_{C,F}$ = 255 Hz). ^{19}F NMR ($CDCl_3$), δ: −103.9 (dd, $J_{H,F\text{-}trans}$ = 50.0 Hz, $J_{H,F\text{-}cis}$ = 17.3 Hz). Partial MS, *m/z* (I_{rel} (%)): 125 $[M - H]^+$ (8), 111 $[M - Me]^+$ (43), 91 (29), 77 (19), 68 (28), 55 (27), 41 (100).

1-Fluoro-2-methylcyclopentene (6). A pyrolyzate (0.76 g) obtained from 1-(1-fluorovinyl)-1-methylcyclopropane (**4**) (3.00 g, 30 mmol) at 600 °C was distilled at an atmospheric pressure to give fluorocyclopentene **6** (0.66 g, 22%) as a colorless liquid, b.p. 72—74 °C (≥98% purity). ^{1}H NMR ($CDCl_3$), δ: 1.59 (br.s, 3 H, Me); 1.86 (m, 2 H, H(4)); 2.20 (m, 2 H, H(3)); 2.40 (m, 2 H, H(5)). ^{13}C NMR ($CDCl_3$), δ: 10.6 (s, Me); 18.7 (d, C(4), $^3J_{C,F}$ = 9.3 Hz); 29.2 (d, C(5), $^2J_{C,F}$ = 21.7 Hz); 32.1 (d, C(3), $^3J_{C,F}$ = 8.1 Hz); 128.7 (d, C(2), $^2J_{C,F}$ = 40.7 Hz); 155.3 (d, C(1), $^1J_{C,F} \approx 269$ Hz). ^{19}F NMR ($CDCl_3$), δ: −131.4 (br.s.). Partial MS, *m/z* (I_{rel} (%)): 99 $[M - H]^+$ (38), 84 (48), 67 (20), 55 (32), 43 (100).

Thermolysis of 1-(1-fluorovinyl)-1-methylspiropentane (5) (0.12 g, 0.9 mmol) at 390 °C gave a mixture (0.081 g) of 5-fluoro-4-methylspiro[2.4]hept-4-ene (**7**) (~80%) and 1-fluoro-2-methyl-3-methylidenecyclohex-1-ene (**8**) (16%). The total yield of these products was ~65%. Compound **7** was isolated by preparative GLC (~98% purity), while compound **8** was enriched to ~85%. Analogously, the thermolysis of spiropentane **5** (0.12 g, 0.9 mmol) at 440 °C gave a mixture (0.074 g, ~62%) containing spiroheptene **7** (56—58%), fluorocyclohexene **8** (~22%), *o*-xylene (~13%), and some amounts of minor products.

Compound 7. Found (%): C, 75.61; H, 8.59. $C_8H_{11}F$. Calculated (%): C, 75.85; H, 8.52. ^{1}H NMR ($CDCl_3$), δ: 0.39, 0.62 (both m, 2 H each, H(1), H(2)); 1.26 (q, 3 H, Me, J = 2.3 Hz); 1.90 (br.dd, 2 H, H(7), $^3J \approx 7.4$ and 7.8 Hz); 2.52 (m, 2 H, H(6)). ^{13}C NMR ($CDCl_3$), δ: 6.0 (s, Me); 9.7 (s, C(1), C(2)); 26.4 (d, C(3), $J_{C,F}$ = 9.5 Hz); 28.0 (d, C(6), $J_{C,F}$ = 21.0 Hz); 30.3 (d, C(7), $J_{C,F}$ = 7.5 Hz); 113.0 (d, C(4), $J_{C,F}$ = 10.8 Hz); 153.9 (d, C(5), $J_{C,F}$ = 270 Hz). ^{19}F NMR ($CDCl_3$), δ: −126.3 (br.s). Partial MS, *m/z* (I_{rel} (%)): 126 $[M]^+$ (100), 111 $[M - Me]^+$ (70), 109 (48), 79 (20).

Compound 8. ^{1}H NMR ($CDCl_3$), δ: 1.76 (q, 3 H, Me, J = 2.2 Hz); 1.79 (m, 2 H, H(5)); 2.32 (m, 4 H, H(4), H(6)); 4.77, 4.82 (both m, 1 H each, $=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 9.2 (d, Me, $J_{C,F}$ = 8.8 Hz); 22.4 (d, C(5), $J_{C,F}$ = 9.2 Hz); 26.6 (d, C(6), $J_{C,F}$ = 27.2 Hz); 31.6 (s, C(4)); 107.1 (d, $=CH_2$, $J_{C,F}$ =10.9 Hz); 116.2 (d, C(2), $J_{C,F}$ =17.5 Hz); 143.8 (d, C(3), $J_{C,F}$ = 8.2 Hz); 159.1 (d, C(1), $J_{C,F} \approx 262$ Hz). ^{19}F NMR ($CDCl_3$), δ: −100.6 (br.s). Partial MS, *m/z* (I_{rel} (%)): 126 $[M]^+$ (100), 111 $[M - Me]^+$ (85), 109 (50), 79 (43), 51 (20), 39 (50).

Thermolysis of 6-(2,3,3-trifluorocyclobut-1-enyl)-4,5-diazaspiro[2.4]hept-4-ene (10). ***A.*** A pyrolyzate (0.24 g) obtained from pyrazoline **10** (0.41 g, 2 mmol) at 370 °C was distilled *in vacuo* (T_{bath} 60—65 °C, 6 Torr) to give 2,3,3-trifluoro-1-(spiropent-1-yl)cyclobutene (**11**) (72 mg, 22%; ~96% purity). A pyrolyzate (0.11 g) obtained from compound **10** at 400 °C

(virtually complete conversion) contained spiropentane **11** (~73%) and 2,3,3-trifluoro-1-(2-methylidenecyclobutyl)cyclobut-1-ene (**12**) (18%). The total yield of these compounds was ~27%. Compounds **11** and **12** were isolated by preparative GLC at 90 °C.

Compound 11. Found (%): C, 61.79; H, 5.04. $C_9H_9F_3$. Calculated (%): C, 62.07; H, 5.21. ^{1}H NMR ($CDCl_3$), δ: 0.88 (m, 4 H, CH_2CH_2); 1.17 (t, 1 H, $H_a(2')$, $^2J \approx {}^3J_{trans}$ = 4.2 Hz); 1.38 (dd, 1 H, $H_b(2')$, ^2J = 4.2 Hz, $^3J_{cis}$ = 7.7 Hz); 2.01 (dd, 1 H, H(1′), J_{trans} = 4.2 Hz, J_{cis} = 7.7 Hz); 2.46 (m, 2 H, H(4)). ^{13}C NMR ($CDCl_3$), δ: 4.9, 5.5 (both s, C(4′), C(5′)); 13.3 (q, C(2′), $J_{C,F}$ = 1.8 Hz); 14.0 (q, C(1′), $J_{C,F}$ = 4.0 Hz); 15.8 (q, C(3′), $J_{C,F}$ = 2.0 Hz); 37.0 (dt, C(4), $J_{C,F}$ = 19.1 and 22.5 Hz); 118.1 (td, CF_2, $^1J_{C,F}$ = 275 Hz, $^2J_{C,F}$ = 26.0 Hz); 128.9 (td, C(1), $J_{C,F} \approx$ 17.0 and 6.0 Hz); 138.3 (dt, =CF, $^1J_{C,F}$ = 337 Hz, $^2J_{C,F}$ = 25.0 Hz). ^{19}F NMR ($CDCl_3$), δ: −111.0, −111.7 (both br.d, CF_2, $^2J_{F,F} \approx$ 203 Hz), −119.8 (br.s, =CF). MS, *m/z* (I_{rel} (%)): 173 $[M - H]^+$ (1), 153 (4), 145 (25), 133 (26), 123 (23), 109 (80), 91 (35), 84 (48), 77 (20), 63 (18), 51 (35), 44 (38), 39 $[C_3H_3]^+$ (100).

Compound 12. ^{1}H NMR ($CDCl_3$), δ: 2.06, 2.25 (both m, 1 H each, H(4′)); 2.64 (m, 5 H, H(4), H(1′), H(3′)); 4.82, 4.88 (both br.q, 1 H each, $=CH_2$). ^{13}C NMR ($CDCl_3$), δ: 21.5 (q, C(4′), $J_{C,F}$ = 1.7 Hz); 29.8 (s, C(3′)); 36.7 (dt, C(4), $J_{C,F} \approx$ 19.0 and 22.0 Hz); 39.6 (q, C(1′), $J_{C,F}$ = 3.8 Hz); 107.2 (s, $=CH_2$); 118.0 (td, CF_2, $^1J_{C,F}$ = 275 Hz, $^2J_{C,F} \approx$ 25.0 Hz); 128.7 (td, C(1), $J_{C,F} \approx$ 17.0 and 6.0 Hz); 136.0 (q, C(2′), $J_{C,F}$ = 4.0 Hz); 139.1 (dt, =CF, $^1J_{C,F}$ = 338 Hz, $^2J_{C,F}$ = 25.0 Hz). ^{19}F NMR ($CDCl_3$), δ: −112.0 (CF_2); −115.7 (=CF).

Thermolysis of 1-cyclopropyl-2,3,3-trifluorocyclobut-1-ene (14) (1.67 g, 11 mmol) at 600 °C gave a mixture (0.90 g) of 1-(trifluorovinyl)cyclopent-1-ene (**15**) (~60%) and 2,3-difluorotoluene (**17**) (32%) (GLC and ^{1}H NMR data). The data on the thermolysis of cyclobutene **14** at 550, 600, and 620 °C are summarized in Table 1. The spectroscopic data for 1-(trifluorovinyl)cyclopentene (**15**) were obtained by subtracting the signals for 2,3-difluorotoluene synthesized according to a known procedure.[14]

Compound 15. ^{1}H NMR ($CDCl_3$), δ: 1.99 (m, 2 H, H(4)); 2.51 (m, 4 H, H(3), H(5)); 6.02 (m, 1 H, =CH). ^{13}C NMR ($CDCl_3$), δ: 23.3 (s, C(4)); 31.6 (dd, C(5), $J_{C,F}$ = 5.6 and 3.2 Hz); 32.6 (s, C(3)); 128.0 (ddd, =CF, $^1J_{C,F}$ = 233 Hz, $^2J_{C,F}$ = 49.5 and 18.0 Hz); 129.5 (dd, C(2), $J_{C,F}$ = 11.8 and 4.4 Hz); 136.5 (q, C(1), $J_{C,F} \approx$ 20.0 Hz); 153.3 (ddd, $=CF_2$, $^1J_{C,F}$ = 242 and 235 Hz, $^2J_{C,F}$ = 49.0 Hz). ^{19}F NMR ($CDCl_3$), δ: −102.5 (dd, ^2J = 71.0 Hz, $^3J_{cis}$ = 27.5 Hz) and −116.4 (dd, $=CF_2$, ^2J = 71.0 Hz, $^3J_{trans}$ = 102.5 Hz); −173.8 (dd, =CF, $^3J_{trans}$ = 102.5 Hz, $^3J_{cis}$ = 27.5 Hz). MS, *m/z* (I_{rel} (%)): 148 $[M]^+$ (100), 127 (30), 97 (31), 79 (46), 67 (17), 39 (35).

Compound 17. ^{1}H NMR ($CDCl_3$), δ: 2.31 (m, 3 H, Me); 6.91 (m, 3 H, Ar). ^{13}C NMR ($CDCl_3$), δ: 14.3 (t, Me, $J_{C,F}$ = 2.9 Hz); 114.5 (d, C(4), $J_{C,F}$ = 17.3 Hz); 123.6 (dd, C(6), $J_{C,F}$ = 6.6 and 5.1 Hz); 126.1 (t, C(5), $J_{C,F}$ = 3.5 Hz); 127.3 (d, C(1), $J_{C,F}$ = 12.5 Hz); 149.4, 150.9 (both dd, C(2), C(3), $^1J_{C,F}$ = 246.5 Hz, $^2J_{C,F}$ = 12.8 Hz). ^{19}F NMR ($CDCl_3$), δ: −139.2, −142.7 (both br.d, ^3J = 24.5 Hz).

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