Aluminum oxide-induced gas-phase ring-opening in methyl substituted *gem*-difluorocyclopropanes, leading to 2-fluorobuta-1,3-dienes and vinylacetylenes*

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A gas-phase pyrolysis of methyl-substituted *gem*-difluorocyclopropanes in a flow-tube reactor in the presence of Al_2O_3 at 185—250 °C gives 2-fluorobuta-1,3-dienes and vinylacetylenes.

Key words: *gem*-difluorocyclopropanes, gas-phase pyrolysis, cyclopropyl-allylic rearrangement, 2-fluorobuta-1,3-dienes, vinylacetylenes, organofluorine compounds.

gem-Chlorofluoro-, *gem*-dichloro-, and *gem*-dibromocyclopropanes are known to undergo thermal and catalytic transformations, leading to dihaloalkenes,[1—4] halodienes,[1,4—8] or haloarenes.[1,9—13] These transformations proceed with a cyclopropyl-allylic rearrangement, which includes opening of a cyclopropane ring and migration of halogen or dehydrohalogenation. For *gem*-chlorofluorocyclopropanes, such processes, as a rule, involve the cleavage of the less strong chlorine-carbon bond.[1,3,5—10] At the same time, the processes of cyclopropyl-allylic transformation were considered uncharacteristic of *gem*-difluorocyclopropanes because of the strong C—F bond, limiting the possibility of this reaction to proceed. In this connection, the thermal transformations of *gem*-difluorocyclopropanes, as a rule, follow alternative directions, including various rearrangements without cleavage of the C—F bond and with preservation of the difluoromethylene fragment in the products[1d,14,15] or thermal fragmentation with elimination of difluorocarbene.[15—17] A formal exception from this rule are thermal reactions of labile *gem*-difluorocyclopropanes included in the bicyclo[3.1.0]-hexene structures (the products of cycloaddition of difluorocarbene to cyclopentadiene or indene), leading to fluoroarenes and resulting from the three-membered ring opening and dehydrofluorination.[9,13] However, there is a suggestion[13] that these reactions can proceed by a biradical process rather than by a typical mechanism of cyclopropyl-allylic transformation. In the present work, we report a discovered possibility to effect skeleton transformations of simple methyl-substituted *gem*-difluorocyclopropanes, which follow a usual type of cyclopropyl-allylic transformation with obtaining of 2-fluorobuta-1,3-dienes, when this reaction is initiated by aluminum oxide under the gas-phase pyrolysis conditions.

Results and Discussion

Earlier, we[18,19] carried out comparative studies to identify specific features of the gas-phase thermal transformations of methyl-substituted *gem*-chlorofluorocyclopropanes in flow-tube reactors containing quartz (SiO_2) or Al_2O_3 as a filling. We found that in the reactor with SiO_2, *gem*-chlorofluorocyclopropanes under the gas-phase pyrolysis conditions at 430—460 °C undergo the skeleton transformations with the formation of 2-fluorobuta-1,3-dienes as a result of the cyclopropane ring opening and dehydrochlorination. Conversely, in the presence of Al_2O_3 the same *gem*-chlorofluorocyclopropanes at 150—250 °C yield 2-chlorobuta-1,3-dienes as a result of the ring opening and dehydrofluorination, probably, due to the ability of Al_2O_3 to efficiently activate the cleavage the C—F bond. It seemed interesting to study a possibility of such activating effect of Al_2O_3 for the gas-phase thermal transformations of *gem*-difluorocyclopropanes.

As the starting compounds, we used *cis*-3,3-difluoro-1,2-dimethylcyclopropane (**1a**), *trans*-3,3-difluoro-1,2-dimethylcyclopropane (**1b**), 1-chloro-2,2-difluoro-1-methylcyclopropane (**1c**), and 2,2-difluoro-1,1-dimethylcyclopropane (**1d**), which were obtained in 23—42% yields by the addition of difluorocarbene, generated from hexafluoropropylene oxide, under conditions of its gas-phase copyrolysis with *cis*-but-2-ene, *trans*-but-2-ene, 2-chloropropene, or isobutylene (Scheme 1).


Scheme 1
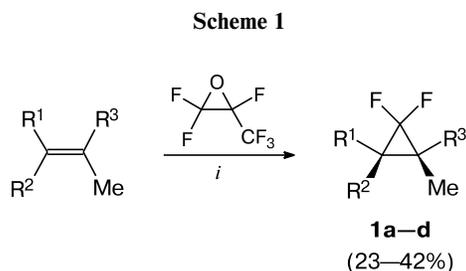
i. 320—350 °C, a flow-tube reactor.

$R^1 = R^3 = H$, $R^2 = Me$ (**a**); $R^1 = Me$, $R^2 = R^3 = H$ (**b**);
$R^1 = R^2 = H$, $R^3 = Cl$ (**c**); $R^1 = R^2 = H$, $R^3 = Me$ (**d**)

It is known[15] that *cis*- and *trans*-3,3-difluoro-1,2-di-methylcyclopropanes **1a,b** under pyrolysis conditions in a static reactor at 297—345 °C undergo only a reversible *cis-trans* isomerization, accompanied by a competing fragmentation with the elimination of difluorocarbene and formation of but-2-enes. We obtained similar results in the pyrolysis of difluorocyclopropanes **1a** and **1b** in a flow-tube reactor. Thus, the gas-phase pyrolysis of *cis*-3,3-difluoro-1,2-dimethylcyclopropane (**1a**) in a quartz flow-tube reactor at 420 °C gave a pyrolysate containing (according to the GLC and NMR data) 35% of the starting cyclopropane **1a**, 45% of *trans*-3,3-difluoro-1,2-dimethylcyclopropane (**1b**), 5% of *cis*-but-2-ene, and 6% of *trans*-but-2-ene (Scheme 2). The pyrolysis of *trans*-3,3-difluoro-1,2-dimethylcyclopropane (**1b**) at 420 °C gave virtually the same composition of the pyrolysate, which contained 34% of **1a**, 47% of the starting **1b**, 5% of *cis*-but-2-ene, and 6% of *trans*-but-2-ene.

Scheme 2
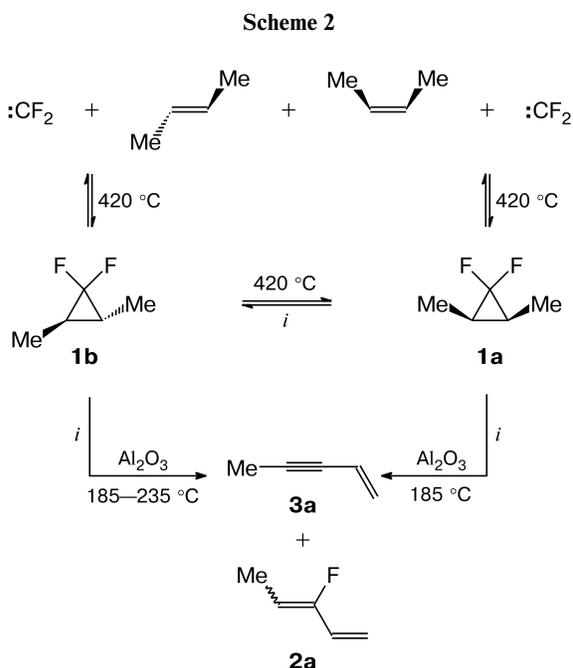
i. A flow-tube reactor.

Essentially different results were obtained in the gas-phase pyrolysis of 3,3-difluoro-1,2-dimethylcyclopropanes (**1a,b**) carried out in the reactor partially filled with granulated Al_2O_3. Under these conditions, the pyrolysis of isomer **1a** at 185 °C led to a mixture of *Z*- and *E*-isomers of 3-fluoropenta-1,3-diene (**2a**) in a 63% total yield (the ratio *Z*-**2a** : *E*-**2a** = 8 : 1) and pent-1-en-3-yne (**3a**) (5% yield) with almost complete conversion of the starting cyclopropane (see Scheme 2, Table 1). The pyrolysis of isomer **1b** under similar conditions at 185 °C led also to isomeric 3-fluoropent-1,3-dienes **2a** (the ratio *Z*-**2a** : *E*-**2a** = = 7 : 1) in a 49% total yield and pent-1-en-3-yne (**3a**) (7% yield), with the conversion of the starting cyclopropane being about 91%. When the temperature of pyrolysis of **1b** was elevated to 235 °C, its conversion was more than 99%, whereas the yield of enyne **3a** increased to 13% and the yield of fluorodienes **2a** decreased to 38% (see Table 1).

Similar transformations were observed in the pyrolysis of 1-chloro-2,2-difluoro-1-methylcyclopropane (**1c**). But in contrast to compounds **1a,b**, chlorodifluoro derivative **1c** turned out to be able to undergo the cyclopropyl-allyl-ic-type skeleton transformations both in the presence of aluminum oxide and in an empty quartz reactor. However, the opening of the three-membered carbocycle took different directions for the two versions of the reaction conditions (Scheme 3). Thus, together with the fragmentation to difluorocarbene and 2-chloropropene **6** as a principal process, the pyrolysis of **1c** in an empty quartz reactor in the flow of nitrogen at 450 °C also included the skeleton cyclopropyl-allylic isomerization, which gave 3-chloro-3,3-difluoro-2-methylpropene (**4**) and 3-chloro-1,1-difluoro-2-methylpropene (**5**) formed by the ring opening at the C(2)—C(3) bond opposite to the CCl(Me)

Table 1. Yields of the products of the gas-phase pyrolysis of difluorocyclopropanes **1a—d** in a quartz flow-tube reactor containing Al_2O_3, depending on the pyrolysis temperature

| **1**	T^a/°C	C^b (%)	Product yields^c (%)			
1a	185	>99	**2a** (63)	**3a** (5)	—	—
			(*Z/E* = 8)			
1b	185	91	**2a** (49)	**3a** (7)	—	—
			(*Z/E* = 7)			
	235	>99	**2a** (38)	**3a** (13)	—	—
			(*Z/E* = 7)			
1c	190	72	**2c** (36)	**3c** (4)	—	—
	250	97	**2c** (48)	**3c** (8)	—	—
1d	200	85	**2d** (33)	**3d** (10)	**7** (7)	**8** (2)
	220	92	**2d** (32)	**3d** (7)	**7** (13)	**8** (3)
	235	95	**2d** (29)	**3d** (4)	**7** (19)	**8** (5)

^{a} Pyrolysis temperature.
^{b} Conversion of **1**.
^{c} The yields were calculated from the NMR spectra of the mixtures of products with an added internal standard (fluorobenzene).

fragment and 1,2-migration of the Cl atom to the methylene or difluoromethylene fragment. No cleavage of the C—F bond took place, and the difluoromethylene fragment remained preserved in the reaction products.

Scheme 3
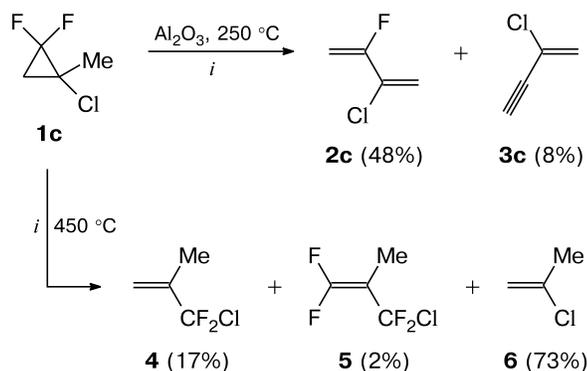
i. A flow-tube reactor.

Note. The product yields were calculated based on the results of analysis of mixtures of products by GLC and NMR.

The gas-phase pyrolysis of **1c** in the presence of Al_2O_3 at 190—250 °C took fundamentally different direction, leading to 3-chloro-2-fluorobuta-1,3-diene (**2c**) as the main product (36—48% yield), as well as (chlorovinyl)-acetylene **3c** (4—8% yield, see Scheme 3, Table 1). No formation of chlorodifluoropropenes **4** and **5** was observed. Thus, in contrast to homogeneous pyrolysis, the transformation of **1c** in the presence of Al_2O_3 proceeded through the ring opening at the C(1)—C(3) bond opposite to the difluoromethylene fragment and is accompanied by the dehydrofluorination.

2,2-Difluoro-1,1-dimethylcyclopropane (**1d**), which does not undergo noticeable transformations under the gas-phase pyrolysis conditions at temperatures below 300 °C in an empty quartz reactor, at 440 °C eliminates difluorocarbene, forming isobutylene as a main product in 30% yield, with the conversion of the starting cyclopropane **1d** being about 54% (Scheme 4). At the same time, the pyrolysis of **1d** in a flow-tube reactor containing Al_2O_3 at 220 °C gave 2-fluoro-3-methylbuta-1,3-diene

(**2d**) (33% yield), isopropenylacetylene (**3d**) (10% yield), 3-methylbut-3-en-2-one (**7**) (7% yield), and 3-methyl-butan-2-one (**8**) (2% yield) with the conversion of the starting cyclopropane **1d** about 85% (see Scheme 4, Table 1).

The results obtained allow us to draw a conclusion that, in contrast to the homogeneous thermal transformations, the heterogeneous pyrolysis of methyl-substituted *gem*-difluorocyclopropanes in the presence of Al_2O_3 proceeds with the formation of 2-fluorobuta-1,3-dienes, typical products of the cyclopropyl-allylic transformation. Apparently, this occurs as a result of the activation by the aluminum oxide of the very strong C—F bond, which initiates the cyclopropane ring opening and dehydrofluorination. The ability of Al_2O_3 to efficiently activate cleavage of the C—F bond is also indicated by the formation of vinylacetylenes **3a—d** observed in the course of the reaction, which formally are the products of dehydrofluorination of fluorodienes **2a—d**. The formation of considerable amounts of ketones **7** and **8** in the pyrolysis of compound **1d** in the presence of Al_2O_3, probably, results from the partial hydrolysis of vinylacetylene **3d** or fluorodiene **2d** upon the reaction with water formed in the reaction of hydrogen fluoride with the surface hydroxy groups of Al_2O_3. Such acid-catalyzed hydrolytic transformations of alkynes, including vinylacetylenes, to ketones are well known.[20]

Experimental

Commercially available isobutylene (99%), *cis*-but-2-ene (99%), *trans*-but-2-ene (99%), 2-chloropropene (98%) (Aldrich), and hexafluoropropylene oxide (99.9%, Poly-Trade Ltd., Russia) were used without additional purification, as well as commercial AOA-1 γ-Al_2O_3 (cylindrical grains 5 × (6—8) mm) (Reakhim, Russia).

GLC analysis was carried out on a Crystal 2000M chromatograph (a Macherey-Nagel OPTIMA-1 capillary column, 30 m × 0.25 mm, carrier gas helium, flame-ionizing detector).

^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer (300.1, 282.4, and 75.4 MHz, respectively) for solutions in $CDCl_3$ containing Me_4Si. Mass spectra were recorded on a Finnigan MAT INCOS-50 instrument (EI, 70 eV, direct injection) or a Trace GC Ultra instrument equipped with a Finnigan MAT DSQII mass detector (EI, 70 eV, temperature of the system 200 °C, an ion trap as a source of ions) and a Thermo TR-5ms SQC capillary chromatographic column (15 m × 0.25 mm).

Scheme 4
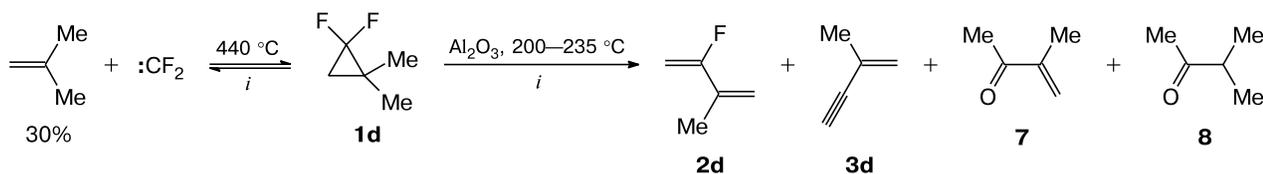
i. A flow-tube reactor.

Synthesis of *gem*-difluorocyclopropanes 1a—d. *cis*-3,3-Difluoro-1,2-dimethylcyclopropane (1a).[21,22] The gas flows of hexafluoropropylene oxide (5.17 mmol min^{-1}), *cis*-but-2-ene (3.41 mmol min^{-1}), and nitrogen (70 mL min^{-1}) were supplied with a constant consumption during 180 min into a quartz flow-tube reactor (400 mm in length and 22 mm in internal diameter) heated in a tube oven to 318—320 °C. The products coming out of the reactor were collected in a trap cooled to −35—−45 °C. The condensate obtained was slowly warmed to room temperature to remove the gaseous components, then sequentially washed with 10% aqueous Na$_2$CO$_3$ and water, dried with Na$_2$SO$_4$. The residue (26.53 g) obtained after filtering off the drying agent was distilled to give *cis*-3,3-difluoro-1,2-dimethylcyclopropane (1a) 14.92 g (23%), b.p. 54—56 °C. The product contained ~1% of *trans*-3,3-difluoro-1,2-dimethylcyclopropane (1b). ^{1}H NMR of 1a (CDCl$_3$, 300.1 MHz), δ: 1.49 (m, 2 H); 1.04 (m, 6 H, 2 CH$_3$). ^{19}F NMR of 1a (CDCl$_3$, 282.4 MHz), δ: −127.9, −156.8 (both br.d, CF$_2$, $^2J_{F,F}$ = 153 Hz). MS, *m/z* (I_{rel} (%)): 106 [M]$^+$ (6), 91 [M − Me]$^+$ (100).

trans-3,3-Difluoro-1,2-dimethylcyclopropane (1b).[21,22] Similarly, the copyrolysis of a mixture of *trans*-but-2-ene (3.41 mmol min^{-1}), hexafluoropropylene oxide (5.17 mmol min^{-1}), and nitrogen (70 mL min^{-1}) at 320—322 °C for 180 min gave a crude product (27.42 g), which was treated as described above and distilled to yield *trans*-3,3-difluoro-1,2-dimethylcyclopropane (1b) (15.72 g, 24%) (b.p. 45—47 °C). The product contained ~1% of *cis*-3,3-difluoro-1,2-dimethylcyclopropane (1a). ^{1}H NMR of 1b (CDCl$_3$, 300.1 MHz), δ: 1.15 (m, 6 H, 2 CH$_3$); 1.05 (m, 2 H). ^{19}F NMR of 1b (CDCl$_3$, 282.4 MHz), δ: −142.5 (m, CF$_2$). MS, *m/z* (I_{rel} (%)): 106 [M]$^+$ (9), 91 [M − Me]$^+$ (100).

1-Chloro-2,2-difluoro-1-methylcyclopropane (1c). Similarly, the copyrolysis of 2-chloropropene (consumption 1.62 mmol min^{-1}) and hexafluoropropylene oxide (consumption 2.78 mmol min^{-1}) in the flow of nitrogen (70 mL min^{-1}) at 320—325 °C for 240 min gave a crude product (38.52 g), which was treated as described above and distilled to yield 1-chloro-2,2-difluoro-1-methylcyclopropane (1c) (15.51 g, 31%) (b.p. 60—62 °C). ^{1}H NMR (CDCl$_3$, 300.1 MHz), δ: 1.71 (m, 3 H, CH$_3$); 1.69—1.51 (m, 2 H). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: −136.1, −139.5 (both br.d, CF$_2$, $^2J_{F,F}$ = 154 Hz). MS, *m/z* (I_{rel} (%)): 111 [M − Me]$^+$ (8), 91 [M − Cl]$^+$ (100), 71 (10), 65 (15).

2,2-Difluoro-1,1-dimethylcyclopropane (1d).[21] Similarly, the copyrolysis of isobutylene (consumption 3.63 mmol min^{-1}) and hexafluoropropylene oxide (consumption 5.83 mmol min^{-1}) in the flow of nitrogen (70 mL min^{-1}) for 240 min gave a crude product (48.32 g), which was treated as described above and distilled to yield 2,2-difluoro-1,1-dimethylcyclopropane (1d) (38.83 g, 42%) (b.p. 40—41 °C). ^{1}H NMR (CDCl$_3$, 300.1 MHz), δ: 0.98 (t, 2 H, J = 8.6 Hz); 1.20 (m, 6 H, 2 CH$_3$). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: −140.2 (m, CF$_2$). MS, *m/z* (I_{rel} (%)): 106 [M]$^+$ (5), 91 [M − Me]$^+$ (100).

Pyrolysis of *gem*-difluorocyclopropanes 1a—d was carried out in flow-tube reactors in a flow of nitrogen 70 mL min^{-1} at atmospheric pressure. Reactor *A* was a 350 mm quartz tube with an internal diameter of 16 mm; reactor *B* was the same quartz tube, filled in the middle part with a layer (10 g, 7.5 cm long) of γ-Al$_2$O$_3$ cylindrical grains, the lower and the upper parts were filled with quartz pieces.

Pyrolysis of *gem*-difluorocyclopropanes 1a—d in reactor *A*. *cis*-3,3-Difluoro-1,2-dimethylcyclopropane (1a) (2.60 g, 24.53 mmol) was added with a syringe at a constant rate over 30 min into an empty flow-tube quartz reactor *A* heated to 420 °C at atmospheric pressure in the flow of nitrogen (70 mL min^{-1}). The pyrolysis products coming out of the reactor were collected in a trap cooled with a mixture of solid CO$_2$—propan-2-ol. The pyrolysate (2.02 g) contained (GLC and NMR data) 35 wt.% of the starting cyclopropane 1a, 45% of *trans*-3,3-difluoro-1,2-dimethylcyclopropane 1b, 5% of *cis*-but-2-ene, and 6% of *trans*-but-2-ene, as well as some minor unidentified products (a total of 8%).

Similarly, the pyrolysis of *trans*-3,3-difluoro-1,2-dimethylcyclopropane (1b) (2.60 g, 24.53 mmol) in reactor *A* at 420 °C over 30 min gave a a pyrolysate (2.07 g) containing (GLC and NMR data) 47 wt.% of the starting *trans*-3,3-difluoro-1,2-dimethylcyclopropane (1b), 34% of *cis*-3,3-difluoro-1,2-dimethylcyclopropane (1a), 5% of *cis*-but-2-ene, and 5% of *trans*-but-2-ene, as well as some minor unidentified products (a total of ~9%).

Similarly, the pyrolysis of 1-chloro-2,2-difluoro-1-methylcyclopropane (1c) (3.00 g, 23.70 mmol) at 450 °C over 30 min gave a pyrolysate (2.01 g) containing (GLC, NMR, and GC-MS data) 2 wt.% of the starting cyclopropane 1c, 66% of 2-chloropropene 6, 25% of 3-chloro-3,3-difluoro-2-methylpropene (4), 3% of 3-chloro-1,1-difluoro-2-methylpropene (5). The yields (in the mixture) were 17% (4), 2% (5), 73% (6).

3-Chloro-3,3-difluoro-2-methylpropene (4). ^{1}H NMR (CDCl$_3$, 300.1 MHz), δ: 5.53 (m, 1 H); 5.20 (m, 1 H); 1.69—1.51 (m, 3 H, CH$_3$). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: −55.8 (m, 2 F, CF$_2$Cl). MS, *m/z* (I_{rel} (%)): 126, 128 [M]$^+$ (27, 9), 91 [M − Cl]$^+$ (100), 71 (4), 65 (20).

3-Chloro-1,1-difluoro-2-methylpropene (5). ^{1}H NMR (CDCl$_3$, 300.1 MHz), δ: 4.10 (m, 2 H); 2.19 (m, 3 H, CH$_3$). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: −90.3 (d, 1 F, =CF$_2$, $^2J_{F,F}$ = 41 Hz); −91.3 (d, 1 F, =CF$_2$, $^2J_{F,F}$ = 41 Hz).

Similarly, the pyrolysis of 2,2-difluoro-1,1-dimethylcyclopropane (1d) (2.60 g, 24.53 mmol) at 440 °C in the flow of nitrogen (70 mL min^{-1}) over 30 min gave a pyrolysate (1.83 g) containing (GLC and NMR data) 66 wt.% of the starting cyclopropane 1d, 26% of isobutylene, and several unidentified minor products, each in the amount of 0.1—4% (a total of about 8%). Isobutylene (0.41 g, 30%) was isolated from the mixture by distillation, collecting it in a trap cooled with a mixture of solid CO$_2$—propan-2-ol.

Pyrolysis of *gem*-difluorocyclopropanes 1a—d in reactor *B* (in the presence of Al$_2$O$_3$). A quartz flow-tube reactor *B* containing Al$_2$O$_3$ (10 g) was heated over 1 h at 450—550 °C in the flow of N$_2$ (300 mL min^{-1}) for the activation (removal of water) of Al$_2$O$_3$, then the reactor was cooled in the flow of N$_2$ to 185 °C. Then, *cis*-3,3-difluoro-1,2-dimethylcyclopropane (1a) (3.00 g, 28.30 mmol) was passed at a constant rate through the reactor at 185 °C in the flow of N$_2$ (70 mL min^{-1}) over 45 min, using a syringe. The pyrolysis products coming out of the reactor were collected in a trap cooled with a mixture of CO$_2$—propan-2-ol. The pyrolysate (1.97 g) was sequentially washed with 10% aqueous Na$_2$CO$_3$ and water, dried with Na$_2$SO$_4$, and distilled to obtain a mixture of the products (1.68 g, b.p. 45—52 °C) containing according to the ^{1}H and ^{19}F NMR spectra (calculated using fluorobenzene as an internal standard) the starting cyclopropane 1a (0.27 mmol), (*Z*)-3-fluoropenta-1,3-diene (*Z*-2a) (15.62 mmol), (*E*)-3-fluoropenta-1,3-diene (*E*-2a) (1.95 mmol), and pent-1-en-3-yne 3a (1.53 mmol). The yields (in the mixture) were 55% (*Z*-2a), 8% (*E*-2a), 5% (3a).

(*Z*)-3-Fluoropenta-1,3-diene (*Z*-2a).[19] ^{1}H NMR (CDCl$_3$, 300.1 MHz), δ: 6.09 (ddd, 1 H, CH=, J_1 = 27.8 Hz, J_2 = 17.4 Hz,

$J_3 = 11.8$ Hz); 5.43 (d, 1 H, $=CH_2$, $J_1 = 17.4$ Hz); 5.09 (d, 1 H, $=CH_2$, $J_1 = 11.8$ Hz); 4.83 (dq, 1 H, CH=CF, $J_1 = 37$ Hz, $J_2 = 6.9$ Hz); 1.72 (dd, 3 H, CH_3, $J_1 = 6.9$ Hz, $J_2 = 1.5$ Hz). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: -127.1 (dd, 1 F, $J_1 = 37.0$ Hz, $J_2 = 27.8$ Hz). MS, *m/z* (I_{rel} (%)):86 [M]$^+$ (100), 85 (65), 71(15), 66 (60), 65 (40) (for the mixture with *Z*-**2a** and *E*-**2a**).

(*E*)-3-Fluoropenta-1,3-diene (*E*-2a).[19] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 6.44 (ddd, 1 H, CH=, $J_1 = 26.5$ Hz, $J_2 = 16.5$ Hz, $J_3 = 12.0$ Hz); 5.55 (d, 1 H, $=CH_2$, $J_2 = 16.5$ Hz); 5.20 (m, 1 H, CH=CF); 5.22 (d, 1 H, $=CH_2$, $J = 12.0$ Hz); 1.70 (m, 3 H, CH_3). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: -120.8 (dd, 1 F, $J_1 = 26.5$, $J_2 = 23.0$ Hz). MS, *m/z* (I_{rel} (%)):86 [M]$^+$ (100), 85 (65), 71 (15), 66 (60), 65 (40) (for the mixture with *Z*-**2a** and *E*-**2a**).

Pent-1-en-3-yne (3a).[23] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 5.83—5.18 (m, 1 H, $C=CH-C≡C-$); 5.56 (d, 1 H, $=CH_2$, $J = 17.5$ Hz); 5.39 (d, 1 H, $=CH_2$, $J = 11.0$ Hz); 1.96 (s, 3 H, CH_3). MS, *m/z* (I_{rel} (%)): 66 [M]$^+$ (100), 63 (15), 51 (7).

Similarly, the pyrolysis of *trans*-3,3-difluoro-1,2-dimethyl-cyclopropane (**1b**) (3.00 g, 28.30 mmol) at 185 °C gave a pyrolysate (2.02 g), which was treated as described above and distilled to obtain a mixture of the products (1.71 g, b.p. 44—54 °C) containing according to the ^1H and ^{19}F NMR spectra (calculated using fluorobenzene as an internal standard) the starting cyclopropane **1b** (2.58 mmol), *Z*-**2a** (12.13 mmol), *E*-**2a** (1.99 mmol), and enyne **3a** (2.07 mmol). The yields (in the mixture) were *Z*-**2a** (43%), *E*-**2a** (6%), **3a** (7%).

Similarly, the pyrolysis of *trans*-3,3-difluoro-1,2-dimethyl-cyclopropane (**1b**) (3.00 g, 28.30 mmol) in reactor *B* at 235 °C gave a pyrolysate (1.72 g), which was treated as described above and distilled to obtain a mixture of the products (1.22 g, b.p. 47—59 °C) containing the starting cyclopropane **1b** (0.23 mmol), *Z*-**2a** (9.23 mmol), *E*-**2a** (1.37 mmol), and propenylacetylene **3a** (3.76 mmol). The yields (in the mixture) were 33% (*Z*-**2a**), 5% (*E*-**2a**), 13% (**3a**).

Similarly, the pyrolysis of 1-chloro-2,2-difluoro-1-methyl-cyclopropane (**1c**) (3.00 g, 23.72 mmol) in reactor *B* in the presence of aluminum oxide upon addition at a constant rate at 190 °C over 45 min resulted in a pyrolysate (2.25 g), which was sequentially washed with aqueous solution of Na$_2$CO$_3$ and water, dried with Na$_2$SO$_4$, and distilled to give a mixture of the products (1.94 g, b.p. 48—59 °C) containing according to the ^1H and ^{19}F NMR spectra (calculated using fluorobenzene as an internal standard) the starting cyclopropane **1c** (6.75 mmol), 3-chloro-2-fluorobuta-1,3-diene (**2c**) (8.56 mmol), and 2-chlorobut-1-ene-3-yne (**3c**) (0.88 mmol). The yields (in the mixture) were 36% (**2c**), 4% (**3c**).

Similarly, the pyrolysis of cyclopropane **1c** (3.00 g, 23.72 mmol) in reactor *B* at 250 °C gave a pyrolysate (2.13 g), which was sequentially washed with aqueous solution of Na$_2$CO$_3$ and water, dried with Na$_2$SO$_4$, and distilled to give a mixture of the products (1.71 g, b.p. 48—57 °C) containing the starting cyclopropane **1c** (0.73 mmol), 3-chloro-2-fluorobuta-1,3-diene (**2c**) (11.35 mmol), and 2-chloro-1-buten-3-yne (**3c**) (1.95 mmol). The yields (in the mixture) were 48% (**2c**), 8% (**3c**).

3-Chloro-2-fluorobuta-1,3-diene (2c).[19] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 5.81 (m, 1 H, $-CCl=CH_2$); 5.52 (m, 1 H, $-CCl=CH_2$); 5.13 (d, 1 H, $-CF=CH_2$, $J = 47.1$ Hz); 4.96 (d, 1 H, $-CF=CH_2$, $J = 16.9$ Hz). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: -110.1 (dd, 1 F, $J_1 = 47.0$ Hz, $J_2 = 16.9$ Hz). MS, *m/z* (I_{rel} (%)): 108, 106 [M]$^+$ (32, 100), 71 [M$^+$ — Cl] 62).

2-Chloro-1-buten-3-yne (3c).[24] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 5.75 (br.s, 1 H, $=CH_2$); 5.69 (br.s, 1 H, $=CH_2$); 3.13 (s, 1 H, C≡CH). MS, *m/z* (I_{rel} (%)): 88, 86 [M]$^+$ (33, 100), 51 [M$^+$ — Cl] (92).

Similarly, the pyrolysis of 2,2-difluoro-1,1-dimethylcyclo-propane (**1d**) (3.00 g, 28.30 mmol) in reactor *B* at 200 °C upon addition at a constant rate over 45 min gave a pyrolysate (1.93 g), which was sequentially washed with 10% aqueous Na$_2$CO$_3$ and water and dried with Na$_2$SO$_4$ to yield a mixture of the products (1.73 g) containing according to the ^1H and ^{19}F NMR spectra (calculated using fluorobenzene as an internal standard) the starting cyclopropane **1d** (4.24 mmol), 2-fluoro-3-methylbuta-1,3-diene (**2d**) (9.45 mmol, isopropenylacetylene **3d** (2.88 mmol), 3-methylbut-3-en-2-one (**7**) (1.85 mmol), and 3-methylbutan-2-one (**8**) (0.60 mmol). The yields (in the mixture) were 33% (**2d**), 10% (**3d**), 7% (**7**), 2% (**8**).

Similarly, the pyrolysis of cyclopropane (**1d**) (3.00 g, 28.30 mmol) at 220 °C gave a pyrolysate (1.87 g), which was sequentially washed with 10% aqueous Na$_2$CO$_3$ and water and dried with Na$_2$SO$_4$ to yield a mixture of the products (1.68 g) containing the starting cyclopropane **1a** (2.28 mmol), diene **2d** (9.18 mmol), isopropenylacetylene **3d** (1.78 mmol), ketone **7** (3.60 mmol), and ketone **8** (0.98 mmol). The yields (in the mixture) were **2d** (32%), **3d** (7%), **7** (13%), **8** (3%).

The mixture was distilled at atmospheric pressure, collecting a fraction (1.06 g) with b.p. 37—45 °C, which contained (^1H and ^{19}F NMR data) 17 mol.% of cyclopropane **1a**, 68 mol.% of fluorodiene **2d**, and 10 mol.% of isopropenylacetylene **3d**. The residue was distilled at reduced pressure to give a mixture of the products (0.32 g, b.p. 43—46 °C (135 Torr)) containing (^1H NMR data) 3-methylbut-3-en-2-one (**7**) (74%) and 3-methylbutan-2-one (**8**) (21%).

Similarly, the pyrolysis of cyclopropane (**1d**) (3.00 g, 28.30 mmol) in reactor *B* at 235 °C gave a pyrolysate (1.80 g), which was sequentially washed with 10% aqueous Na$_2$CO$_3$ and water and dried with Na$_2$SO$_4$ to obtain a mixture of the products (1.57 g) containing the starting cyclopropane **1d** (1.48 mmol), diene **2d** (8.22 mmol), isopropenylacetylene **3d** (1.20 mmol), ketone **7** (5.23 mmol), and ketone **8** (1.46 mmol). The yields (in the mixtures) were 29% (**2d**), 4% (**3d**), 19% (**7**), 5% (**8**).

The mixture was distilled at atmospheric pressure to collect a fraction (0.89 g) with b.p. 37—45 °C) containing (^1H and ^{19}F NMR data) 12 mol.% of cyclopropane **1d**, 75% of fluoro-diene **2d**, and 8% of isopropenylacetylene **3d**. The residue was distilled at reduced pressure to give a mixture of the products (0.46 g, b.p. 42—46 °C (135 Torr)) containing (^1H NMR data) 3-methylbut-3-en-2-one (**7**) (78%) and 3-methylbutan-2-one (**8**) (18%).

2-Fluoro-3-methylbuta-1,3-diene (2d).[19] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 5.46 (m, 1 H, $=CH_2$); 5.10 (m, 1 H, $=CH_2$); 4.71 (d, 1 H, $-CF=CH_2$, $J = 17.8$ Hz); 4.55 (d, 1 H, $-CF=CH_2$, $J = 49.3$ Hz); 1.90 (m, 3 H, Me). ^{19}F NMR (CDCl$_3$, 282.4 MHz), δ: -109.7 (dd, 1 F, $-CF=CH_2$, $J_1 = 49.3$ Hz, $J_2 = 17.8$ Hz). MS, *m/z* (I_{rel} (%)): 86 [M]$^+$ (100), 85 (80), 71 (21), 65 (31), 51 (49).

2-Methylbut-1-en-3-yne (3d).[25,26] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 5.43 (m, 1 H, $C=CH_2$); 5.33 (m, 1 H, $C=CH_2$); 2.90 (s, 1 H, C≡CH); 1.94 (m, 3 H, Me). MS, *m/z* (I_{rel} (%)): 66 [M]$^+$ (100), 65 (84), 51 (36), 50 (30), 40 (45), 39 (70), 28 (36).

3-Methylbut-3-en-2-one (7).[27,28] ^1H NMR (CDCl$_3$, 300.1 MHz), δ: 5.94 (m, 1 H, $C=CH_2$); 5.78 (m, 1 H, $C=CH_2$);

2.31 (m, 3 H, Me); 1.83 (m, 3 H, Me). ^{13}C NMR (CDCl$_3$, 50.3 MHz), δ: 17.3 (CH$_3$), 25.4 (CH$_3$), 125.2 (C=C), 145.2 (C=C), 199.3 (C=O). MS, *m/z* (I_{rel} (%)): 84 [M]$^+$ (83), 69 (76), 43 (100), 41 (87), 39 (30).

3-Methylbutan-2-one (8)^{29}. ^{1}H NMR (CDCl$_3$, 300.1 MHz), δ: 2.60 (m, 1 H, CH); 2.15 (s, 3 H, Me); 1.10 (d, 6 H, 2 Me, *J* =7.0 Hz). ^{13}C (CDCl$_3$, 50.3 MHz), δ: 17.6 (CH$_3$), 26.8 (CH$_3$), 40.9 (CH), 211.2 (C=O). MS, *m/z* (I_{rel} (%)): 86 [M]$^+$ (27), 71(5), 43(100), 41 (15), 39(5).

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