Thermal isomerisation of 1-chloro-1-fluoro-2-vinylcyclopropanes: competition between the vinylcyclopropane–cyclopentene rearrangement and cyclopropyl–allyl transformation

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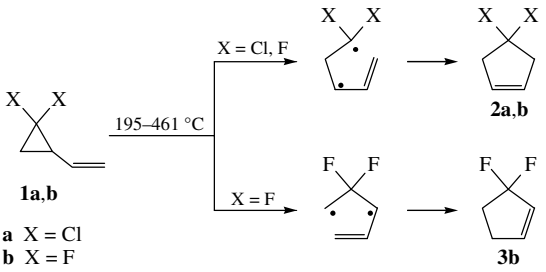
The gas-phase pyrolysis of 1-chloro-1-fluoro-2-vinylcyclopropane and 1-chloro-1-fluoro-2-methyl-2-vinylcyclopropane at 305–360 °C afforded 4-chloro-4-fluorocyclopentenes and chlorofluorobutadienes as a result of competitive vinylcyclopropane–cyclopentene rearrangement and cyclopropyl–allyl isomerisation.

Vinylcyclopropane undergoes selective ring-expansion isomerisation to cyclopentene at elevated temperatures.[1] A similar reaction is also characteristic of 1,1-dichloro-2-vinylcyclopropane **1a**[1,2] and 1,1-difluoro-2-vinylcyclopropane **1b**.[3,4] The tentative mechanism of the vinylcyclopropane–cyclopentene rearrangement of **1a**,**b** involves the homolysis of a C–C bond of the cyclopropane ring adjacent to the vinyl group followed by the 1,5-cyclisation of intermediate biradicals (Scheme 1).[1–4]



Scheme 1

The regioselectivities of the rearrangements of **1a** and **1b** differed in principle. Thus, *gem*-dichloro(vinyl)cyclopropane **1a** was selectively transformed into 4,4-dichlorocyclopentene **2a**[2] at 275–300 °C in a flow reactor upon ring opening with cleavage of the C(1)–C(2) bond, whereas virtually selective homolysis of the C(2)–C(3) bond opposite to the dihalomethylene fragment occurred in *gem*-difluoro(vinyl)cyclopropane **1b** resulting in its isomerisation to 3,3-difluorocyclopentene **3b** as the major product (**3b**:**2b** ratio of 94:6)[3,4] at 195–267 °C in a sealed tube[3] or at 384–461 °C in a flow reactor.[4]

These results prompted investigation into thermolysis of *gem*-chlorofluoro(vinyl)cyclopropanes where competitive effects of the chlorine and fluorine atoms might appear. 1-Chloro-1-fluoro-2-vinylcyclopropane **4a**[5] and 1-chloro-1-fluoro-2-methyl-2-vinylcyclopropane **4b**[5] were chosen as model compounds; these were obtained by addition of chlorofluorocarbene, generated from $CHCl_2F$ under conditions of phase-transfer catalysis, to butadiene or isoprene, respectively.† Thermolysis of compounds **4a**,**b** was carried out in a quartz flow reactor at 305–360 °C.‡

† *Synthesis of compounds* **4a**,**b**. A 50% aqueous solution of KOH (220 g) was added dropwise over 2 h to a vigorously stirred solution of a diene (butadiene or isoprene) (1.0 mol), $CHCl_2F$ (1.2 mol) and benzyltriethylammonium chloride (1.5 g) in dichloromethane (150 ml), at –5 to –10 °C, then the mixture was additionally stirred for 8 h and diluted with water. The organic layer was distilled to give 0.57 mol of cyclopropane **4a** (*E*/*Z* = 0.65) (bp 87–89 °C)[5] (yield 57%) or 0.78 mol of cyclopropane **4b** (*E*/*Z* = 1.0) (bp 109–110 °C)[5] (yield 78%).

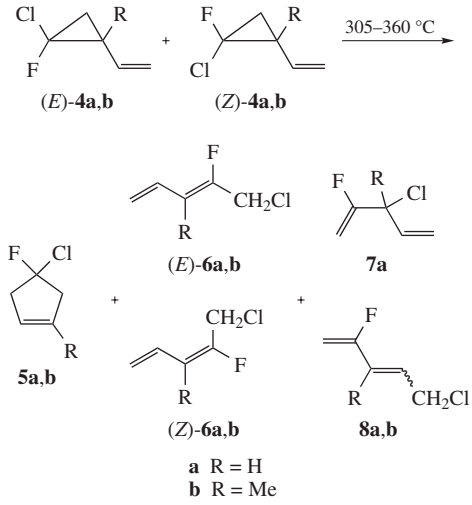
‡ *Pyrolysis of compounds* **4a**,**b** was carried out in a flow mode under atmospheric pressure by feeding cyclopropanes **4** (with 10% of 1,2-difluorobenzene added as the internal standard) at a constant rate of 0.15 g min^{-1} into a heated quartz tube reactor (300×22 mm) under a flow of nitrogen (60 ml min^{-1}). The pyrolysis products were collected in a dry ice–acetone cooled trap and further analysed using GLC, NMR spectroscopy and GLC-MS.

Table 1 Composition of pyrolysis products of compound **4a** (*E*/*Z* = 0.65) at 320–360 °C.

T/°C	Pyrolysate composition (%)						
	4a[a]	**5a**	(*E*)-**6a**	(*Z*)-**6a**	**7a**	**8a**	Other products[b]
320	71	7	7	2	5	3	5
330	51	10	13	4	7	5	10
335	38	14	18	4	8	6	12
340	28	17	21	5	9	8	12
350	12	21	26	6	5	12	18
360	5	23	26	6	4	13	23

[a]The (*E*)-**4a**:(*Z*)-**4a** ratio in reaction mixtures remains within 0.65±0.05. [b]Total amount of unidentified minor products and resins.

It was found that *gem*-chlorofluoro(vinyl)cyclopropanes **4a**,**b** differed substantially from structurally similar *gem*-dichloro- and *gem*-difluorocyclopropanes **1a**,**b** in the character of thermal transformations. Thus, the pyrolysis of compound **4a** (the *E*:*Z* = = 0.65) at 320–360 °C resulted in a mixture of products comprising, along with expected 4-chloro-4-fluorocyclopentene **5a**, chlorofluorobutadienes **6a**–**8a**, their total yield exceeding 2–3 times that of cyclopentene **5a** (Scheme 2, Table 1).



Scheme 2

The pyrolysis of compound **4b** (*E*:*Z* = 1.0) gave similar results: at 305–360 °C, it was converted into chlorofluorocyclopentene **5b** and a mixture of chlorofluorobutadienes (*E*)-**6b**, (*Z*)-**6b** and **8b** (Scheme 2, Table 2).

Products **4**–**8** were isolated by preparative GLC and unambiguously identified.§ According to NMR and GLC data, the reaction mixtures also contained several minor unidentified components (from 0.5 to 4% each, overal 4–10% depending on temperature); the degree of resinification (5–15%) increased with pyrolysis temperature.

It is evident from Tables 1 and 2 that no substantial changes in the ratio of the major reaction products occurred with an increase in the pyrolysis temperature in the interval studied and the concomitant increase in the degree of conversion of compounds **4a**,**b**. Note that the percentage of reaction products (*E*)-**6a**,**b** exceeded considerably that of (*Z*)-**6a**,**b**. The (*E*)-**4a**,**b**:(*Z*)-**4a**,**b** ratios in pyrolysis products obtained at different temperatures were virtually the same as the isomer ratios in the starting cyclopropanes. This suggests similar reactivities of stereoisomers **4a**,**b** under conditions of gas-phase pyrolysis.

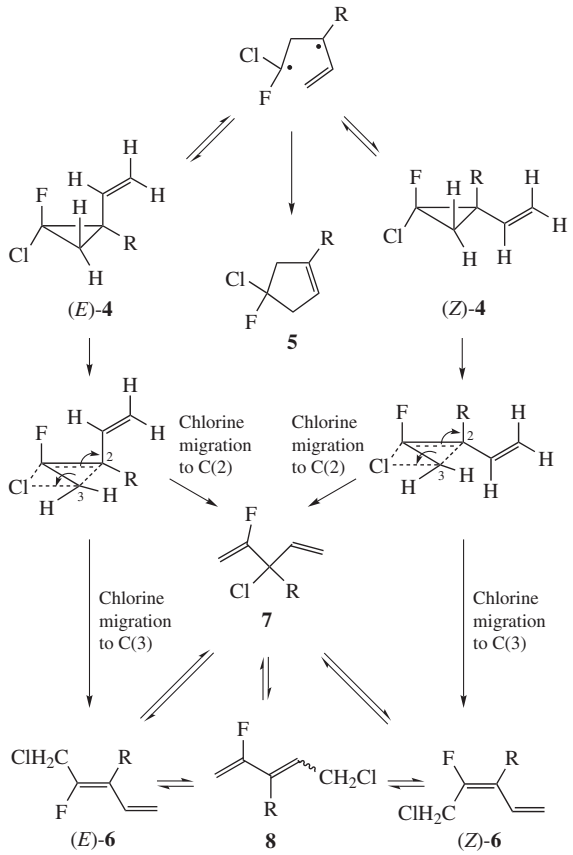
Table 2 Content of pyrolysis products of compound **4b** (*E*/*Z* = 1.0) at 305–360 °C.

T/°C	Pyrolysate composition (%)					
	4b[a]	**5b**	(*E*)-**6b**	(*Z*)-**6b**	**8a**	Other products[b]
305	64	10	9	7	6	4
315	40	16	13	9	10	12
320	33	18	15	10	11	13
335	20	21	18	10	15	16
350	9	24	20	12	18	17
360	3	23	20	11	18	25

[a]The (*E*)-**4b**:(*Z*)-**4b** ratio in reaction mixtures remains within 1.00±0.05. [b]Total amount of unidentified minor products and resins.

The results obtained can be accounted for by competition between two pathways of the thermal transformation of **4**, *viz.*, the rearrangement into cyclopentenes, which is typical of vinylcyclopropanes, and transformation of the cyclopropyl–allyl type.[6,7] The latter occurs as ring opening with the cleavage of the C(2)–C(3) bond with chlorine migration to carbon atoms C(2) or C(3) of the cleaved ring and formation of chlorofluorobutadienes **6**–**8** (see Scheme 3).

According to the classical studies on the mechanism of cyclopropyl to allyl transformation of the series of halocyclopropanes,[7] the isomerisation of **4** into chlorofluorobutadienes **6**–**8** proceeds as a concerted electrocyclic process, which implies the stereospecific transformation of (*E*)-**4a**,**b** into diene (*E*)-**6a**,**b** and (*Z*)-**4a**,**b** into (*Z*)-**6a**,**b**. With consideration of the steric effects, the reactivity of (*Z*)-**4a** was expected to be lower than that of (*E*)-**4a**. The deviations in the stereochemical consequences observed in the pyrolysis of **4** (Tables 1 and 2) from those expected for the cyclopropyl to allyl isomerisation according to the classical mechanism, *viz.*, similar reactivities of stereoisomers (*Z*)-**4a**,**b** and (*E*)-**4a**,**b**, as well as the absence of correlation between the degrees of their conversion and the percentage of



Scheme 3

§ For (*E*)-**4a**: ^{1}H NMR ($CDCl_3$) δ: 1.41–1.54 (m, 1H, ring), 2.08–2.39 (m, 2H, ring), 5.18–5.37 (m, 2H, H_2C=CH), 5.43–5.62 (m, 1H, H_2C=C*H*). ^{19}F NMR ($CDCl_3$) δ: –147.7 (dd, 1F, CFCl, ^3J 16.4 Hz, ^3J 7.8 Hz). MS (EI, 70 eV) *m*/*z* (%): 122 and 120 $[M]^+$ (3 and 9), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (40).

For (*Z*)-**4a**: ^{1}H NMR ($CDCl_3$) δ: 1.18–1.28 (m, 1H, ring), 1.55–1.63 (m, 1H, ring), 1.73–1.89 (m, 1H, ring), 5.18–5.37 (m, 2H, H_2C=CH), 5.43–5.62 (m, 1H, H_2C=C*H*). ^{19}F NMR ($CDCl_3$) δ: –130.2 (ddd, 1F, CFCl, ^3J 17.4 Hz, ^3J 17.0 Hz, ^3J 7.3 Hz). MS (EI, 70 eV,) *m*/*z* (%): 122 and 120 $[M]^+$ (2 and 6), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (31).

For **4b** [mixture of (*E*)-**4b** and (*Z*)-**4b**]: ^{1}H NMR ($CDCl_3$) δ: 1.20–1.68 (m, 2H, ring), 1.37–1.39 (m, 3H, Me), 5.11–5.32 (m, 2H, H_2C=CH), 5.64–5.82 (m, 1H, H_2C=C*H*). ^{19}F NMR ($CDCl_3$): the spectrum contains two signals with approximately equal integral intensities with δ –138.7 (ddq, 1F, CFCl, ^3J 15.6 Hz, ^3J 8.1 Hz, ^4J 1.8 Hz) and –139.2 (ddq, 1F, CFCl, ^3J 16.4 Hz, ^3J 7.4 Hz, ^4J 2.0 Hz). MS (EI, 70 eV) *m*/*z* (%): 99 $[M - Cl]^+$ (18), 80 $[M - Cl - F]^+$ (32), 79 $[M - Cl - HF]^+$ (68), 77 (22), 53 (36), 51 (45), 39 (62), 27 (100).

For **5a**: ^{1}H NMR ($CDCl_3$) δ: 3.13 (d, 4H, 2CH_2, ^3J 20.8 Hz), 5.73–5.77 (m, 2H, CH=CH). ^{19}F NMR ($CDCl_3$) δ: –92.7 (qw, 1F, CFCl, ^3J 20.8 Hz). MS (EI, 70 eV) *m*/*z* (%): 122 and 120 $[M]^+$ (8 and 23), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (29).

For **5b**: ^{1}H NMR ($CDCl_3$) δ: 1.77 (br. s, 3H, Me), 3.02 (d, 2H, CH_2, ^3J 21.0 Hz), 3.10 (d, 2H, CH_2, ^3J 21.0 Hz), 5.29–5.36 (m, 1H, CH=). ^{19}F NMR ($CDCl_3$) δ: –92.5 (qw, 1F, CF, ^3J 21.0 Hz). MS (EI, 70 eV) *m*/*z* (%): 136 and 134 $[M]^+$ (1 and 3), 99 $[M - Cl]^+$ (66), 79 $[M - Cl - HF]^+$ (94), 39 (100), 27 $[C_2H_3]^+$ (94).

For (*E*)-**6a**: ^{1}H NMR ($CDCl_3$) δ: 4.11 (d, 2H, CH_2Cl, ^3J 18.2 Hz), 5.19 (d, 1H, =CH_2, ^3J 10.1 Hz), 5.30 (d, 1H, =CH_2, ^3J 17.3 Hz), 5.62 (dd, 1H, CH=CF, ^3J 31.7 Hz, ^3J 10.1 Hz), 6.59 (ddd, 1H, CH=, ^3J 17.3 Hz, ^3J 10.1 Hz, ^3J 10.1 Hz). ^{19}F NMR ($CDCl_3$) δ: –111.6 (dt, 1F, CF, ^3J 31.7 Hz, ^3J 18.2 Hz). MS (EI, 70 eV) *m*/*z* (%): 122 and 120 $[M]^+$ (14 and 43), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (31).

For (*Z*)-**6a**: ^{1}H NMR ($CDCl_3$) δ: 4.26 (d, 2H, CH_2Cl, ^3J 20.4 Hz), 5.23 (d, 1H, =CH_2, ^3J 10.1 Hz), 5.32 (d, 1H, =CH_2, ^3J 15.3 Hz), 5.97 (dd, 1H, CH=CF, ^3J 16.2 Hz, ^3J 10.1 Hz), 6.33 (ddd, 1H, CH=, ^3J 15.3 Hz, ^3J 10.1 Hz, ^3J 10.1 Hz). ^{19}F NMR ($CDCl_3$) δ: –107.3 (dt, 1F, CF, ^3J 20.4 Hz, ^3J 16.2 Hz). MS (EI, 70 eV) *m*/*z* (%): 122 and 120 $[M]^+$ (13 and 42), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (32).

For (*E*)-**6b**: ^{1}H NMR ($CDCl_3$) δ: 1.84 (d, 3H, Me, ^4J 3.5 Hz), 4.33 (d, 2H, CH_2Cl, ^3J 22.9 Hz), 5.24 (dd, 1H, =CH_2, ^3J 10.0 Hz, ^3J 1.8 Hz), 5.38 (br. d, 1H, =CH_2, ^3J 17.0 Hz), 6.51 (ddd, 1H, CH=, ^3J 17.0 Hz, ^3J 10.0 Hz, ^4J 2.0 Hz). ^{19}F NMR ($CDCl_3$) δ: –109.6 (br. t, 1F, CF, ^3J 22.9 Hz). MS (EI, 70 eV) *m*/*z* (%): 99 $[M - Cl]^+$ (31), 79 $[M - Cl - HF]^+$ (81), 53 (31), 51 (61), 45 (32), 39 (50), 27 $[C_2H_3]^+$ (100).

For (*Z*)-**6b**: ^{1}H NMR ($CDCl_3$) δ: 1.82 (d, 3H, Me, ^4J 2.9 Hz), 4.28 (d, 2H, CH_2Cl, ^3J 23.1 Hz), 5.23 (d, 1H, =CH_2, ^3J 10.8 Hz), 5.38 (br. d, 1H, =CH_2, ^3J 17.5 Hz), 6.87 (ddd, 1H, CH=, ^3J 17.5 Hz, ^3J 10.8 Hz, ^4J 1.5 Hz). ^{19}F NMR ($CDCl_3$) δ: –113.1 (br. t, 1F, CF, ^3J 23.1 Hz). MS (EI, 70 eV) *m*/*z* (%): 136 and 134 $[M]^+$ (1 and 3), 99 $[M - Cl]^+$ (43), 79 $[M - Cl - HF]^+$ (76), 77 (57), 53 (24), 51 (63), 45 (32), 39 (43), 27 $[C_2H_3]^+$ (100).

For **7a**: ^{1}H NMR ($CDCl_3$) δ: 4.68 (dd, 1H, CF=CH_2, ^3J 46.3 Hz, ^2J 3.5 Hz), 4.79 (dd, 1H, CF=CH_2, ^3J 15.8 Hz, ^2J 3.5 Hz), 4.88 (dd, 1H, CHCl, ^3J 14.8 Hz, ^3J 7.8 Hz), 5.34 (d, 1H, H_2C=C, ^3J 10.3 Hz), 5.47 (d, 1H, H_2C=C, ^3J 17.0 Hz), 6.02 (ddd, 1H, C=CH, ^3J 17.0 Hz, ^3J 10.3 Hz, ^3J 7.8 Hz). ^{19}F NMR ($CDCl_3$) δ: –105.3 (ddd, 1F, CF, ^3J 46.3 Hz, ^3J 15.8 Hz, ^3J 14.8 Hz). MS (EI, 70 eV) *m*/*z* (%): 122 and 120 $[M]^+$ (9 and 35), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (32).

For **8a** (*E*- or *Z*-isomer): ^{1}H NMR ($CDCl_3$) δ: 4.16 (d, 2H, CH_2Cl, ^3J 6.1 Hz), 4.56 (dd, 1H, =CH_2, ^3J 48.1 Hz, ^2J 4.1 Hz), 4.70 (dd, 1H, =CH_2, ^3J 15.9 Hz, ^2J 4.1 Hz), 6.10–6.18 (m, 2H, CH=CH). ^{19}F NMR ($CDCl_3$) δ: –111.0 (ddd, 1F, CF, ^3J 48.1 Hz, ^3J 25.6 Hz, ^3J 15.9 Hz). MS (EI, 70 eV) *m*/*z* (%): 122 and 120 $[M]^+$ (11 and 41), 85 $[M - Cl]^+$ (100), 65 $[M - Cl - HF]^+$ (34).

For **8b** (*E*- or *Z*-isomer): ^{1}H NMR ($CDCl_3$) δ: 1.87 (br. s, 3H, Me), 4.20 (d, 2H, CH_2Cl, ^3J 7.8 Hz), 4.65 (dd, 1H, =CH_2, ^3J 48.9 Hz, ^2J 3.1 Hz), 4.80 (dd, 1H, =CH_2, ^3J 18.4 Hz, ^2J 3.1 Hz), 6.17 (br. t, 1H, C=CH, ^3J 7.8 Hz). ^{19}F NMR ($CDCl_3$) δ: –109.8 (dd, 1F, =CF, ^3J 48.9 Hz, ^3J 18.4 Hz). MS (EI, 70 eV) *m*/*z* (%): 99 $[M - Cl]^+$ (32), 79 $[M - Cl - HF]^+$ (71), 77 (52), 53 (40), 51 (82), 45 (40), 51 (82), 45 (40), 39 (55), 27 $[C_2H_3]^+$ (100).

dienes (*E*)-**6a**,**b** and (*Z*)-**6a**,**b** in the pyrolysis products, can be related to the reversible isomerisation of dienes **6**–**8** induced by the 1,3-allylic shift of chlorine and, probably, to the reversible *E*–*Z* isomerisation of dihalo(vinyl)cyclopropanes **4a**,**b**. An alternative explanation assumes a non-concerted two-step conversion of **4** into **6**–**8** involving homolysis of the C(2)–C(3) bond and subsequent rearrangement of the corresponding intermediate biradical with chlorine migration.

The revealed specificity of thermal transformations of *gem*-chlorofluoro(vinyl)cyclopropanes **4** and the observed differences in the pathways of their thermal rearrangements from those of analogous *gem*-difluoro- and *gem*-dichloro(vinyl)cyclopropanes **1a**,**b** can be explained by competition between two different effects of chlorine and fluorine that can manifest themselves in elementary steps of the thermally induced ring opening of a halogen-substituted cyclopropane. Thus, the selective isomerisation[2] of 1,1-dichloro-2-vinylcyclopropane **1a** in 4,4-dichlorocyclopentene **2a** is accounted for by the known ability of the chlorine atoms to efficient stabilising the carbon-centred radical, so that the gain in the energy upon ring opening of cyclopropane **1a** with homolysis of the C(1)–C(2) cyclopropane bond is much higher than that upon alternative cleavage of the C(2)–C(3) bond preceding the cyclopropyl–allyl rearrangement. Conversely, the prevailing effect governing the direction of ring opening in 1,1-difluoro-2-vinylcyclopropane **1b** is related to the well-known[3,8] property of the fluorine atom of inducing structural and kinetic destabilisation of the C–C bond in the three-membered carbocycle opposite to the difluoromethylene fragment. This together with the weak radical-stabilising effect of fluorine determine the observed[3,4] selective thermally induced isomerisation of compound **1b** to **3b** involving cleavage of the C(2)–C(3) bond. On the other hand, the isomerisation of **1b** according to the mechanism of the cyclopropyl–allyl transformation implies highly energy-consuming cleavage of the strong C–F bond. Therefore, this cannot compete with the vinylcyclopropane–cyclopentene rearrangement.

In chlorofluoro(vinyl)cyclopropanes **4**, a decrease in the radical-stabilising effect of one chlorine atom (as compared with the effect of two chlorine atoms in dichlorocyclopropane **1a**) and the expected smaller destabilising effect of the fluorine atom (as compared with that in difluorocyclopropane **1b**) should make activation barriers for the processes involving ring opening of the three-membered carbocycle in **4** with cleavage of the C(2)–C(3) and C(1)–C(2) bonds closer to each other. As a consequence, the thermolysis of chlorofluoro(vinyl)cyclopropanes **4** results in comparable yields of the vinylcyclopropane–cyclopentene rearrangement and the cyclopropyl–allyl transformation products.

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