33. The Halide-Promoted Fragmentation of 1-Chloro-1-fluoro-2-(α-silylalkyl)cyclopropanes: A New Entry to Fluorodienes[1])

by **Manfred Schlosser***, **Rachel Dahan**, and **Sylvain Cottens**

Institut de Chimie organique de l'Université, Rue de la Barre 2, CH-1005 Lausanne (Switzerland)

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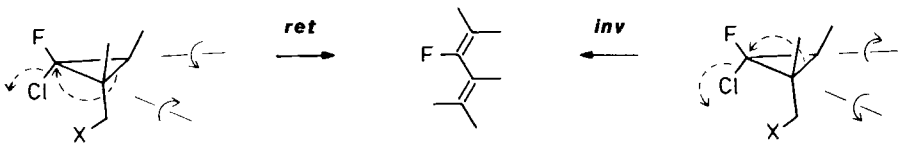
Summary

When heated in the presence of tetrabutylammonium fluoride or chloride, 1-chloro-1-fluoro-2-(trimethylsilyl)methyl-cyclopropanes (**1**, **2**, and **3**) undergo smooth ring-opening fragmentation to afford 2-fluoro-butadienes (**4**, **5** and **6**, resp.) with high yields. Despite unfavorable geometries, the reaction is concerted and the inversion mode of rotation dominates over the retention mode by a factor of roughly 100.

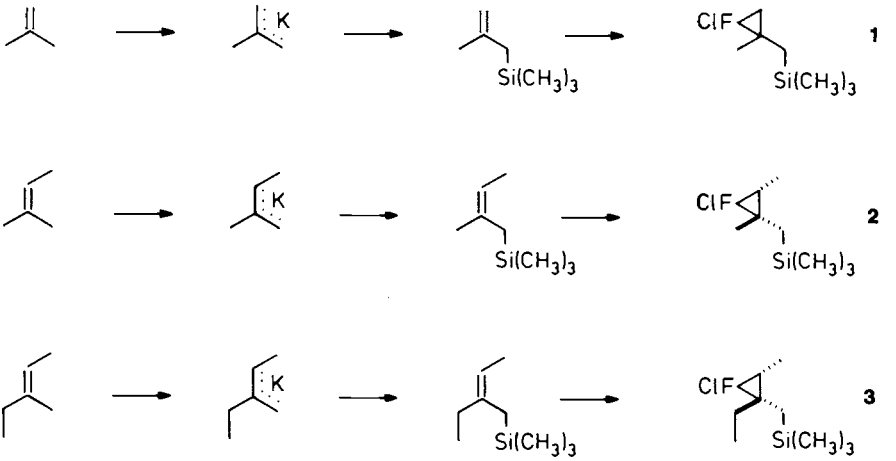
Upon treatment with reducing agents such as Zn, α-haloalkyl-chlorofluoro-cyclopropanes undergo a ring-opening fragmentation affording 2-fluorodienes [2]. This fragmentation may be brought about employing either of two stereoelectronically different processes: a retention-like ('*ret*') or an inversion-like ('*inv*') mode. Although a general preference for the latter was observed, this stereoselectivity of the cleavage mechanism proved to depend heavily on the nature of the reducing agent, for example whether acid-washed or copper-coated Zn was used [3]. In order to escape from ambiguities due to heterogeneous reaction conditions, we wanted to replace the exocyclic halogen atom by another electrofugal leaving group the elimination of which would no longer require metals but could be affected with soluble, nucleophilic reagents. Our choice fell on the trimethylsilyl group.



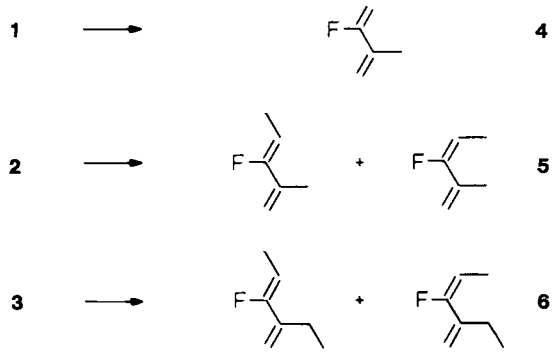
The synthesis of suitable model compounds was straightforward. The olefins 2-methyl-1-propene, 2-methyl-2-butene and 3-methyl-2-pentene were metalated with BuLi in the presence of KO*t*Bu [4]. After stirring overnight to establish the torsional equilibrium of the allylpotassium intermediates [5], chlorotrimethylsilane was added.

[1]) Part XIII of the series 'Organofluorine Compounds'; for part XII see [1].

The phase-transfer-catalyzed reaction [6] with dichlorofluoromethane and KOH converted the intermediate (*Z*)-allylsilanes into the chlorofluorocyclopropanes **1**, **2**, and **3**, respectively.

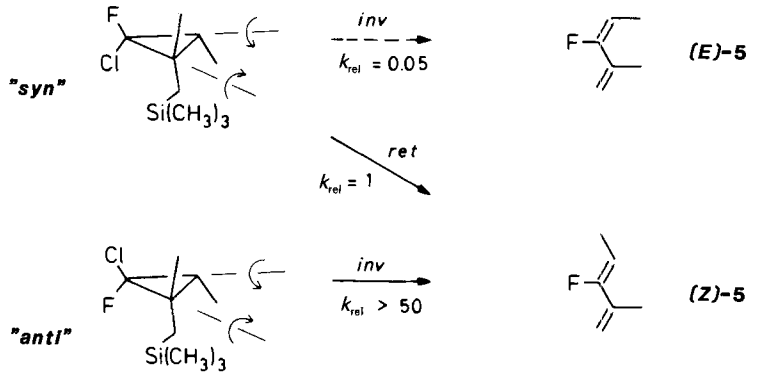


Upon heating diethyleneglycol dimethyl ether solutions in the presence of tetrabutylammonium fluoride to 130 or 140 °C, a smooth fragmentation of the cyclopropanes **1**, **2** and **3** took place producing 2-fluoro-3-methyl-1,3-butadiene (**4**), 3-fluoro-2-methyl-1,3-pentadiene (**5**), and 2-ethyl-3-fluoro-1,3-pentadiene (**6**), respectively. Remarkably enough, tetrabutylammonium *chloride* was found to promote the ring-opening fragmentation almost as efficiently as the corresponding *fluoride*. Since both salts, however, are hydrated to various degrees, it is difficult to compare their reaction rates in a meaningful and reproducible fashion.

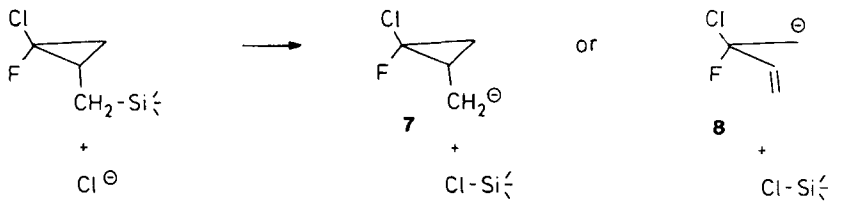


In order to elucidate the stereochemical course of the fragmentation reaction, the pure *'syn'*-diastereoisomer of cyclopropane **2** (*'syn'*-**2**) and a diastereoisomeric mixture rich in the *'anti'*-component (*'anti'*-**2**) were studied separately. Under the impact of tetrabutylammonium fluoride or chloride the *'anti'*-isomer disappeared very rapidly affording exclusively the fluorodiene (*Z*)-**5**. As revealed by competition experiments,

the *'syn'*-isomer reacted at least 50 times more slowly and gave a 95 : 5 mixture of (*Z*)- and (*E*)-**5**. In this case, the inversion mode generating (*E*)-**5** is clearly disfavored for steric reasons [7]: the obligatory disrotatory motion together with the given geometrical disposition of the leaving group obliges two bulky moieties, a methyl and a (trimethylsilyl)methyl group, to rotate toward each other and thus to build up considerable repulsion.



The reaction conditions unequivocally rule out a non-concerted mechanism. The formation of either of the possible intermediates, carbanions **7** and **8**, would be a highly endothermal process[2]).



Thus, we can conclude that the fragmentation of α-haloalkyl-chlorofluorocyclopropanes takes a concerted pathway. This is remarkable because two of the involved orbitals, those of the C,Cl bond and the opposite ring bond, are perpendicularly oriented with respect to each other ('concertedness turning around a corner' [3]). Furthermore, the fragmentation reaction prefers clearly an inversion over a retention mode of ring opening.

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[2]) Approximate heterolytic bond dissociation energies and electron affinities: Si-C 75, Si-Cl 90, Si-F 135, ≥C · 0, Cl · 85, and F · 80 kcal/mol.

Experimental Part

General Remarks. See [2b].

1. Allyl-silanes. – a) *Trimethyl-(2-methyl-2-propen-1-yl)silane.* At −75° and under vigorous stirring, 16.8 g (0.15 mol) of KO*t*Bu were added within 15 min to a solution of 0.15 mol of BuLi and 8.4 g (0.15 mol) of 2-methyl-1-propene in 115 ml of hexane and 100 ml of THF. After 10 h at −50°, the suspension was cooled again to −75°, treated with 20 ml (0.16 mol) of chlorotrimethylsilane, warmed to 25°, and poored into 100 ml of ice water. The aq. layer was extracted with Et_2O (3 × 50 ml), and the combined org. layers were washed with H_2O (3 × 10 ml) before drying ($CaSO_4$) and removal of the solvents through a *Widmer* column. Distillation gave 9.6 g (50%) of the analytically pure silane, b.p. 93–96°. Anal. calc. for $C_7H_{16}Si$ (128.3): C 65.54, H 12.57; found: C 65.49, H 12.63.

b)*(Z)-Trimethyl-(2-methyl-2-buten-1-yl)silane.* The same procedure applied to 10.5 g (0.15 mmol) of 2-methyl-2-butene led to 9.7 g (45%) of product, b.p. 60–63°/80 Torr. Anal. calc. for $C_8H_{18}Si$ (142.3): C 67.52 H 12.74; found: C 67.40, H 12.54.

2. Chlorofluorocyclopropanes. – a) *1-Chloro-1-fluoro-2-methyl-2-(trimethylsilyl)methyl-cyclopropane* (**1**). A three-necked flask with dry-ice condenser was cooled to 0° and filled with 25 ml of 55% aq. KOH (360 mmol), 0.1 g (0.4 mmol) of 1,4,6,7,10,13,16-hexaoxacyclooctadecane ('18-crown-6'), 5.1 g (40 mmol) of trimethyl-(2-methyl-2-propen-1-yl)-silane and 10 ml (70 mmol) of dichlorofluoromethane (*Freon-21*). After vigorous stirring during 1 h at 0° and 2 h at 25°, the org. phase was collected, washed (2 × 20 ml H_2O), dried ($CaSO_4$), and evaporated. The product (**1**) distilled at 73–75°/30 Torr: 4.7 g (60%). ^{19}F-NMR ($CDCl_3$, 84.7 MHz): the two *'syn/anti'*-diastereoisomers had formed in a 1:1 ratio (−62 and −64 ppm, *d*, J = 12 and 15, resp.). Anal. calc. for $C_8H_{16}ClFSi$ (194.7): C 49.34, H 8.28; found: C 49.17, H 8.02.

b) *1-Chloro-1-fluoro-2,3-dimethyl-2-(trimethylsilyl)methyl-cyclopropane* (**2**). Under the same conditions 5.7 g (40 mmol) of trimethyl-(2-methyl-2-buten-1-yl)silane gave 5.5 g (66%) of **2**; b.p. 90–92°/30 Torr. ^{19}F-NMR: *'syn/anti'*-ratio 3:1 (−60, *d*, J = 21, and −74, *s*, $J < 5$, resp.). Anal. calc. for $C_9H_{19}ClFSi$ (208.7): C 51.80, H 8.65; found: C 51.77, H 8.69.

Careful distillation through a spinning-band column yielded a fraction having a 2:1 *'syn/anti'*-ratio. On the other hand, the attempted separation of the diastereoisomeric mixture by prep. GLC (3 m 20% *SE-30**, 140°; 3 m 15% *C-20M**, 125°) resulted in selective destruction of *'anti'*-**2** and provided pure *'syn'*-**2**.

c) *1-Chloro-2-ethyl-1-fluoro-3-methyl-2-(trimethylsilyl)methyl-cyclopropane* (**3**). As above 6.3 g (40 mmol) of (2-ethyl-2-buten-1-yl)trimethylsilane afforded 4.5 g (51%) of **3**, b.p. 73–75°/12 Torr. ^{19}F-NMR: *'syn/anti'*-ratio 3:1 (−60, *d*, J = 18, and −71, *s*, $J < 5$, resp.). Anal. calc. for $C_{10}H_{20}ClFSi$ (222.8): C 53.91, H 9.05; found: C 53.94, H 9.13.

3. Fluoro-dienes. – a) *Analytical Scale Reactions.* A solution of 2.5 mmol of **2**, either the pure *'syn'*-component or the 2:1 *'syn/anti'*-mixture, and of 0.25 mmol of $Bu_4NF \cdot 3H_2O$ in 5 ml of diethyleneglycol dimethyl ether was heated to 130°. In intervals samples were removed and analyzed by GLC [3] and NMR. In parallel runs, $Bu_4NF \cdot 3H_2O$ was replaced by $Bu_4NCl \cdot \frac{1}{2}H_2O$ which proved to be slightly more reactive. The chloride-catalyzed fragmentation of *'syn/anti'*-**2** produced in the initial stages, when only *'anti'*-**2** was consumed, exclusively the (*Z*)-isomer of *3-fluoro-2-methyl-1,3-pentadiene* (**5**). The remaining pure *'syn'*-component, however, gave rise also to trace amounts of the (*E*)-isomer (see *Table*).

The half-reaction times can be estimated as 2.5 and ≤ 1.5 min for the fluoride- and chloride-promoted fragmentation, respectively, of *'anti'*-**2** and approximates 150 min in the case of *'syn'*-**2** regardless of which halide catalyst is used.

Table. *Bu_4NCl-catalyzed Fragmentation of* 'syn'- *and* 'anti'-*Chlorofluorocyclopropane* **2** *Affording (Z)- and (E)-Fluorodiene* **5**. Product composition (relative concentrations) as a function of time *t*.

t [min]	*'syn'*-**2**	*'anti'*-**2**	(*Z*)-**5**	(*E*)-**5**
0	67	33	0	0
5	67	0	33	0
15	63	0	37	0
40	60	0	40	0
80	45	0	52	3
120	38	0	59	3
900	< 3	0	95	3

b) *Preparative Scale Reactions.* A mixture of 25.0 mmol of the chlorofluorocyclopropane (**1–3**), 7.8 g (25 mmol) of $Bu_4NF \cdot 3H_2O$ and 50 ml of diethyleneglycol dimethyl ether was heated 4 h to 140°. During this period, a slow current of N_2 was allowed to stream through the reaction vessel before it passed through a trap which was placed in an ice bath. The trap contained the desired fluorodienes **4–6** in approximate yields of 65%. *'Fluoro-isoprene'* (**4**) and *3-fluoro-2-methyl-1,3-pentadiene* (**5**) were identified by comparison with authentic materials [2b] [3]. The condensate of *2-ethyl-3-fluoro-1,3-pentadiene* (**6**) was taken up in 5 ml of pentane and, after removal of the solvent using a spinning band column, submitted to a bulb-to-bulb distillation (95–100°/760 Torr). At the expense of substantial loss of product, it was finally purified by prep. GLC (3 m 20% *C-20M*, 80°). NMR ($CDCl_3$, 56.4 MHz): the (*Z*)- and (*E*)-isomer were present in a 10:1 ratio; −59 (*d*, *J* = 38, (*Z*)); −65 (*d*, *J* = 24, (*E*)). ^{1}H-NMR ($CDCl_3$, 80 MHz): 5.1 (*m*, 3 H); 2.18 (*q*, *J* = 7.5, 2 H); 1.73 (*dd*, *J* = 7, 3, 3 H); 1.10 (*t*, *J* = 7.5, 3 H). MS (250°): 114 (53, M^+), 79 (100). Anal. calc. for $C_7H_{11}F$ (114.2): C 73.65, H 9.71; found: C 73.61, H 10.13.

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