ADDITION OF DIHALOCARBENES TO VINYL FLUORIDES. CHEMICAL CONSEQUENCES OF FLUORINE SUBSTITUTION. PART 3+

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Dedicated to the memory of Professor Miloš Hudlický.

1-Fluoro-1-phenylethene (**1a**) or 1-(4-chlorophenyl)-1-fluoroethene (**1b**) and 2-fluorooct-1-ene (**4**), on reaction with chloroform and sodium hydroxide, in a two-phase system in the presence of a phase transfer catalyst, gave the corresponding dichlorocyclopropanes in good yields. In a competition experiment, **1a** was shown to be slightly more reactive than styrene itself. AM1 calculations predict reasonable activation barriers for these reactions although the relative reactivity observed in the experiment is not reproduced. For the (*E*)- and (*Z*)-1-fluoro-2-phenylethenes (**3**), higher activation barriers were calculated, in agreement with the observation that these alkenes did not react with dichlorocarbene under these conditions. The dibromocarbene addition to **1a** gave 1,1-dibromo-2-fluoro-2-phenylcyclopropane (**8**), which on heating with silver salts in acetic acid yielded 3-acetoxy-2-bromo-1-fluoro-1-phenylprop-1-ene (**9**) by a cyclopropyl-allyl rearrangement.

Keywords: [2+1]-Cycloaddition; Cyclopropanes; Cyclopropanation; Fluoroalkenes; Dihalogen carbenes; Cyclopropyl-allyl rearrangement; AM1 calculations.

Substituted cyclopropanes continue to be attractive target molecules, both as important structural motifs of biological activity[1] and as building blocks for organic synthesis[2]. Furthermore, much effort has been made in the chemistry of fluorinated compounds since the dramatic effect of a fluorine substituent on the properties and the reactivity of compounds has become well known[3].

Continuing our investigations of reactions of vinyl fluorides[4], we became also interested in carbene additions to these compounds[5a]. There are only

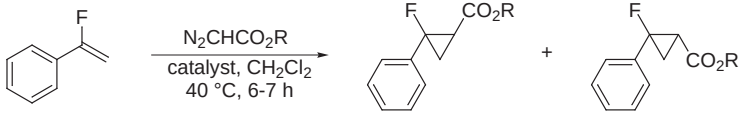
+ For Part 2, see ref.[23]

few examples of such reactions known in the literature. Taguchi *et al.* demonstrated the diastereoselective cyclopropanation of fluorinated allylic alcohol derivatives using the Simmons–Smith reaction[6], and Sloan and Kirk published a synthesis of a racemic fluorinated ethyl cyclopropanecarboxylate from a β-fluoro-α,β-unsaturated carboxylate and diazomethane[7]. Also a few examples of dihalocarbene additions to vinyl fluorides have been reported. Haszeldine *et al.*[8] added dichlorocarbene to vinyl fluoride to yield 1,1-dichloro-2-fluorocyclopropane. Similarly, also α,ω-diarylperfluoropolyenes[9] or substituted 1,2-difluoroethenes[10] were reacted with dichlorocarbene.

Herein, we report our results on the reactivity of simple vinyl fluorides to dichloro- and dibromocarbenes and the application of a so formed dibromofluorocyclopropane in a subsequent cyclopropyl-allyl rearrangement.

RESULTS AND DISCUSSION

Earlier investigations have shown that simple vinyl fluorides such as substituted α- or β-fluorostyrenes are weak dienophiles in Diels–Alder reactions[4a,4g]. On the other hand, 2-fluoroalkenes have been proved to be good substrates for the reaction with diazoacetates[5a] (Scheme 1).



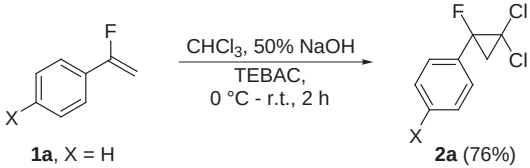
R = Et, *t*-Bu, (-)-menthyl

SCHEME 1

Also stepwise electrophilic additions, such as bromofluorinations are successful with vinyl fluorides[11]. Now, we reacted several 2-fluoroalkenes prepared by a two-step procedure from the corresponding 1-alkenes by bromofluorination[12] and subsequent HBr elimination[4b,11,13] with dichloro- and dibromocarbene. The carbenes were prepared *in situ* according to the Makosza method[14]. In this way, 1-fluoro-1-phenylethene (**1a**) in chloroform was stirred with 50% aqueous NaOH in the presence of benzyltriethylammonium chloride (TEBAC) as a phase transfer catalyst at room temperature for 2 h to give, after work-up, 76% of 1,1-dichloro-2-fluoro-2-phenylcyclopropane (**2a**). The corresponding reaction of 1-(4-chlorophenyl)-1-fluoroethene (**1b**), because of the electron-withdrawing effect of chlorine, proceeded slower and gave **2b** in 77% yield (Scheme 2).

In order to determine the influence of the 1-fluoro substituent in 1-phenylethene on the reactivity of the double bond, we performed compe-

tition experiments. An equimolar mixture of freshly distilled styrene and freshly distilled **1a** in chloroform was treated at once with a large excess (7.5 equivalents per mol of olefin) of 50% aqueous NaOH in the presence of catalytic amounts of TEBAC at 0 °C. The consumption of the alkenes was followed by gas chromatography (GC). Graphical analysis of the results makes the higher reactivity of **1a** clear (Fig. 1).



1a, X = H
1b, X = Cl

2a (76%)
2b (77%)

SCHEME 2

Using Eq. (*1*), previously used for the calculation of relative rate constants by Skell and Garner in dihalocarbene addition to non-fluorinated alkenes[15], it was calculated that the reaction of **1a** is faster by a factor of ≈1.9 compared to the reaction of styrene itself.

$$\frac{k_x}{k_y} = \frac{\log (n_x / n_{x,0})}{\log (n_y / n_{y,0})}, \qquad (1)$$

$n_{x,0}/n_{y,0}$ = molar amounts of the alkenes X or Y at $t = 0$; n_x/n_y = final molar amount of the alkenes X or Y.

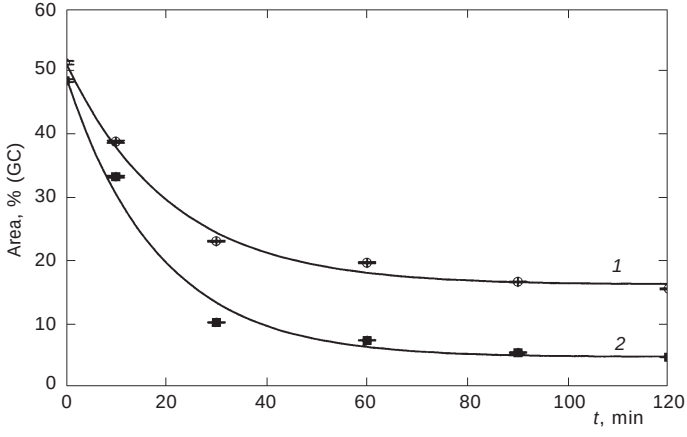


FIG. 1
Consumption of styrene (*1*) and **1a** (*2*) in dependence of the reaction time

Calculation of the HOMO and LUMO energies of the alkenes (Table I) suggests that the electrophilic[16] dichlorocarbene in a synchronous cycloaddition should react faster with styrene having the higher HOMO energy compared to **1a**. The opposite, however, was found in the experiment. On the other hand, although the HOMO energies of the styryl fluorides **3** (86 : 14 mixture of *E*- and *Z*-isomers) in solution are higher compared to those of styrene and **1a**, the former alkenes did not react with dichlorocarbene at 0 °C at all. Even after heating the reaction mixture to 60 °C for several hours, the reactants were recovered in the same ratio of stereoisomers. This observation is in agreement with resulst of Yagupolskii *et al.*[9] The authors described that (*E*)-1,2-difluoro-1,2-diphenylethene did not react with dichlorocarbene. We also found that the styryl fluorides **3** are much less reactive compared to **1a** in the copper-catalyzed reactions with diazoacetates[5a].

In order to get a qualitative picture of possible reasons for the increased reactivity of **1a** compared to styrene in dichlorocarbene addition, we performed semiempirical MO calculations by the AM1 method[17]. The optimizations of the transition states of the [2+1]-cycloaddition reactions were performed for the gas phase and for a solution model (in chloroform), taking into account the PTC conditions[14]. Using molecular partition functions, the entropy of the transition states was calculated. Since the AM1 heat of formation is referred to 298 K, the entropy values were also calculated for that temperature.

The calculations suggest a non-symmetric attack of the carbene at a preferred atom of the double bond. After optimization of the transition state, the lone pair of the carbene is directed away from the double bond, due to

TABLE I
Frontier orbital energies (AM1) for the reactants in eV

Reactant	In vacuum		In chloroform (ε_r = 4.9)	
	HOMO, eV	LUMO, eV	HOMO, eV	LUMO, eV
Styrene	–8.998	+0.019	–9.210	–0.198
1a	–9.284	–0.175	–9.447	–0.302
(*E*)-**3**	–8.964	–0.259	–9.110	–0.389
(*Z*)-**3**	–8.915	–0.189	–9.085	–0.348
$:CCl_2$	–10.166	–1.105	–10.196	–1.020

frontier orbital interactions, maximizing the overlap with its π* orbital. Thus, for each reaction two transition states showing the carbene attack at C1 or C2 are obtained, which would lead to the same cyclopropane (Scheme 3).

SCHEME 3

Two general observations were made (see Table II): $\Delta H^{\neq}$ is larger (2–3 kcal mol^{-1}) in solution than in the gas phase, and the entropic contribution to the Gibbs energy of activation, $\Delta G^{\neq}$, is as large as or larger than the activation enthalpy $\Delta H^{\neq}$ for all reactions. A high activation entropy has already been calculated for additions of electrophilic carbenes earlier[18]. The solvent effect indicates that the transition states are not polar enough to profit from the higher polarizability of the solvent. With this finding, we can argue that in the attack at C2, the partial positive charge at the α-carbon, which in the reaction of **1a** would be stabilized by fluorine and the phenyl group, is not very high.

Comparing the barriers of the reactions of styrene and **1a**, a significant increase (4.3 kcal mol^{-1}) in $\Delta H^{\neq}$ is observed in the gas phase, if **1a** is at-

TABLE II
Activation enthalpies and Gibbs energies (AM1) of the reaction of dichlorocarbene with styrene and **1a** and **3** at 298 K in kcal mol^{-1}

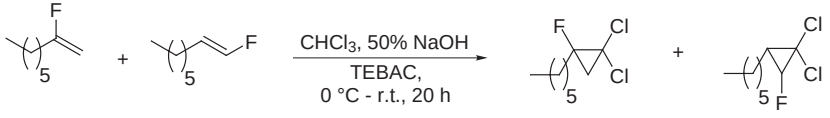
	In vacuum				In chloroform (ε_r = 4.9)			
	approach to α-C		approach to β-C		approach to α-C		approach to β-C	
	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$	$\Delta H^{\neq}$	$\Delta G^{\neq}$
Styrene	10.6	26.4	4.1	19.7	13.1	28.9	6.3	21.9
1a	14.9	30.0	5.0	19.9	[a]	[a]	7.4	22.2
(*E*)-**3**	11.7	27.4	9.0	25.0	14.6	30.3	11.7	27.7
(*Z*)-**3**	11.6	27.4	8.7	24.8	14.0	29.0	11.3	26.5

[a] No transition state structure for the attack at α-C has been found, attack at β-C was obtained.

tacked at C1. Within the solvent model, such a transition state derived from **1a** is not even a stationary point. We interpret this as a repulsive interaction of the carbene lone pair with the fluorine atom and the phenyl ring. The repulsive interaction with the phenyl group of styrene – besides electronic stabilization of the partial charges at C1 – would explain why the bond to C2 is formed easier than to C1. The transition states in which the carbene approaches the unsubstituted sp^2-carbon atom of styrene and **1a** have the lowest barriers in the gas phase (19.7 or 19.9 kcal mol^{-1}) and in chloroform (21.9 or 22.2 kcal mol^{-1}). All other reactions are much slower. In the styrylfluorides **3**, there is no unsubstituted sp^2-carbon atom and therefore no way to avoid the repulsive interaction mentioned above.

Thus, neither the frontier orbital energies, nor the small differences in the calculated activation energies (AM1) can explain the higher reactivity of **1a** than that of styrene observed in the experiment. However, the observation that (*E*)-**3** and (*Z*)-**3** did not react under the reported conditions is reflected in the very high activation barriers, which are 4–5 kcal mol^{-1} higher compared to those calculated for compound **1a**.

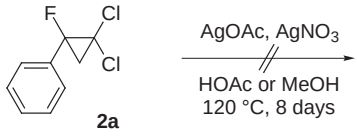
In addition to the mentioned aromatic vinyl fluorides, also aliphatic analogues were investigated. Thus, in the crude product of the reaction of a mixture of 2-fluorooctene (**4**), (*E*)- and (*Z*)-1-fluorooctene (**5**) (82 : 15 : 3) with dichlorocarbene (Makosza method[14]), besides 1,1-dichloro-2-fluoro-3-hexylcyclopropane (**6**), only <5% of 1,1-dichloro-2-fluoro-2-hexylcyclopropane (**7**), was found by ^{19}F NMR spectroscopy (see Scheme 4). The analogous treatment of (*Z*)-1-fluorononon-1-ene, prepared according to Burton *et al.*[19], did not give any cyclopropane.



4 **5** **6** **7**

SCHEME 4

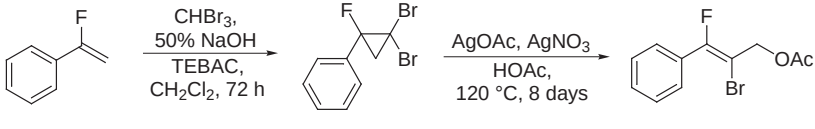
Subsequently, we investigated the Ag^+-induced cyclopropyl-allyl rearrangement by acetolysis and methanolysis, of 1,1-dichloro-2-fluoro-2-phenylpropane (**2a**) analogously to the procedure described by Molchanov and Kostikov[20]. However, even after variation of the used silver salts and very long reaction time, no ring opening occurred. After refluxing **2a** with $AgOAc/AgNO_3$ (1 : 1) in glacial acetic acid for 8 days, or in methanol at 120 °C in a sealed tube for 8 days (Scheme 5), the starting material was recovered almost quantitatively.



2a

SCHEME 5

Thus, we decided to introduce a better leaving group and synthesized the corresponding dibromocyclopropane **8** by treatment of **1a** in freshly distilled bromoform with 50% NaOH in the presence of a catalytic amount of TEBAC. After three days stirring at room temperature and usual work-up, **8** was isolated by bulb-to-bulb distillation with 54% yield. Subsequent heating of **8** with an 1 : 1 mixture of silver acetate and silver nitrate in glacial acetic acid at 150 °C for 8 h, besides unreacted **1a** gave 3-acetoxy-2-bromo-1-fluoro-1-phenylprop-1-ene (**9**) (63%, GC). No other products were detected (see Scheme 6).



1a **8** (54%) **9** (63%, GC)

SCHEME 6

A very slow cyclopropyl-allyl rearrangement was observed by Weyerstahl *et al.*[21] and Molchanov and Kostikov[20] also for reactions of 1-bromo-1-fluorocyclopropanes with silver salts. Disrotatory ring opening, which was found in cyclopropyl-allyl rearrangements of non-fluorinated dihalocyclopropanes[22], leads to an allylic cation, which should be stabilized better in the fluorinated benzylic position. However, the product resulting from an addition of acetate to this position was not found. Obviously, the styrene derivative **9** is thermodynamically more stable and is formed either directly from the allylic cation or by allylic rearrangement of an unstable primary product.

EXPERIMENTAL

General Methods

NMR spectra of *ca* 20% solutions in $CDCl_3$ were recorded on a Bruker WM 300 or Varian Unity 600 Plus spectrometers at 300 or 600 MHz (^{1}H), at 75 or 150 MHz (^{13}C) and at 282 or 564 MHz (^{19}F) and are reported in ppm (δ-scale) downfield from TMS (^{1}H), acetone-d_6 (^{13}C), $CDCl_3$ (^{13}C), or $CFCl_3$ (^{19}F). Coupling constants (*J*) are given in Hz. Mass spectra were recorded by GC/MS coupling (EI, 70 eV) using a Varian GC 3400 (50 m HP-1, i.d. 0.2 mm,

film 0.52 μm, carrier gas N_2) coupled to a mass spectrometer Finnigan MAT 8230. Thin-layer chromatography was done on coated Merck plate 60 F_{254}, column chromatography with Merck silica gel 60 (0.063–0.2 mm). Elemental analyses were performed at the micro-analytical laboratory of the Organic Chemistry Institute at the University of Münster. Styrene and bromoform were distilled prior to using. All other reagents purchased from suppliers were used without further purification.

1,1-Dichloro-2-fluoro-2-phenylcyclopropane (**2a**)

1-Fluoro-1-phenylethene[4g] (**1a**; 2.0 g, 16.4 mmol) and benzyltriethylammonium chloride (TEBAC, 150 mg, 0.66 mmol) were dissolved in chloroform (20 ml). At 0 °C, 50% aqueous NaOH (5 ml, 62.5 mmol) was added dropwise with vigorous stirring. After 30 min at this temperature, the mixture was stirred at room temperature for another 2 h. Subsequently, the reaction mixture was poured into ice-water. The phases were separated and the aqueous was extracted with CH_2Cl_2 (2 × 20 ml). The combined organic phases were washed with HCl (0.1 mol l^{-1}, 20 ml), 5% aqueous $NaHCO_3$ (20 ml) and water. After drying with anhydrous $MgSO_4$ the solvent was removed and the residue was distilled after column filtration over 5 cm alumina (pentane). Compound **2a** was isolated as a colorless oil of sweet odor. Yield 2.50 g (76%); b.p. 65–70 °C/1.5 Torr (200 Pa). IR (film, NaCl): 3 093/3 066/3 037 m (ν(C–H_{arom})); 1 955/1 887/1 813 w; 1 651 s (ν(C=C_{arom})); 1 606 w; 1 498 m (ν(C=C_{arom})); 1 405 s; 1 414 m; 1 346 m; 1 276 m; 1 237 s (ν(C–F)); 1 058 s; 1 041 s; 985 m; 864 m; 781 s (δ(H_{arom}), "out of plane"); 696 s. ^{1}H NMR (600 MHz): 2.19 dd, 1 H, $^3J_{H(cis)F}$ = 20.4, $^2J_{HF}$ = 9.8 (3-CH_a); 2.26 dd, 1 H, $^3J_{H(trans)F}$ = 12.2 , $^2J_{HF}$ = 9.8 (3-CH_b); 7.4–7.5 m, 5 H (H_{arom}). ^{13}C NMR (150 MHz): 30.1 dt, $^2J_{CF}$ = 12.7 (C-3); 60.4 ds, $^2J_{CF}$ = 15.3 (C-1); 81.9 ds, $^1J_{CF}$ = 236.5 (C-2); 127.9 d (C_{arom}); 128.5 d (C_{arom}); 129.7 d (C_{arom}); 132.0 ds, $^2J_{CF}$ = 20.3 (C-4_{arom}). ^{19}F NMR (564 MHz): –162.9 ddd, $^3J_{H(trans)F}$ = 12.2, $^3J_{H(cis)F}$ = 20.4, $^4J_{FH}$ = 1.0. GC/MS (70 eV): 208/206/204 (3/19/28) [M^+]; 203 (3); 171/169 (22/72) [M^+ – Cl]; 167 (6); 149 (6) [169 – HF]; 134/133 (22/100) [171/169 – HCl]; 107 (16); 101 (4); 83 (6); 77 (3) [$C_6H_5^+$]; 74 (8); 67 (12); 51 (12) [$C_4H_3^+$]; 50 (8). For $C_9H_7Cl_2F$ (205.1) calculated: 52.72% C, 3.44% H; found: 52.53% C, 3.42% H.

1,1-Dichloro-2-(4-chlorophenyl)-2-fluorocyclopropane (**2b**)

According to the above procedure, 1-(4-chlorophenyl)-1-fluoroethene[5a] (**1b**; 0.31 g, 2.0 mmol) and TEBAC (23 mg, 0.1 mmol) in chloroform (10 ml) were reacted with 50% aqueous NaOH (0.6 ml, 7.5 mmol) at room temperature for 20 h. Yield 0.41 g (77%). IR (film, NaCl): 3 095/3 011/2 981 m (ν(C–H_{arom})); 1 905/1 715 w; 1 601 m (ν(C=C_{arom})); 1 496 s; 1 412 s; 1 346 m; 1 283 m; 1 238 s (ν(C–F)); 1 090 s; 1 059 s; 1 042 s; 1 016 s; 987 m; 866 m; 830 s; 779 s; 747 m; 652 m. ^{1}H NMR (300 MHz): 2.18 dd, 1 H, $^3J_{H(cis)F}$ = 15.5, $^2J_{HH}$ = 10.0 (3-CH_a); 2.23 dd, 1 H, $^3J_{H(trans)F}$ = 10.5, $^2J_{HH}$ = 10.0 (3-CH_b); 7.4–7.5 m, 5 H (H_{arom}). ^{13}C NMR (75 MHz): 30.2 dt, $^2J_{CF}$ = 10.2 (C-3); 60.1 ds, $^2J_{CF}$ = 15.3 (C-1); 81.3 ds, $^1J_{CF}$ = 236.5 (C-2); 128.8 d (C_{arom}); 129.3 d (C_{arom}); 130.2 s (C_{arom}); 130.4 ds, $^2J_{CF}$ = 20.3 (C-4_{arom}). ^{19}F NMR (282 MHz): –155.8 dd, $^3J_{H(trans)F}$ = 10.5, $^3J_{H(cis)F}$ = 15.5. GC/MS (70 eV): 244/242/240/238 (0/0.5/3/3) [M^+]; 207/205/203 (100/60/9) [M^+ – Cl]; 187/185/183 (8/8/1) [207/205/203 – HF]; 169/167 (94/32) [207/205/203 – HCl]; 133 (40) [169/167 – HCl]; 132 (10); 101 (9); 91 (4); 84 (6); 75 (6); 66 (4); 51 (4) [$C_4H_3^+$].

1,1-Dichloro-2-fluoro-2-hexylcyclopropane (**6**)

According to the above procedure, 2-fluorooct-1-ene[4b] (**4**) in a mixture with 15% of (*E*)- and 3% of (*Z*)-1-fluorooct-1-ene (**5**) (0.4 g, 3 mmol) and TEBAC (23 mg, 0.1 mmol) in chloroform (10 ml) were reacted with 50% aqueous NaOH (1.0 ml, 12.5 mmol) at room temperature for 20 h. Yield 0.48 g (85%) of a mixture (95 : 5, ^{19}F NMR) of **6** and **7**. ^{1}H NMR (300 MHz): 0.9 t, 3 H, $^{3}J_{HH}$ = 6.7 (9-CH_3); 1.2–1.45 m, 10 H (4-CH_2, 5-CH_2, 6-CH_2, 7-CH_2, 8-CH_2); 1.78–2.06 m, 2 H (3-CH_2). ^{13}C NMR (75 MHz): 14.0 q (C-9); 22.5 t (C-8); 24.5 t (C-6); 28.8 t (C-5); 31.6 t (C-7); 31.2 dt, $^{2}J_{CF}$ = 15.3 (C-4); 32.0 ds, $^{2}J_{CF}$ = 20.3 (C-3); 60.9 ds, $^{2}J_{CF}$ = 134.8 (C-1); 81.5 ds, $^{1}J_{CF}$ = 239.1 (C-2). ^{19}F NMR (282 MHz): –177.1 m. GC/MS (70 eV): 216/214/212 (0/0.4/0) [M^+]; 195 (0.2); 194 (0.1) [M^+ – HF]; 179/177 (0.2/0.1) [M^+ – Cl]; 169 (0.2); 166 (1.2); 116 (9); 102 (12); 96 (7); 83 (16); 81 (18); 70 (62); 69 (50); 56 (100); 55 (56); 53 (14); 43 (58) [$C_3H_7^+$]; 41 (70) [$C_3H_5^+$]; 39 (37).

The regioisomer **7** was detected by its ^{19}F NMR shift of –200.7 dd, $^{2}J_{HF}$ = 64.9, $^{3}J_{HF}$ = 21.0.

1,1-Dibromo-2-fluoro-2-phenylcyclopropane (**8**)

At 0 °C, a vigorously stirred mixture of compound **1a**[4g] (2.44 g, 20 mmol), ethanol (0.5 ml), TEBAC (150 mg, 0.66 mmol) and bromoform (3.6 ml, 40 mmol) in dichloromethane (20 ml) was treated dropwise with 50% aqueous NaOH (10 ml, 125 mmol). After 1 h the mixture was allowed to warm up to room temperature and stirring was continued for 72 h. The mixture was poured into ice water, the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 20 ml). The combined organic layers were washed with HCl (0.1 mol l^{-1}, 20 ml), with 5% aqueous $NaHCO_3$ (2 × 10 ml) and with water (1 × 10 ml). After drying with magnesium sulfate the solvent was evaporated and the product was isolated by bulb-to-bulb distillation. Yield 2.9 g (49%); b.p. 90–95 °C/0.3 Torr (40 Pa, oven tempera-

TABLE III
Relative contents (±0.5%, GC) of styrene and 1-fluoro-1-phenylethene (**1a**) in the reaction with dichlorocarbene

Time, min	Portions, GC (±0.5%)	
	α-fluorostyrene	styrene
0	48.6	51.4
10	33.5	39.0
30	10.5	23.3
60	7.6	19.8
90	5.6	16.7
120	4.8	15.5

ture). IR (film, NaCl): 3 085/3 064/3 034/2 926 m (ν(C–H_{arom})); 1 952/1 890/1 800 w; 1 713 w; 1 651 s (ν(C=C_{arom})); 1 604 w; 1 497 w; 1 450 s; 1 424 w; 1 409 w; 1 342 w; 1 277 w; 1 230 m (ν(C–F)); 1 176 w; 1 108 w; 1 052 s; 1 024 s; 972 m; 860 m; 766 s (δ(H_{arom}), "out of plane"); 720 m; 695 s; 670 s (ν(C–Br)). ^{1}H NMR (600 MHz): 2.36 dd, 1 H, $^3J_{H(cis)F}$ = 18.9, $^2J_{HH}$ = 10.1 (3-CH_a); 2.47 dd, 1 H, $^3J_{H(trans)F}$ = 11.1, $^2J_{HH}$ = 10.1 (3-CH_b); 7.4–7.5 m, 5 H (H_{arom}). ^{13}C NMR (150 MHz): 28.9 ds, $^2J_{CF}$ = 15.3 (C-1); 32.0 dt, $^2J_{CF}$ = 10.7 (C-3); 81.1 ds, $^1J_{CF}$ = 234.0 (C-2); 128.0 d (C_{arom}); 128.4 d (C_{arom}); 129.8 d (C_{arom}); 133.1 ds, $^2J_{CF}$ = 22.9 (C-4$_{arom}$). ^{19}F NMR (564 MHz): –155.85 dd, $^3J_{H(trans)F}$ = 11.1, $^3J_{H(cis)F}$ = 18.9. GC/MS (70 eV): 296/294/292 (0.5/1.2/0.4) [M^+]; 217/215 (50/50) [M^+ – Br]; 193/195 (2/2) [215/213 – HF]; 134/133 (54/100) [215/213 – HBr]; 113 (3) [133 – HF]; 109 (7); 107 (14); 106 (4); 81 (5); 77 (3) [$C_6H_5^+$]; 66 (33); 57 (14); 51 (8) [$C_4H_3^+$]. For $C_9H_7Br_2F$ (294.0) calculated: 36.77% C, 2.40% H; found: 37.05% C, 2.61% H.

Competitive Addition of Dichlorocarbene to Styrene and 1-Fluoro-1-phenylethene (**1a**)

Equimolar amounts of freshly distilled styrene (104 mg, 1 mmol) and **1a** (122 mg, 1 mmol) were dissolved in chloroform (10 ml), TEBAC (18 mg, 0.07 mmol) was added. The solution was cooled 0 °C and maintained at this temperature during the reaction. 50% aqueous NaOH (0.6 ml, 15 mmol) was added in one portion while the mixture was stirred vigorously. Samples were taken after the times shown in Table III and analyzed by GLC after work-up as described above.

Silver(I)-Induced Cyclopropyl-Allyl Rearrangement of 1,1-Dibromo-2-fluoro-2-phenylcyclopropane (**8**)

In a sealed vessel, 1,1-dibromo-2-fluoro-2-phenylcyclopropane (**8**; 197 mg, 0.5 mmol) in glacial acetic acid (5 ml) was heated to 150 °C with a mixture of silver acetate (166 mg, 1 mmol) and silver nitrate (169 mg, 1 mmol) for 8 h. After cooling to room temperature, the mixture was poured into ice-water, neutralized with dilute NaOH, and extracted with diethyl ether (3 × 10 ml). The combined organic layers were washed with HCl (0.1 mol l^{-1}, 10 ml), with 5% aqueous $NaHCO_3$ (2 × 10 ml) and with water. After drying with anhydrous magnesium sulfate, the solvent was removed, the residue was filtered through a short column containing alumina (eluting with pentane) and analyzed by GC. Besides 37% of starting material, 63% of the desired product **9** was found.

3-Acetoxy-2-bromo-1-fluoro-1-phenylprop-1-ene (**9**). ^{1}H NMR (300 MHz): 2.08 s, 3 H (5-CH_3); 4.82 d, 2 H, $^4J_{HF}$ = 1.7 (3-CH_2); 7.3–7.5 m, 5 H (H_{arom}). ^{13}C NMR (75 MHz): 20.8 q (C-5); 65.2 t (C-3); 100.8 ds (C-2); 124.2 d (C_{arom}); 127.4 d (C_{arom}); 127.7 d (C_{arom}); 132.1 ds (C-3$_{arom}$); 156.8 ds, $^1J_{CF}$ = 226.4 (C-1); 175.8 s (C-4). ^{19}F NMR (282 MHz): –77.8 s. GC/MS (70 eV): 275/273 (0.2/0.1) [M^+ + H]; 274/272 (0.5/0.3) [M^+]; 231/229 (1.1/1.2) [M^+ – C_2H_3O]; 215/213 (2/3) [M^+ – $C_2H_3O_2$]; 194 (8); 193 (45) [M^+ – Br / 215/213 – HF]; 152 (10); 151 (100) [193 – C_2H_2O]; 134 (15) [193 – $C_2H_3O_2$]; 133 (42) [193 – $C_2H_4O_2$]; 120 (3); 103 (10); 101 (3); 89 (2); 86 (4); 77 (3) [$C_6H_5^+$]; 63 (2); 57 (3); 51 (3) [$C_4H_3^+$]; 50 (2); 43 (20) [$C_2H_3O^+$].

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