DEHYDROHALOGENATIONS OF cis- AND trans-1-BROMO-2-FLUOROCYCLOHEXANES

M. HUDLICKY

Department of Chemistry, Virginia Polytechnic Institute and State
University, Blacksburg, Virginia   24061 (U.S.A.)

SUMMARY

    Reactions of both diastereomeric vicinal bromofluorocyclohexanes with
sodamide, sodium methoxide, potassium tert-butoxide, and triethylamine were
studied.   cis-1-Bromo-2-fluorocyclohexane eliminated almost exclusively
hydrogen bromide giving mainly 1-fluorocyclohexene and a small amount of 3-
fluorocyclohexene.   trans-1-Bromo-2-fluorocyclohexane eliminated prefer-
entially hydrogen fluoride on treatment with sodamide.   Potassium tert-
butoxide eliminated hydrogen bromide and yielded 3-fluorocyclohexene and a
small amount of 1,3-cyclohexadiene, whereas sodium methoxide converted
trans-1-bromo-2-fluorocyclohexane to 3-fluorocyclohexene and 3-methoxy-
cyclohexene.   Possible mechanisms and stereochemistry of the preferential
elimination of hydrogen fluoride are discussed and new interpretations are
offered.

INTRODUCTION

    In 1979, Lee and Bartsch [1] reported that a mixture of sodamide and
sodium tert-butoxide in tetrahydrofuran ('complex base') caused prefer-
ential elimination of hydrogen fluoride from trans-1-chloro-2-fluorocyclo-
hexane and trans-1-bromo-2-fluorocyclohexane, giving 85% yields of 1-
chlorocyclohexene and of 1-bromocyclohexene, respectively.   No 1-fluoro-
cyclohexene was detected.   This preferential elimination of fluoride ion,
'poorer halogen leaving group', was found only with trans-1,2-dihalocyclo-
alkanes and was linked to the so called 'complex base' [2].

    Prior to this observation, elimination of hydrogen fluoride in
preference to hydrogen chloride was noticed in the reaction of 1H,2-chloro-

decafluorocyclohexanes and of 1H,1,2-dichlorononafluorocyclohexanes with aqueous potassium hydroxide. Those diastereomers that contained hydrogen and fluorine in trans-positions eliminated preferentially hydrogen fluoride, and only to a lesser extent also hydrogen chloride. The other diastereomers with hydrogen trans to chlorine eliminated only hydrogen chloride [3].

Elimination of hydrogen fluoride in preference to hydrogen bromide was observed in a reaction of dimethyl and diethyl α-bromo-α'-fluorosuccinates with potassium phthalimide [4] and during the treatment of dimethyl and diethyl α-bromo-α'-fluorosuccinates with sodium azide [5] and with potassium acetate [5]. Later, the preferential elimination of "poorer halogen" was studied in diastereomeric 1,2-dihaloacenaphthenes [6] and in erythro- and threo-α-bromo-α'-fluorosuccinic acids [7].

The examples quoted [3,6,7] partly contradict the claim that only 'complex bases' caused preferential elimination of 'poorer halogen leaving groups' exclusively by a syn-elimination process [1,2]. In order to find out more about the mechanism of this rather rare reaction, a more thorough study was carried out with cis- and trans-1-bromo-2-fluorocyclohexanes.
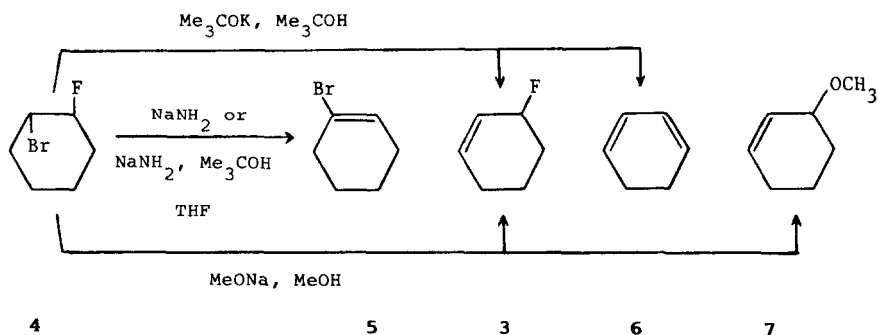

RESULTS

cis-1-Bromo-2-fluorocyclohexane 1 eliminated rather easily (3 h at 50°) almost exclusively hydrogen bromide by a conventional trans-elimination, probably by E2 mechanism. This finding is in agreement with the literature [1,8]. The reaction took place with sodium methoxide or potassium tert-butoxide, and the reaction product was predominantly (90-92%) 1-fluorocyclohexene 2 plus a small amount (8-10%) of 3-fluorocyclohexene 3. In the reaction of 1 with three mols of sodamide in tetrahydrofuran, only 2 but no 3 was identified by ^{19}F NMR in the reaction mixture after 25 hours at room temperature.

1   2   3
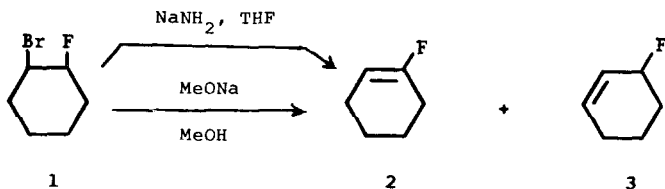
On the other hand, the products of dehalogenation of trans-1-bromo-2-fluorocyclohexane **4** depended on the base used, on its excess, and on the temperature and the time of the reaction. The so called "complex base", sodamide and sodium tert-butoxide in tetrahydrofuran, eliminated hydrogen fluoride and yielded 1-bromocyclohexene **5**. Only traces of 3-fluorocyclohexene and no 1-fluorocyclohexene were detected. The same results were obtained with sodamide alone in tetrahydrofuran at room temperature.

Potassium tert-butoxide reacted with trans-1-bromo-2-fluorocyclohexane much more slowly. Refluxing was necessary to bring about the reaction

Me$_3$COK, Me$_3$COH

NaNH$_2$ or

NaNH$_2$, Me$_3$COH

THF

MeONa, MeOH

4   **5**   **3**   **6**   **7**

which resulted in the elimination of hydrogen bromide to give 3-fluorocyclohexene **3**. This derivative, described by Olah et al. [9] as an easily decomposing compound, is indeed very unstable and decomposed within hours even in non-polar solvents at room temperature, reacting strongly with glass and forming dark blue-green decomposition products containing 1,3-cyclohexadiene **6**.

3-Fluorocyclohexene was also obtained when trans-1-bromo-2-fluorocyclohexane **4** was refluxed with sodium methoxide. Again the reaction was slow, leaving considerable amounts of the starting material unreacted. The product of the elimination of hydrogen bromide, 3-fluorocyclohexene **3**, was on prolonged refluxing and especially at higher temperatures (120° in a sealed tube) converted to 3-methoxycyclohexene **7**.

This compound could have arisen either from nucleophilic displacement of bromine followed by elimination of hydrogen fluoride, or else by primary preferential dehydrobromination to 3-fluorocyclohexene which then reacted with sodium methoxide. Since 3-fluorocyclohexene was also found in the reaction of trans-1-bromo-2-fluorocyclohexane with potassium tert-butoxide, the second interpretation is more plausible.

In most experiments carried out with sodamide, potassium tert-butoxide, sodium methoxide, and even triethylamine, both halogens were always eliminated, as ascertained by titrations of bromide and fluoride ions in the reaction mixtures. The ratios of bromide to fluoride varied over a range of 0.62-12.8:1. Selected examples of the titrations are presented in Table 1.

TABLE 1

Titrimetric Determination of Bromide and Fluoride Ions After

Dehydrohalogenation of trans-1-Bromo-2-fluorocyclohexane

Base	Equiv.	Temp. °C	Time, h	%* Br⁻ + F⁻	% Br	% F	Ratio Br:F
Et$_3$N	3.0	130	65	20.6	9.9	10.7	0.92:1
MeONa	1.5	Reflux	9	73.1	59.8	13.3	4.5:1
Me$_3$COK	3.0	Reflux	3	103.6	88.2	15.4	5.7:1
NaNH$_2$	3.1	R.T.	12.75	133.2	51.2	82.0	0.62:1

* Maximum total halogen is 200%, since there are two halogens per one mol
  of the bromofluoro compound.

Identification of products was carried out by means of gas-liquid chromatography and ^{1}H and ^{19}F NMR. The product of dehydrobromination of cis-1-bromo-2-fluorocyclohexane, 1-fluorocyclohexene 2, could be chromato-graphically separated from the unreacted starting material. The minor product, 3-fluorocyclohexene 3, could only be identified by NMR. In the reaction of trans-1-bromo-2-fluorocyclohexene with sodamide, 1-bromocyclo-hexene 5 was isolated by gas-liquid chromatography. The main product of dehydrobromination of trans-1-bromo-2-fluorocyclohexane, 3-fluorocyclo-hexene 3, could not be isolated because of its instability. It was identified by NMR. Also the by-products resulting from the elimination or displacement of fluorine in 3, i.e., 1,3-cyclohexadiene 6 and 3-methoxy-cyclohexene 7, respectively, were detected in the reaction mixtures by means of NMR.

DISCUSSION

In agreement with the literature [1], cis-1,2-dihalocyclohexanes suffer elimination of the more reactive halogen, in the present case bromine, regardless of the base used. In contrast to the literature statements [1], preferential elimination of hydrogen fluoride from trans-1-bromo-2-fluorocyclohexane **4** to form 1-bromocyclohexene **5** does not occur only by the action of 'complex base,' sodamide and sodium tert-butoxide, but by sodamide alone. On the other hand, potassium tert-butoxide or sodium methoxide alone do not eliminate hydrogen fluoride but hydrogen bromide to give 3-fluorocyclohexene **3**.

The formation of predominantly 1-fluorocyclohexene **2** from cis-1-bromo-2-fluorocyclohexane **1**, and of exclusively 3-fluorocyclohexene **3** from trans-1-bromo-2-fluorocyclohexane **4** with alkoxides is not difficult to understand: In **1** there are three hydrogens β to bromine, two of which are trans and consequently in a favorable (antiperiplanar) position required for the elimination. The predominance of 1-fluorocyclohexene **2** over 3-fluorocyclohexene **3** is in agreement with Zaitsev's rule and may be caused by higher acidity of hydrogen on the carbon holding fluorine. In trans-1-bromo-2-fluorocyclohexane **4**, there are also three β-hydrogens, but only one of them is in the trans-configuration to bromine. Therefore, hydrogen bromide is eliminated against the Zaitsev rule to form 3-fluorocyclohexene **3** as the sole fluorinated product. The results of alkoxide-promoted elimination of hydrogen bromide from cis- and trans-1-bromo-2-fluorocyclohexanes thus parallel the classical examples of elimination of hydrogen chloride from menthyl- and neomenthyl chlorides [10].

What remained puzzling was that only sodamide, and not alkaline alkoxides, caused preferential elimination of hydrogen fluoride from trans-1-bromo-2-fluorocyclohexane, and that the elimination of hydrogen fluoride occurred by a syn-process. The explanation offered by Lee and Bartsch [1], that the driving force for the preferential elimination of hydrogen fluoride by a syn-mode is favored by complexation of fluorine in preference to bromine in the transition state with 'complex bases' in such a way that sodium forms a tighter ionic bond with fluorine than with bromine, does not seem satisfactory. In other cases of preferential elimination of hydrogen fluoride from vicinal bromofluorides, neither the strength and nature of the base nor the mutual position of the two halogens mattered [5-7].

The finding that not only the 'complex base' $NaNH_2$-tert-BuONa but also sodamide alone (but neither potassium tert-butoxide nor sodium methoxide)

cause exclusive elimination of hydrogen fluoride in preference to hydrogen bromide from trans-1-bromo-2-fluororcyclohexane **4** can be explained by the formation of hydrogen bonds in the transition state. These can occur only between bromofluorocyclohexanes and the amide ion which possesses hydrogens capable of forming hydrogen bonds. Such a possibility does not exist for methoxide nor for tert-butoxide anions.

This explains the propensity for the preferential elimination of hydrogen fluoride from the trans isomer **4** where both conformations, aa (**8**) and ee (**9**) allow for six-membered transition states with the amide ion.

Br

H

H

N

H

8 F

H

H

Br

F

H

9 H N H

F

Br

H

10 N H

H

Br

H

N

H

H F H

11 H
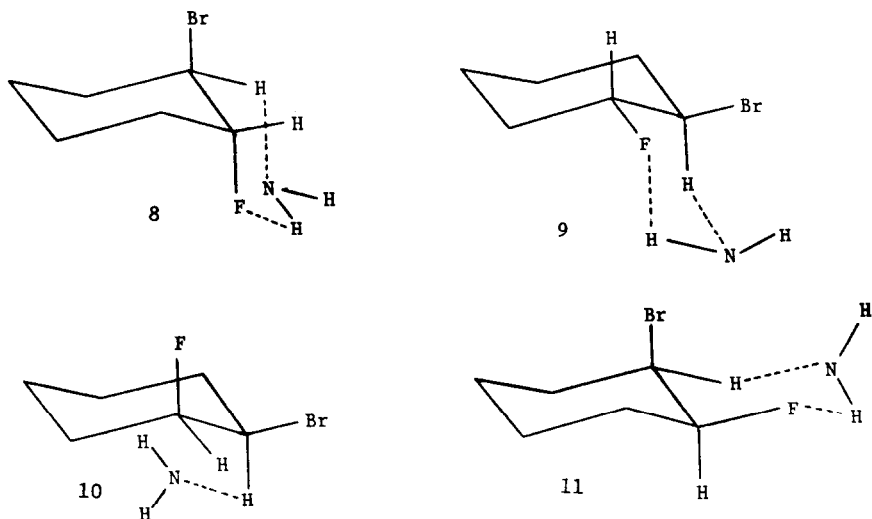
H---F Bond impossible

Since the hydrogen on carbon 1 (holding bromine) is the most acidic of all the hydrogens present in the molecule [7], it is this hydrogen which is capable of forming a hydrogen bond with nitrogen of the amide ion and is therefore eliminated in preference to hydrogens on carbon 3 in trans-1-bromo-2-fluorocyclohexane **4**. That is why 1-bromocyclohexene was isolated as the only reaction product, the isomeric 3-bromocyclohexene not being detected by NMR even in traces. Because of the 'acidity' of the hydrogen on carbon 1, the mechanism of dehydrofluorination may be E_1cB (or that proceeding via Bunnett's 'variable transition state'). Such transition states do not require anti alignment of the elements to be eliminated, and the elimination takes place in a syn mode.

In cis-1-bromo-2-fluorocyclohexane 1, a hydrogen-bonded transition state is sterically impossible in ea conformation (10) but is feasible in ae conformation (11). However, the ae conformation is the only one in which bromine and a hydrogen in a β-position occupy an anti-periplanar conformation indispensable for E2 elimination of hydrogen bromide. Hydrogen bonds in this conformation are stabilizing the transition state with β-hydrogen in anti-periplanar position to bromine. Thus, this conformation provides ideal conditions for the elimination of hydrogen bromide by the classical E2 mechanism. Consequently dehydrobromination takes precedence over dehydrofluorination and gives 1-fluorocyclohexane 2. It is not surprising that also the other β-hydrogen may be eliminated as well giving 3-fluorocyclohexene 3.

It is of interest to compare the results of the dehydrohalogenation of 1-bromo-2-fluorocyclohexanes with dehydrohalogenations of diastereomeric 1-hydro-2-chlorodecafluorocyclohexanes and 1-hydro-1,2-dichlorononafluoro-cyclohexanes reported by Tatlow and coworkers [3]. In these compounds, elimination of hydrogen fluoride in preference to hydrogen chloride occurs predominantly, but not exclusively, only in diastereomers with hydrogens in trans-position to fluorines. The ratios of the elimination of hydrogen fluoride to hydrogen chloride in the two above examples were 6.2:1 and 4.2:1, respectively. The diastereomers with hydrogens trans to chlorines lose only hydrogen chloride. Both the elimination of hydrogen fluoride and that of hydrogen chloride by the anti-mode from the antiperiplanar position suggest the possibility of the E2 process. A good explanation of the syn-elimination of hydrogen chloride occurring to a lesser extent from the diastereomers having hydrogen and chlorine in cis-positions is offered by the authors who consider E1cB carbanion mechanism as a possibility [3]. This mechanism is very likely because of the strong acidity of hydrogen caused by the presence of three fluorine atoms on the two adjacent carbons [7]. A strong support for the participating carbanion mechanism is the isotope exchange accomplished by treatment of the compounds with potassium hydroxide in deuterium oxide [3]. It is not surprising that the carbanion once formed loses chlorine as a better leaving group.

EXPERIMENTAL SECTION

General Methods. Titrations were carried out by standardized solutions of sulfuric acid, mercuric nitrate, and thorium nitrate. Determination of bromide was carried out mercurimetrically according to

Votocek [11] using sodium nitroprusside as the indicator. Titration of fluoride was based on Winter-Willard's thorimetric method using a modified indicator [12] (equal parts of 0.05% aqueous solution of sodium alizarin-sulfonate and 0.01% aqueous solution of indigo carmine) which changes a green to a pink-purple color. Gas-liquid chromatography was carried out on a Gow-Mac thermal detector chromatograph model 150 using Carbowax 20M as the stationary phase and helium as a carrier gas. ^{1}H NMR spectra were taken on a Bruker WP270SY supercon spectrometer with TMS as the internal standard. ^{19}F NMR spectra were measured on a Varian EM 390 at 84.6 MHz with fluorotrichloromethane (Fll) and HFB as internal standards. The fluorine chemical shifts are negative upfield (east) from Fll.

Materials. All the chemicals were reagent grade, dried and distilled as appropriate. Dimethylaminosulfur trifluoride (DAST) was a commercial product of Aldrich Chemical Co. and was used without prior distillation.

cis-1-Bromo-2-fluorocyclohexane (1). The title compound was prepared according to the literature [13] from cyclohexene oxide via trans-2-fluorocyclohexanol (43.9%) which was converted to 1 in 37.6% yield. The product was 98% pure according to gas-liquid chromatography, bp 87-89 °C (27 mm), 84-86 °C (23 mm) (lit. bp 68-69 °C (14 mm) [13], 77.0-78.0 °C (22 mm)) [14]. ^{1}H NMR ∂ 1.65 (m, 2 H), 1.73 (m, 2 H), 2.00 (m, 2 H), 2.10 (m, 2 H), 4.25 (dm, 1 H, CHBr, J = 19.5 Hz), 4.64 (dq, 1 H, CHF, J = 48 Hz) (lit. [14] 1.0-2.6 (m, 8 H), 3.8-5.1 (m, 2 H). ^{19}F NMR -185 (m).

trans-1-Bromo-2-fluorocyclohexane (4). **(a) From cyclohexene.** Since the procedure used here was more suitable and gave higher yields than that reported in the literature [15], it is described in detail. In a 250 mL polyethylene bottle fitted with a plastic-coated magnetic stirring bar, 59 g (2.95 mol) of anhydrous hydrogen fluoride was cooled in a dry ice-acetone bath. Anhydrous ether (100 mL) precooled in a dry ice bath was added over a 5 min period. Then 28.3 g (0.345 mol) of cyclohexene and 46.5 g (0.337 mol) of N-bromoacetamide were added portionwise alternately over a period of 25 min. The reaction vessel was kept in the dry ice bath for 1.5 h and allowed to warm to room temperature overnight. The dark gray-violet solution was poured over 85 g of ice, 25 mL of ether was added, and the mixture was neutralized by portionwise addition of 157 g (1.48 mol, 2.96 equiv.) of sodium carbonate. Efficient stirring was necessary to prevent overflowing of the foaming solution. The temperature was maintained between 13-27 °C by adding ice in 20 g batches (80 g altogether). The two-layer liquid was decanted, the solids were filtered with suction and washed with 70 mL of ether. The organic layer and the ether extract were

combined; the aqueous phase was extracted with two 20 mL portions of dichloromethane; the combined organic solutions were washed with two 5 mL portions of water, dried with magnesium sulfate and evaporated at 20-21 °C (47 mm). The residue (62.75 g) was fractionated to give 53.05 g (86.95%) of chromatographically pure **4**, distilling at 74.5-76.5 °C (19 mm) (lit. 76-78 °C (16 mm) [16], 67-70 °C (14 mm)) [17]. ^{1}H NMR ∂ 1.40 (m, 2 H), 1.56 (m, 2 H), 1.78 (m, 2 H), 2.25 (m, 2 H), 4.01 (m, 1 H, CHBr), 4.50 (dm, 1 H, CHF, J = 47 Hz) (lit. [17] ^{1}H NMR ∂ 1.0-2.6 (br m, 8 H), 4.03 (m, 1 H, CHBr), 4.53 (m, 1 H, CHF, J = 49.5 Hz)). ^{19}F NMR -168.6 (lit. -167.98 [18], -165.3 [19]).

(b) From _trans_-2-Bromocyclohexanol. A solution of 3.56 g (0.02 mol) of _trans_-2-bromocyclohexanol in 3 mL of dichloromethane was added over a period of 10 min to a solution of 3.56 g (0.022 mol, 10% excess) of diethylaminosulfur trifluoride (DAST) in 10 mL of dichloromethane and the mixture was stirred magnetically under argon in a dry ice bath at -78 °C. After 1.5 h at -78 °C, the mixture was allowed to warm to room temperature and was decomposed with 10 mL of water. The organic layer was separated, washed with 4 mL of water, and neutralized to pH 7 with a 5% solution of sodium bicarbonate. The aqueous layers were extracted with 1 mL of dichloromethane and the original organic layer was combined with the extract, washed with 2 mL of water, and dried with absorbent cotton. Distillation afforded 2.41 g (66.6%) of chromatographically pure **4**, bp 75-78 °C (25 mm), identical with that prepared from cyclohexene. The replacement of the hydroxyl by fluorine occurred with complete retention of configuration.

1-Fluorocyclohexene (2). **a) From Cyclohexanone.** Compound 2 was prepared from 4.9 g (0.05 mol) of cyclohexanone and 13.0 g (0.08 mol) of DAST in 54 mL of triglyme and 1 mL of 30% oleum according to the literature [20] in a 38% yield, bp 92-94 °C (lit. [13] bp 96 °C). ^{1}H NMR ∂ 1.54 (m, 2 H), 1.73 (m, 2 H), 2.01 (m, 2 H), 2.13 (m, 2 H), 5.14 (dt, 1 H, =CH, J = 18.4 Hz) (lit. [14] 1.66 (m, 4 H), 2.11 (m, 4 H), 5.07 (br d, 1 H, J = 16.8 Hz)). ^{19}F NMR -100.5 (br s) (lit. [21] -101.1).

b) From _cis_-1-Bromo-2-fluorocyclohexane. A solution of 1.84 g (0.01 mol) of **1** in 7.5 ml (0.015 mol) of 2 N sodium methoxide in methanol was heated at 50°C for 3 h. The reaction mixture containing crystals of sodium bromide was diluted with 10 ml of water, neutralized to pH 3 with 1.5 ml of concentrated hydrochloric acid, and the heavier layer was separated and dried with absorbent cotton. According to ^{19}F NMR the product (0.7 g)

contained 45% (0.0021 mol) of the recovered 1 and 55% (0.0032 mol) of 2. Preparative chromatography over Carbowax 20 M afforded 0.12 g (12%) of pure 1.

3-Fluorocyclohexene (3). To 2.6 mL (3.2 g, 0.02 mol) of diethylamino-sulfur trifluoride (DAST) in a 25 mL flask fitted with a magnetic stirring bar and a pressure equalizing separatory funnel and placed in a cooling bath of dry ice and acetone was added, under argon, 1.92 g (0.02 mol) of 2-cyclohexen-1-ol over a period of 15 min. The bath was kept at -30 to -50 °C to maintain the mixture fluid. After storing at -78 °C for 2.5 h, the mixture was allowed to warm to room temperature over a period of 40 min, then cooled to 0 °C and poured onto ice and a solution of sodium bicarbonate. At pH 7, the upper yellow layer was separated and dried with absorbent cotton to give 1.17 g (60%) of crude 3. The compound decomposed quickly at room temperature in agreement with the literature [9]. ^{1}H NMR ∂ 1.50-2.20 (m, 2 H), 4.90 (dm, 1 H, CHF, J = 49.5 Hz), 5.78 (m, 1 H, =CH), 5.96 (m, 1 H, =CH). ^{19}F NMR -166.8 (br d, J = 49.5 Hz).

1-Bromocyclohexene (5). Compound 5 was prepared according to the literature [22] from 1.81 g (0.01 mol) of 4, 1.20 g (0.03 mol) of sodamide, and 1.11 g (0.015 mol) of _tert_-butyl alcohol in 10 mL of tetrahydrofuran in 47% yield, bp 140-145 °C (lit. [23] 164-6 °C, 69 °C (35 mm); 48 °C (13 mm)) [24]. ^{1}H NMR ∂ 1.68 (m, 4 H), 2.06 (m, 2 H), 2.38 (m, 2 H), 6.00 (m, 1 H) (lit. [24] 1.2-2.5 (m, 8 H), 5.94 (1 H, =CH)).

3-Methoxycyclohexene (7). To a solution of 1.47 g (0.015 mol) of 2-cyclohexen-1-ol in 5 mL of THF was added portionwise 0.98 g (0.02 mol) of 50% sodium hydride in paraffin oil followed by 2.29 g (0.016 mol) of methyl iodide, and the reaction mixture was stirred under argon at room temperature for 24 h. Regular work-up gave 1.58 g (94%) of 7, bp 126-7 °C (lit. [25] 45-50 °C (30 mm)). The distillate was purified by preparative gas-liquid chromatography to remove small amounts of THF. ^{1}H NMR ∂ 1.47-1.88 (m, 4 H), 2.00 (m, 2 H), 3.34 (s, 3 H, OCH$_3$), 3.75 (m, 1 H, CHO), 5.72-5.88 (m, 2 H, =CH) (lit. [24] 3.41 (s, 3 H), 3.83 (m, 1 H, CHO), 5.93 (m, 2 H, =CH)).

Elimination Experiments with _trans_ 1-Bromo-2-fluorocyclohexane.

(a) Eliminations Using Sodamide. To a stirred mixture of 0.60 g (0.015 mol, 3 equiv.) of sodamide in 5.0 mL of anhydrous THF was added 0.90 g (0.005 mol) of 4 over a period of 4 min. The grey mixture was stirred at room temperature for 12 h, then poured onto ice. The lighter layer was separated, and the aqueous layer was diluted with 5 mL of water and then extracted with two 1 mL portions of dichloromethane. The organic solutions

were washed with 1 mL of water, dried with absorbent cotton, and evaporated
in vacuo at 60-75 °C. The residue (0.49 g) still containing THF was
purified by preparative gas-liquid chromatography over Carbowax 20 M to
give pure 5. No fluorine-containing material was present in the crude
product.

   (b) Eliminations Using 'Complex Bases'. These were carried out as
described in the preparation of 5 [22].

   (c) Eliminations Using Potassium tert-Butoxide. In a side-arm flask
fitted with a magnetic stirring bar, a septum, and a reflux condenser, 1.68
g (0.015 mol) of freshly sublimed potassium tert-butoxide was dissolved in
9 mL of dry tert-butyl alcohol under reflux. Through the septum, 1.81 g
(0.01 mol) of 4 was added over a period of 6 min. Refluxing was continued
while 1 mL samples were withdrawn to follow the reaction progress by gas-
liquid chromatography and ^{1}H and ^{19}F NMR. After 1 h 15 min, the reaction
did not contain any starting material and was composed of 89% of 3-fluoro-
cyclohexene 3 and 11% of 1,3-cyclohexadiene 6 (δ $-CH_2-$ 2.14, $-CH-$ 5.81).
Authentic 3 showed exactly the same chemical shifts.

   (d) Eliminations Using Sodium Methoxide. A solution of 0.90 g (0.005
mol) of 4 in 3.8 mL (0.0075 mol) of 2 N sodium methoxide in methanol
(prepared by dissolving sodium in methanol) was refluxed under argon while
samples were withdrawn for analysis by gas-liquid chromatography, ^{1}H and
^{19}F NMR, and by titration of the aqueous phases for bromide and fluoride
(after neutralization with dilute sulfuric acid and evaporation in vacuo).
In the above experiment, after 9 h, the reaction mixture contained 32.5% of
unreacted 4, 62.5% of 3-fluorocyclohexene 3, and 5% of 3-methoxycyclo-
hexane 7. Any attempts to isolate 3-fluorocyclohexene 3 failed because the
compound decomposed to highly colored intermediates and polymers.

   Elimination Experiments with cis-1-Bromo-2-fluorocyclohexane (1).
a) Elimination using sodamide was carried out in the way discribed for the
trans-isomer using the same amounts of 1, sodamide and THF. After 22 hours
at room temperature, the work-up gave a mixture of 40% of unreacted 1 and
60% of 2, ^{19}F NMR -100.7 ppm.

   b) Elimination using sodium methoxide was carried out as described in
the paragraph b on the preparation of 1-fluorocyclohexene.

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