SYNTHESIS OF α-FLUORO-β-LACTONES AND THEIR THERMAL CONVERSION TO 1-FLUOROALKENES

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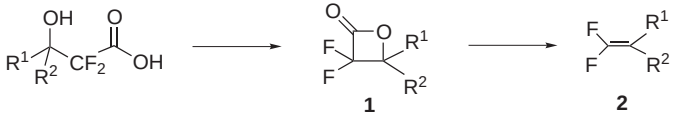
Dedicated to the memory of Professor Miloš Hudlický, a pioneering chronicler of organofluorine chemistry.

α-Fluoro-β-lactones have been synthesized and isolated for the first time from α-fluoro-β-hydroxy acids by using the couple TsCl/DMAP as lactonization agent. A detailed description of the synthesis and spectroscopic properties of α-fluoro-β-lactones is presented. Preliminary results indicate that thermolysis of these new β-lactones produces 1-fluoroalkenes.
Keywords: β-Lactones; Fluorine; Fluoroalkenes; Decarboxylation; Thermolysis; Hydroxy acids; Alkenes.

β-Lactones have been the subject of study for more than a century, not only because of the challenge of their synthesis, but also because they undergo thermal decarboxylation to form alkenes[1]. For the last few years our efforts in this area have focused on the synthesis and study of the chemical behavior of fluorinated β-lactones, compounds that had been only briefly mentioned in the literature before our investigations[2]. The preparation of a number of α,α-difluoro-β-lactones **1** was reported, along with an X-ray structure study[3] and an investigation of their use as precursors for the thermal generation of 1,1-difluoroalkenes[4] **2** (Scheme 1).



SCHEME 1

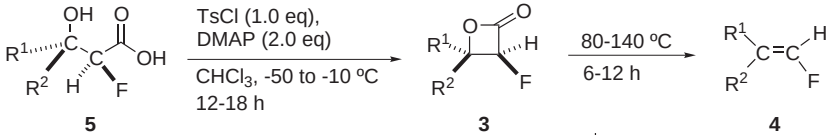
The structures of such α,α-difluoro-β-lactones were compared to those of non-fluorinated analogs, and a detailed computational and experimental kinetic study of the thermal decarboxylation of α,α-difluoro-β-lactones **1** was reported. Evidence was presented in favor of a concerted decarboxylative pathway *via* a highly asynchronous transition state that is sensitive to the medium[5,6].

Methods for the synthesis of 1-fluoro- and 1,1-difluoroalkenes are of considerable interest, because of the interesting chemical properties and potential bioactivity of such compounds[7,8]. In particular, a number of approaches to the synthesis of 1-fluoroalkenes have been published[9], some of them leading to such products in a stereocontrolled manner[10].

It was our intent in the current study to determine whether the methodology that we had developed for preparation of difluoro-β-lactones **1** could be applied to the synthesis of monofluoro-β-lactones **3**, and, if so, whether such monofluoro-β-lactones **3** would be useful thermal sources of 1-fluoroalkenes[4] **4**. In fact, it was possible, using slightly modified procedure, to prepare α-fluoro-β,β-dialkyl-β-lactones **3**, and preliminary results indicate that the thermolysis of these lactones will be useful intermediates for the 1-fluoroalkenes **4**.

RESULTS AND DISCUSSION

Our approach to synthesizing α-fluoro-β-lactones **3** (Scheme 2) was very similar to that which we developed for the synthesis of α,α-difluoro-β-lactones **1** (Scheme 1)[4]. Modifications were necessary in each of the steps in order for consistent results to be obtained. As expected, α-fluoro-β-hydroxy esters, synthesized from ketones using our modified Reformatsky procedure[11,12], were appropriate starting materials by way of their respective α-fluoro-β-hydroxy acids[12] **5**.



5 **3** **4**

3-5	R^1	R^2
a	Bn	Bn
b	Ph	Bn
c	Bn	Ph
d	Ph	Me
e	Ph	Ph

SCHEME 2

*Lactonization of α-Fluoro-β-hydroxy Acids **5***

Unexpectedly, most of the conventional reagents for carboxyl group activation failed to give a clean lactonization process. Whereas benzenesulfonyl chloride/pyridine couple in chloroform worked well with the α,α-difluoro-β-hydroxy acids[4], it gave rise to complex product mixtures when applied to the α-monofluoro system. Adam's typical lactonization procedure of benzenesulfonyl chloride in pyridine[13] led to a 50% conversion to the α-fluoro-β-lactone **3** along with about 25% of α-fluoroalkenoic acid. This result made isolation and purification of lactone **3** very difficult, in particular because of its easy ring opening regenerate the carboxylic acid **5** during aqueous work-up. The product composition suggests some competition between carboxyl and hydroxyl group activation pathways, which is not the case when lactonizing non-fluorinated acids[13]. Similar complex product mixtures were obtained when the lactonization was attempted using *p*-toluenesulfonyl chloride/pyridine, both in toluene and in chloroform. Mitsunobu conditions (with DEAD/PPh_3 couple)[14] proved to be totally inactive in THF towards lactonization of α-fluoro-β-hydroxy acids **5**.

The method that eventually proved suitable for preparation of α-fluoro-β-lactones **3** involved the use of one equivalent of the starting α-fluoro-β-hydroxy acid **5** with one equivalent of *p*-toluenesulfonyl chloride and two equivalents of *N*,*N*-dimethylaminopyridine in anhydrous chloroform. This method resulted in full conversion of acids **5** to a mixture of the respective α-fluoro-β-lactones **3** and 1-fluoroalkenes **4**. The results are summarized in Table I. As was the case in our synthesis of α,α-difluoro-

TABLE I
Preparation of α-fluoro-β-lactones

Acid	R^1	R^2	Diastereomer	Yields, %	
				Lactone[a]	Alkene
5a	Bn	Bn	–	**3a** (82)	–
5b	Ph	Bn	*R**,*R**	**3b** (77)	–
5c	Bn	Ph	*R**,*S**	**3c** (57)	**4c** (20) (*Z*)
5d	Ph	Me	*R**,*R**	**3d** (30)	**4d** (4) (*E*)
5e	Ph	Ph	–	**3e** transient	**4e** ≈ quant

[a] Stereochemistry presumed, based on known stereochemistry of acid precursor **5**.

β-lactones **1**, α-fluoro-β-hydroxy acids that were prepared from aldehydes, rather than ketones, were not effective substrates in the lactonization reaction.

When at least one aromatic ring is attached to the β-position, lactone formation is usually accompanied to some extent by 1-fluoroalkene formation. In the extreme case (R^1 = R^2 = Ph), acid **5e** was converted directly to 1,1-diphenyl-2-fluoroethylene (**4e**), perhaps *via* the intermediate lactone[15] **3e**. By carrying out the lactonization reaction at –50 °C, one can generally avoid direct conversion of the acids to the 1-fluoroalkene or at least significantly diminish the extent of such decarboxylation *in situ*. However, diphenyl lactone **3e** mentioned above, must be extremely prone to decarboxylation, since only alkene **4e** is obtained, even at –50 °C.

As depicted in Scheme 2, lactonization of acid **5b** (*R**,*R** diastereomer, R^1 = Ph, R^2 = Bn) proceeds stereospecifically to form lactone **3b** only, with no accompanying eliminative decarboxylation. On the other hand, lactonization of diastereomeric acid **5c** (the *R**,*S** isomer) gave rise to significant amounts of *in situ* formed 1-fluoroalkene **4c** in addition to the lactone **3c**. Acid **5d** gave a poor conversion and produced a mixture of alkene and lactone. In this case the lactone, although identified in the mixture by its NMR and IR spectra, was not isolated, nor was it studied further. Acid **5a** (R^1 = R^2 = Bn) gave lactone **3a** cleanly, along with traces of recovered acid **5a** (probably due to its hydrolytic reformation during work-up.)

Spectral Properties of α-Fluoro-β-lactones

The α-fluoro-β-lactones **3** exhibit the expected carbonyl IR absorption band at 1 825–1 830 cm^{-1} typical of the β-lactone ring, along with a shoulder (sometimes a strong peak) at 1 850–1 865 cm^{-1}.

Their ^1H NMR spectra are characterized by the presence of a doublet in the region of 5 to 6 ppm (downfield in comparison to the analogous signal in the spectrum of the α-fluoro-β-hydroxy acid **5** and α-fluoro-β-hydroxy ester precursors), with a geminal coupling constant $^2J_{HF}$ of 53–54 Hz. The same coupling constant is observed in the ^{19}F NMR spectrum, typically as a doublet at –190 to –200 ppm. These signals usually appear at higher field than those of the precursor esters and acids **5**.

Due to the carbon-fluorine coupling, the ^{13}C NMR spectra of the α-fluoro-β-lactones **3** exhibit characteristic doublets for each of the carbons in the lactone framework. The doublets of the lactone carbonyl carbons in the 164 ppm region appear at a higher field in comparison to those of the ester or acid precursors. Another important feature of their ^{13}C NMR spectra

is the chemical shift of C4, typically at 82–85 ppm, which is significantly downfield compared to the analogous signals of the ester or acid precursors, which are generally found between 72–76 ppm.

*Thermal Decarboxylation of α-Fluoro-β-lactones **3***

Although the mechanism of the thermal decarboxylation of β-lactones remains controversial, its effectively concerted character has been exploited in the past to carry out stereospecific syntheses of alkenes[16]. It has also served as a tool for estimating the extent of carboxyl *vs* hydroxyl group activation during the course of lactonization processes of non-fluoro-substituted hydroxy acid precursors[17]. If a concerted *syn* decarboxylation process were to occur for lactones **3**, stereospecific formation of 1-fluoroalkenes **4** with predictable stereochemistry would be observed. In fact, the preliminary results are consistent with probable stereospecific decarboxylation. Heating a neat sample of (*R**,*R**)-4-benzyl-3-fluoro-4-phenyloxetan-2-one (**3b**) at 100 °C for 8 h gave 1-fluoro-2,3-diphenyl-1-propene quantitatively (>98% *E*-isomer **4b** as determined by ^{19}F NMR). Likewise, neat pyrolysis at 80 °C of the more reactive (*R**,*S**)-diastereomer **3c** led to virtually pure (*Z*)-1-fluoro-2,3-diphenyl-1-propene (**4c**). It was found that carrying out the decarboxylations at temperatures higher than necessary led to increasing loss of stereoselectivity.

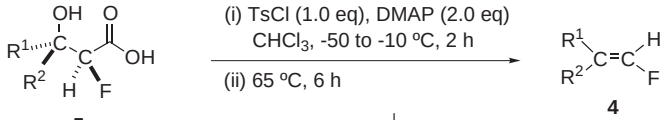
The *E*- *vs* *Z*-configurations of fluoroalkenes **4b** and **4c** were assigned based upon the larger *trans*-allylic, four-bond F-H coupling between the vinylic fluorine and the CH_2 group of the benzyl substituent in (*E*)-alkene **4b**, than for the analogous *cis*-allylic F-H coupling present in (*Z*)-alkene **4c**. This NMR-based stereochemical assignment must be considered preliminary, and a more complete study of the decarboxylation process is in progress.

Dibenzyl-substituted lactone **3a** was much less reactive and required heating to 135 °C overnight to undergo decarboxylation with complete conversion to alkene **4a**.

One-Pot Decarboxylation Reaction of α-Fluoro-β-Hydroxy Acids

If one is simply interested in preparing the 1-fluoroalkenes **4**, there is no need to isolate the β-lactones **3** at all. It should generally be possible to carry out an *in situ* procedure that produces the alkenes **4** directly from their hydroxy acid precursors **5** in good yield and with equally good

stereoselectivity. A preliminary examination of such reactions was carried out, as shown in Scheme 3, affording alkenes **4** in 93–96% isolated yield.



5 **4**

4,5	R^1	R^2
b	Ph	Bn
c	Bn	Ph
e	Ph	Ph

SCHEME 3

CONCLUSIONS

The first synthesis of α-fluoro-β-lactones **3** has been accomplished *via* lactonization of α-fluoro-β,β-dialkyl-β-hydroxy acids **5**. Preliminary studies of the thermal decarboxylation of these α-fluoro-β-lactones **3**, or the direct decarboxylative dehydration of the precursor hydroxy acids **5** led to highly stereoselective formation of 1-fluoroalkenes **4**.

EXPERIMENTAL

All chemicals were used as supplied from manufacturers without further purification. High resolution mass spectra and elemental analyses were obtained from the mass spectrometry and elemental analysis laboratories at the University of Florida. Satisfactory elemental analyses were not obtained for any of the α-fluoro-β-lactones **3** because of their high instability. However, all of them gave satisfactory HRMS analyses. NMR analyses were recorded in $CDCl_3$ at 300 MHz for ^1H, at 75.46 MHz for ^{13}C and at 282 MHz for ^{19}F spectra. Chemical shifts (δ) are given in ppm, coupling constants (*J*) in Hz. TMS was used as internal standard for ^1H and ^{13}C, and $CFCl_3$ for ^{19}F NMR spectra. Samples for IR analysis were prepared as mulls of Nujol (wavenumbers are given in cm^{-1}).

All α-fluoro-β-hydroxy acids **5** were prepared according to our recent published procedure[12].

Syntheses of α-Fluoro-β-lactones **3**. General Procedure

Starting α-fluoro-β-hydroxy acids **5** were dissolved in anhydrous chloroform (20 ml/g of **5**) and 2.0 equivalents of DMAP were added immediately. The flask was sealed, and the resultant solution was cooled to –50 °C. In another flask a solution of 1.0 equivalent of *p*-toluenesulfonyl chloride in anhydrous chloroform (10 ml/g of TsCl) was prepared and this solution was added dropwise, to the first solution while cooling the mixture and stirring vigorously. The mixture was kept in the bath until it warmed to –10 °C and then was kept in the freezer for 18 h. The solvent was removed on a rotary evaporator, using dry N_2 to relieve pressure once evaporation was completed. The white residue was extracted with dry hex-

anes[18] with vigorous stirring over 0.5 h under dry N_2. The solution, which contained the product, was carefully filtered and evaporated, and the resulting crude α-fluoro-β-lactones **3** were then recrystallized from hexane.

4,4-Dibenzyl-3-fluorooxetan-2-one (**3a**). From 0.299 g (1.0 mmol) of starting acid **5a**, 0.220 g (82%) of **3a** was obtained as a white solid; m.p. 97–98 °C (dec.). ^{1}H NMR: 7.39–7.25 m, 8 H; 7.14–7.11 dd, $^3J_{HH}$ = 7.5, $^3J_{HF}$ = 2.4, 2 H (aromatic signals); 5.30 d, $^2J_{HF}$ = 53, 1 H (CH of the lactone ring); 3.35 dd, $^2J_{HH}$ = 15, $^3J_{HF}$ = 2.4, 1 H; 3.20 d, $^2J_{HH}$ = 15, 1 H; 3.07 dd, $^2J_{HH}$ = 15, $^3J_{HF}$ = 1.8, 1 H; 2.93 d, $^2J_{HH}$ = 15, 1 H (benzylic H's). ^{19}F NMR: –200.8 d, $^2J_{HF}$ = 53. ^{13}C NMR: 39.4 d, $^3J_{CF}$ = 4.5; 40.2; 85.7 d, $^2J_{CF}$ = 19; 92.6 d, $^1J_{CF}$ = 228; 127.7; 127.9; 128.9; 129.0; 130.4; 130.7 d, $^4J_{CF}$ = 1.5; 133.4; 133.9; 164.2 d, $^2J_{CF}$ = 22. HRMS (EI): $[M]^{\bullet+}$ 270.1056; calculated for $C_{17}H_{15}FO_2$ 270.1056. IR (Nujol): 1 826.3 (strong), 1 865.2.

(R,R*)-4-Benzyl-3-fluoro-4-phenyloxetan-2-one* (**3b**). From 0.137 g (0.5 mmol) of **5b**, 0.098 g (76.5%) of product was obtained as a white solid; m.p. 89–92 °C (dec.). ^{1}H NMR: 7.34–7.27 m, 3 H; 7.20–7.06 m, 5 H; 6.94–6.87 m, 2 H (aromatic signals); 5.70 d, $^2J_{HF}$ = 54, 1 H (CH of the lactone ring); 3.53 dd, $^2J_{HH}$ = 14, $^3J_{HF}$ = 2.1, 1 H; 3.40 d, $^2J_{HH}$ = 15, 1 H (benzylic H's). ^{19}F NMR: –196.8 d, $^2J_{HF}$ = 54. ^{13}C NMR: 41.6 d, $^3J_{CF}$ = 3.6; 87.3 d, $^2J_{CF}$ = 20; 96.9 d, $^1J_{CF}$ = 232; 125.3; 127.3; 128.3; 128.6; 128.8; 130.8; 132.8; 137.4; 164.1 d, $^3J_{CF}$ = 22. HRMS (EI): $[M]^{\bullet+}$ 256.0896; calculated for $C_{16}H_{13}FO_2$ 256.0900. IR (Nujol): 1 854.9 (shoulder), 1 828.0 (strong).

(R,S*)-4-Benzyl-3-fluoro-4-phenyloxetan-2-one* (**3c**). From 0.412 g (1.5 mmol) of **5c**, 0.275 g (74.8%) of a mixture of products, consisting of 74% lactone **3c** and 26% 1-fluoroalkene **4c**, from which **3c** was obtained pure by recrystallization from hexane; m.p. 77–80 °C (dec.). ^{1}H NMR: 7.33–7.25 m, 6 H; 7.15–7.10 m, 2 H (aromatic signals); 5.53 d, $^2J_{HF}$ = 54, 1 H (CH of the lactone ring); 3.48 dd, $^2J_{HH}$ = 15, $^3J_{HF}$ = 0.9, 1 H; 3.36 d, $^2J_{HH}$ = 15, 1 H (benzylic H's). ^{19}F NMR: –192.0 d, $^2J_{HF}$ = 54. ^{13}C NMR: 45.1; 86.5 d, $^2J_{CF}$ = 20; 93.4 d, $^1J_{CF}$ = 231; 126.2; 127.9; 128.7; 128.8; 129.0; 130.6; 133.1; 134.8; 163.7 d, $^3J_{CF}$ = 23. HRMS (EI): $[M]^{\bullet+}$ 256.0896; calculated for $C_{16}H_{13}FO_2$ 256.0900. IR (Nujol): 1 849.9, 1823.4 (two strong bands).

(R,R*)-3-Fluoro-4-methyl-4-phenyloxetan-2-one* (**3d**). From 0.200 g (1.0 mmol) of **5d**, after evaporation of the chloroform, rinsing with ethyl acetate, careful filtration and evaporation of ethyl acetate, 0.060 g (34%) of product was isolated as a mixture of products consisting of 89% lactone **3d** and 11% 1-fluoroalkene **4d**. Characterization of **3d** was done as the mixture. ^{1}H NMR: 7.10–7.20 m, 5 H; 5.46 d, $^2J_{HF}$ = 54, 1 H (CH of the lactone ring); 1.81 d, $^4J_{HF}$ = 3.3 (β-methyl). ^{19}F NMR: –194.6 d, $^2J_{HF}$ = 54. ^{13}C NMR: 22.0 d, $^3J_{CF}$ = 4.5; 85.1 d, $^2J_{CF}$ = 21; 96.2 d, $^1J_{CF}$ = 232; 124.3; 128.7; 129.0; 129.1; 139.4; 164.8 d, $^3J_{CF}$ = 22. IR (Nujol): 1 839.3 (strong).

1-Fluoroalkenes **4** from α-Fluoro-β-lactones **3**. General Procedure

A dry vial, flame-dried and purged with dry N_2, was charged with the α-fluoro-β-lactone **3**, sealed tightly with a nalgene cap and teflon, and heated at the specified temperature overnight. A yellow oil was formed in each case. The reaction mixture was cooled with dry ice, the vial was opened, and the resultant oil was dissolved in $CDCl_3$ and analyzed by NMR. In all the cases a full conversion to the respective 1-fluoroalkene **4** was achieved, and their ^{1}H, ^{19}F and ^{13}C NMR spectra were very clean with no further purification being required.

2-Benzyl-1-fluoro-3-phenyl-1-propene (**4a**). Heating of 100 mg (0.37 mmol) of 4,4-dibenzyl-3-fluorooxetan-2-one (**3a**) at 140 °C overnight gave 81 mg (97%) of fluoroalkene **4a**. ^{1}H NMR: 7.23 t, $^3J_{HH}$ = 7.2, 5 H; 7.17 dd, $^3J_{HH}$ = 7.2, $^4J_{HF}$ = 2.2, 2 H; 7.09 td, $^3J_{HH}$ = 7.2,

$^4J_{HF}$ = 1, 3 H; 6.52 d, $^2J_{HF}$ = 86, 1 H; 3.39 d, $^4J_{HF}$ = 2.5, 2 H; 3.02 d, $^4J_{HF}$ = 3.3, 2 H. ^{19}F NMR: –135.6 d, $^2J_{HF}$ = 86. ^{13}C NMR: 31.9 d, $^3J_{CF}$ = 5.1; 35.2 d, $^3J_{CF}$ = 6.6; 121.8 d, $^2J_{CF}$ = 6.3; 126.4; 126.7; 128.7; 129.2; 129.2; 138.6 d, $^4J_{CF}$ = 2.7; 139.0 d, $^4J_{CF}$ = 2.4; 145.2 d, $^1J_{CF}$ = 255. HRMS (EI): $[M]^{\bullet+}$ 226.1158; calculated for $C_{16}H_{15}F$ 226.1158. IR (Nujol): 1 683, 1 602.

(E)-1-Fluoro-2,3-diphenyl-1-propene (**4b**). Heating of 100 mg (0.47 mmol) of (*R**,*R**)-4-benzyl-3-fluoro-4-phenyloxetan-2-one (**3b**) at 100 °C overnight gave 77 mg (93%) of fluoroalkene **4b** (traces (2%) of the *Z*-isomer **4c** were also observed). ^{1}H NMR: 7.30–7.12 m, 10 H; 6.97 d, $^2J_{HF}$ = 85, 1 H; 3.87 d, $^4J_{HF}$ = 3.3, 2 H. ^{19}F NMR: –130.5 dt, $^2J_{HF}$ = 85, $^4J_{HF}$ = 3.0. ^{13}C NMR: 33.0 d, $^3J_{CF}$ = 5.1; 123.8 d, $^2J_{CF}$ = 9.0; 126.3; 127.0 d, $^4J_{CF}$ = 3.0; 127.7; 128.6; 128.6; 128.7; 136.4 d, $^3J_{CF}$ = 8.4; 138.9 d, $^4J_{CF}$ = 2.4; 146.8 d, $^1J_{CF}$ = 261. HRMS (EI): $[M]^{\bullet+}$ 212.1002; calculated for $C_{15}H_{13}F$ 212.1001. IR (Nujol): 1 657, 1 600.

(Z)-1-Fluoro-2,3-diphenyl-1-propene (**4c**). Heating of 100 mg (0.47 mmol) of (*R**,*S**)-4-benzyl-3-fluoro-4-phenyloxetan-2-one (**3c**) at 100 °C overnight gave 75 mg (91%) of fluoroalkene **4c** (traces (1%) of the *E*-isomer **4b** were observed). ^{1}H NMR: 7.37 d, $^4J_{HH}$ = 7.5, 2 H; 7.32–7.13 m, 8 H (aromatic signals); 6.65 dt, $^2J_{HF}$ = 84, $^4J_{HF}$ = 1.2, 1 H; 3.61 d, $^4J_{HF}$ = 3.9, 2 H. ^{19}F NMR: –129.9 dt, $^2J_{HF}$ = 84, $^4J_{HF}$ = 3.9. ^{13}C NMR: 36.8 d, $^3J_{CF}$ = 6.6; 121.5 d, $^2J_{CF}$ = 1.8; 126.6; 127.6; 128.4; 128.5 d, $^4J_{CF}$ = 4.5; 128.6; 128.8; 134.9; 138.8 d, $^4J_{CF}$ = 2.7; 146.2 d, $^1J_{CF}$ = 264. HRMS (EI): $[M]^{\bullet+}$ 212.1002; calculated for $C_{15}H_{14}F$ 212.1001. IR (Nujol): 1 658, 1 602.

1-Fluoroalkenes **4** from α-Fluoro-β-hydroxy Acids **5**: One-Pot Lactonization-Decarboxylation. General Procedure

The starting 2-fluoro-3-hydroxy acids **5** were dissolved in anhydrous chloroform (20 ml/g of **5**) and 2.0 equivalents of DMAP were added immediately. The resultant solution was cooled to –50 °C. In another flask a solution of 1.1 equivalents of *p*-toluenesulfonyl chloride in anhydrous chloroform (10 ml/g of TsCl) was prepared and added very slowly (dropwise) to the first solution, while cooling and stirring vigorously. The reaction mixture was allowed to stand in the bath until it warmed to 0 °C (usually 2 h), and then it was heated 15 h in an oil bath at 65 °C. For **5e** (R^1 = R^2 = Ph) it was not necessary to warm up the reactant mixture to perform the total conversion to the 1-fluoroalkene **4e**. The progress of the reaction was monitored by ^{19}F NMR spectroscopy. Upon completion of the reaction, the solvent was evaporated and the white residue extracted with dry hexanes by vigorous stirring for 0.5 h under a blanket of dry N_2. The solution was carefully filtered and evaporated to give the products as yellow oils.

(E)-1-Fluoro-2,3-diphenylprop-1-ene (**4b**). Starting from 0.139 g (0.5 mmol) of **5b**, 0.103 g (96%) of a yellow oil was isolated, having the same spectral properties as that obtained by decarboxylation of **3b**. ^{19}F NMR analysis of the crude reaction mixture showed a signal at –130.5 ppm (d, $^2J_{HF}$ = 84) (99% conversion, 100% stereoselective to the *E*-1-fluoroalkene) and a small signal at –197.1 ppm (d, $^2J_{HF}$ = 47) (1%) characteristic of acid **5b** (by-product from hydrolysis).

(Z)-1-Fluoro-2,3-diphenylprop-1-ene (**4c**). Starting from 0.139 g (0.5 mmol) of **5c**, 99 mg (93%) of a yellow oil was isolated with the same spectral properties as the one obtained from decarboxylation of **3c**. ^{19}F NMR analysis of the crude reactant mixture showed a signal at –129.9 (d, $^2J_{HF}$ = 86) (99%) and a small signal at –130.5 (d, $^2J_{HF}$ = 85) (1%) characteristic of the *E*-isomer **4b** (100% conversion, 99% stereoselective).

2-Fluoro-1,1-diphenylethylene (**4e**). Starting from 0.136 g (0.52 mmol) of **5e**, 100 mg (95%) of a yellow oil was isolated, having the same spectral properties as reported in the literature[9f,9m,9p]. ^{19}F NMR analysis of the crude reaction mixture showed only a signal at –128.5 (d, $^{2}J_{HF}$ = 83.8) (100% conversion). ^{1}H NMR: 7.29–7.18 m, 7 H; 7.16–7.08 m, 3 H; 6.84 d, $^{2}J_{HF}$ = 83, 1 H. ^{19}F NMR: –128.5 d, $^{2}J_{HF}$ = 84. ^{13}C NMR: 126.5 d, J_{CF} = 5.4; 146.1 d, J_{CF} = 269; and aromatic signals. IR (Nujol): 1 659, 1 637.

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REFERENCES AND NOTES

1. For recent reviews, see: a) Pommier A., Pons J.-M.: *Synthesis* **1993**, 441; b) Mulzer J. in: *Comprehensive Organic Synthesis* (B. M. Trost and I. Flemming, Eds), Vol. 6, p. 323. Pergamon, Oxford 1991; c) Searles S. in: *Comprehensive Heterocyclic Chemistry* (A. R. Katrizky and C. W. Rees, Eds), Vol. 7, Part 5, p. 363. Pergamon, Oxford 1984.
2. a) England D. C., Solomon L., Krespan C. G.: *J. Fluorine Chem.* **1973/74**, *3*, 63; b) England D. C., Krespan C. G.: *J. Org. Chem.* **1968**, *33*, 816.
3. Abboud K., Dolbier W. R., Jr., Ocampo R.: *Acta Crystallogr., Sect.C: Cryst. Struct. Commun.* **1997**, *53*, 1923.
4. a) Dolbier W. R., Jr., Ocampo R., Paredes R.: *J. Org. Chem.* **1995**, *60*, 5378; b) Ocampo R., Dolbier W. R., Jr., Paredes R.: *J. Fluorine Chem.* **1998**, *88*, 41.
5. Ocampo R., Dolbier W. R., Jr., Bartberger M. D., Paredes R.: *J. Org. Chem.* **1997**, *62*, 109.
6. Morao I., Lecea B., Arrieta A., Cossío F. P.: *J. Am. Chem. Soc.* **1997**, *119*, 816.
7. Smart B. E. in: *Organofluorine Chemistry: Principles and Commercial Applications* (R. E. Banks, B. E. Smart and J. C. Tatlow, Eds), p. 57. Plenum Press, New York 1994.
8. a) Robins M. J., Neschadimenko V., Ro B. O., Yuan C. S., Borchardt R. T., Wnuk S. F.: *J. Org. Chem.* **1998**, *63*, 1205; b) Liu S. M., Yuan C. S., Borchardt R. T.: *J. Med. Chem.* **1996**, *39*, 2347; c) Bey P., McCarthy J. R., McDonald I. A.: *ACS Symp. Ser.* **1991**, *456*, 105; d) Pirrung M. C., Chen J. L., Rowley E. G., McPhail A. T.: *J. Am. Chem. Soc.* **1993**, *115*, 7103; e) Welch J. T.: *Tetrahedron* **1987**, *43*, 3123.
9. a) Chen C., Wilcoxen K., Huang C. Q., Strack N., McCarthy J. R.: *J. Fluorine Chem.* **2000**, *101*, 285; b) Chen C., Wilcoxen K., Strack N., McCarthy J. R.: *Tetrahedron Lett.* **1999**, *40*, 827; c) Tsai H. J., Lin K. W., Ting T. H., Burton D. J.: *Helv. Chim. Acta* **1999**, *82*, 2231; d) Lee S. H., Riediker M., Schwartz J.: *Bull. Korean Chem. Soc.* **1998**, *19*, 760; e) Bohlmann R.: *Tetrahedron Lett.* **1994**, *35*, 85; f) Tius M. A., Kawakami J. K.: *Tetrahedron* **1995**, *51*, 3997; g) Kunugi A., Yamane K., Yasuzawa M., Matsui H., Uno H., Sakamoto K.: *Electrochim. Acta* **1993**, *38*, 1037; h) McCarthy J. R., Matthews D. P., Edwards M. L., Stemerick D. M., Jarvi E. T.: *Tetrahedron Lett.* **1990**, *31*, 5449; i) Matsuo N., Kende A. S.: *J. Org. Chem.* **1988**, *53*, 2304; j) Purrington S. T., Pittman J. H.: *Tetrahedron Lett.* **1987**, *28*, 3901; k) Reutrakul V., Rukachaisirikul V.: *Tetrahedron Lett.* **1983**, *24*, 725; l) Boche G., Fährmann U.: *Chem. Ber.* **1981**, *114*, 4005; m) Hayashi S., Nakai T., Ishikawa N.: *Chem. Lett.* **1980**, 651; n) Hayashi S., Nakai T., Ishikawa N., Burton D. J., Naae D. G., Kesling H. S.:

Chem. Lett. **1979**, 983; o) Eckes L., Hanack M.: *Chem. Ber.* **1978**, *111*, 1253; p) Burton D. J., Greenlimb P. E.: *J. Org. Chem.* **1975**, *40*, 2796; q) Elkik E., Le Blanc M.: *C. R. Seances Acad. Sci., Ser. C* **1969**, *269*, 173.

10. a) Chen C., Wilcoxen K., Zhu Y. F., Kim K. I., McCarthy J. R.: *J. Org. Chem.* **1999**, *64*, 3476; b) Lin J., Welch J. T.: *Tetrahedron Lett.* **1998**, *39*, 9613; c) McCarthy J. R., Huber E. W., Le T. B., Kaskovics F. M., Matthews D. P.: *Tetrahedron* **1996**, *52*, 45; d) Kuroboshi M., Yamada N., Takebe Y., Hiyama T.: *Tetrahedron Lett.* **1995**, *36*, 6271; e) McCarthy J. R., Mathews D. P., Paolini J. P.: *Org. Synth.* **1995**, *72*, 216; f) McCarthy J. R., Matthews D. P., Stemerick D. M., Huber E. W., Bey P., Lippert B. J., Snyder R. D., Sunkara P. S.: *J. Am. Chem. Soc.* **1991**, *113*, 7439; g) van Steenis J. H., van der Gen A.: *Eur. J. Org. Chem.* **2001**, 897.
11. a) Shen Y., Qi M.: *J. Chem. Res., Synop.* **1993**, 222; b) Linderman R. J., Graves D. M.: *J. Org. Chem.* **1989**, *54*, 661; c) Brandänge S., Dahlman O., Mörch L.: *J. Am. Chem. Soc.* **1981**, *103*, 4452.
12. Ocampo R., Dolbier W. R., Jr., Abboud K., Zuluaga F.: *J. Org. Chem.* **2002**, *67*, 72.
13. Adam W., Baeza J., Liu J.-C. : *J. Am. Chem. Soc.* **1972**, *94*, 2000.
14. Pansare S. V., Huyer G., Arnold L. D., Vederas J. C.: *Org. Synth.* **1991**, *70*, 1 and 10.
15. By using less than 2 equivalents of DMAP, ^{19}F NMR analysis of an early sample of the reactant mixture makes possible to see the transient peak corresponding to the intermediate 3-fluoro-4,4-diphenyloxetan-2-one at –188.9 d, $^{2}J_{HF}$ = 51.
16. a) Mulzer J., Pointner A., Chucholowski A., Brüntrup G.: *J. Chem. Soc., Chem. Commun.* **1979**, 52; b) Noyce D. S., Bannit E. H.: *J. Org. Chem.* **1966**, *31*, 4043.
17. a) Adam W., Narita N., Nishizawa Y.: *J. Am. Chem. Soc.* **1984**, *106*, 1843; b) Mulzer J., Brüntrup G., Chucholowski A.: *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 622.
18. Ethyl acetate was used instead of hexanes for the isolation of **3d** because of its low solubility in hexanes.