ELSEVIER

Journal of Fluorine Chemistry 88 (1998) 23–27

JOURNAL OF FLUORINE CHEMISTRY

Substituent effects on the regioselectivity in fluorination of allylic alcohols with DAST

Abdelghani Boukerb [a], Danielle Grée [b], Mohammed Laabassi [a], René Grée [b,*]

[a] *Faculté des Sciences, Université de Batna, Avenue Chahid El Hadi Boukhlouf, DZ 05000 Batna, Algeria*

[b] *Laboratoire de Synthèses et Activations de Biomolécules, associé au CNRS, ENSCR, Avenue du Général Leclerc, 35700 Rennes, France*

Received 30 June 1997; accepted 12 September 1997

Abstract

The regioselectivity of the fluorination of various allylic and β-dienoic alcohols with DAST has been studied. Substituent effects are important in these reactions; a strong preference for the secondary fluorides versus the primary ones is observed, especially in the case of alkyl and aryl substituted derivatives. © 1998 Elsevier Science S.A.

Keywords: DAST; Fluorination; Allylic systems; Regioselectivity; Fluorine NMR

1. Introduction

It has been well established that the introduction of fluorine atoms into biomolecules can induce important modifications of their biological properties[1–9]. Therefore, the control of the regio-, stereo-, and enantioselectivity of the fluorination is of much interest.[1] A few years ago we initiated a program dealing with the challenging problem of selective monofluorination in a position vicinal to unsaturated systems and its application to the synthesis of natural product analogs; we demonstrated in several instances that transition metal complexes can control the regio- and stereoselectivity of the nucleophilic fluorination [15,16].

Reactions of allylic alcohols with nucleophilic fluorinating agents are known to be susceptible to an allylic shift. In the case of DAST for instance, this was first reported by Middleton: reaction of crotyl alcohol **1** gives mixtures of **2** and **3** (28:72 in diglyme and 36:64 in isooctane, GLC estimate) [17] (Scheme 1).

Many applications of this type of reaction have been subsequences described in various families of natural products.[2] The competition between fluorination with and without transposition of fluorine is extremely substrate-dependent and since these examples are obtained with complex structures, it appears very difficult to rationalize the results.[3] It is interesting to note that the regioselectivity problem is not limited to DAST since other fluorinating agents give similar results;[4] for instance, α-fluoroenamines react with various allylic alcohols, either primary or secondary and tertiary bearing alkyl type substituents, to give mixtures of fluorinated derivatives with and without allylic shift [33–36].[5]

The systematic study of the substituent effects on the course of the reaction of allylic alcohols with DAST appears to be of interest, not only in mechanistic terms of but also for synthetic purposes. In this study, reactions of DAST with a number of selected, simple model alcohols bearing aliphatic and aromatic substituents were investigated. In each case, the regioisomeric ratios have been carefully established by high field NMR spectrometry (^{1}H, ^{13}C and ^{19}F) directly on the crude reaction mixtures.

2. Results and discussion

With simple aliphatic systems, as expected, a low regioselectivity is observed. Upon treatment with DAST in dichloromethane, crotyl alcohol **1** gives compounds **2** and **3** in a 27:73 ratio (NMR estimate, which is in good agreement with

* Corresponding author. Tel.: +33-02-99-87-13-83; fax: +33-02-99-87-13-84; e-mail: rene.gree@univ-rennes1.fr.

[1] For some recent reviews, see Refs. [10–14].

[2] For representative examples, see Refs. [18–29].

[3] These problems are discussed in a recent review. See Ref. [30].

[4] For an interesting recent discussion about the mechanistic aspects of the reaction of aminosulfur trifluorides with alcohols, see Ref. [31]. See also a recent synthesis of difluorallyl compounds, in Ref. [32].

[5] For some applications of α-fluoroenamines, see Ref. [37].

PII S0022-1139(98)00115-8

Middleton's results [17]). With the isopropyl derivative **4**, the respective fluorinated compounds **5** and **6** are formed in a 2:3 ratio.

In both cases, structures of both regioisomers were established from their NMR spectra, taking advantage of the fluorine-to-proton and fluorine-to-carbon coupling constants. Particularly relevant are the methyl group signals: they appear as dd with a $^{3}J_{HF} \approx 24$ Hz in the case of **3** and **6** whereas these coupling constants are very small ($^{5}J_{HF} \approx 2$ Hz) for the methyl group in a vinylic position (**2** and **5**). Similarly in ^{13}C NMR, the methyl groups signals are close to 21 ppm with a $J_{CF} \approx 25$ Hz in the case of **3** and **6** while they are around 17 ppm with a small J_{CF} (≈ 2 Hz) for **2** and **5**. This is clearly exemplified in the case of **7**, prepared by the same route, and used as a reference compound (Scheme 2).

Also notable are the chemical shifts in ^{19}F NMR which appear highly characteristic: allylic CH_2F appear below -200 ppm while the corresponding CH(R)F are close to -165 ppm. This is in good agreement with Middleton's results on derivatives **2** (-210 ppm) and **3** (-171.6 ppm) [17]. Other NMR data for all these compounds (see Section 3) are also in excellent agreement with the indicated structures.

In contrast to the alkyl groups, which have little effect on the regioselectivity of fluorination of allyl alcohols with DAST, this regioselectivity is strongly affected by the phenyl substituent: the reaction of **8** with DAST occurs with complete transposition giving exclusively the conjugated system **10**. The same derivative is obtained directly from alcohol **9** (Scheme 3).

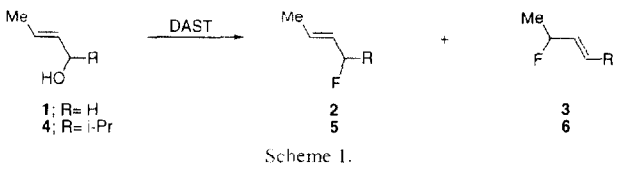
In this case, the fluorination leads clearly to the most conjugated, and probably also the most stable, derivative. However, it must be noticed that the reaction of cinnamyl alcohol **11** with DAST yields, under the same conditions, a 34:66 mixture of **12** and **13**. It is interesting to note that this ratio could be obtained only by NMR on the crude reaction mixture: **13** appears to be very sensitive and decomposes during chromatography on silica gel, with **12** being the only isolated regioisomer. This result, obtained with **11**, is important since it indicates a preference for the formation of the *secondary* fluoride versus the primary, in spite of the conjugation of the aryl group with the double bond observed only in the case of **12** (Scheme 4).

Several dienyl alcohols have also been studied. Sorbyl alcohol **14** reacts with DAST to give a 1:9 mixture of primary fluoride **15** and completely transposed fluorinated diene **16** (Scheme 5).

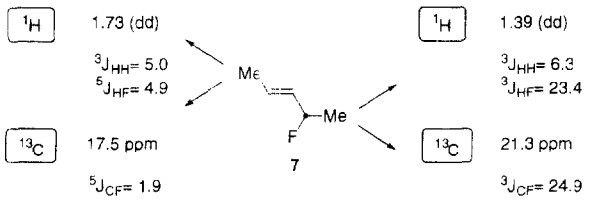
The structures of **15** and **16** were elucidated from their NMR spectra using the same criteria for **2** and **4**. It is worth noticing that divinylcarbinol **17** gives, on reaction with DAST, exactly the same result with identical 1:9 ratio of **15** and **16**. This appears to be in good agreement with the possible involvement of a pentadienyl carbenium ion intermediate.

The introduction of electron withdrawing substituents was anticipated to have also a strong influence on the regioselectivity of the fluorination and this has been confirmed with an ester group. Under the same conditions, the reaction of **18a** (R = H) with DAST occurred smoothly and gave compounds **19a** and **20a** in a 4:1 ratio (Scheme 6).

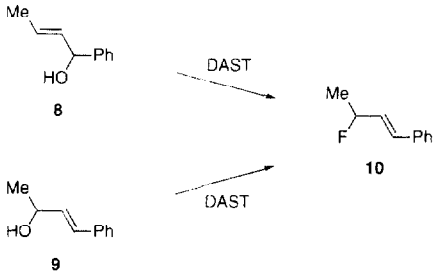
We have demonstrated earlier that in the case of **18b** (R = Me) the reaction leads exclusively to **19b** [15]. Thus, there is a clear preference for the dienyl system conjugated with the ester group.



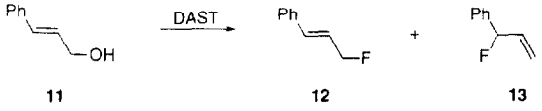
Scheme 1.



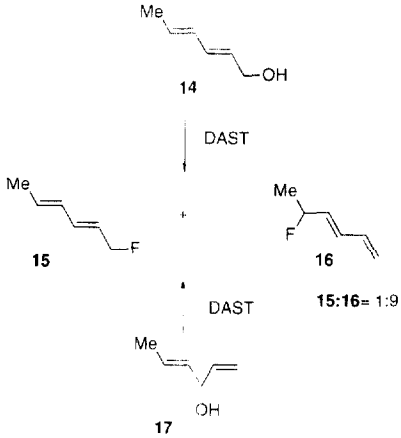
Scheme 2.



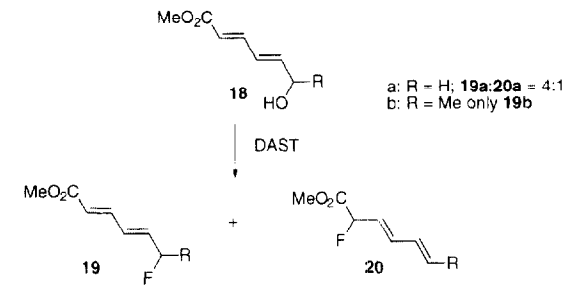
Scheme 3.



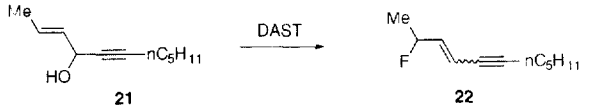
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

Finally, it also appeared interesting to consider an alcohol such as **21** with both an allylic and a propargylic position. On treatment with DAST, it gave only rearranged product **22** (as a 72:28 mixture of the *E* and *Z* isomer) (Scheme 7). In agreement with earlier reports describing fluorination of propargylic alcohols, no transposition in allenyl systems was observed.[6]

In conclusion, the present results appear to support the existence of stabilized allylic or pentadienyl carbenium ions as intermediates (at least, under the reaction conditions used here). Furthermore, these results indicate that the regioselectivity in this type of fluorination is strongly influenced by the substituents of the starting alcohol. The two key factors appear to be as follows.

1) The nature (primary and secondary) of the final products: the secondary fluorides are always obtained preferentially to the primary ones, except in the case of the systems conjugated with electron withdrawing groups such as **19a**.

2) The preference for the formation of the most conjugated and therefore, thermodynamically the most stable systems.

When both factors are acting in the same direction, the reactions are completely regioselective. In the other cases, the first factor appears predominant.

Further studies are underway to confirm the above relationships though the present results appear already to be good guidelines for the design of synthetic strategies towards the preparation of molecules selectively fluorinated in β-positions to unsaturated systems. Such studies as well as their application to the preparation of natural product analogs are being actively pursued in our laboratory.

3. Experimental section

3.1. General methods

^1H, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ solutions with a Bruker ARX 400 spectrometer at 400, 376 and 100 MHz respectively. Chemical shifts are quoted in ppm from internal Me_4Si for ^1H and ^{13}C and from internal CCl_3F for ^{19}F (negative upfield). When appropriate, signal assignments have been confirmed by 2D NMR experiments. Mass spectra were recorded with a Varian MAT 311 spectrometer at the «Centre Régional de Mesures Physiques de l'Ouest» (Rennes). Silica plates (Merck) were used for TLC analysis and the column chromatography was performed on silica gel Geduran Si60 (230–400 mesh, Merck). Mixtures of ether and low boiling ($\leq 60°C$) petroleum ether, or a mixture of ether and pentane were used as eluents. CH_2Cl_2 was distilled from P_4O_{10} just before use. DAST (Aldrich or Acros) was used as received.

3.2. General procedure for the fluorination of allylic and dienoic alcohols

An alcohol (1 mmole) in CH_2Cl_2 (4 ml) was added under nitrogen at room temperature to a solution of DAST (1.2 mmole) in CH_2Cl_2 (4 ml). After 5 min, solid Na_2CO_3 (125 mg, 1 eq.) was added. The organic phase was then washed twice with a 1 M aqueous Na_2CO_3 followed by water and then dried over $MgSO_4$. The solvent was removed either using a rotatory evaporator (for **10**, **12** + **13** and **22**) or distilled off under atmospheric pressure in other cases. The fluorinated compounds were purified by flash chromatography on silica gel using a 1:9 mixture of ether and *n*-pentane as eluent. After the removal of the solvents (same conditions as above), the crude products were examined h. NMR and MS investigations. The reactions carried out with excess DAST (1.5 eq.) directly in an NMR tube (in $CDCl_3$) proceeded quantitatively and gave the same ratios of products as in preparative runs. The given yields correspond to, NMR pure, products obtained after distillation of the solvents. Lower yields are obtained in the case of the derivatives with a low molecular mass, due to their high volatility.

Yield: 36% (**2:3** = 27:73); 1-fluoro-2-butene **2**; ^1H NMR: 1.73 (m, 3H, H_4); 4.75 (dd, 2H, J = 47.5 and 6.4, H_1); 5.27 (dm, 1H, J = 17.2, H_2); 5.75–5.56 (m, 1H, H_3). ^{19}F NMR δ = −207.7. Litt. [17]: −210. ^{13}C NMR: 17.6 (J = 2.5, C_4); 83.5 (J = 159.5, C_1); 125.7 (J = 16.3, C_2); 132.5 (J = 12.3, C_3).

2-fluoro-3-butene **3**; ^1H NMR: 1.37 (dd, 3H, J = 23.7 and 6.4, H_1); 5.02 (dqt, 1H, J = 48.2 and 6.4, H_2); 5.15 (d, 1H, J = 1.08, H_4); 5.96–5.79 (m, 2H, H_3 and H_4). ^{19}F NMR δ = −170.4. Litt. [17]: −171.6. ^{13}C NMR: 20.9 (J = 23.7, C_1); 89.9 (J = 163.4, C_2); 116.0 (J = 11.7, C_4); 137.7 (J = 16.3, C_3).

Yield: 43% (**5:6** = 2:3); 2-methyl-3-fluoro-4-hexene **5**; ^1H NMR: 0.92 (dd, 6H, J = 26.2 and 6.9, H_1); 1.78–1.73 (m, 3H, H_6); 1.88 (dm, 1H, J = 21.7, H_2); 4.52 (dt, 1H, J = 47.9 and 7.0, H_3); 5.80–5.49 (m, 2H, H_5 and H_4). ^{19}F NMR δ = −174.1. ^{13}C NMR: 17.6 (J = 18.1, C_1); 17.7 (J = 17.2, C_1); 17.8 (J = 2.2, C_6); 32.9 (J = 22.2, C_2); 98.8 (J = 166.7, C_3); 128.2 (J = 19.3, C_4). 131.5 (J = 12.5, C_5).

[6] See, for instance, Refs. [38–40].

2-fluoro-5-methyl-3-hexene **6**; ^{1}H NMR: 1.03 (dd, 6H, J=6.8 and 1.7, H_6); 1.42 (dd, 3H, J=23.4 and 6.3, H_1); 2.38–2.28 (m, 1H, H_5); 5.01 (dqt, 1H, J=48.5 and 6.3, H_2); 5.80–5.49 (m, 2H, H_3 and H_4). ^{19}F NMR δ= −162.8. ^{13}C NMR: 21.5 (J=24.9, C_1); 21.9 (J=1.3, C_6); 22.0 (J=1.2, C_6); 30.6 (J=1.4, C_5); 90.6 (J=160.6, C_2); 126.8 (J=19.2, C_3); 141.2 (J=11.0, C_4). HRMS (**5**+**6** mixture): found: 116.100 $C_7H_{13}F$ requires: 116.1001.

2-fluoro-3-pentene **7** (Yield: 42%): ^{1}H NMR: 1.39 (dd, 3H, J=23.4 and 6.3, H_1); 1.73 (dt, 3H, J=4.9 and 1.5, H_5); 5.00 (dqt, 1H, J=48.5 and 6.7, H_2); 5.60 (dddq, 1H, J=15.4, 9.4, 7.0, 1.6, H_3); 5.78 (ddq, 1H, J=15.4, 6.4, 4.6, H_4). ^{19}F NMR δ= −162.6. ^{13}C NMR: 17.5 (J=1.9, C_5); 21.3 (J=24.9, C_1); 90.3 (J=160.0, C_2); 129.3 (J=11.6, C_4); 131.0 (J=18.8, C_3).

3-fluoro-1-phenyl-1-butene **10** (Yield: 71%); ^{1}H NMR: 1.54 (dd, 3H, J=23.4 and 6.4, H_1); 5.26 (dqtd, 1H, J=48.2, 6.4, 1.0, H_2); 6.30 (ddd, 1H, J=16.1, 12.1, 6.4, H_3); 6.64 (dd, 1H, J=16.1 and 4.1, H_4) 7.5–7.2 (m, 5H, arom.). ^{19}F NMR δ= −166.0. ^{13}C NMR: 21.5 (J=24.6, C_1); 90.2 (J=163.1, C_2); 126.7 (J=1.5, arom.); 128.1 (J=0.7, arom.); 128.6 (arom.); 128.8 (J=18.9, C_3); 131.8 (J=11.8, C_4); 136.1 (J=1.7, arom.). HRMS: found: 150.084 $C_{10}H_{11}F$ requires 150.0845.

Yield: 76% (**12:13**=34:66); 1-fluoro-3-phenyl-2-propene **12** (Yield: 18%); ^{1}H NMR: 5.01 (ddd, 2H, J=47.0, 6.1, 1.3, H_1); 6.36 (ddt, 1H, J=15.9, 11.9, 6.1, H_2); 6.69 (dd, 1H, J=15.9, 5.2, H_3); 7.42–7.27 (m, 5H, arom.). ^{19}F NMR δ= −210.8. ^{13}C NMR: 83.4 (J=160.8, C_1); 123.0 (J=16.0, C_2); 126.2 (J=1.0, arom.); 127.7 (J=1.1, arom.); 128.1 (J=0.9, arom.); 133.7 (J=12.3, C_3); 135.3 (J=2.4, arom.). HRMS: found: 136.069 C_9H_9F requires 136.0688.

1-fluoro-1-phenyl-2-propene **13**; ^{1}H NMR: 5.33 (dt, 1H, J=10.5 and 1.2, H_3); 5.43 (ddt, 1H, J=17.2, 3.6, 1.3, H_3); 5.86 (ddt, 1H, J=47.5, 6.0, 1.2, H_1); 6.09 (dddd, 1H, J=17.1, 13.6, 10.5, 6.1, H_2). ^{19}F NMR δ= −169.6. ^{13}C NMR: 93.4 (J=167.0, C_1); 116.8 (J=11.1, C_3); 125.5 (J=5.9, arom.); 127.8 (J=2.1, arom.); 127.9 (J=4.4, arom.); 135.4 (J=22.2, C_2); 137.8 (J=20.6, arom.).

Yield: 68% (**15:16**=1:9); (*2E,4E*)-1-fluoro hexa-2,4-diene **15**: Characteristic NMR data: ^{1}H NMR: 4.84 (dd, J=47.4 and 6.4, H_1); 1.78–1.72 (m, H_6); ^{19}F NMR δ= −208.7. ^{13}C NMR: 18.0 (J=1.8, C_6); 83.2 (J=160.6, C_1); 123.9 (J=15.5, C_2); 130.2 (J=4.0, C_4 or C_5); 132.1 (J=4.7, C_4 or C_5); 135.3 (J=12.5, C_3).

(*3E*)-2-fluoro hexa-3,5-diene **16**; ^{1}H NMR: 1.40 (dd, 3H, J=23.4 and 6.4, H_1); 5.08 (dqt, 1H, J=47.9 and 6.3, H_2); 5.30–5.11 (m, 2H, H_6); 5.75 (ddd, 1H, J= 14.8, 12.9, 6.4, H_3); 6.40–6.20 (m, 2H, H_4, H_5). ^{19}F NMR δ= −166.7. ^{13}C NMR: 21.2 (J=24.4, C_1); 89.5 (J=162.5, C_2); 118.0 (J=3.2, C_6); 132.3 (J=11.7, C_4); 132.5 (J=18.6, C_3); 135.7 (J=2.6, C_5). HRMS (**15**+**16** mixture): found: 100.068 C_6H_9F requires 100.0688.

Yield: 81% (**19a:20a**=4:1); (*2E,4E*) methyl-6-fluoro-2,4-hexadienoate **19a**; ^{1}H NMR: 5.00 (ddd, 2H, J=46.2, 5.1, 1.5, H_6); 5.97 (dqt, 1H, J=15.4 and 0.7, H_2); 6.20 (ddtt, 1H, J=17.7, 15.4, 4.4, 0.7, H_5); 6.46 (m, 1H, J=15.4, 11.0, 3.3, 1.5, 0.7, H_4); 7.31 (dddd, 1H, J=15.4, 11.0, 1.2 and 0.7, H_3). ^{19}F NMR δ= −218.1. ^{13}C NMR: 51.7 (CO_2CH_3); 81.5 (J=166.4, C_6); 122.5 (J=2.7, C_2); 129.7 (J=12.3, C_4); 135.5 (J=15.8, C_5); 143.0 (J=2.2, C_3); 167.1 (C_1).

(*3E*) methyl-2-fluoro-hexa-3,5-dienoate **20a**; ^{1}H NMR: 5.38 (d, 1H, J=10.5, H_6); 5.57–5.41 (m, 2H, H_6 and H_2); 5.94–5.84 (m, 1H, H_5); 6.11 (dt, 1H, J=15.8 and 1.7, H_4); 6.93 (ddd, 1H, J=18.6, 15.8, 4.4, H_3). ^{19}F NMR δ= −179.3. ^{13}C NMR: 51.8 (CO_2CH_3); 90.8 (J=171.5, C_2); 119.3 (J=11.2, C_6); 121.4 (J=10.3, C_4); 133.4 (J=20.4, C_5); 143.5 (J=20.9, C_3); 166.2 (C_1).

Yield: 73% (**22E:22Z**=72:28); (*3E*) 2fluoro-5-yn-3-undecene **22E**; ^{1}H NMR: 0.90 (t, 3H, J=7.0, H_{11}); 1.41 (dd, 3H, J=23.5 and 6.4, H_1); 1.60–1.40 (m, 8H); 5.07 (dqtd, 1H, J=47.9, 6.4, 1.2, H_2); 5.73 (dm, 1H, J=15.9, H_4); 6.05 (ddd, 1H, J=15.9, 13.7, 6.0, H_3). ^{19}F NMR δ= −169.3. ^{13}C NMR: 14.0 (C_{11}); 19.4, 21.1 (J=24.1, C_1); 22.2, 28.33, 31.07, 77.8 (J=2.4, C_5 or C_6); 89.2 (J=165.1, C_2); 92.6 (J=2.6, C_5 or C_6); 112.2 (J=13.6, C_4); 140.0 (J=18.4, C_3).

(*3Z*) 2-fluoro-5yn-3-undecene **22Z**; ^{1}H NMR: 0.90 (t, 3H, J=7.0, H_{11}); 1.43 (dd, 3H, J=23.6 and 6.4, H_1); 5.55 (dqt, 1H, J=48.4 and 6.3, H_2); 5.59 (dm, 1H, J=10.8, H_4); 5.90 (dt, 1H, J=10.8 and 8.1, H_3). ^{19}F NMR δ= −169.5. ^{13}C NMR: 14.0 (C_{11}); 19.5, 20.9 (J=25.0, C_1); 22.1, 28.30, 31.06, 75.7 (J=4.4, C_5 or C_6); 87.8 (J=159.2, C_2); 97.4 (J=1.9, C_5 or C_6); 112.0 (J=12.0, C_4); 140.1 (J=21.9, C_3). HRMS (mixture of **22E** and **22Z**): found: 168.131 $C_{11}H_{17}F$ requires 168.1314.

Acknowledgements

We thank Dr. J. Doyon for fruitful discussions and the French–Algerian cooperation program for financial support.

References

[1] R. Filler, Y. Kobayashi, Biomedicinal Aspects of Fluorine Chemistry, Elsevier Amsterdam, 1982.
[2] J. Mann, J. Chem. Soc. Rev. 16 (1987) 381.
[3] J.T. Welch, Tetrahedron 43 (1987) 3123.
[4] J.T. Welch, S. Eswarakrishnan, Fluorine in Bioorganic Chemistry, Wiley-Interscience, New York, 1991.
[5] J.T. Welch (Ed), Selective Fluorination in Organic and Bioorganic Chemistry, ACS symposium series 456, Washington DC, 1991.
[6] R.H. Abeles, T.A. Alston, J. Biol. Chem. 265 (1990) 16705.
[7] T. Hayashi, V.A. Soloshonok, Tetrahedron Asymmetry 5 (1994) 1.
[8] I. Ojima, J.R. McCarthy, J.T. Welch (Eds.), Biomedical Frontiers of Fluorine Chemistry, ACS symposium series 639, Washington DC, 1996 and references cited therein.
[9] D. O'Hagan, H.S. Rzepa, Chem. Commun., (1997) 645.
[10] J.A. Wilkinson, Chem. Rev. 92 (1992) 505.
[11] P. Bravo, G. Resnati, Tetrahedron Asymmetry 1 (1990) 661.
[12] G. Resnati, Tetrahedron 49 (1993) 9385.
[13] O.A. Mascaretti, Aldrichim. Acta 26 (1993) 47.

[14] M.A. Tius, Tetrahedron 51 (1995) 6605.
[15] D.M. Grée, C.J.M. Kermarrec, J.T. Martelli, R. Grée, J.P Lellouche, L.J. Toupet, J. Org. Chem. 61 (1996) 1918.
[16] C. Kermarrec, V. Madiot, D. Grée, A. Meyer, R. Grée, Tetrahedron Lett. 37 (1996) 5691.
[17] W.J. Middleton, J. Org. Chem. 40 (1975) 574.
[18] B.E. Cross, P. Hendley, J. Chem. Soc. Perkin Trans. 1 (1975) 2523.
[19] J.H. Bateson, B.E. Cross, J. Chem. Soc. Perkin Trans. 1 (1974) 2409.
[20] R.E. Banks, B.E. Cross, J. Chem. Soc. Perkin Trans. 1 (1977) 512.
[21] B.E. Cross, A. Erasmuson, P. Filippone, J. Chem. Soc. Perkin Trans. 1 (1981) 1293.
[22] T. K Bannai, T. Toru, T. Oba, T. Tanaka, N. Okamura, K Watanabe, A. Hazato, S. Kurozumi, Tetrahedron 39 (1983) 3807.
[23] E. Ohshima, S. Takatsuto, N. Ikekawa, H.F. Deluca, Chem. Pharm. Bull. 32 (1984) 3518.
[24] T. Ando, N. Koseki, I. Yashuhara, N. Matsuo, T. Ishiwatari, Biosci. Biotechnol. Biochem. 56 (1992) 1581.
[25] Y.L. Li, K. Luthman, U. Hacksell, Tetrahedron Lett. 33 (1992) 4487.
[26] J.K. Sutherland, R.G. Whitehead, G.M. Davies, J. Chem. Soc. Chem. Commun., 1993, p. 464.
[27] G. Neef, G. Ast, G. Michl, W. Schwede, H. Vierhufe, Tetrahedron Lett. 35 (1994) 8587.
[28] P. Marwah, J.B. Thoden, D.R. Powell, H.A. Lardy, Steroids 61 (1996) 453.
[29] S. Kaneko, M. Shikano, T. Katoh, S. Terashima, Synlett, 1997, p. 447.
[30] R.L. Grée, J.P. Lellouche, in V.A. Soloshonok (Ed.), EPC Synthesis of Fluoro-Organic Compounds: Stereochemical Challenges and Biomedicinal Targets, Wiley, Chichester, UK, in print.
[31] D.F. Shelhamer, A.A. Briggs, B.M. Miller, J.M. Prince, D.H. Scott, V.L. Healey, J. Chem. Soc. Perkin Trans. 2 (1996) 973.
[32] F. Tellier, R. Sauvetre, Tetrahedron Lett. 56 (1995) 4223.
[33] Munyemana, PhD Thesis, University of Louvain La Neuve, Belgium, 1991.
[34] B. Ernst, T. Winkler, Tetrahedron Lett. 30 (1989) 3081.
[35] B. Ernst, A. De Mesmaeker, B. Wagner, T. Winkler, Tetrahedron Lett. 31 (1990) 6167.
[36] J.M.D. Tronchet, A.P. Bonenfant, Helv. Chim. Acta 64 (1981) 2322.
[37] A. Colens, L. Ghosez, Nouv. J. Chim. 1 (1977) 371.
[38] Y. Matsumura, T. Shimada, T. Nakayama, M. Urushira, T. Asai, Y. Morizawa, A. Yasuda, Tetrahedron 51 (1995) 8771.
[39] F. Benayoud, G.D. Hammond, Chem. Commun., (1996) 1447.
[40] F. Benayoud, D.J. De Mendonca, C.A. Digits, G.A. Moniz, T.C. Sanders, G.B. Hammond, J. Org. Chem. 61 (1996) 5159 and references therein.