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Rearrangement routes to selectively fluorinated compounds

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Abstract

Fluoroallylic alcohols are easy to synthesise by a variety of routes using one or two carbon fluorinated building blocks. Sigmatropic rearrangement then transforms these intermediates into species in which the fluorine atom (or atoms) is borne on an sp^3-hybridised carbon. Alternatively, allylic alcohols can be transformed into fluorinated vinyl ether derivatives; rearrangement then affords products in which the fluorine atoms occupy a different and complementary location with respect to a carbonyl function.

Keywords: Fluorinated allylic alcohols; Sigmatropic rearrangement; Synthetic approaches; Building blocks

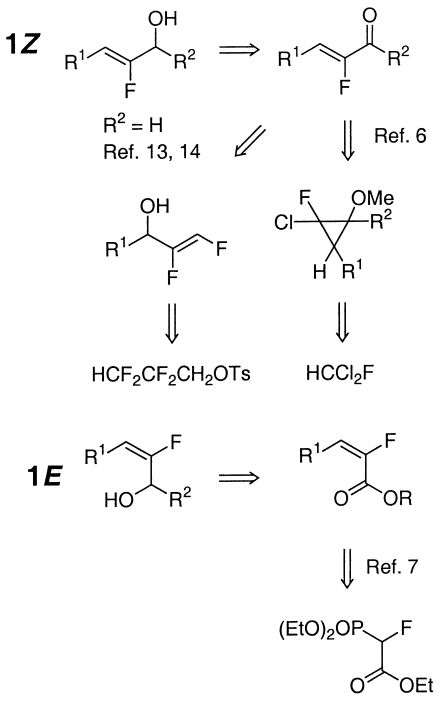
1. Introduction

Sigmatropic rearrangements are most attractive reactions for the interconversion of selectively fluorinated substrates and for the elaboration of simple and readily-available fluorinated building blocks. With correct design of the rearrangement system, fluorine atom substituent effects can be exploited to the full, allowing thermal rearrangements to occur at unusually low temperatures, or, providing a driving force for changes in the equilibrium position.

Rather than attempting to catalogue all the different classes of rearrangement in which transformations of fluorinated compounds appear [1], this short review will attempt to show the strategic importance of rearrangement reactions within the canon of organofluorine chemistry, systematising on the location of the fluorine atoms in the rearrangement template, and choosing convenient entry points to the chemistry. Rearrangements which have found very few synthetic applications (Cope and variants, vinylcyclopropane and divinylcyclopropane rearrangements) will not be treated at this stage nor will polar rearrangements or reactions which afford apparent rearrangement products via S_N2'-type mechanisms [2–4].

2. On the potential of β-fluoroallylic alcohols

Recently, this topic was reviewed admirably by Allmendinger [5], one of the main contributors to the area. The β-fluoroallylic alcohols are fairly accessible (Scheme 1) from simple enol ethers using the alkoxycyclopropane ring-opening chemistry of Schlosser [6] (to afford *Z*-alkenyl stereoisomers 1*Z*), or commonly, from carbonyl compounds using chemistry described initially by Machleidt [7] in a Wadsworth–Horner–Emmons variant [8–12] that affords the *E*-congeners 1*E*. Recent approaches by Funabiki [13,14]



Scheme 1

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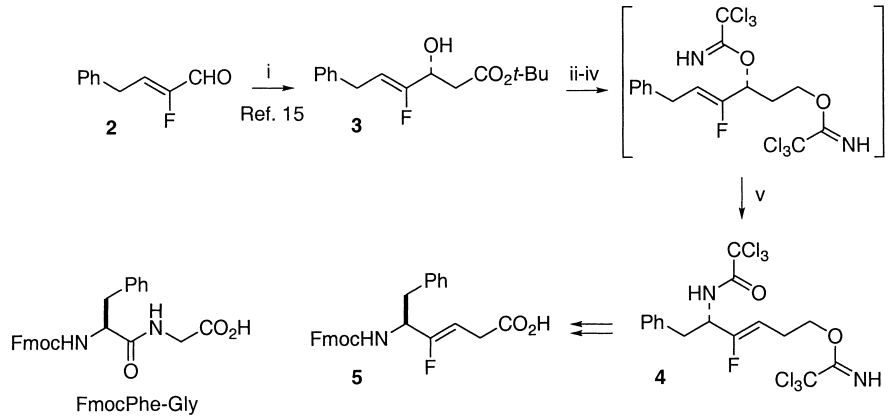
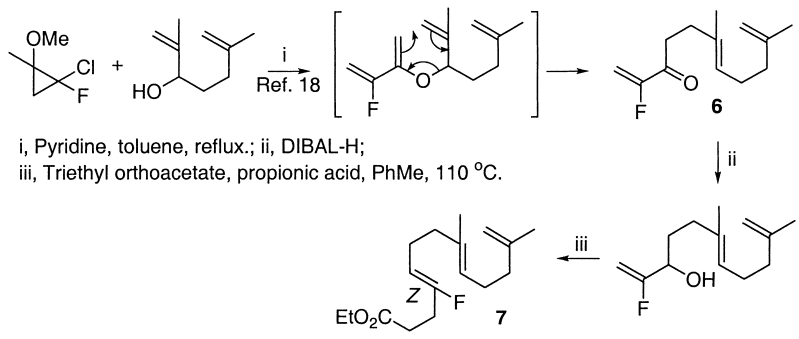


i, $Cp(DAG\text{-}O)_2TiOC(^tBuO)=CH_2$, toluene, -70 °C, 80 %, ee = 93 %; ii, $LiAlH_4$, ether, 78 %; iii, cat. NaH, hexane, THF; iv, Cl_3CCN, ether; v, xylene, 140 °C, 73 % (from **3**).

Scheme 2

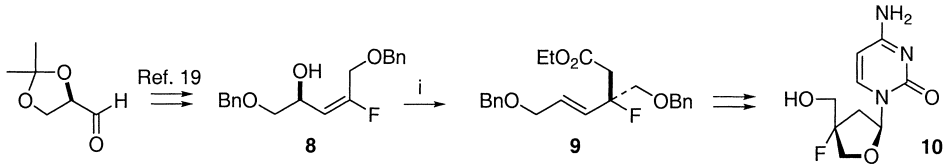
employ 2*H*-tetrafluoropropanol in a route which exploits a metallated fluoroenol tosylate intermediate and lead to fluorinated acrylaldehydes of *Z*-configuration (selective 1,2-reduction affords the alcohols) so a degree of stereocomplementarity exists. Direct Overman rearrangement has been used to install the amino group in a route to an interesting class of peptide isosteres, wherein the fluoroalkene mimics the rather rigid and highly polarised amide function [15–17]. For example, Scheme 2 shows the asymmetric synthesis of a Phe-Gly dipeptide isostere. Fluoroenal **2** was prepared by Schlosser methodology and taken through an asymmetric aldol sequence to afford allylic alcohol **3** in high enantiomeric purity. Reduction to the diol set the stage for immediate rearrangement in refluxing xylene with efficient chirality transfer to afford **4** which could be elaborated to the Fmoc-protected dipeptide isostere **5**. Reaction conditions for the rearrangement are typical for secondary allylic alcohols and therefore do not appear to be affected by the presence of the fluorine atom substituent.

Rearrangements that form C–C bonds have also been published; these relocate the fluoroalkenyl group from a terminal position to a site within a chain while controlling configuration, an attractive feature when the difficulties of stereoselective fluoroalkene synthesis are considered. However, there are limitations therein; the chair-like transition states populated by Claisen rearrangements almost invariably dispose alkyl substituents in pseudo-equatorial environments with (in these cases) a *Z*-configured alkene being formed. Nevertheless, the method has its uses; for example, Johnson and co-workers [18] were able to use eponymous Claisen rearrangements to construct complex polyenes containing a fluoroalkenyl unit of the correct configuration for use in their studies of biomimetic cascade cyclisations. In Scheme 3, epoxycyclopropane ring opening occurs in the presence of a dienol which undergoes Claisen rearrangement to afford complex fluoroenal **6**. Reduction and orthoester Claisen rearrangement then affords fluorotrienoate **7** in which the new alkenyl group configuration is controlled accurately. A recent publication by Chu and co-workers used the Johnson-Claisen rearrangement to synthesise 3′-fluoro-apionucleosides (Scheme 4) [19]. Allylic alcohol **8** was prepared by standard means, and rearranged to afford **9** in high enantiomeric purity. Novel nucleosides such as **10** were synthesised from this pivotal intermediate. It should be noted that the fluorine atom has been located at a tertiary stereogenic centre with control of configuration, a task which is difficult to complete by other methods.



i, Pyridine, toluene, reflux.; ii, DIBAL-H;
iii, Triethyl orthoacetate, propionic acid, PhMe, 110 °C.

Scheme 3



i, Triethyl orthoacetate, propionic acid, 130 °C, 7hr.

Scheme 4

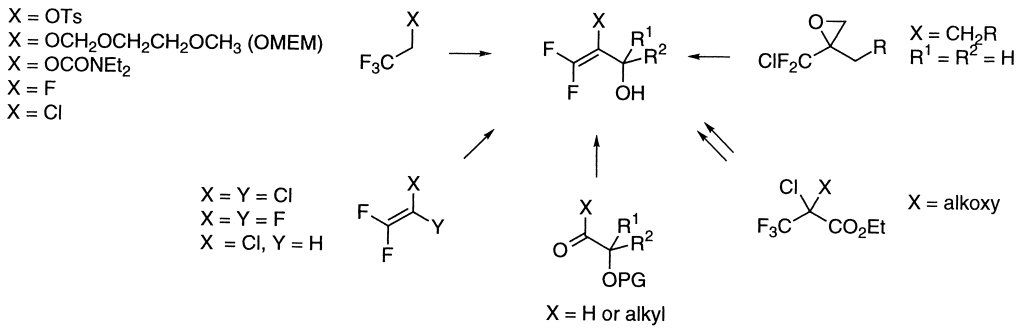
3. γ-Difluoroallylic alcohols: versatile intermediates

3.1. Using γ-fluoro- and γ,γ-difluoroallylic alcohols

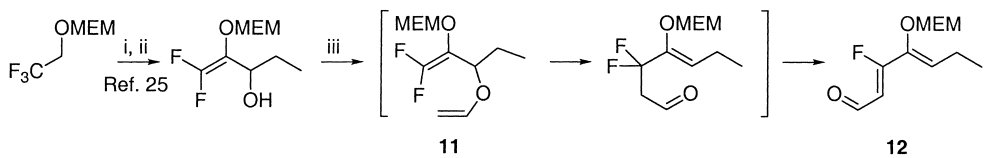
One of the most powerful and concise routes to a wide range of highly-functionalised gem-difluorocompounds involves the sigmatropic rearrangement of a γ,γ-difluoroallylic alcohol. These starting materials are relatively easy to synthesise from metallated fluoroalkenes [20], by dehydrofluorination of trifluoroethyl ethers [21], or using ylide methods from chlorodifluoromethyl ketones. Scheme 5 shows the range of species available via two-carbon chain extension using vinyl organometallic reagents from fluoroalkenes or trifluorethanol derivatives, or by difluoromethylenation as described initially by Burton [22] and reviewed recently [23], and improved by Motherwell [24]. An epoxide ring-opening route also allows chlorodifluoromethylketones to be used directly, releasing products in which the α-carbon of the alkene bears two carbon substituents [25].

Claisen rearrangements have been carried out by a number of groups, including our own [26]. Basing our investigation on initial contributions by Taguchi [28], Jarvi [29] and Kumadaki [30], we have confirmed that β,β-difluorinated carbonyl derivatives can be synthesised generally and rapidly from difluoroallylic alcohols under fairly mild conditions (Table 1). This chemistry complements the well known Reformatsky reaction of ethyl bromodifluoroacetate, and the chemistry of Lang and others (Section 4.1), wherein the two fluorine atoms are located α-to a carbonyl function in the rearrangement products.

The rearrangements appear to be assisted by the rehybridisation from sp^2 to sp^3 of the CF_2 centre though there appear to be no reported reaction kinetics in the literature for compounds of this type. A striking example is shown in Scheme 6; normally, the Dauben-Dietsch Claisen is carried out in two steps [27]. Allyl vinyl ether formation occurs under mild conditions with mercury(II)ion catalysis; a more rigorous thermic regime (150–250°C) then follows isolation. However, in the case of **11**, rearrangement occurred in situ at a low temperature (<40°C) and was followed by dehydrofluorination to afford dienal **12**. High reactivity was also reported by Jarvi and co-workers [29]. In contrast, when competition between rearrangement sites was possible within the same molecule, as in **13** [31], both possible reactions ran at similar rates and two amides **14** and **15** were isolated; obviously, this substrate is complicated by the presence of the oxygen function but the result suggests that the rehybridisation effect is not expressed strongly at the (presumably early with respect to C–C bond making)



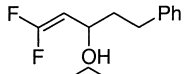
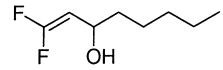
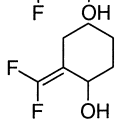
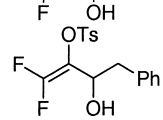
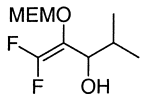
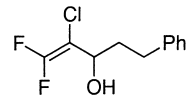
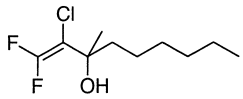
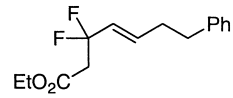
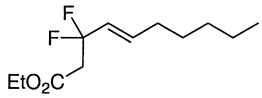
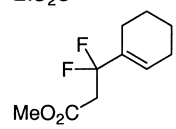
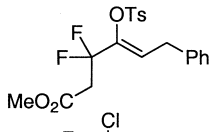
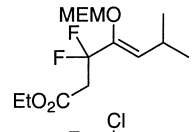
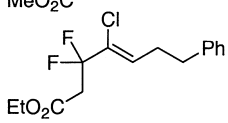
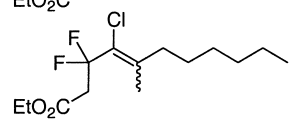
Scheme 5



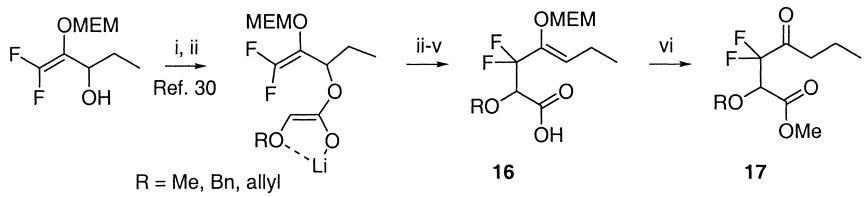
i, LDA, THF, -78 °C; ii, EtCHO, iii, $Hg(OAc)_2$, Ethyl vinyl ether, reflux.

Scheme 6

Table 1

Entry	Substrate	Conditions[a]	Product	Yield (%)
1 [28]		TEOA, PhMe 110°C, 5 h		76
2 [28]		TEOA, PhMe 110°C, 5 h		37
3 [28]		TMOA, PhMe 110°C, 5 h		78
4 [29]		TEOA, neat 120°C, 1.5 h		84
5 [26]		TEOA, neat 140°C, 0.75 h		64
6 [30]		TEOA, neat 140°C, 6 h		90
7 [30]		TEOA, neat 140°C, 8 h		15

[a] All reactions required a propionic acid catalyst and the appropriate alcohol was allowed to distill from the reaction mixture.

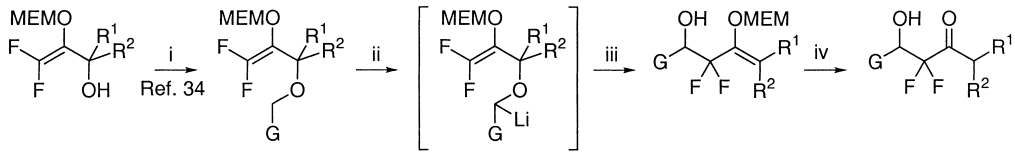


i, $ROCH_2CO_2H$, EDC, DMAP, DCM, 0 °C, 18 hr; ii, LDA, THF, -78 °C; iii, TMSCl, -78 °C; iv, Warm to r.t.; v, H_3O^+; vi, $SOCl_2$, MeOH, 0 °C.

Scheme 7

transition state. More reactive silyl ketene acetals were generated from the enolates of the corresponding alkoxyesters (Scheme 7) at low temperature (−78°C); rearrangement then occurred on warming to afford **16** which could be esterified and deprotected in one pot to afford the difluorinated ketoesters **17** [32]. In the case of dienol **13**, we found that rearrangement of the derived silyl ketene acetal only occurred on the non-fluorinated allylic fragment to afford acid **18**, and that cleavage of the enol acetal followed simply upon standing in chloroform and ketoacid **19** was isolated [33]. The basis of regioselectivity in the Claisen rearrangement of these and related dienyl systems is something we are attempting to elucidate.

A significant limitation upon ester enolate-dependent rearrangements arises as a consequence of the two fluorine atom substituents. Ester enolates fragment readily to ketenes and alkoxide anions, and the inductive electron withdrawing effect of the two fluorine atom substituents would be expected to stabilise the alkoxide anion lowering the barrier to ketene formation. In contrast to the preliminary result reported by Jarvi [29] for ester **20**, we found that Ireland procedures (conditions from [29]) could not be used to rearrange our alcohols; ester enolates only existed for long enough to be trapped when a stabilising chelating substituent was present. Zinc enolates have also been used directly in [3,3]-rearrangements following the procedures developed by Kazmaier [34], opening a route to β,β-difluorinated-γ-oxoamino acids **21**, an unusual class of natural product analogue with relatively unexplored potential [35].



R^1, R^2 = H or alkyl
G = Ph, $CH{=}CH_2$, $C(Me){=}CH_2$, C≡CTIPS
X = Cl or Br
TIPS = Triisopropylsilyl

i, GCH_2X, NaOH, PTC; ii, LDA, THF, -78 °C; iii, Warm to -30 °C; iv, $SOCl_2$, MeOH, 0 °C.

Scheme 8

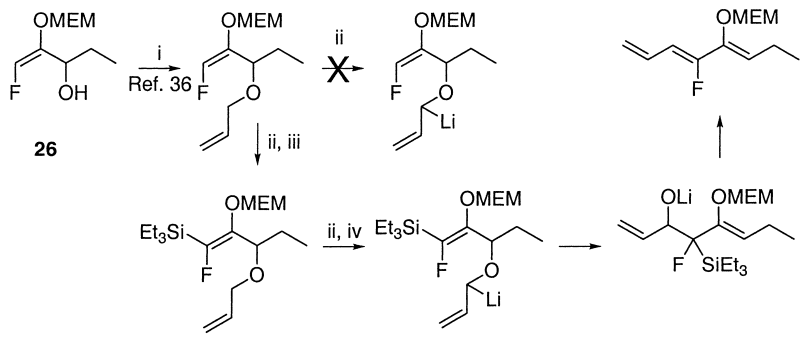
The [2,3]-Wittig rearrangement also shows considerable power (Scheme 8): we were able to generate a range of difluoroalcohols with great potential for further oxygenation [36,37]. In this frontier orbital controlled rearrangement, the low LUMO energy of the fluorinated allylic component in **22** resulted in exclusive [2,3]-Wittig rearrangement to **23**. Subjecting these products to [methoxy(ethoxy)]methyl- or MEM-cleavage affords aldol-type species, assembled from trifluoroethanol, a simple aldehyde or ketone and an allylic halide.

Other rearrangements have formed bonds between a CF_2 centre and sulfur or phosphorus [38–40]; for example irreversible Evans–Mislow rearrangement to afford sulfoxides such as **24** occurred readily when our difluoroallylic alcohols were treated with phenylsulfenyl chloride. The reverse reaction could not be induced by exposure to triethylphosphite. Phosphine oxides such as **25** could be prepared by an analogous reaction. The full potential of these heteroatomic [2,3]-rearrangements and their products is not known.

Z-Monofluoroallylic alcohols, for example **26**, can be prepared stereoselectively from the difluoro-congeners by reduction and [3,3]-rearrangements have been reported, under slightly more forcing conditions than those used for the more highly fluorinated species. Our attempts to perform highly stereoselective [2,3]-Wittig rearrangements (Scheme 9) were unsuccessful because of competitive metallation at the exposed vinylic position [41]; blocking the acidic position with a triethylsilyl-group allowed rearrangement to proceed, though we isolated an unstable triene formed in a subsequent Peterson elimination. Attempts to run chelated ester enolate [3,3]-rearrangements on the monofluoroalcohols have to data been unsuccessful, even though the methylene protons in the ester should be considerably more acidic than the allylic ethereal methylene protons in the [2,3]-Wittig substrate. However when the vinylic metallation site is blocked with an alkyl group as in **27**, highly stereoselective rearrangements can be induced (Scheme 10). We used our published chemistry of HCFC-133a [42] and ideas of Normant to assemble the alcohols stereoselectively in one pot. Derivatisation and deprotonation followed and a range of products which all contain a single fluorine atom at a tertiary centre have been prepared [43].

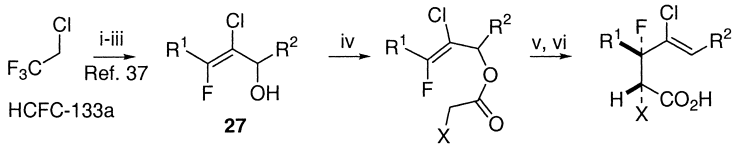
3.2. Rearrangements of perfluoroalkyl-substitututed systems

The two systems, represented by **28** and **29** are very readily available, and are, in principle interconvertible (Scheme 11). Whereas the latter is being exploited in powerful rearrangement chemistry, the potential of the



i, $H_2C{=}CHCH_2Br$, NaOH, Bu_4NHSO_4; ii, n-BuLi, THF, -78 °C; iii, Et_3SiCl; iv, Warm to -30 °C.

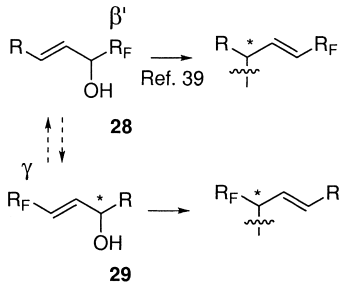
Scheme 9



R^1 = Me or Benzyl
R^2 = alkyl or aryl
X = alkoxy

i, n-BuLi, THF, -78 °C; ii, R^2CHO; iii, R^1Li; iv, XCH_2COCl; v, LDA, THF, -78 °C; vi, Me_3SiCl, -78 °C then warm to 0 °C.

Scheme 10



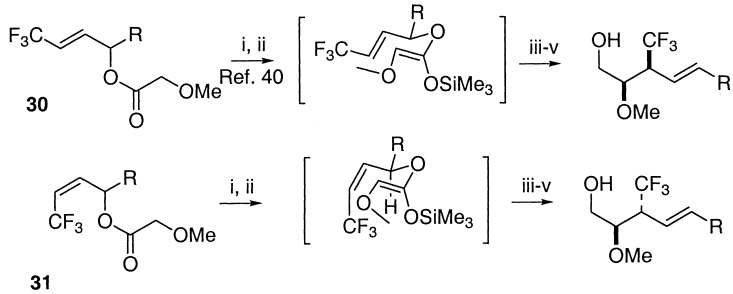
Scheme 11

former for the chain extension of perfluoroalkanes does not appear to be a well-worked theme [44].

3.3. Fluorination at the γ-position

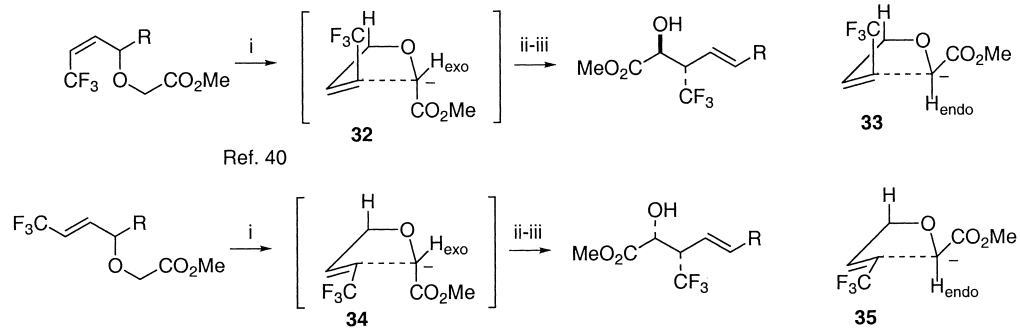
The system can be entered from the corresponding perfluoroalkynyl anion addition to an aldehyde; double bond configuration can then be controlled by Lindlar or complex metal hydride reduction. Products of rearrangements of these systems contain a perfluoroalkyl group at an sp^3 stereogenic centre, or as a double bond substituent and high levels of control and degree of flexibility are possible. The former category have been studied in depth by the Tokyo Institute of Technology group. The rearrangements of the γ-trifluorinated alcohols described by Kitazume and Yamazaki [45] reveal the bulk of the trifluoromethyl group and the power of the electron withdrawing effect it exerts. Silyl ketene acetal rearrangements (Scheme 12) occurred with the usual sense of diastereoselectivity (*E*-alcohol (**30**) to *syn* product (>99 : 1 *syn* : *anti*) and *Z*-alcohol (**31**) to *anti* product (up to 98 : 2 *anti* : *syn*)) indicating that the trifluoromethyl group can occupy pseudo-axial and pseudo-equatorial orientations without excessive non-bonded repulsions being incurred. However, non-bonded repulsions were more significant in the smaller ring [2,3]-Wittig transition state (Scheme 13). Highly selective *Z* to *anti* induction (>99 : 1 *anti* : *syn*) was observed via proposed transition state **32** in which the C–CF_3 and C–CO_2Me bonds are close to antiperiplanar; diastereoisomeric transition state **33** is expected to be higher in energy. However, the E to *syn* reaction was considerably less stereoselective; the energy of transition state **34** may be raised closer to that of **35** by the presence of a *gauche* repulsion between the trifluoromethyl and methoxycarbonyl groups, lowering the energy difference, and thus the selectivity, between them.

Rearrangement procedures were deployed to achieve efficient transmission of chirality from resolved secondary trifluoroallylic alcohols. Similar results were reported for Eschenmoser and Johnson variant rearrangements using similar alcohols [46]. Indeed both *E*- and *Z*-diastereoisomers underwent rearrangement with efficient chirality transfer via these simpler procedures. These represent an efficient strategy for the synthesis of enantiomerically pure compounds that contain a trifluoromethyl group. By analogy, more extended perfluoroalkyl groups could be located at secondary stereogenic centres using this approach though steric bulk must be considered. In our own chemistry (Scheme 14), we have found that the apparent bulk of

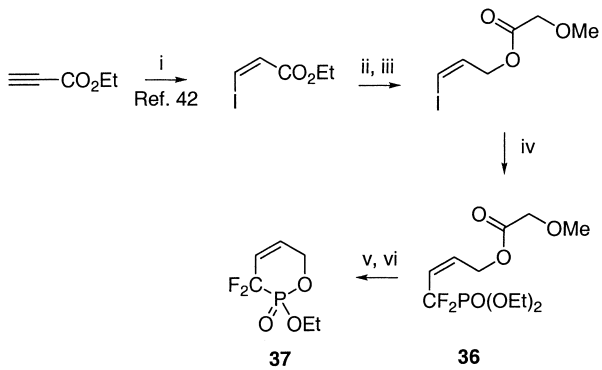


i, LDA, THF, -78 °C; ii, TMSCl, -78 °C; iii, Warm to r.t.; iv, H_3O^+; v, $LiAlH_4$, THF, 0 °C.

Scheme 12



Scheme 13



Scheme 14

the difluoromethylenephosphonato group subverts completely the ability of **36** to attain the cyclic transition states required for [3,3]-rearrangement; enolate generation was followed by fragmentation and formation of cyclic phosphonate **37** in all cases, despite an exhaustive investigation of reaction conditions (more than 30 variations of base, temperature and stoichiometry) [47].

4. Systems with fluorination in the vinylic fragment

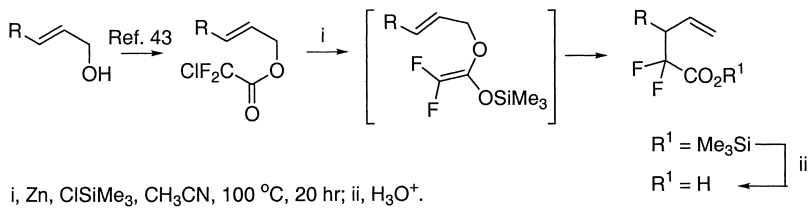
There are extremely direct transformations available for the preparation of fluorinated acid derivatives; the methodology described in this section is attractive because it operates by the facile synthesis of oxygen–carbon bonds and then reorganises through rearrangement avoiding the need for direct C–C bond synthesis to a fluorinated unit, or C–F bond synthesis by fluorination. A high degree of functionality can be installed and stereocontrol can be achieved.

4.1. α,α-Difluorocarboxylic acid derivatives

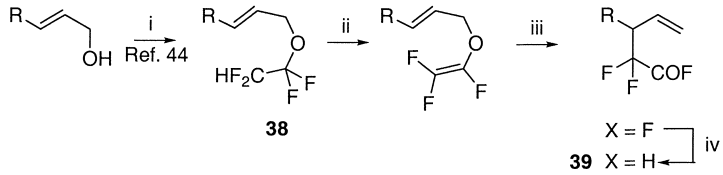
The conversion of simple allylic alcohols to chlorodifluoroacetate esters was followed by exposure to zinc in acetonitrile containing chlorotrimethylsilane in a procedure described by Lang (Scheme 15). The silyl ketene acetals formed in situ underwent the so-called [3,3]-Reformatskii Claisen rearrangement [48] to afford attractive products with enormous potential for further functionalisation. Lang and co-workers made unexplained comments about the instability of the immediate acid products yet it seems surprising that there are no reports of further usage. Products of the same level and pattern of functionality were described by Gelb (based upon initial findings by Normant) [49]; lithium alkoxides of allylic alcohols underwent addition/elimination with tetrafluoroethylene to afford allyl trifluorovinyl ether **38**. Facile room temperature [3,3]-rearrangement followed (Scheme 16) and the immediate acid fluoride product **39** was processed through out to a PLA_2 inhibitor. Again, this method has not been applied by other groups, perhaps less surprisingly in view of problems associated with handling tetrafluoroethylene.

4.2. α-Monofluorinated acids [3,3]-rearrangement

Related chemistry was described recently by the group of Sauvêtre and Tellier (Scheme 17) [50]. The trifluorvinylsi-

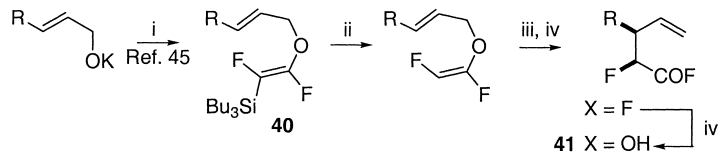


Scheme 15



i, 5 % NaH, C_2F_4, THF, -5 °C; ii, n-BuLi, THF, -60 °C; iii, Warm to r.t.; iv, H_2O, 25 °C.

Scheme 16



i, CF_2=CFSiBu_3, THF, -90 °C; ii, F^- cat., -80 °C; iii, Warm to -30 °C; iv, H_2O.

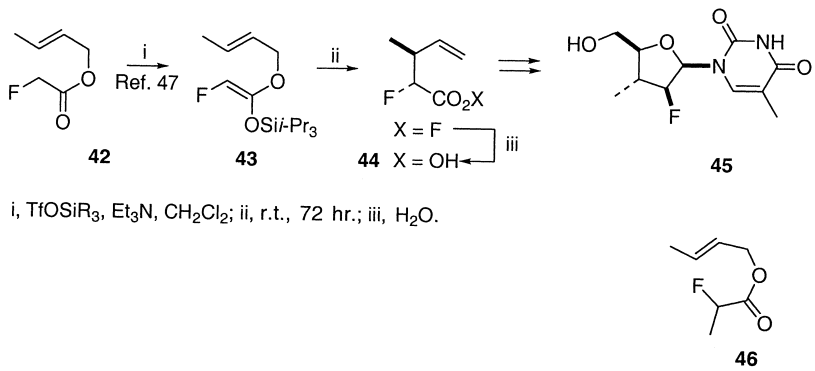
Scheme 17

lanes are readily available and the presence of a trialkylsilyl group activates the process of addition/elimination allowing the smooth development of allyl vinyl ether **40** with reasonable control over configuration. Desilylation (with TBAF) then sets the stage for a particularly facile (−60°C!) rearrangement affording an α-fluorinated acid fluoride **41** in which the relationship between the fluorinated stereogenic centre and the adjacent methine was controlled to a potentially useful level. A chair transition state predicts the formation of the major diastereoisomer shown from silane **40**. This chemistry echoes much earlier studies by Nakai in which a phenylsulfinyl group serves as the activator [51]. Fluoride loss terminated those sequences but in principle, that approach also exploits the accelerative effect of fluorine atom substitution upon rearrangements of this type.

Perhaps the most powerful methodological developments in this area were made by Welch (Scheme 18); fluoroacetate esters **42** were used to address α-monofluorinated acids at different levels of substitution. Control of enolate configuration is critical to the whole undertaking and the highest levels of control were achieved with the bulky triisopropylsilyl triflate reagent which afforded the *Z*-silylketene acetal **43** [52]. Rearrangement through a chair transition state then correlates this relationship with that observed between the two new stereogenic centres in the product **44**. The rearrangements of esters of *Z*-allylic alcohols were most stereoselective but even the rearrangements of the *E*-congeners afforded higher levels of diastereoselection than the methodology of Sauvêtre and Tellier [50]. Asymmetric versions are available (using the C_2-symmetric *trans*-(2R,5R)-2,5-dimethyl-pyrrolidine auxiliary) [53] and Welch and co-workers applied the methodology successfully in syntheses of nucleoside analogues **45** [54]. At a higher level of substitution, the corresponding propionates **46** failed to rearrange with control of internal asymmetric induction so that the location of a fluorine atom substituent at a tertiary stereogenic centre cannot be addressed by this method.

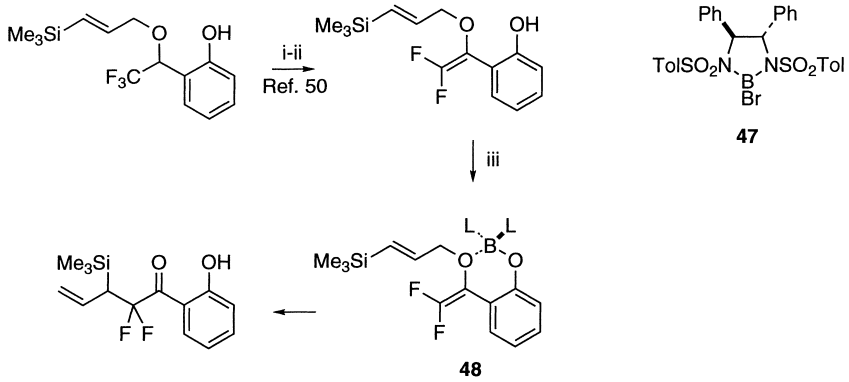
4.3. α,α-Difluoroketones via [3,3]-rearrangement

Seminal work was reported by Jarvi et al.; indeed, their 1985 paper delineated an approach in which allyl trifluoroethyl ethers could be converted to allyl vinyl systems by dehydrofluorination/metallation with the incorporation of

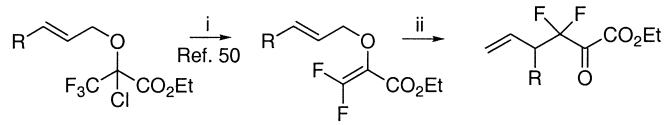


i, $TfOSiR_3$, Et_3N, CH_2Cl_2; ii, r.t., 72 hr.; iii, H_2O.

Scheme 18



Scheme 19



Scheme 20

different substituents at the α′-position. The main weakness of this method lies in the inconvenience of using anhydrous trifluoroacetaldehyde. Rearrangement occurred under extremely mild conditions though once again, there were no reports of subsequent use of this chemistry until a recent paper by the Taguchi group who developed a rare asymmetric catalytic method (Scheme 19) [55]. Locating chiral Lewis acid catalyst **47** in the binding site in **48** allowed the enantiotopic faces of the allylic system to be distinguished. Though the *ee* for the most selective reaction was relatively low and it was not clear how the educt could be processed in a versatile manner, this report represents a current landmark in the area. Shi has also used trifluoromethyl precursors to launch Claisen rearrangements in a concise route to difluorinated unsaturated ketoacids (Scheme 20) [56].

5. Conclusion

Rearrangement chemistry as described in this article represents a flexible and strategically powerful tool which can be used to synthesise a range of mono- and difluoro-compounds from simple and often readily-available starting materials. High levels of functionality can often be achieved yet there are relatively few published target syntheses that use the methods described herein. Significant achievement may be expected in the future.

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