

# Polyfluorovinyl lithium reagents and their use in synthesis

Paul L. Coe\*

School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

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## Abstract

The use of polyfluorovinyl lithium reagents in synthesis since their original discovery almost simultaneously by Seyferth and Tarrant and their development by Normant is reviewed. More recent developments in the field using CFC replacements as starting materials has given a new impetus to the use of these important reagents as building blocks for the development of new materials. These new reactions are also reviewed. © 1999 Elsevier Science S.A. All rights reserved.

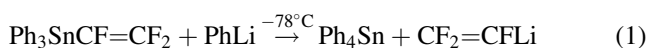
*Keywords:* Fluorovinyl lithium reagents; Reactions; New methodology; CFC replacements; Solvent effects; Trifluorovinyl group reactions

## 1. Introduction

With the increasing need for methodology for the regio and stereospecific introduction of fluorine into compounds with potential biological activity the use of fluorovinyl groups has for some time been of interest, particularly in the light of their ready manipulation to other functions by addition/elimination, cyclisation, hydrolysis and rearrangement reactions. This review will explore the generation and reactions of unstabilised polyfluorovinyl lithium reagents and some of the down stream reactions of the products from this chemistry.

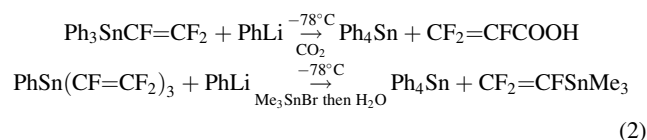
## 2. Discussion

The first reported synthesis of trifluorovinyl lithium was by Seyferth et al. [1] who showed the reaction of phenyl lithium with tris (trifluorovinyl)phenylstannane:



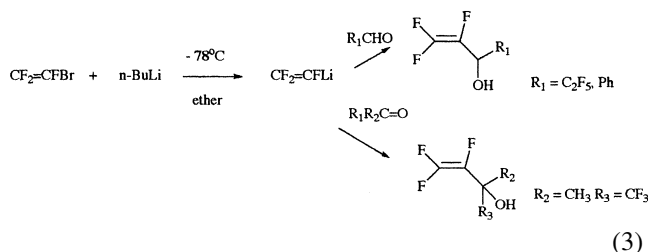
Although this work was pioneering as a route to trifluorovinyl lithium it was clearly very cumbersome and expensive. In this work the authors suggested that the reagent was stable in pentane at  $-40^\circ\text{C}$  but rapidly decomposed at  $0^\circ\text{C}$ . The stability of the reagent in ether even at  $-78^\circ\text{C}$  appeared to be very low (see below). Nevertheless, using this method

it was possible to obtain new stannanes and also to prepare trifluoroacrylic acid:

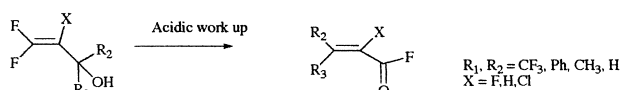


The first practical synthesis of trifluorovinyl lithium from the reaction of lithiumalkyls with trifluorovinyl bromide was reported by Tarrant et al. [2], who also showed that it was possible to obtain products derived from the reagent. At this stage the potential instability of the lithium reagent was recognised in that there is a very strong possibility of lithium fluoride elimination leading initially to alkynes which may then react further. Tarrant also carried out a more detailed study than Seyferth had done and showed that there were a number of factors involved in obtaining a good yield of product. Firstly, he showed that at  $-78^\circ\text{C}$  the reagent in ether solution is stable for 6 h without significant loss of yield and even after 24 h there was only a 10% fall in yield. At  $-27^\circ\text{C}$  the reagent was much more unstable, but a good yield of product could be obtained by consecutive addition of small aliquots of the alkyl lithium reagent and then the substrate. Even at  $0^\circ\text{C}$  using the consecutive addition procedure reasonable yields were obtained. It was also found in all cases that the more dilute the solution the more stable was the reagent at a given temperature. Using this procedure a number of trifluorovinyl-substituted compounds were formed:

\*Tel.: +44-121-414-4360; fax: +44-121-414-4403.

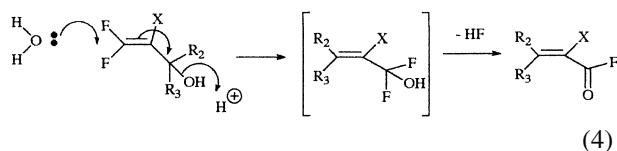


In the course of this work Tarrant et al. [3] discovered two important features of trifluorovinyl-substituted compounds. Firstly, they were very susceptible to hydrolysis:

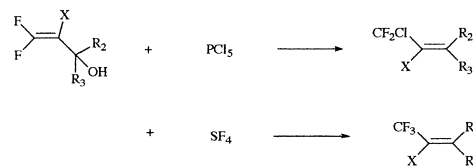


See Table 1

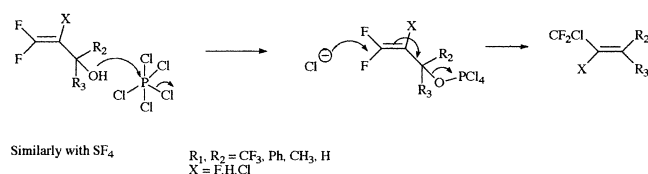
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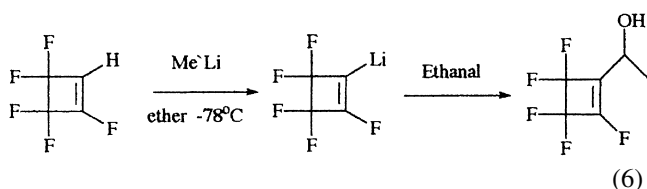
Secondly, some interesting rearrangements occurred on reaction with some Lewis acids:



via



Following the work of Stephens and coworkers [4], who showed that 1H-pentafluorocyclobutene reacted with methyl lithium in a standard metallation reaction, gave the corresponding lithium:



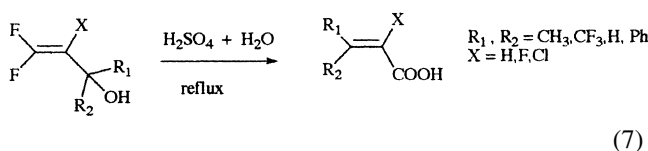
Tarrant investigated the reactions of polyfluoro and polyfluorohaloethenes, all of which contained at least one hydrogen atom, with butyl lithium in ether at  $-100^\circ\text{C}$ . These reactions afforded a range of new polyfluorovinyl lithium reagents and represented the next major advance in

Table 1

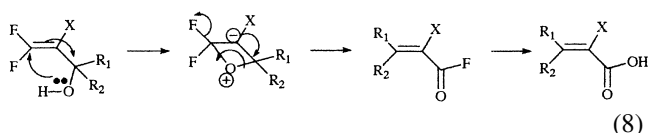
Reactions of fluoroalkenes with *n*-butyl lithium and carbonyl compounds

Alkene	Carbonyl compound	Product
CF <sub>2</sub> =CHF	CH <sub>3</sub> COCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=CFCOOH
CF <sub>2</sub> =CHF	CF <sub>3</sub> COCH <sub>3</sub>	(CF <sub>3</sub> ) <sub>2</sub> C(OH)CF=CF <sub>2</sub>
CF <sub>2</sub> =CHCl	CH <sub>3</sub> COCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=CClCOOH
CF <sub>2</sub> =CHCl	CH <sub>3</sub> COCF <sub>3</sub>	(CH <sub>3</sub> )(CF <sub>3</sub> )C(OH)CCl=CF <sub>2</sub>
CF <sub>2</sub> =CHCl	CF <sub>3</sub> COCH <sub>3</sub>	(CF <sub>3</sub> ) <sub>2</sub> C(OH)CCl=CF <sub>2</sub>
CF <sub>2</sub> =CHCl	PhCHO	PhCH=CClCOOH
CF <sub>2</sub> =CH <sub>2</sub>	CH <sub>3</sub> COCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C(OH)C <sub>4</sub> H <sub>9</sub>
CF <sub>2</sub> =CHBr	CH <sub>3</sub> COCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C=CHCOOH
CFCl=CHCl	CH <sub>3</sub> COCH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> C(OH)CCl=CClF
CFCl=CHCl	CH <sub>3</sub> COCF <sub>3</sub>	(CH <sub>3</sub> )(CF <sub>3</sub> )C(OH)CCl=CFCl

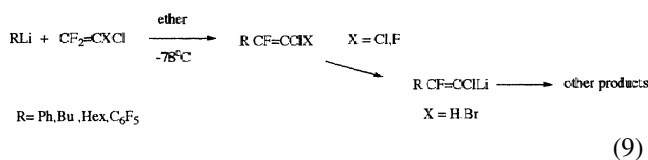
this field. The reactions he studied are shown in Table 1. In most cases the resulting lithium reagent was trapped by reaction with a range of carbonyl compounds, depending on the work up procedure and the structure of the product alcohol, he was able to isolate reasonable yields of either the alcohols or the corresponding carboxylic acid derivatives. These latter resulted from the facile reaction of the fluoro-vinyl function with nucleophiles:



Tarrant and coworkers [5] postulated that an internal allylic reaction with oxyanion formed in the initial reaction was a possible reaction pathway. An alternative, and in the light of more recent results more likely pathway, is a direct attack on the alkene in an S<sub>N</sub>2' reaction as shown below:



The main problem in this work was the availability of starting materials which at that time were difficult to prepare or only available within specialist groups. This situation was eventually resolved by Normant who, following the work of Dixon [6] and our work using pentafluorophenyl lithium [7] which had shown that chlorotrifluoroethene reacted with lithium reagents in ether at  $-80^\circ\text{C}$  by an addition–elimination reaction,

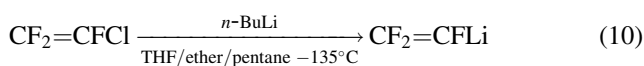


From that he discovered a route to trifluorovinyl lithium from the readily available chlorotrifluoroethene. In our work [7] we had shown that the product composition was depen-

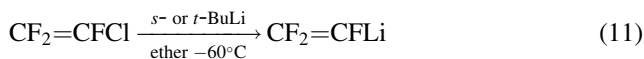
Table 2  
Reaction of trifluorovinyl lithium with carbonyl compounds

Carbonyl Compound	Acid	Derivatives
Acetophenone	2-Fluoro-3-phenylbutenoic acid	Ethyl ester, <i>N,N</i> -diethylamide
Cyclohexanone	2-Fluorocyclohexylidene acetic acid	Ethyl ester
Propanone	2-Fluoro-3-methylbutenoic acid	Acid only
Benzaldehyde	2-Fluoro-3-phenylpropenoic acids	<i>N,N</i> -diethylamide
Hexenal	2-Fluoro-oct-2-enoic acid	<i>N,N</i> -diethylamide
But-2-enal	2-Fluoro-hex-2-enoic acid	Acid only

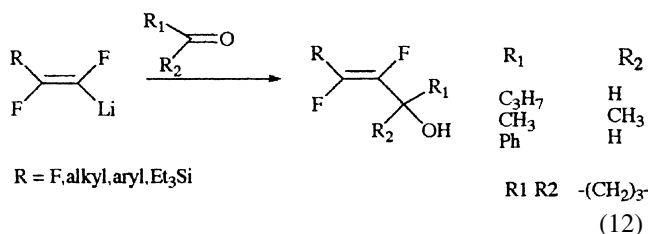
dent on the solvent and the salts present, as well as the need for low temperatures. Without reference to this work, Normant et al. [8] showed that it was possible by using *n*-butyl lithium in a solvent mix of pentane/ether/THF, which would be salt-free in pentane solution, at  $-135^{\circ}\text{C}$ , to obtain a halogen/metal exchange reaction to give a “quantitative yield” of trifluorovinyl lithium. This is in contrast to the previously observed addition–elimination reaction:



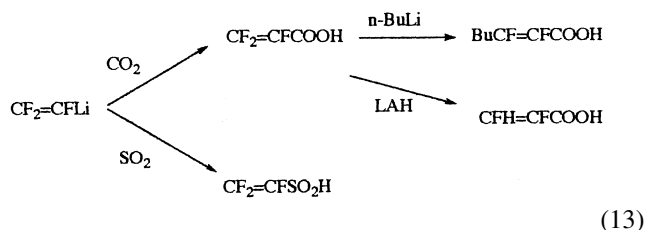
It was suggested that the THF was very important for the halogen metal interchange to occur, unfortunately this also increases the instability of the reagent once formed, so that at temperatures above  $-80^{\circ}\text{C}$  rapid decomposition took place. This reagent system, however, was shown to react with carbonyl compounds as described by Tarrant, most of the intermediate alcohols were characterised by spectroscopic methods only and were hydrolysed to the corresponding acyl fluorides which in turn were converted to fully characterised esters or amides as shown in Table 2. Although this work was an advance in that it used a cheaper more readily available starting material it still required rather specialist conditions. This problem was solved when Normant and coworkers [9] found that it was possible by using the stronger bases, *sec*- or *tert*-butyl lithium, to exchange the chlorine atom in ether at  $-60^{\circ}\text{C}$  without concomitant addition–elimination reactions taking place:



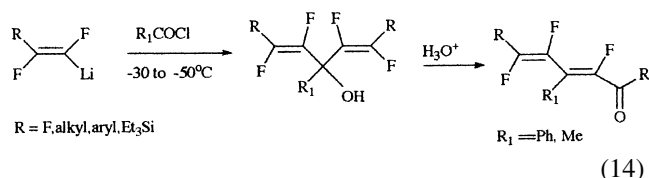
The reagents prepared by the new method reacted with carbonyl compounds [8] in similar reactions to those described earlier by Tarrant:



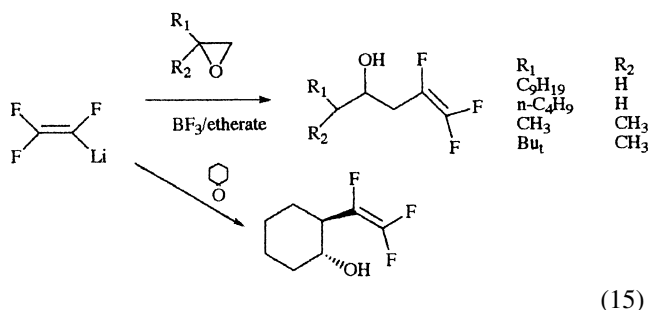
This also reacted with  $\text{CO}_2$  and  $\text{SO}_2$  [10]:



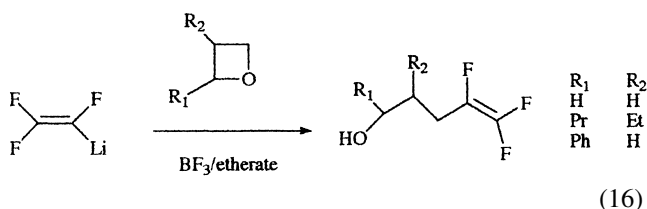
Somewhat surprisingly trifluoroacrylic acid reacted almost completely via Michael type reactions with both lithium–aluminium hydride and butyl lithium in an addition–elimination process to yield the difluorovinyl analogue as a 1:1*E:Z* (Eq. (13)) mixture. Reaction with acyl halides proved to be very useful, the first formed ketone readily reacted with more lithium reagent to afford a bis-polyfluorovinyl carbinol which then hydrolysed to form an unsaturated acid as shown in [9].



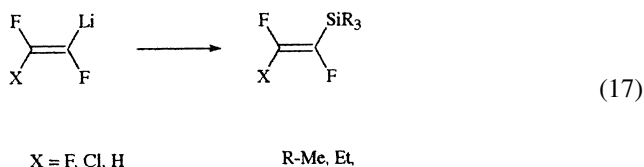
The polyfluoroalkenyl lithium reagents in general did not react with epoxides at low temperatures and the threshold temperature for reaction to take place seems to be above the decomposition temperature of the reagent. This was overcome by the use of a Lewis acid catalyst, usually boron trifluoride etherate, when reaction occurred in good yield [9]:



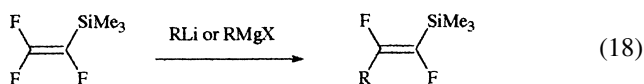
Oxetanes reacted similarly to afford the expected carbinals [11]:



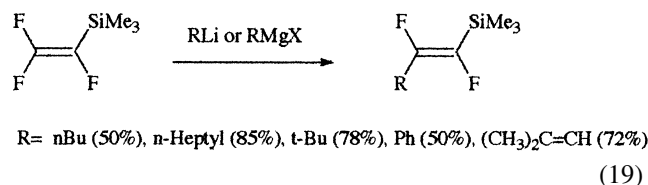
The reaction of trifluorovinyl lithium with trialkylsilyl halides, first described by Seyferth et al. [1] and significantly improved by Normant and coworkers [12], afforded a range of trifluorovinyl trialkylsilanes as shown below:



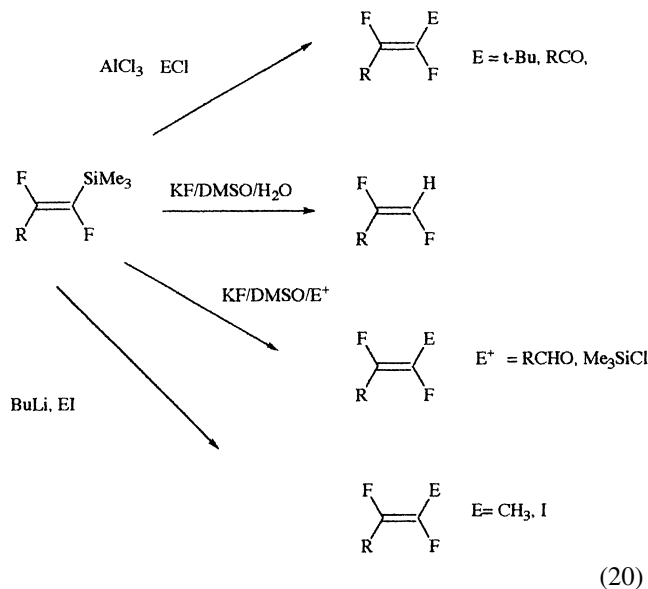
These compounds proved to be very useful precursors for a wide range of new fluorovinyl compounds. Normant and coworkers showed [12,13] that reaction of these compounds with alkyl and aryl lithium reagents or with the corresponding Grignard reagents afforded the alkyl or aryl difluorovinyl silanes which were shown to be formed almost exclusively in the *Z* configuration:



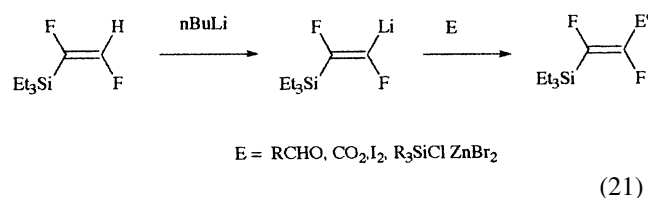
These compounds themselves showed a wide range of reactivity. Firstly, it was observed that protodesilylation by fluoride ion in moist DMSO yielded the corresponding *E*-1,2-difluoroalkenes. Further, it was found that if the reaction was carried out in dry DMSO with added electrophiles a smooth formation of the corresponding tri-substituted ethene occurred. Examples of this reaction are shown below:



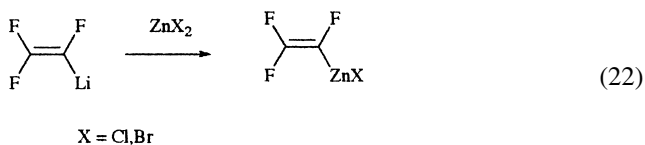
This type of reaction was extended to include Fiedel-Crafts type reactions as shown below:



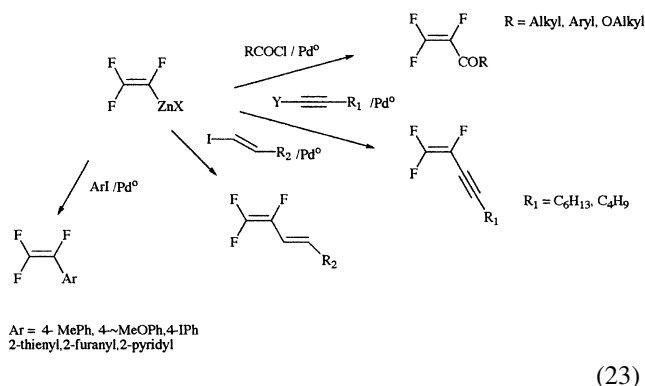
Normant and coworkers [14] also showed that LAH reduction of trifluorovinyltrimethylsilane afforded the corresponding *E*-1,2-difluorovinyl derivative. The introduction of the proton in these reactions gave the possibility for metallation reactions to be investigated and examples of these reactions are shown below:



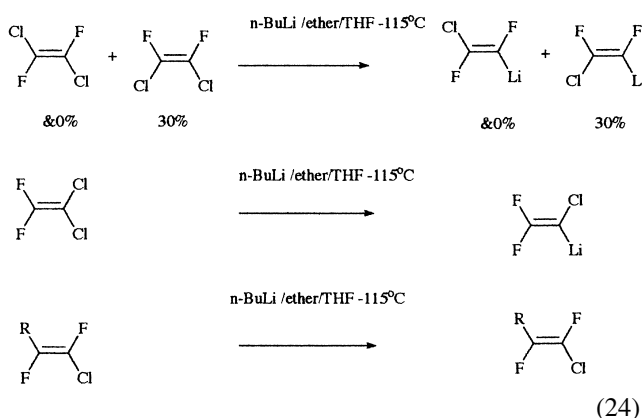
This work thus led to the development of a significant downstream chemistry for the introduction of fluoroalkenyl functions within molecules and provided new methodology for the synthetic chemist. A further important development of this work was the reaction of polyfluorovinyl lithium reagents with zinc halides to yield the corresponding zinc reagents [14,15]:



These reagents were shown to be much more stable than the lithium species, in keeping with the known properties of zinc organometallics, being stable for many hours at room temperature. This stability has led to their use in  $\text{Pd}^0$  mediated cross coupling reaction with a wide variety of substrates [16]:



Thus, the work of the Normant group built on the original work of Tarrant and confirmed the downstream chemistry reported by the latter and extended its range because of the development of a more reliable synthesis. In an extension of the original Tarrant study, but using the newer synthetic procedure, Normant found that it was indeed possible to form lithio compounds from 1,2-dichloro-1,1-difluoroethene, 1,1-difluoroethene and 1,2-dichloro-1,2-difluoroethene as shown in [17,18]:

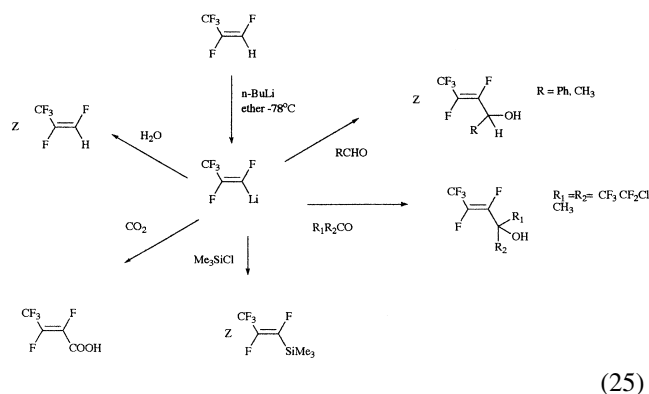


These reagents all gave parallel reactions to those described above for the trifluorovinyl analogue.

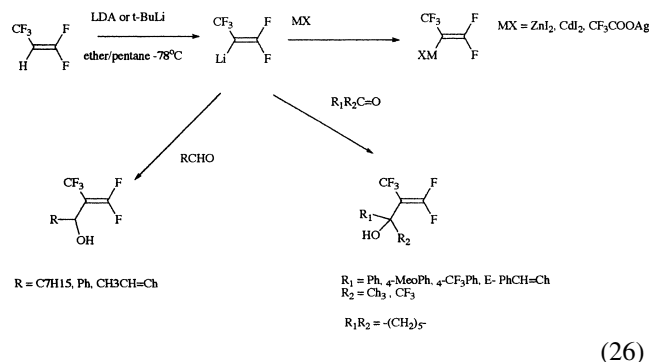
Although there are some reports of the use of trifluorovinyl lithium reagents in synthesis subsequent to the work of Normant reported in a review in 1990 [19], there were no significant new developments in this kind of chemistry for several years. Most of the new chemistry for the introduction of polyfluorovinyl groups and their downstream chemistry uses trifluoroethanol as the fluorine source leading to stabilised lithium reagents has been reported in a review by Percy [20,21] who has carried out much of this work.

The formation of higher homologues of trifluorovinyl lithium has been less well studied. This is mainly due to a lack of good methods for the formation of the required starting materials but also due to the even greater instability of the lithium reagents when formed and in general the more stable zinc reagents have been preferred [22]. 1-Pentafluoropropenyl lithium was first reported by Tarrant et al. [23] who showed that 1-H pentafluoropropene could be metallated with butyl lithium in hexane/ether at  $-78^{\circ}\text{C}$ . It was

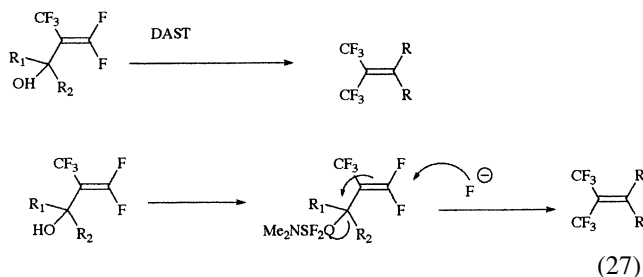
shown that the reagent reacted with aldehydes and ketones, as expected, to give the appropriate *sec*- or *tert*-alcohols. The reaction with acyl halides followed the same pattern as found for trifluorovinyl lithium in that the first formed ketone appeared to be more reactive than the acyl halide and even using molar equivalents the *tert*-alcohol was always the major product. The lithium reagent also reacted with carbon dioxide to form perfluorocrotonic acid and with chlorotrimethylsilane to give the expected silane. These reactions are summarised as below:



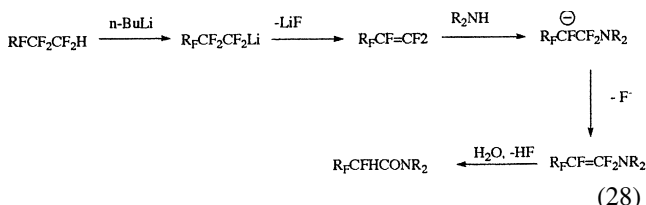
An unusual and unresolved puzzle was found in this reaction. The starting material for the formation of the lithium reagent was a 1:1 mixture of *E* and *Z* isomers whereas the products were exclusively the *Z* isomer, and this was true in all cases when products were isolated yields of >75%. The isomeric 2-pentafluoropropenyl lithium has only been produced more recently by Burton et al. [24] who showed that it was possible to metallate 2-H pentafluoropropene with *tert*-butyl lithium or LDA but obtained no significant yield with *n*-butyl lithium as reagent. The lithium reagent was shown to react with a number of metal halides to give a new series of 2-pentafluoropropenyl metal derivatives of which the more stable zinc reagent was investigated in detail:



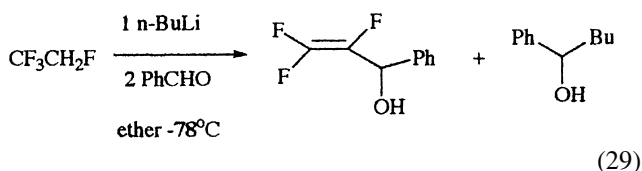
Subsequently, Lu and Burton [25] described the reaction of the lithium reagent with aldehydes and ketones. In an interesting use a rearrangement reaction of the derived carbinols, first shown to occur by Tarrant et al. [3] using  $\text{SF}_4$  and later by ourselves [26] using DAST or pyridine/HF, to form trifluoromethylated alkenes:



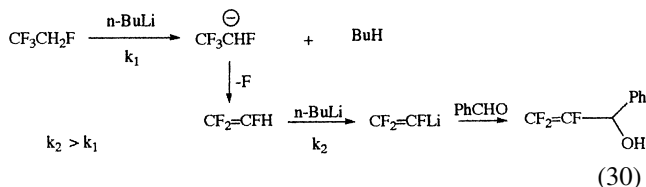
The impetus for new developments in the area of trifluoro and polyfluorohalovinyl lithium chemistry came from the so-called Montreal Protocol banning the use of CFCs, the starting material for Normant type work. There was a need for chemistry to be developed from these replacement materials such as HFC **134a** ( $\text{CF}_3\text{CH}_2\text{F}$ ) and HCFC **133a** ( $\text{CF}_3\text{CH}_2\text{Cl}$ ). Very early work by Andreades [27] showed that it was possible to carry out metallation reactions on hydrofluorocarbons at low temperatures to obtain the corresponding perfluoroalkyl lithium reagents, a similar reaction [28] using lithium diethylamide as base afforded, after work up, the corresponding *N,N*-dialkylamide derivative as shown below:



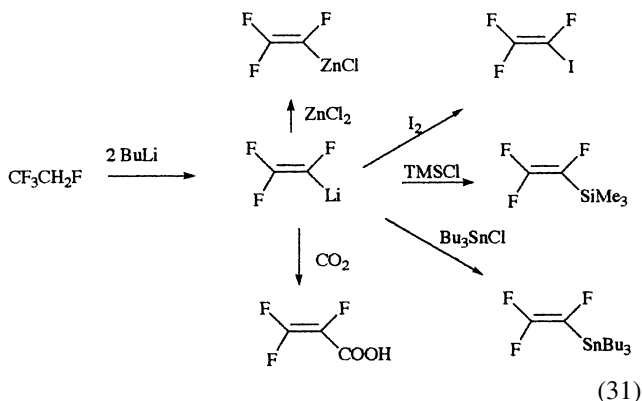
The proposal that the first formed lithium reagent eliminated fluoride ion to give the corresponding alkene which then reacted with diethylamine proved to be very interesting (see below). These reactions were carried out at  $-10^\circ\text{C}$  at which temperature we would not have expected the lithium reagent to be stable. These reactions prompted us to investigate the reaction of **134a** with strong bases in the hope of obtaining tetrafluoroethyl lithium. In the initial reaction using butyl lithium and an excess of **134a** in the presence of benzaldehyde in the manner described by Tarrant and coworkers [5] we obtained a mixture of two products in the ratio of 1:4. These were identified as phenyl trifluorovinylmethanol and butyl phenyl methanol, the latter being the product from the reaction of benzaldehyde with butyl lithium [30].



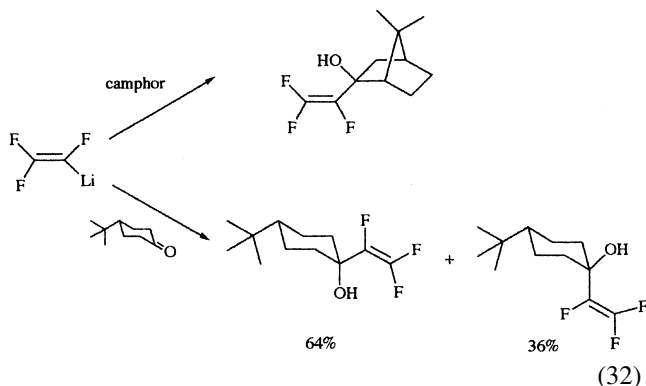
Thus, it appears that a possible mechanism to explain this result as shown is that one proton in **134a** is removed by the base to give the tetrafluoroethyl anion:



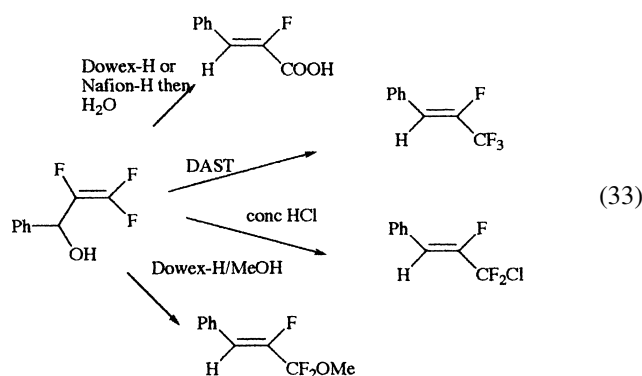
We, subsequently, showed this is very unstable (see below), cf., the half-life of pentafluoroethyl lithium is 8 h at  $-78^\circ\text{C}$  [29], this anion then loses fluoride ion to give trifluoroethene. It is known [5] that trifluoroethene reacts with butyl lithium to give trifluorovinyl lithium and it would appear that under the right conditions this reaction is faster than either deprotonation of **134a** or reaction with carbonyl compounds. This interesting result suggested to us that by careful control of the conditions we might be able to develop a new route to trifluorovinyl lithium. We found that the ideal conditions we required to obtain the reagent were to add the base (two equivalents relative to the electrophile) to an excess of **134a** at  $-78^\circ\text{C}$ , to stir this mixture at this temperature for 1 h. The electrophile was then added and the mixture was warmed slowly to ambient temperature. In this way we did not observe any products associated with reaction of the base with the electrophile [23]. To test that our reagent, generated in a different way to those previously used, reacted in the same manner as described previously, we repeated some of the reported reactions using this system with iodine, carbon dioxide, chlorotrimethylsilane, chlorotributylstannane, 4-*tert*-butylcyclohexanone and benzaldehyde as electrophile



and added some novel procedures [33,35] these new reactions are shown below:



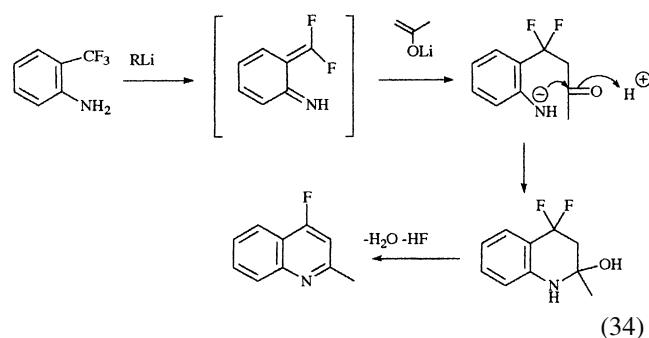
We had thus established what is now the simplest route to trifluorovinyl lithium and had shown that its reactions follow the same pattern observed by previous workers. During the course of this study we found that the method of work up of the reaction was very important. As noted earlier, because of the ready reaction of the trifluorovinyl group with nucleophiles, particularly when the trapping electrophile was a carbonyl compound, hydrolysis to the  $\alpha,\beta$ -unsaturated acyl fluorides using an acidic work up with moderately strong acid proved to be the norm. A similar but cleaner reaction was observed using either Dowex-H or Nafion-H resins. We found, however, by using aqueous ammonium chloride in the work up we could obtain the first formed trifluorovinyl alcohol containing a trace of the acyl fluoride in the reaction with benzaldehyde:



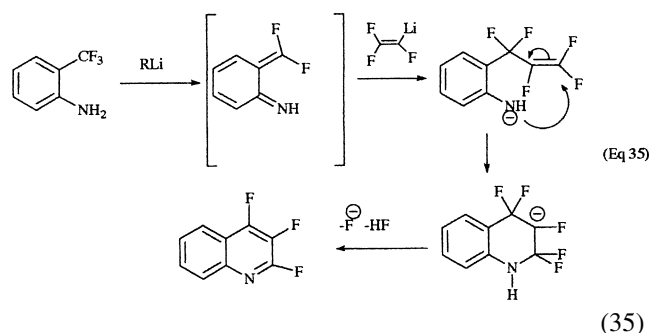
If the work up was carried out using DAST or THF/HF or pyridine/HF, we obtained the corresponding 1-phenyl-2,3,3,3-tetrafluoropropene whilst using concentrated hydrochloric acid afforded the 3-chlorotrifluoro analogue [31]. Interestingly, the ratio of 36:64 for the two isomers formed in the reaction with *tert*-butylcyclohexanone, indicates on the basis of literature evidence [32], that the trifluorovinyl lithium is between methyl and ethyl magnesium iodides in size. Although the methodology described above works well on a laboratory scale and the use of alkyl lithium reagents is now becoming industrially more acceptable it would be ideal to use a more readily available base. There has so far been no literature report of acidity measurements for **134a**. Therefore, we decided to investigate the use of alternative bases, particularly those which were unlikely to react with the added electrophile, in order to see if it is possible to develop an even simpler system to prepare that trifluorovinyl anion. From our results it is clear that under the conditions we employed only very strong organic bases reacted to give the desired anion. Thus, although *tert*-butyl lithium and LDA gave similar results to *n*-butyl lithium, there was no advantage in using these reagents in preference to butyl lithium. When was reacted **134a** with DBU in the presence of chlorotributylstannane and although the yield was very small we were able to trap the tetrafluoroethyl anion, thus suggesting that our original mechanistic postulate has some credence. A number of other bases including potassium *tert*-butoxide, 1,4-diazabicyclo[2,2,2]octane and

triethylamine gave no significant reaction. Thus, we had established that the simplest route to trifluorovinyl lithium is our original reaction using butyl lithium [33].

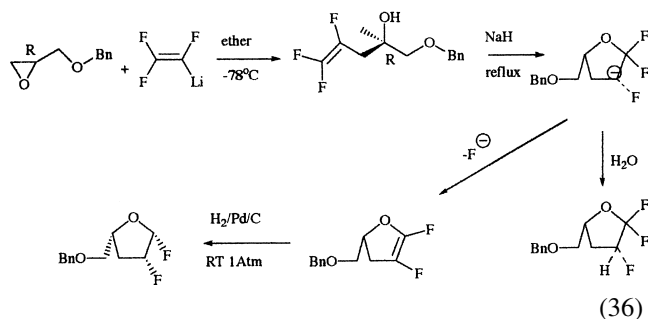
We next investigated the use of this reaction in some new chemistry aimed at making use of the reactivity of the trifluorovinyl group towards nucleophiles in order to produce fluorinated heterocycles. The first example of the chemistry involves the formation of fluoroquinoline derivatives as potential precursors for quinolone anti-bacterials. Strekowski has shown that reaction of lithium enolates [34] with 2-amino-benzotrifluoride readily forms 4-fluoroquinoline:



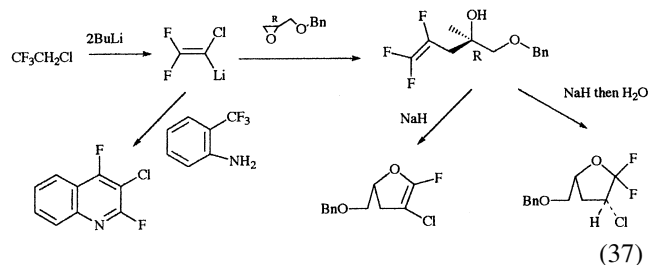
If the mechanism proposed by Strekowski is correct a similar reaction with trifluorovinyl lithium should lead to 2,3,4-trifluoroquinoline. The reaction between an excess of the lithium reagent and 2-amino-benzotrifluoride give the desired material in good yield [35]:



Although we have only carried out this reaction with 2-amino-benzotrifluoride the potential for this reaction is clear since there is a wide range of suitable benzotrifluoride derivatives available. The second reaction we investigated was the ring opening of the chiral epoxide, *R*-3-benzyloxy-1,2-epoxy propane (*R*-*O*-benzylglycidol) in the presence of boron trifluoride etherate. This reaction followed the pattern as reported by Normant and coworkers [9] for the opening of epoxides by trifluorovinyl lithium to give the expected trifluorovinyl derivative. We found that this alcohol in the presence of excess sodium hydride in an unusual 5-endo-trig cyclisation yielded optically pure *R*-5-(benzyloxymethyl)-2,3-difluoro-4,5-dihydrofuran, catalytic hydrogenation of this latter yielded 1(*R*),2(*R*),3(*R*)-5-(benzyloxymethyl)-2,3-difluoro-tetrahydrofuran:



This reaction sequence represents a very simple stereospecific *de novo* synthesis of a dideoxy-aldopentose derivative, which is clearly capable of adaptation to other systems. Recently, others have used this methodology to prepare a number of trifluorovinyl phosphines [36]. Since the reaction with **134a** was so successful we investigated a similar reaction but using **133a**. We showed [35] that it is equally simple to prepare 1-chloro-2,2-difluorovinyl lithium in good yield. We showed that it reacts in the same way as described by Normant with carbonyl compounds and carries out similar reactions to those described above with 2-aminobenzotrifluoride and with *R*-*O*-benzylglycidol [37]:



Recently, the use of this reagent has been extended by Percy and coworkers [38] to other substrates. We believe this work reopens the field of polyfluorovinyl lithium chemistry with the development of a simpler methodology than previously described using cheap readily available starting materials. This allied to some of the elegant chemistry reported by Percy using the polyfluorovinyl function provides an exciting prospect for future developments in the approach to fluorine introduction into bioactive molecules.

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