The hydrofluorocarbon 1,1,1,2-tetrafluoroethane (HFC-134a) as a ready source of trifluorovinyllithium

James Burdon,*[a] Paul L. Coe,[a] Iain B. Haslock[a] and Richard L. Powell[b]

[a] *School of Chemistry, The University of Birmingham, Birmingham, UK B15 2TT*
[b] *ICI Klea, PO Box 8, The Heath, Runcorn, Cheshire, UK WA7 4QD*

Trifluorovinyllithium has been synthesised in high yield from 1,1,1,2-tetrafluoroethane (HFC 134a) by treatment with butyllithium at −78 °C, and then treated with a variety of electrophiles in one-pot reactions.

Originally introduced as refrigerants in the 1930s, the chlorofluorocarbons (CFCs) and hydrofluorocarbons (HCFCs) have also proved vitally important to the development of synthetic organofluorine chemistry. Even today the majority of work in this area depends upon fluorinated substrates whose origin can be traced back to commercially produced CFCs or HCFCs. However, the implication of these chlorine-containing compounds in the depletion of the ozone layer has resulted in agreements which have lead to CFCs being phased out already (1994 in the European Union), or will do so very soon (1995 in the rest of the developed world), for refrigeration, air-conditioning, foam-blowing, aerosol propellants and other applications where the substances could be released into the atmosphere. HCFCs are also to be phased out, but on a longer timescale (probably >2015).

Although a recent dispensation has been given that the use of CFCs for research and analysis can continue, this will be reviewed in 1996: in any case, as large-scale manufacture ceases, the availability of these compounds as research chemicals will decrease. The challenge for organofluorine research chemists will therefore be the development of alternative, non-CFC based syntheses to key intermediates. At present, the CFCs are being replaced in part by the non-chlorine containing hydrofluorocarbons (HFCs) 1,1,1,2-tetrafluoroethane, difluoromethane, pentafluoroethane and 1,1,1-trifluoroethane and these are commercially available. Clearly these substances are potentially valuable reagents for new synthetic methods in organofluorine chemistry and provide opportunities for replacing CFC-based syntheses. This paper describes the very promising results we have obtained from one such HFC, 1,1,1,2-tetrafluoroethane (HFC 134a) **1**, which is now manufactured world-wide on an annual scale of tens of thousands of tonnes.

Although polyfluorovinyllithium reagents have been known for some time and some of their chemistry has been investigated, first by Tarrant[1] and later by Normant[2] and Dolbier,[3] their preparation required stringent conditions and used reagents which are not now readily available.

Here we report a simple preparation of trifluorovinyllithium **2** from 1,1,1,2-tetrafluoroethane (HFC-134a) **1**. On treatment with butyllithium in diethyl ether at −78 °C, **1** gave trifluorovinyllithium **2** in high yield, presumably *via* the route shown in Scheme 1.

$$\underset{\mathbf{1}}{CF_3CFH_2} \xrightarrow{i} [\underset{\mathbf{3}}{CF_3CFHLi} \xrightarrow{-LiF} CF_2{=}CFH] \xrightarrow{i} \underset{\mathbf{2}}{CF_2{=}CFLi} \xrightarrow{ii} CF_2{=}CFE$$

Scheme 1 *Reagents and conditions*: i, BuLi (hexane), Et_2O, −78 °C; then 2 mol dm^{-3} HCl (see text for benzaldehyde work-up); ii, E = electrophile—see Table 1

The lithium **2** is stable for several hours at −78 °C, but if allowed to warm towards room temperature it decomposed to a black material. Treatment of the lithium **2**, prepared in our way, with a variety of electrophiles gave the expected products in fair to good yields (Table 1). It follows that trifluorovinyllithium **2** is now as readily available as any organo-lithium compound and that it can be made and used without any specialised equipment.

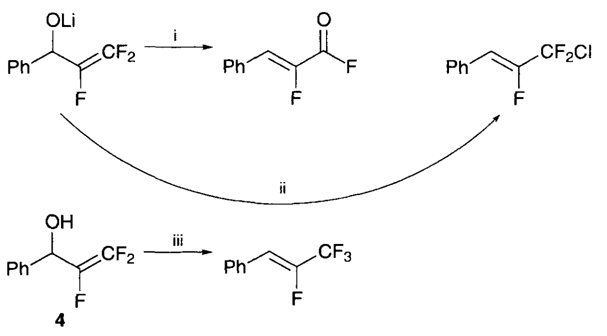
Confirmation that tetrafluoroethyllithium **3** was indeed an intermediate (Scheme 1) was provided by treatment of the ethane **1** with LDA and then tributyltin chloride when $CF_3CFHSnBu_3$ was obtained.

With benzaldehyde, the product shown in Table 1 was only obtained when methanol was added at the end of the reaction: when hydrochloric acid was used instead, the reactions shown in Scheme 2 occurred [a similar rearrangement took place when the normal product **4** was treated with diethylaminosulfur trifluoride (DAST)]. This allylic rearrangement is known in the field of fluorine research.[2a,3]

Table 1 Products derived from trifluorovinyllithium and various electrophiles

Electrophile	Product	Yield (%)
Iodine	$CF_2{=}CFI$	59
CO_2	$CF_2{=}CFCO_2H$	68
Me_3SiCl	$CF_2{=}CFSiMe_3$	70
Bu_3SnCl	$CF_2{=}CFSnBu_3$[a]	67
4-*tert*-Butylcyclohexanone	4-$Bu^tC_6H_9(OH)CF{=}CF_2$	56
PhCHO	$PhCH(OH)CF{=}CF_2$[b]	74

[a] See text for reaction using LDA. [b] See Scheme 2 and text for work-up under different conditions.



Scheme 2 *Reagents and conditions*: i, 1 mol dm^{-3} HCl, room temp.; ii, 10 mol dm^{-3} HCl, room temp.; iii, DAST (start at −78 °C and finish at room temp.)

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References

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