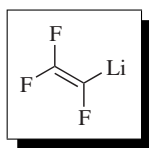


Trifluorovinyl lithium



[683-78-3] C_2F_3Li (MW 87.96)
 InChI = 1/C2F3.Li/c3-1-2(4)5;/rC2F3Li/c3-1(4)2(5)6
 InChIKey = JPRWLTHIUDZUTF-ZFWLYPEZAJ

(reagent is used for introduction of trifluorovinyl group)

Physical Data: stable for several hours as 1.2 M solution in diethyl ether¹ or pentane² at $-27^\circ C$. At higher temperatures, it is decomposed into lithium fluoride and a high boiling viscous oil.² The stability is significantly increased in more dilute solutions.² ^{19}F NMR spectrum has been recorded, and further validated by computational methods.³⁻⁵

Solubility: soluble in THF,⁴ diethyl ether, pentane.¹

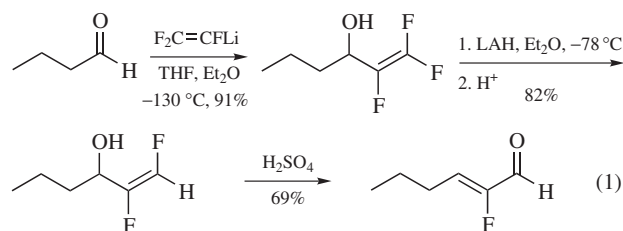
Preparative Methods: prepared by a variety of methods. The lithium-halogen exchange reaction has commonly been used: (1) *n*-BuLi^{2,6} or MeLi⁷⁻⁹ and $CF_2=CFX$ ($X = Cl, 4, 10, 11$ Br, 2, 7, 9 or I^{6,8}) at -78 to $-100^\circ C$; or (2) *sec*- or *t*-BuLi and $CF_2=CFCl$ at $-60^\circ C$. If the exchange reaction is conducted at higher temperatures, 1,2-difluoro-1-chloro-1-hexene can be obtained as a result of the addition-elimination of $CF_2=CFCl$.¹¹ Trifluorovinyl lithium is produced in nearly quantitative yield in the proton exchange reaction of trifluoroethylene, $CF_2=CFH$, with *n*-BuLi in: (1) diethyl ether at $-100^\circ C$,¹²⁻¹⁴ or (2) THF/ether/pentane (5:3:3) at $-135^\circ C$.¹⁵ In the reaction of PhLi with phenyl-tris(perfluorovinyl)tin, $Ph(CF_2=CF)_3Sn$, in diethyl ether at -35 to $-40^\circ C$, the formation of trifluorovinyl lithium is observed in low yield.^{1,16} Analogously, *n*-BuLi is reacted with *n*-butyl-tris(perfluorovinyl)tin, $Bu(CF_2=CF)_3Sn$, in pentane.¹ In a recently developed method,^{5,17-22} the treatment of 1,1,1,2-tetrafluoroethane, CF_3CFH_2 , with 2 equiv of *n*-BuLi in ether at $-78^\circ C$, generates trifluorovinyl lithium in high yield. The elimination, where CF_3CFH_2 is converted to 1,1,2-trifluoroethene, $CF_2=CFH$, is proposed as a first step in the reaction. This is corroborated by introducing Bu_3SnCl to the reaction mixture to obtain tributyltin derivative $CF_3CFHSnBu_3$ exclusively. This method is advantageous, and more used than others, because of widely available and quite inexpensive starting materials.²³

Purification: the reagent is used in diethyl ether solution without any purification.

Handling, Storage, and Precautions: as with most alkyl lithium reagents. Trifluorovinyl lithium should be kept at $-27^\circ C$ or below, under argon atmosphere.² It has been found that the stability is greater in pentane than in diethyl ether.¹ In THF the reagent is decomposed at $-80^\circ C$ or higher.^{10,11} After prolonged time at low temperatures the solution of this reagent turns brown. When the solution becomes dark brown and a precipitate is formed, use is no longer recommended.² The reagent is recommended to be used a few hours upon its preparation.

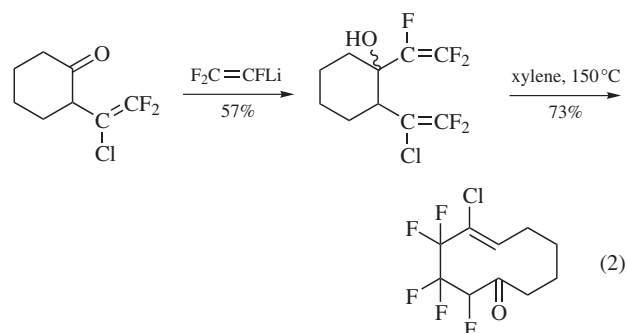
Nucleophilic Addition Reactions. In the reaction of trifluorovinyl lithium with aldehydes and ketones, alcohols are obtained

in good yields.^{2,11,14,15,22,24} This reaction has been used in the synthesis of α -fluoro- α,β -unsaturated aldehydes (eq 1).

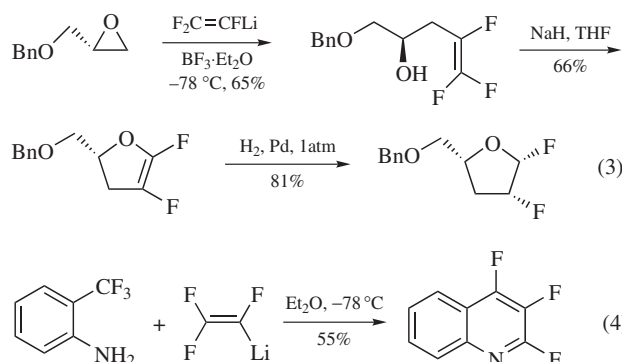


In conjugated 1,4-additions of trifluorovinyl lithium to α,β -unsaturated carbonyl compounds, the trifluorovinyl group can be effectively introduced at the β -position.⁸ This method requires aluminum-tris(2,6-diphenylphenoxide) to activate the carbonyl compound, and importantly it is more effective than the organo-copper-mediated conjugated additions. Trifluorovinyl lithium presents a useful synthon to *E/Z* isomers of α,β -difluoro- α,β -unsaturated alcohols or acids.¹¹ Two trifluorovinyl equivalents readily add to acid chlorides to form bis(α,β -difluoro)allylic alcohols. Acid-promoted rearrangements of such formed alcohols give rise to fluorinated dienic carboxylic acids.¹¹ Carboxylation of trifluorovinyl lithium using gaseous CO_2 affords trifluoroacrylic acid in a very good 80% yield.²⁵ Nucleophilic addition of trifluorovinyl lithium to epoxides or oxetanes can be promoted by boron trifluoride etherate.²⁶ This method allows the preparation of β,γ - or γ,δ -trifluoro-unsaturated alcohols in 60–90% or 50–70% yield, respectively.²⁶

Ring Formation Reactions. Unsaturated fluorinated alcohols, produced in the reaction of trifluorovinyl lithium with carbonyl compounds, epoxides, and oxetanes, present great precursors for subsequent ring formation reactions, and for the preparation of fluorinated cyclic, medium to large ring, ketone compounds.²⁷ For instance, fluorinated cyclodecanone can be synthesized via thermal oxy-Cope rearrangement of α -trifluorovinyl-substituted cyclohexanone in 73% yield (eq 2).²⁷ A stereoselective synthesis of biologically important arabinose derivatives can be achieved using trifluorovinyl lithium.¹⁸ Reaction with commercially available (*R*)-glycidol produces an optically active allyl alcohol. When treated with a large excess of sodium hydride, this alcohol forms dihydrofuran derivative, which after subjected to catalytic hydrogenation exclusively affords a fluoro derivative of arabinose (eq 3). Importantly, the hydrogenation reaction is stereoselective.¹⁸ The syntheses of a wide range of polyhalogenated quinolines can be completed by reacting



substituted aminobenzotrifluorides with trifluorovinyllithium.²⁸ For example, in the reaction with 2-aminobenzotrifluoride, at -78°C , 2,3,4-trifluoroquinoline is synthesized in 55% yield (eq 4).²⁸



Reactions with Other Electrophiles. Trifluorovinyllithium has been shown to react with the boron electrophiles BCl_3 , $\text{BCl}_2(\text{OMe})$, $\text{BCl}(\text{OMe})_2$, and $\text{CF}_2=\text{CFB}(\text{OMe})_2$ to generate (fluoroorgano)fluoroboranes and -borates.²¹ The preparation of silanes containing trifluorovinyl groups can also be effectively accomplished.^{7,12} Thus, triethyltrifluorovinylsilane is prepared in 79% yield upon treating triethylchlorosilane with trifluorovinyllithium.¹³ Perfluorovinyl phosphines of the type $\text{PPh}_m(\text{CF}=\text{CF}_2)_n$ or $\text{P}(\text{CF}=\text{CF}_2)_n\text{Cl}_m$ ($n+m=3$) have all been derived in high yields in the reactions of trifluorovinyllithium and chloro-substituted phosphines.^{23,29} The addition of main-group or transition-metal halides (i.e., Me_3SnCl , HgCl_2 , $\text{Mn}(\text{CO})_5\text{Br}$, *cis*- $[\text{Pt}(\text{PBU}_3)_2\text{Cl}_2]$, or $\text{Cp}_2\text{M}(\text{CF}=\text{CF}_2)_n\text{X}_{2-n}$ where $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Ti}$ or Zr ; and $\text{X} = \text{Cl}$ or F) to trifluorovinyllithium results in the formation of metal perfluorovinyl complexes.^{5,20,23,30}

Related Reagents. Vinyllithium; Trichlorovinyllithium; 2,2-Difluoroethenyllithium; 1-Chloro-2,2-difluoroethenyllithium.

- Seyferth, D.; Wada, T.; Raab, G., *Tetrahedron Lett.* **1960**, 22, 20.
- Tarrant, P.; Johncock, P.; Savory, J., *J. Org. Chem.* **1963**, 28, 839.
- Kvíčala, J.; Czernek, J.; Böhm, S.; Paleta, O., *J. Fluorine Chem.* **2002**, 116, 121.
- Kvíčala, J.; Hrabal, R.; Czernek, J.; Ivana, B.; Paleta, O.; Pelter, A., *J. Fluorine Chem.* **2002**, 113, 211.

- Banger, K. K.; Brisdon, A. K., *J. Organomet. Chem.* **1999**, 582, 301.
- Cowley, A. H.; Taylor, M. W., *J. Am. Chem. Soc.* **1969**, 91, 1929.
- Tarrant, P.; Oliver, W. H., *J. Org. Chem.* **1966**, 31, 1143.
- Maruoka, K.; Shimada, I.; Akakura, M.; Yamamoto, H., *Synlett* **1994**, 847.
- Chang, I. S.; Price, J. T.; Tomlinson, A. J.; Willis, C. J., *Can. J. Chem.* **1972**, 50, 512.
- Gillet, J. P.; Sauvêtre, R.; Normant, J. F., *Synthesis* **1986**, 538.
- Gillet, J. P.; Sauvêtre, R.; Normant, J. F., *Synthesis* **1986**, 355.
- Drakesmith, F. G.; Stewart, O. J.; Tarrant, P., *J. Org. Chem.* **1968**, 33, 472.
- Drakesmith, F. G.; Richardson, R. D.; Stewart, O. J.; Tarrant, P., *J. Org. Chem.* **1968**, 33, 286.
- Tarrant, P.; Summerville, R. H.; Whitfield, Jr., R. W., *J. Org. Chem.* **1970**, 35, 2742.
- Normant, J. F.; Foulon, J. P.; Masure, D.; Sauvêtre, R., *Synthesis* **1975**, 122.
- Seyferth, D.; Welch, D. E.; Raab, G., *J. Am. Chem. Soc.* **1962**, 84, 4266.
- Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L., *Chem. Commun.* **1996**, 49.
- Coe, P. L.; Burdon, J.; Haslock, I. B., *J. Fluorine Chem.* **2000**, 102, 43.
- Dimartino, G.; Percy, J. M., *Chem. Commun.* **2000**, 2339.
- Banger, K. K.; Brisdon, A. K.; Gupta, A. M., *Chem. Commun.* **1997**, 139.
- Adonin, Y. N.; Bardin, V. V., *Organometallics* **2004**, 23, 535.
- Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L., *J. Fluorine Chem.* **1999**, 99, 127.
- Barnes, N. A.; Brisdon, A. K.; Ellis, M. J.; Pritchard, R. G., *J. Fluorine Chem.* **2001**, 112, 35.
- Sauvêtre, R.; Masure, D.; Normant, J. F., *Synthesis* **1978**, 128.
- Sauvêtre, R.; Masure, D.; Chuit, C.; Normant, J. F., *C. R. Acad. Sci.* **1979**, 335.
- Dubuffet, T.; Sauvêtre, R.; Normant, J. F., *J. Organomet. Chem.* **1988**, 341, 11.
- Dimartino, G.; Gelbrich, T.; Hursthouse, M. B.; Light, M. E.; Percy, J. M.; Spencer, N. S., *Chem. Commun.* **1999**, 2535.
- Burdon, J.; Coe, P. L.; Haslock, I. B.; Powell, R. L., *J. Fluorine Chem.* **1997**, 85, 151.
- Banger, K. K.; Banham, R. P.; Brisdon, A. K.; Cross, W. I.; Damant, G.; Parsons, S.; Pritchard, R. G.; Sous-Pedrares, A., *J. Chem. Soc., Dalton Trans.* **1999**, 427.
- Brisdon, A. K.; Crossley, I. R.; Pritchard, R. G.; Warren, J. E., *Inorg. Chem.* **2002**, 41, 4748.

Veselin Maslak, Zhiqing Yan, & Jovica D. Badjic
The Ohio State University, Columbus, OH, USA