The Preparation and Reactions of Some Fluorine-Containing Vinyl Organometallic Compounds

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A series of fluorine-containing vinyl organometallic reagents have been prepared *via* bromine or proton exchange in halo olefins. The stability and mechanism of rearrangement of carbinols formed by their reaction with carbonyl compounds are discussed.

We have been interested for some time in the preparation and reactions of fluorine-containing unsaturated organometallic reagents. In previous papers we have discussed the preparation of trifluorovinyl-,[1] trifluoroisopropenyl-,[2] and trifluoropropynyllithium[2] and studied their reaction with carbonyl compounds[1,2] and triethylchlorosilane.[2] We have also made a preliminary report on the reaction of trifluorovinylmagnesium bromide with carbonyl compounds.[3]

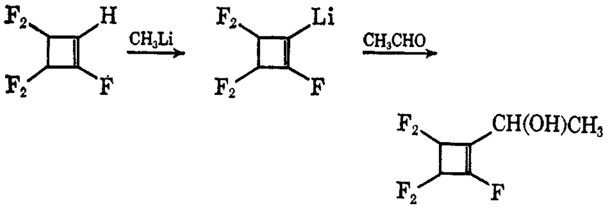
We now wish to report the preparation of a series of fluorine-containing vinyllithium reagents. Several of these have been prepared by a process involving proton exchange in halo olefin srather than by the more conventional halogen exchange procedure, *e.g.*

$$CF_2{=}CFH + C_4H_9Li \xrightarrow{\text{ether}} CF_2{=}CFLi + C_4H_{10}$$
$$\text{(at least 79\%)}$$

This type of olefin metallation reaction has been used extensively in recent years by Köbrich and coworkers in connection with their interest in the mechanism of carbenoid reactions.[4] They prepared a number of bromo- and chloroalkenyllithium reagents which were stable at low temperatures in ether or tetrahydrofuran, *e.g.*[5]

$$CCl_2{=}CClH + C_4H_9Li \xrightarrow[-110^\circ]{\text{THF}}$$
$$CCl_2{=}CClLi + C_4H_{10} \xrightarrow{CO_2} CCl_2{=}CClCOOH\ (31\%)$$

There is a recent report[6] of the metallation of 1-H fluorocycloalkenes using methyllithium. The resulting perfluorocycloalkenyllithium reagent was characterized by reaction with acetaldehyde to give 1-(perfluorocycloalken-1-yl)ethanol (see eq 1). There are two main advantages of proton exchange over halogen exchange in fluoro olefins: (1) the process is not reversible and (2) the starting olefins are usually less expensive or more readily available.

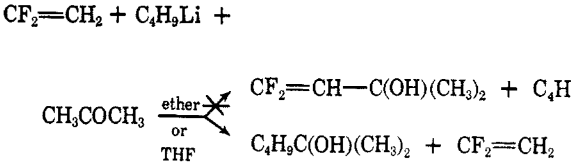


(1)

Apart from trifluorovinyllithium, we have prepared 1-chloro-2,2-difluorovinyllithium and 1,2-dichloro-2-fluorovinyllithium by this method. These preparations merely involved the addition of a solution of butyllithium in mixed solvent (pentane–ether, 1:1) to an equimolar quantity of the halo olefin in ether solution at −100°. The reaction mixture was then allowed to warm to −78° prior to the dropwise addition of an ether solution of the carbonyl compound.

Reaction of 1,2-difluoroethylene with butyllithium in ether did not afford 1,2-difluorovinyllithium.

Similarly, attempts to prepare 2,2-difluorovinyllithium by reaction of butyllithium with vinylidine fluoride in ether or tetrahydrofuran were unsuccessful. The only product obtained on addition of acetone to the above mixture was *n*-butyldimethylcarbinol, formed by reaction of unchanged butyllithium with the ketone (eq 2). 2,2-Difluorovinyllithium was, however, prepared *via* an exchange metallation involving 2,2-difluorovinyl bromide and butyllithium (eq 3).



$$CF_2{=}CH_2 + C_4H_9Li + CH_3COCH_3 \xrightarrow[\text{THF}]{\text{ether or}} \begin{cases} \cancel{CF_2{=}CH{-}C(OH)(CH_3)_2 + C_4H_{10}} \\ C_4H_9C(OH)(CH_3)_2 + CF_2{=}CH_2 \end{cases} \quad (2)$$

$$CF_2{=}CH_2 \xrightarrow[\text{light}]{Br_2} CF_2BrCH_2Br \xrightarrow[60\text{–}70^\circ]{\text{KOH}}$$
$$CF_2{=}CHBr \xrightarrow{C_4H_9Li} CF_2{=}CHLi + C_4H_9Br \quad (3)$$

Attempts to prepare 1-fluorovinyllithium by reaction of vinyl fluoride with butyllithium were unsuccessful. 1-Fluorovinyllithium was obtained by treatment of 1-fluorovinyl bromide with butyllithium (eq 4). As can be seen from the above scheme, treatment of 1,2-dibromo-1-fluoroethane with alkali afforded some monofluoroacetylene as well as the required 1-fluorovinyl bromide. On attempted distillation of the mixture, the acetylene decomposed with accompanying flashes, minor explosions, and carbon deposition.

$$CH_2{=}CHF \xrightarrow[\text{light}]{Br_2} CH_2BrCHFBr \xrightarrow[60\text{–}70^\circ]{\text{KOH}}$$
$$CH_2{=}CFBr + HC{\equiv}CF \xrightarrow{C_4H_9Li} CH_2{=}CFLi + C_4H_9Br \quad (4)$$

Reactions of 2,2-difluorovinyl bromide and 1-fluorovinyl bromide with butyllithium gave the desired lithium reagent and an equimolar amount of butyl bromide. The latter was isolated in low yields (up to 44%), indicating poor conversion into the vinyllithium reagent. This is in contrast to the preparation of trifluorovinyllithium in at least 73% yield by reaction of

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(1) P. Tarrant, P. Johncock, and J. Savory, *J. Org. Chem.*, **28**, 839 (1963).

(2) F. G. Drakesmith, O. J. Stewart, and P. Tarrant, *ibid.*, **33**, 280 (1968).

(3) P. Tarrant and R. D. Richardson, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p 17M.

(4) G. Köbrich, *et al.*, *Angew. Chem. Intern. Ed. Engl.*, **6**, 41 (1967).

(5) G. Köbrich and K. Flory, *Chem. Ber.*, **99**, 1773 (1966).

(6) S. F. Campbell, R. Stephens, and J. C. Tatlow, *Chem. Comm.*, 151 (1967).

trifluorovinylbromide with an alkyllithium compound.[1] The olefins described have, however, contained protons as well as bromine atoms and it is not inconceivable, in view of the reactions described above, that a possible competing reaction (to halogen exchange) involves proton exchange followed by elimination of lithium bromide as shown in eq 5 and 6. However, no products resulting

$$\begin{array}{l} CF_2{=}CHBr + C_4H_9Li \longrightarrow \\ \qquad CF_2{=}CLiBr \xrightarrow{-LiBr} [:C{=}CF_2] \\ \qquad\qquad\qquad \downarrow \\ \qquad\qquad\qquad \text{further reactions} \end{array} \quad (5)$$

$$\begin{array}{l} CH_2{=}CFBr + C_4H_9Li \longrightarrow \\ \qquad CHLi{=}CFBr \xrightarrow{-LiBr} CF{\equiv}CH \\ \qquad\qquad\qquad \downarrow{\scriptstyle C_4H_9Li} \\ \qquad\qquad\qquad \text{further reactions} \end{array} \quad (6)$$

from this type of process have been isolated on reaction of these lithium reagents with carbonyl compounds. There is, however, some precedent for this type of reaction in the literature. Reaction of vinyl bromide with butyllithium in ether at 0° followed by carbonation gave acetylene dicarboxylic acid (34%)[7] (see eq 7). The

$$\begin{array}{l} CH_2{=}CHBr + C_4H_9Li \xrightarrow[0^\circ]{\text{ether}} CHLi{=}CHBr \xrightarrow{-LiBr} \\ CH{\equiv}CH \xrightarrow{C_4H_9Li} LiC{\equiv}CLi \xrightarrow{CO_2} HO_2CC{\equiv}CCO_2H\ (34\%) \end{array} \quad (7)$$

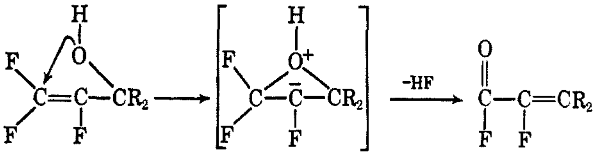
postulated mechanism involved exchange of a proton rather than bromine, elimination of lithium bromide, and dimetallation of the resulting acetylene. Köbrich and Flory have reported an interesting example of competing proton and halogen exchange. Treatment of 1,2-dichlorovinyl bromide with butyllithium in tetrahydrofuran afforded 1,2-dichloro-2-bromovinyllithium *via* proton exchange whereas similar treatment in ether promoted halogen exchange and gave 1,2-dichlorovinyllithium[5] (eq 8).

$$ClLiC{=}CClBr \xleftarrow[\text{THF}]{C_4H_9Li} ClHC{=}CBrCl \xrightarrow[\text{ether}]{C_4H_9Li} ClHC{=}CClLi \quad (8)$$

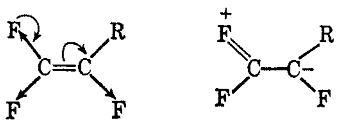
Knunyants, *et al.*,[8] discovered that the reaction of acetaldehyde, benzaldehyde, and acetone with trifluorovinylmagnesium iodide afforded α-fluoro-α,β-unsaturated acid fluorides (eq 9). They postulated a mech-

$$CF_2{=}CFMgI + \begin{matrix} RCHO \\ \text{or} \\ RR_1CO \end{matrix} \longrightarrow \left[\begin{matrix} RCH(OH)CF{=}CF_2 \\ \text{or} \\ RR_1C(OH)CF{=}CF_2 \end{matrix}\right] \longrightarrow \begin{matrix} RCH{=}CFCOF \\ \text{or} \\ RR_1C{=}CFCOF \end{matrix} \quad (9)$$

anism which involved a rearrangement of the trifluorovinyl carbinol and suggested that the rate of rearrangement was dependent upon the nature of the substituents in the reacting carbonyl compound. The mechanism of this reaction necessarily involved initial attack by the free-electron pair of the oxygen atom on the terminal carbon atom. Subsequent elimination of hydrogen fluoride from the intermediate afforded the acid fluoride (eq 10). It is well known that fluoro olefins containing terminal difluoromethylene groups are particularly susceptible to attack by nucleophiles.[9] The driving force for this reaction is normally attributed to the mesomeric effect of a vinylic fluorine atom tending to return electron density to the π system *via* a nonbonding electron pair.



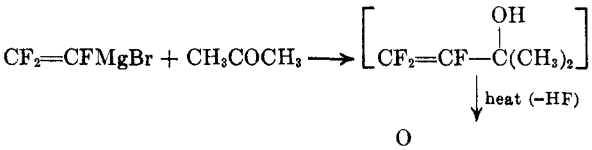
(10)



In our earlier work[1] on the reactions of trifluorovinyllithium the carbinol formed by treatment of the latter with benzaldehyde, 1-trifluorovinylbenzyl alcohol, was found to be unstable to heat but could be isolated as its urethane derivative (53%) by treatment with α-naphthyl isocyanate before heating. On the other hand, reaction of trifluorovinyllithium with perfluoroalkyl-substituted carbonyl compounds (trifluoroacetone and pentafluoropropionaldehyde) gave stable carbinols. Their stability was attributed to the decrease in nucleophilicity of oxygen atom due to the presence of the electron-withdrawing perfluoroalkyl groups.

It was decided to extend this work by preparing a number of other fluorine-containing vinylorganometallic reagents and also by studying the stability of carbinols formed by their reaction with carbonyl compounds.

Trifluorovinylmagnesium bromide, on reaction with a number of nonfluorine-containing carbonyl compounds in tetrahydrofuran, gave unstable alcohols. On attempted purification by distillation, these rearranged (sometimes violently), with accompanying evolution of hydrogen fluoride, to give acyl fluorides which were hydrolyzed immediately to the corresponding α-fluoroalkenylcarboxylic acid (Table I). This reaction depicted in eq 11 provides a useful general method for the preparation of α-fluoroalkenylcarboxylic acids. Although the yields obtained were low these may be improved by using trifluorovinyllithium in place of the Grignard reagent (see below). The alternative method for the preparation of this type of compound involves reaction of an aldehyde with ethyl fluoroacetate.[10,11]



$$\begin{array}{l} CF_2{=}CFMgBr + CH_3COCH_3 \longrightarrow \left[CF_2{=}CF{-}\overset{OH}{\overset{|}{C}}(CH_3)_2\right] \\ \qquad\qquad\qquad\qquad\qquad\qquad \downarrow{\scriptstyle \text{heat }(-HF)} \\ \qquad HOOC{-}CF{=}C(CH_3)_2 \xleftarrow{H_2O} F\overset{O}{\overset{\|}{C}}{-}CF{=}C(CH_3)_2 \end{array} \quad (11)$$

α-fluoro-β-methylcrotonic acid (17%)

Reaction of trifluorovinylmagnesium bromide with fluorine-containing carbonyl compounds afforded more stable carbinols (Table I). Reaction with trifluoroacetaldehyde gave trifluoromethyltrifluorovinylcarbinol

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(7) H. Gilman and H. A. Haubein, *J. Am. Chem. Soc.*, **67**, 1420 (1945).

(8) R. N. Sterlin, R. D. Yatsenko, and I. L. Knunyants, *Khim. Nauka i Promy.*, **3**, 540 (1958); *Chem. Abstr.*, **53**, 4195 (1959).

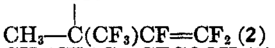
(9) R. D. Chambers and R. H. Mobbs, "Advances in Fluorine Chemistry," Vol. 4, Butterworth and Co., London, 1965, p 50.

(10) E. D. Bergmann and J. Shahak, *J. Chem. Soc.*, 4033 (1961).

(11) E. D. Bergmann and D. Schwarcz, *ibid.*, 1524 (1956).

TABLE I

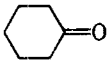
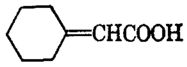
REACTION OF TRIFLUOROVINYLMAGNESIUM BROMIDE WITH CARBONYL COMPOUNDS IN TETRAHYDROFURAN

Carbonyl compd	Product	Yield, %	Physical properties
CH_3COCH_3	$(CH_3)_2C{=}CFCOOH$ (1)	17	Mp 64–66°, S-benzylisothiuronium salt mp 174.5°
CH_3COCF_3	 $CH_3{-}\overset{OH}{\overset{\mid}{C}}(CF_3)CF{=}CF_2$ (2)	29	Bp 98°, $n^{24}D$ 1.3340
	$CH_3(CF_3)C{=}CFCOOH$ (3)	11	Bp 100–108° (26 mm)
$CH_3COC_6H_5$	$C_6H_5C(CH_3){=}CFCOOH$ (4)	14	Mp 128–129° (lit.[a] 129–130.2°)
$C_6H_5COC_6H_5$	$(C_6H_5)_2C{=}CFCOOH$ (5)	32	Mp 160–162°
HCHO	$CH_2{=}CFCOOH$ (6)	3	Mp 52° (sublimes to give an amorphous solid which softens between 130–140°; lit.[10] 51.5–52°)
CH_3CHO	$CH_3CH{=}CFCOOH$ (7)	11	Mp 114–115° (lit.[10] mp 111–112°), p-nitrobenzyl ester mp 75–76°
CF_3CHO	$CF_3CH(OH)CF{=}CF_2$ (8)	53	Bp 95–96°, $n^{24}D$ 1.3200
C_6H_5CHO	$C_6H_5CH{=}CFCOOH$ (9)	16	Mp 155–156° (lit.[11] mp 157°), S-benzylisothiuronium salt mp 205–206°

[a] E. F. Silversmith, Y. Kitahara, M. C. Caserio, and J. D. Roberts, *J. Am. Chem. Soc.*, **80**, 5840 (1958).

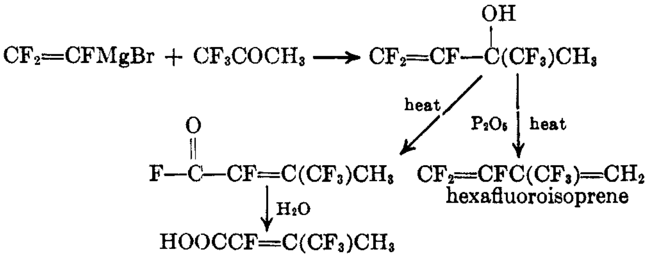
TABLE II

REACTION OF FLUOROÖLEFINS WITH BUTYLLITHIUM FOLLOWING THE ADDITION OF CARBONYL COMPOUNDS

Olefin	Carbonyl compd	Product (%)	Physical properties
$CF_2{=}CFH$	CH_3COCH_3	$(CH_3)_2C{=}CFCOOH$ (30) **(10)**	See Table I
$CF_2{=}CFH$	CF_3COCF_3	$(CF_3)_2C(OH)CF{=}CF_2$ (63) **(11)**	Bp 86°, $n^{24}D$ 1.3000
$CF_2{=}CFH$	CO_2	$CF_2{=}CFCOOH$ (56.5) **(12)**	Isolated as its S-benzylisothiuronium salt, mp 140–142°
$CF_2{=}CClH$	CH_3COCH_3	$(CH_3)_2C{=}CClCOOH$ (15) **(13)**	Mp 85–86° (lit.[a] mp 85–86°)
$CF_2{=}CClH$	CH_3COCF_3	$CH_3(CF_3)C(OH)CCl{=}CF_2$ (61) **(14)**	Bp 105–106°, $n^{25}D$ 1.3620
$CF_2{=}CClH$	CF_3COCF_3	$(CF_3)_2C(OH)CCl{=}CF_2$ (56) **(15)**	Bp 93–93.5°, $n^{24}D$ 1.3315
$CF_2{=}CClH$	C_6H_5CHO	$C_6H_5CH{=}CClCOOH$ (44) **(16)**	Mp 139–140° (lit.[b] mp 140–141°)
$CF_2{=}CH_2$	CH_3COCH_3	$(CH_3)_2C(OH)C_4H_9$ (52) **(17)**	Bp 139°, $n^{28}D$ 1.4146 (lit. bp 139.4–140.4°, $n^{25}D$ 1.4126)
$CF_2{=}CHBr$	CH_3COCH_3	$(CH_3)_2C{=}CHCOOH$ (9) **(18)** C_4H_9Br (16) **(19)**	Mp 66–68° (lit.[c] mp 69°)
$CF_2{=}CHBr$	CH_3COCF_3	Unstable product C_4H_9Br (44)	
$CF_2{=}CHBr$	CF_3COCF_3	C_4H_9Br (44)	
$CF_2{=}CHBr$		 (25) **(20)** C_4H_9Br (34)	Mp 90° (lit.[d] mp 90–91°) S-benzylisothiuronium salt mp 168–170°
$CFH{=}CFH$	CH_3COCH_3	No products isolated	
$CH_2{=}CFBr$	$CH_3CH_2COCH_3$	Inseparable mixture of products C_4H_9Br (24)	
$CFCl{=}CClH$	CH_3COCH_3	$(CH_3)_2C(OH)CCl{=}CClF$ (60) **(21)**	Bp 98–99° (90 mm), $n^{25}D$ 1.4627
$CFCl{=}CClH$	CH_3COCF_3	$CH_3(CF_3)C(OH)CCl{=}CClF$ (66) **(32)**	Bp 136–138°, $n^{24}D$ 1.4601 (isomer A), 1.4105 (isomer B)

[a] M. U. S. Sultanbawa and P. Veeravagu, *J. Chem. Soc.*, 4113 (1958). [b] M. Le Corre and E. Levas, *Compt. Rend.*, **260**, 3414 (1965); *Chem. Abstr.*, **63**, 4157 (1965). [c] A. A. Morton, M. L. Brown, M. E. T. Holden, R. L. Letsinger, and E. E. Magat, *J. Am. Chem. Soc.*, **67**, 2224 (1945). [d] R. P. Linstead, *J. Chem. Soc.*, 355 (1927).

(53%), which was completely stable to distillation. Two products were obtained from reaction with trifluoroacetone. One was α-fluoro-β-trifluoromethylcrotonic acid (11%), formed from the expected alcohol *via* rearrangement and hydrolysis of the resulting acid fluoride, and the second product was the expected alcohol (29%). The latter was dehydrated by heating with phosphorus pentoxide to give hexafluoroisoprene, which may be a useful monomer (eq 12).

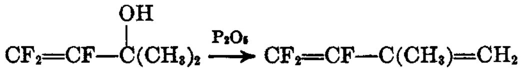


α-fluoro-β-trifluoromethylcrotonic acid (11%) (12)

Seyferth and coworkers[12] prepared trifluorovinyllithium by treating triphenyl(trifluorovinyl)tin with phenyllithium. We described a more convenient synthesis of this reagent (in at least 73% yield) involving treatment of bromotrifluoroethylene with an alkyllithium in either.[1] As described earlier, we have now prepared trifluorovinyllithium by reaction of trifluoroethylene with butyllithium. The lithium reagent was characterized by reaction with carbon dioxide to give trifluoroacrylic acid. The latter, which was known to be extremely hygroscopic,[13] was isolated as its S-benzylisothiuronium salt (56.5%). .

Reaction of trifluorovinyllithium with acetone gave a good yield of dimethyltrifluorovinyl carbinol in solution (Table II). Attempts to distil this product led to its rearrangement and the product on hydrolysis was α-fluoro-β-methylcrotonic acid (30%). This was a considerably higher yield than that obtained using trifluorovinylmagnesium bromide in tetrahydrofuran (Table I).

An attempt was made to obtain a pure sample of dimethyltrifluorovinylcarbinol by removal of the solvents at room temperature under vacuum. It was hoped to dehydrate the alcohol and thus obtain trifluoroisoprene (eq 13). The carbinol obtained (infrared absorp-



$$CF_2{=}CF{-}\overset{OH}{\overset{\mid}{C}}(CH_3)_2 \xrightarrow{P_2O_5} CF_2{=}CF{-}C(CH_3){=}CH_2 \quad (13)$$

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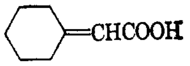
(12) D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters*, **22**, 20 (1960).

(13) A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, **76**, 479 (1954).

TABLE III

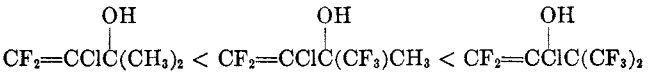
ANALYSES

Compd	Calcd			Found		
	C, %	H, %	F, %	C, %	H, %	F, %
$(CH_3)_2C=CFCOOH$	50.85	5.93	16.10	50.87	6.06	16.37
S-Benzylisothiuronium salt of $(CH_3)_2C=CFCOOH$	54.92	5.99		55.15	6.13	
$CH_3(CF_3)C(OH)CF=CF_2$	30.92	2.06		30.84	2.27	
$CH_3(CF_3)C=CFCOOH$	34.88	2.33		34.78	2.63	
$C_6H_5C(CH_3)=CFCOOH$	66.66	5.00		66.61	5.07	
$(C_6H_5)_2C=CFCOOH$	74.38	4.54		74.46	4.59	
$CH_3CH=CFCOOH$	46.15	4.81		46.30	4.89	
p-Nitrobenzyl ester of $CH_3CH=CFCOOH$	55.23	4.18		55.00	4.30	
$CF_3CH(OH)CF=CF_2$	26.67	1.11		26.43	1.23	
$C_6H_5CH=CFCOOH$	65.06	4.22		65.14	4.12	
S-Benzylisothiuronium salt of $C_6H_5CH=CFCOOH$	61.44	5.12		61.49	5.28	
$(CF_3)_2C(OH)CF=CF_2$			68.59			68.71
S-Benzylisothiuronium salt of $CF_2=CFCOOH$	45.20	3.77	19.52	45.01	3.61	19.50
$(CH_3)_2C=CClCOOH$	44.61	5.20		44.39	4.99	
$(CF_3)_2C(OH)CCl=CF_2$			57.46			57.40
$(CH_3)_2C(OH)C_4H_9$	72.41	13.80		72.18	13.71	
S-Benzylisothiuronium salt of 	62.75	7.20		62.62	7.26	
$(CH_3)_2C(OH)CCl=CClF$	34.68	4.05	10.99	34.82	4.04	11.22
$CH_3(CF_3)C(OH)CCl=CClF$ (isomer A)	26.43	1.76		26.63	1.95	
$CH_3(CF_3)C(OH)CCl=CClF$ (isomer B)	26.43	1.76		26.53	1.94	

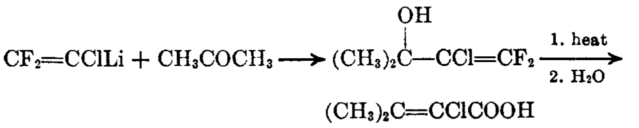
tion: OH, 2.99 μ; $CF=CF_2$, 5.65 μ) was only 90% pure (by glpc). Further manipulation to obtain greater purity resulted in rearrangement of the alcohol. A sample (90% purity) was cooled and phosphorus pentoxide added. On warming to room temperature, a vigorous reaction took place and a product distilled from the reaction flask. Infrared spectral evidence (no absorption due to OH; $CF_2=CF$, 5.57 μ; $CH_2=CH$, 6.08 μ) suggested that this was trifluoroisoprene but again the sample was only 90% pure (by glpc). Rapid polymerization prevented further purification or analysis.

Reaction of trifluorovinyllithium with hexafluoroacetone gave bis(trifluoromethyl)trifluorovinylcarbinol in good yield (Table II). This alcohol was stable to distillation and this fact provides further evidence for the enhancement of alcohol stability by trifluoromethyl group substitution.

Since 1-chloro-2,2-difluorovinyllithium contained a terminal difluoromethylene group, the product of its reaction with acetone would be expected to be unstable and rearrange to give α-chloro-β-methylcrotonic acid on heating followed by hydrolysis (eq 14). This acid was, in fact, isolated in low yield (15%). Reaction of the above lithium reagent with trifluoroacetone gave the expected carbinol ($CF_2=CClC(OH)(CF_3)CH_3$) in good yield (61%). The latter was apparently sufficiently stable to allow purification by distillation and preparative-scale glpc, but on allowing to stand for a few days at room temperature evolution of a small quantity of hydrogen fluoride was observed. Bis(trifluoromethyl)-1-chloro-2,2-difluorovinylcarbinol, obtained from reaction of hexafluoroacetone with 1-chloro-2,2-difluorovinyllithium, was completely stable on heating and on standing for long periods at room temperature. Thus the stability of the alcohols produced again increased with increasing trifluoromethyl group substitution, *i.e.*



$$CF_2=CCl\overset{OH}{\overset{|}{C}}(CH_3)_2 < CF_2=CCl\overset{OH}{\overset{|}{C}}(CF_3)CH_3 < CF_2=CCl\overset{OH}{\overset{|}{C}}(CF_3)_2$$

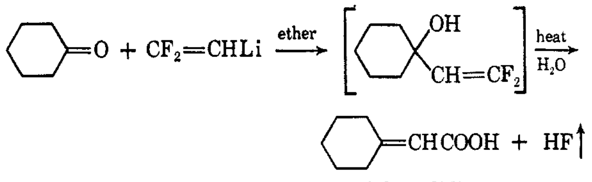


$$CF_2=CClLi + CH_3COCH_3 \longrightarrow (CH_3)_2\overset{OH}{\overset{|}{C}}-CCl=CF_2 \xrightarrow[2.\ H_2O]{1.\ heat} (CH_3)_2C=CClCOOH$$

α-chloro-β-methylcrotonic acid (15%) (14)

The product of reaction of 1-chloro-2,2-difluorovinyllithium with benzaldehyde rearranged on distillation to give α-chlorocinnamic acid (44%). The phenyl group is therefore not a sufficiently good electron acceptor to prevent attack on the difluoromethylene group. A similar result had been obtained previously on reaction of trifluorovinyllithium with benzaldehyde.[1]

A number of ketones were added to 2,2-difluorovinyllithium and the order of stability of the resulting tertiary alcohols was in agreement with the mechanism proposed for the rearrangement. The product from reaction with acetone, 2,2-difluorovinyldimethylcarbinol, rearranged even in ether solution without heating to give a low yield (9%) of β-methylcrotonic acid. 1-(2,2-Difluorovinyl)cyclohexylcarbinol, formed from reaction of cyclohexanone with 2,2-difluorovinyllithium, was a little more stable (eq 15). The alcohol did not rearrange on standing at room temperature. However, on attempted solvent removal by distillation (pot temperature 45°), rearrangement obviously occurred since the color of solution darkened considerably and hydrogen fluoride evolution was observed (eq 15).



(15)

cyclohexylidine
acetic acid (25%)

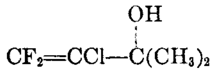
Cyclohexylidine acetic acid (25%) was isolated on removal of the solvent followed by treatment with aqueous alkali. It had been hoped that the rearrangement of the alcohol would not take place readily since product formation required the formation of an exocyclic double bond. The latter is known to be an energetically unfavorable process. Reaction of 2,2-difluorovinyllithium with trifluoroacetone and hexafluoroacetone gave alcohols which were apparently stable to distillation. Infrared spectra showed absorption due to OH (2.8 μ) and $CF_2{=}CH$ (5.92 μ). These alcohols rearranged, or otherwise decomposed, on attempted further purification by preparative-scale glpc. No pure products were isolated from these two reactions.

Finally, 1,2-dichloro-2-fluorovinyllithium was prepared by a metallation reaction and was shown to give stable carbinols on reaction with acetone and trifluoroacetone, *e.g.*

$$CClF{=}CClH + C_4H_9Li \longrightarrow CClF{=}CClLi + C_4H_{10}$$

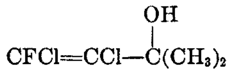
$$CClF{=}CClLi + CH_3COCH_3 \longrightarrow (CH_3)_2C(OH)CCl{=}CClF \quad (60\%)$$

The fact that 1,2-dichloro-2-fluorovinyllithium gave stable alcohols whereas analagous products from 1-chloro-2,2-difluorovinyllithium were unstable must be related directly to the comparative effects of chlorine and fluorine on the terminal carbon atoms of the molecules.



$CF_2{=}CCl{-}C(OH)(CH_3)_2$

unstable



$CFCl{=}CCl{-}C(OH)(CH_3)_2$

stable

Again an analogy exists in the attack of fluoro olefins by nucleophiles. Those fluoro olefins with terminal difluoromethylene groups are readily attacked in this position due to the mesomeric effect of vinylic fluorine as described earlier. Nucleophilic attack on fluoro olefins with terminal chlorofluoromethylene group does not readily occur and the reason given is that mesomeric electron release by vinylic chlorine is much less efficient than that by fluorine in a similar position since chlorine and carbon are of different size and p–π interaction is not so easily achieved.[9] The extent of this effect can be observed by comparing the acid strength of $CF_2{=}CFCOOH$ ($K_a \times 10^5 = 1580$) and $CCl_2{=}CClCOOH$ ($K_a \times 10^5 = 6200$).[13]

The starting 1,2-dichloro-1-fluoroethylene consisted of a mixture of equal amounts of geometric isomers but the isomeric products were in the ratio 4:1 in each case. One of the isomer of $CFCl{=}CCl(OH)(CH_3)_2$ isomerized on the preparative-scale glpc column. It has been suggested[14] that the vinyllithium group can be caused to react with a high degree of steric configuration retention but there have also been reports of loss of configuration of such compounds.[15]

Experimental Section[16]

Preparation and Reactions of Trifluorovinylmagnesium Bromide.—Trifluorovinyl bromide (0.3 mole) was dissolved in dry redistilled tetrahydrofuran (250 ml). A portion (10 ml) of this solution was added at room temperature to magnesium turnings (0.33 g-atom) in a four-necked flask equipped with a stirrer, dropping funnel, cooled (−78°) condenser, and nitrogen sweep. Initiation usually occurred immediately and the reaction flask was then immersed in a bath of ice water and the remainder of the halide solution added at the rate of 50 g/hr.

The Grignard solution was stirred for 1 hr at 0° and the carbonyl compound (0.3 mole) was then added slowly enough to prevent any temperature increase. After 1–2 hr, wet tetrahydrofuran, water, and 6 *N* hydrochloric acid were added in that order. The mixture was extracted with sodium bicarbonate and then water. The residue was steam distilled and the distillate extracted with ether. The extracts were dried ($CaSO_4$) and the products isolated by distillation and/or preparative-scale glpc.

The bicarbonate extract was acidified and the precipitated acidic products extracted in ether. The ether was dried ($CaSO_4$) and removed by distillation. The acidic product in the residue was purified by recrystallization or sublimation.

Reactions of Lithium Reagents Formed *via* Proton Exchange in Fluoro Olefins.—The fluoro olefin (0.05 mole) was transferred to a three-necked flask containing ether (120 ml) and the solution cooled to −100° under nitrogen. A solution of butyllithium (0.05 mole) in a mixed solvent of 32 ml of pentane and 32 ml of ether was precooled to −78° and then added dropwise to the reaction mixture. The latter was maintained at −100° for 30 to 60 min and then allowed to warm to −78°. At this stage the carbonyl compound (0.05 mole) was added in ether (30 ml) solution.

Volatile ketones were transferred to flask containing phosphorus pentoxide and then bubbled into the reaction flask. The reaction mixture was allowed to attain room temperature slowly.

The lithium salts of the products were hydrolyzed by addition of water (20 ml) followed by 6 *N* hydrochloric acid (20 ml) to the reaction mixture. Normally a white solid was precipitated, which redissolved on stirring. The organic layer was separated and dried (Drierite), and the solvents were removed by distillation. The products were again purified by distillation and preparative-scale glpc. Where carboxylic acids were formed, a violent reaction normally occurred during product distillation with the simultaneous evolution of hydrogen fluoride. The acid was isolated by extraction with aqueous sodium bicarbonate solution, acidification of the extract, and further extraction with ether. The latter was removed after drying ($CaSO_4$) and the residue purified by recrystallization (water) or sublimation.

Preparation and Reactions of 2,2-Difluorovinyllithium.—Vinylidene fluoride was bubbled into bromine (illumination) and a quantitative yield of 1,2-dibromo-1,1-difluoroethane, bp 91–92° (lit.[17] 91°), was obtained. The latter (0.312 mole) was treated with potassium hydroxide pellets (1.43 mole) at 60–80°. Vigorous mechanical stirring was maintained throughout the reaction and 1-bromo-2,2-difluoroethylene, bp 6° (lit.[18] bp 6.1°), distilled directly from the reaction flask in high yield (90%).

2,2-Difluorovinyl bromide (0.05 mole) was transferred from phosphorus pentoxide to a flask containing ether (100 ml) under nitrogen. The flask was then cooled to −78° and similarly cooled solutions of butyllithium (0.05 mole) in hexane and the carbonyl compound (0.05 mole) in ether (40 ml) were then added dropwise and alternatively in four equal aliquots. The reaction mixture was then allowed to warm slowly to room temperature.

The work-up procedure was identical with that described above for reactions with lithium reagents formed *via* proton exchange.

Preparation and Reaction of 1-Fluorovinyllithium.—Vinyl fluoride was bubbled into bromine under illumination and a good yield (88%) of 1,2-dibromo-1-fluoroethane bp 121–122° (lit.[19] bp 122.5°) was obtained.

The above dibromide (0.5 mole) was added dropwise to potassium hydroxide pellets (1.8 mole). No reaction was observed until the flask was heated (vigorous stirring) to 60°. Heating was continued at 60–80° until no more gaseous product was evolved (3 hr). The volatile products were condensed in a Dry Ice–acetone cooled trap which necessarily contained an inhibitor (α-pinene) to prevent polymerization. Phosphorus pentoxide was added and an attempt was made to distil the product. This was achieved only with difficulty since there was presumably some monofluoroacetylene present, which decomposed with accompanying explosions and carbon deposition.

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[19] F. Swarts, *Bull. Acad. Roy. Belg.*, 728 (1909).

Monofluoroacetylene is known to decompose at its boiling point.[20] As a consequence of this, yields of 1-fluorovinyl bromide, bp 6–8° (lit.[21] bp 6.8°) varied considerably in successive runs (20–45%). Attempts to repeat the experiment in mineral oil gave similar results and no 1-fluorovinyl bromide was obtained from the reaction carried out in ethanol.

The preparation and reaction of 1-fluorovinyllithium were then carried out in a manner similar to that described previously for 2,2-difluorovinyllithium.

Registry No.—1, 15051-86-2; 1 S-benzylisothiuronium salt, 15051-85-1; 2, 1869-14-3; 3, 15051-83-9; 4, 708-84-9; 5, 15052-21-8; 6, 430-99-9; 7, 2365-87-9; 7 p-nitrobenzyl ester, 15156-69-1; 8, 15052-24-1; 9, 350-90-3; 9 S-benzylisothiuronium salt, 15052-26-3; 11, 15052-92-3; 12 S-benzylisothiuronium salt, 15053-97-1; 13, 15052-93-4; 14, 15052-94-5; 15, 15053-98-2; 16, 1727-39-5; 17, 625-23-0; 18, 541-47-9; 20, 1552-91-6; 20 S-benzylisothiuronium salt, 15052-99-0; 21, 5851-65-0; 22, 15053-01-7.

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Quantitative Studies in Stereochemistry. B. Photochemistry. II. Solvent and Basicity Effects on the Ratio of Diastereomeric Glycols Formed in the Ultraviolet-Promoted Bimolecular Reduction of Acetophenone-7-C^{14} and Benzaldehyde-7-C^{14}

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Substitution of various media for the 2-propanol customarily employed in the photopinacolization of acetophenone produced small but real changes in the ratio of *dl/meso* diastereomers formed. Values from 1.03 (cyclohexane) to 1.31 (50% aqueous 2-PrOH) were observed. In the presence of strong base in 2-propanol, *dl/meso* ratios as high as 3:1 were found. It is proposed that the more stereoselective reactions in base result from the combination of radical anions with ketyl radicals. The *dl/meso* ratios for benzaldehyde were observed to be lower than those for acetophenone under identical reaction conditions. The glycols proved stable to the strongly alkaline reaction conditions.

A recent report[1] from this laboratory described the ratio of diastereomeric acetophenone pinacols resulting from the ultraviolet irradiation of acetophenone-7-C^{14} in slightly acidic 2-propanol. Employing wavelengths above 3000 A, a remarkably constant predominance of the *dl*-pinacol over the *meso* form in an 11:10 ratio was observed irrespective of time, concentration of ketone, intensity of radiation, and degassing.

The possibility of carrying out the pinacolization reaction in other than neutral or slightly acidic media was not seriously considered during the early part of the investigation; strongly acidic media might induce the pinacols present to rearrange, while alkaline media are routinely avoided in photopinacolizations to the point of adding sufficient acid to insure nonbasicity. This latter practice derives from reports by Bachmann[2,3] that the pinacol derived from benzophenone cleaved in alkaline media to benzhydrol plus regenerated ketone rapidly and in sufficiently good yield to make the method of synthetic value. This report has been confirmed with a change in mechanism by Cohen and Sherman[4] who have utilized this reaction for analytical purposes.[5] Data are hereby offered to indicate that the pinacolization of acetophenone does indeed occur in basic as well as acidic media but with quite different stereochemical consequences.

To provide some significant comparisons, the stereochemistry of the photochemical bimolecular reduction of benzaldehyde was also studied. The use of this system was designed to permit a comparison of the relative importance of the methyl group in acetophenone with the aldehydic hydrogen in benzaldehyde in determining the resultant stereochemistry. This system lent itself well to examination; the labeled aldehyde was commercially available, the diastereomeric hydrobenzoins were conveniently accessible by standard synthetic techniques (see Experimental Section), and their identities have been satisfactorily established.[6]

Additional stereochemical information was obtained from selected variations in temperature and the composition of the solvent/donor. The stabilities of the pinacols and glycols were also examined.

Results and Discussion

The *dl/meso* ratios of diastereomers formed are tabulated in Table I. It is probably most convenient to examine the stereochemistry of the acetophenone system first. The data may be divided into two distinct ranges, 1.0 to 1.3 and above 2.4. Most significant is the high stereoselectivity arising from the use of strong bases in the reaction media. The authors would like to propose that a radical anion II results from base attack upon the ketyl radical I,[1] reaction 1.

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