Ethylation at Low Temperatures.—The apparatus used for ethylation was similar to that used for *t*-butylation.[1] A glass flask was charged with 0.022 mole of toluene and the toluene frozen with liquid nitrogen. The glass flask was then evacuated and 0.022 or 0.21 mole of ethyl fluoride and 0.022 or 0.21 mole of boron fluoride condensed onto the frozen toluene. The flask was then immersed in a Dry Ice bath or a low temperature bath at the melting point of chlorobenzene (−45°) or toluene (−95°). The vapor pressure was measured by a manometer. The yellow solution formed in the flask. After the solution had been kept for several hours in the cold bath, a valve which connected the flask to an evacuated glass vessel cooled with liquid nitrogen was opened. Any volatile material was thus withdrawn and condensed in the vessel. This procedure was continued for about 2 hr and the valve then closed. The withdrawn volatile material in the vessel was allowed to warm and was then transferred to another glass gas reservoir. A small amount of colorless liquid which had a high vapor pressure, remained in the vessel at room temperature. The liquid, which might be hydrogen fluoride, was completely evaporated. The gas was introduced into the gas reservoir and a white deposit was found in the vessel which had corroded. The gas introduced into the reservoir was analyzed with a 15-cm, 60°-sector-type mass spectrometer made in our laboratory. The boron fluoride and ethyl fluoride peaks were observed at *m/e* 68, 67, 49, 48, 30, 29, etc. and at *m/e* 47, 46, 45, 33, 28, 27, 26, etc. Silicon fluoride peaks were observed at *m/e* 85, 66, 47, 28, etc. For comparison, commercial hydrogen fluoride was evaporated in the above glass vessel at room temperature and the resulting gas was analyzed. Peaks were observed at *m/e* 85, 66, 47, 28, etc. Analysis of the gas withdrawn from the 1:1:1 complex at −45 or −80° gave a spectrum in which the peak intensities for ethyl fluoride were much lower than those for boron fluoride and silicon fluoride.

The gas obtained by evaporation of the nonionized ethyl fluoride–boron fluoride complex at −80° was analyzed. The intensities of the peaks due to boron fluoride and ethyl fluoride were high, but no peaks due to silicon fluoride were detected at *m/e* = 85, etc.

Ammonia was added to the liquid and the mixture allowed to warm to room temperature. The flask was slightly corroded. The liquid was separated from the white solid and directly analyzed with a Hitachi Perkin-Elmer Programmed Temperature Gas Chromatograph Model F 6 D using a Golay column HB-2000 (length, 45 m; i.d., 0.5 mm) coated with polypropylene glycol (UCON oil 50-HB-2000 Poly) and a hydrogen flame ionization detector. The column temperature was 120° with a dry nitrogen gas flow rate of approximately 4.5 cc/min. The accuracy of measurements of *ortho*, *meta*, and *para* isomers in monoethyltoluenes was checked by analyses of standard samples of isomers obtained from Tokyo Kagaku Sieki Co. The *meta* and *para* isomers were not separated sufficiently well on the above capillary column, although it was possible to separate the *ortho* isomer from the combined *meta* and *para* isomers.

Registry No.—Boron fluoride, 7637-07-2; ethyl fluoride, 353-36-6; $C_2H_5F{-}BF_3$ complex, 373-60-4; $C_6H_5CH_3{-}C_2H_5F{-}BF_3$, 4601-90-5; $C_6H_5CH_3$, 108-88-3.

The Preparation and Reactions of Lithium Derivatives of Trifluoropropene and Trifluoropropyne

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3,3,3-Trifluoroisopropenyllithium has been prepared by exchange metallation between 3,3,3-trifluoroisopropenyl bromide and an alkyllithium reagent. The unsaturated fluoroorganic lithium compound is unstable even below −90° decomposing by elimination of lithium fluoride to produce 1,1-difluoroallene. Reaction of butyllithium with 1,1,1-trifluoropropyne has given 3,3,3-trifluoropropynyllithium which is stable up to 0°. Good yields of unsaturated alcohols have been obtained on reaction of each of the above lithium compounds with carbonyl compounds. Some of the alcohols have been dehydrated to give high yields of fluorine-containing substituted butadienes, which may give useful polymeric products. Reactions with triethylchlorosilane and the synthetic limitations of the lithium reagents are also discussed.

Many fluoroorganic lithium and Grignard reagents have been prepared by exchange metallation between alkyllithium and Grignard reagents and fluoroorganic compounds containing bromine,[1] iodine,[2] or "acidic" hydrogen[3,4] atoms.

Here we report the preparation of 3,3,3-trifluoroisopropenyllithium and 3,3,3-trifluoropropynyllithium.

The former reagent was prepared by reaction of trifluoroisopropenyl bromide with butyllithium (eq 1).

$$CF_3CBr{=}CH_2 + C_4H_9Li \longrightarrow CF_3CLi{=}CH_2 + C_4H_9Br \quad (1)$$

Trifluoroisopropenyl bromide was prepared by quantitative bromination of trifluoropropene, followed by dehydrobromination by potassium hydroxide in the absence of solvent (eq 2). This method proved more

$$CF_3CH{=}CH_2 \xrightarrow{Br_2} \underset{100\%}{CF_3CHBrCH_2Br} \xrightarrow[\text{no solvent}]{KOH} \underset{100\%}{CF_3CBr{=}CH_2} \quad (2)$$

suitable than that reported in the literature[5] and gave the product in quantitative yield. The extent of exchange was determined by the amount of butyl bromide produced. When the exchange reaction was conducted at temperatures higher than −90°, the yield of useful products obtained by reaction of trifluoroisopropenyllithium and a carbonyl compound was low compared with the actual amount of lithium reagent produced as indicated by the butyl bromide formed. Apparently, the lithium reagent underwent decomposition before the desired reaction could occur.

Thus, the problem became an experimental one of preparing the fluoroorganic lithium compound and preventing its decomposition before the carbonyl compound was added.

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

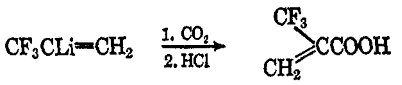
(2) R. N. Sterlin, L. N. Pinkina, I. L. Knunyants, and L. F. Nezgovorov, *Khim. Nauka i Promy.*, **4**, 809 (1959); *Chem. Abstr.*, **54**, 10837 (1960).

(3) R. D. Chambers, F. G. Drakesmith, and W. K. R. Musgrave, *J. Chem. Soc.*, 5045 (1965).

(4) F. G. Drakesmith, R. D. Richardson, O. J. Stewart, and P. Tarrant, in press.

(5) A. L. Henne and M. Nager, *J. Am. Chem. Soc.*, **73**, 1042 (1951).

The exchange reactions were normally carried out by adding a solution of butyllithium in hexane or pentane and ether, cooled to −78°, to a solution of 3,3,3-trifluoroisopropenyl bromide in diethyl ether at temperatures lower than −90°. If the bromide was added to the butyllithium solution, side reactions occurred giving products due to addition–elimination,[6] *e.g.*, $CF_2{=}CBrCH_2C_4H_9$. Attempts to prepare trifluoroisopropenyllithium by exchange in other solvents were not successful. In hexane solution, exchange did not occur, and in tetrahydrofuran solution extensive degradation took place and no useful products were obtained. Two techniques for the preparation of trifluoroisopropenyllithium and its reaction with carbonyl compounds were applied. When the carbonyl compound was liquid, it was convenient to add alternate aliquots of butyllithium and carbonyl compound to the trifluoroisopropenyl bromide solution. In this way, the reaction could be performed at temperatures from −100 to −90°; the desired lithium reagent as it was formed immediately reacting with the carbonyl compound. When the carbonyl compound was a gas, however, as in the carbonation reaction to produce 2-trifluoromethyl acrylic acid, a different technique was necessary. Here butyllithium was added to trifluoroisopropenyl bromide solution cooled to −110 ± 3°; after allowing to warm to −100° over 15 min, carbon dioxide was passed into the reaction mixture. 2-Trifluoromethyl acrylic acid was obtained in 56% yield (eq 3).



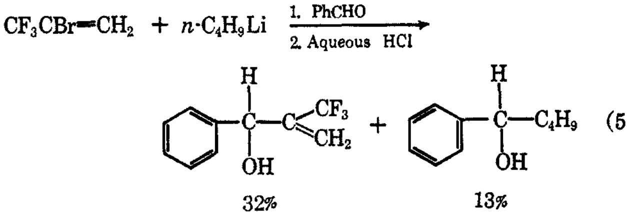
$$CF_3CLi{=}CH_2 \xrightarrow[2.\ HCl]{1.\ CO_2} (CF_3)(CH_2{=})CCOOH \qquad (3)$$

By applying either of these techniques it was possible to prepare 3,3,3-trifluoroisopropenyllithium and allow it to react with carbonyl compounds before extensive decomposition could occur.

A study of the decomposition reaction showed that it provided a useful synthetic route to 1,1-difluoroallene. When 3,3,3-trifluoroisopropenyllithium was prepared at −90° and allowed to warm to room temperature, lithium fluoride was produced almost quantitatively together with 1,1-difluoroallene in 72% yield (eq 4).

$$CF_3CLi{=}CH_2 \longrightarrow CF_2{=}C{=}CH_2 + LiF \qquad (4)$$

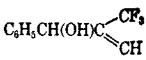
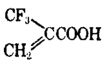
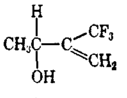
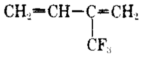
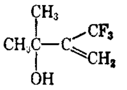
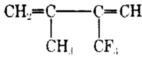
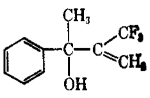
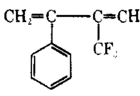
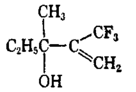
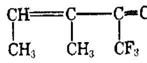
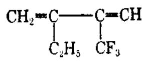
3,3,3-Trifluoroisopropenyllithium was prepared and allowed to react with benzaldehyde using the aliquot technique to give α-(trifluoroisopropenyl)benzyl alcohol in 32% yield (eq 5).



If the type of reaction described above could be accomplished with carbonyl compounds in general, then it seemed likely that reaction with compounds to produce alcohols possessing hydrogen on an α-carbon atom would afford a general route to substituted butadienes. This proved to be the case, and trifluoroisopropenyllithium was shown to react normally with a number of carbonyl compounds to give alcohols, which on heating with phosphorus pentoxide gave high yields of fluorine-containing substituted butadienes. (See Table I). Whereas the reactions of trifluoroisopropenyllithium with the above carbonyl compounds were normal, the reaction with trifluoroacetone was anomolous. Several experiments under varying conditions were performed, but in none was the expected product, methyltrifluoromethyltrifluoroisopropenylcarbinol obtained (see Scheme I). Instead, mixtures were obtained of methylbutyltrifluoromethylcarbinol (I), 1,1,1,5,5,5-hexafluoro-2-methylpentan-4-on-2-ol (II), and a pyran derivative (III), owing to the cyclization reaction of trifluoroacetone.[7]

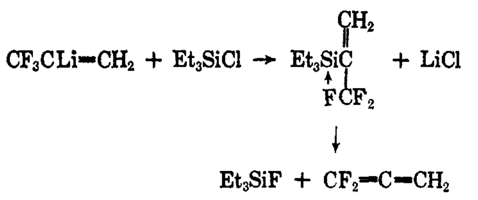
TABLE I

REACTIONS OF TRIFLUOROISOPROPENYLLITHIUM WITH CARBONYL COMPOUNDS AND DEHYDRATION PRODUCTS

Carbonyl compounds	Product	Yield, %	Dehydration product	Yield, %
C_6H_5CHO		32		
CO_2		56		
CH_3CHO		44		84
$(CH_3)_2CO$		46		49
$C_6H_5COCH_3$		51		82
$C_2H_5COCH_3$		42	Isomeric mixture of  and 	78

Apparently, trifluoroisopropenyllithium preferentially abstracts a proton from trifluoroacetone rather than attacking the carbonyl function.

In an attempt to prepare a trifluoroisopropenyl derivative of silicon, the reaction between trifluoroisopropenyllithium and triethylchlorosilane was investigated (see eq 6). The formation of the desired lithium reagent was successful, as indicated by the amount of butyl bromide produced, but the only prod-



$$CF_3CLi{=}CH_2 + Et_3SiCl \rightarrow Et_3SiC({=}CH_2)CF_2F + LiCl \qquad (6)$$
$$\downarrow$$
$$Et_3SiF + CF_2{=}C{=}CH_2$$

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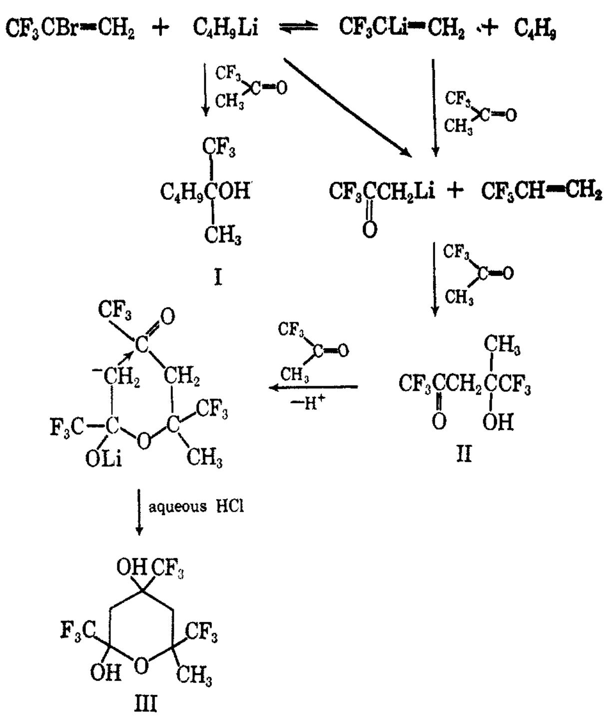
[6] R. Fontanelli and D. Sianesi, *Ann. Chim.*, **55**, 862 (1965); *Chem. Abstr.*, **64**, 578 (1966).

[7] A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5147 (1954).

SCHEME I



uct obtained was triethylfluorosilane in small yield (11%). Most of the chlorosilane was recovered unreacted. Lithium fluoride and chloride were obtained in 61 and 29% yields, respectively. The exact mechanism of this reaction and the route by which the fluorosilane was produced are not clear, but possibly initial formation of triethyl(trifluoroisopropenyl)silane, followed by fluorine migration to the silicon atom with elimination of difluoroallene took place. It is known that β-chlorinated alkylsilanes are unstable to heat[8] and decompose to give chlorosilane and alkene. Silicon perfluoroalkoxides undergo a similar rearrangement.[9] Lithium fluoride does not react with triethylchlorosilane under the conditions used. Dixon[10] found that a number of fluoro olefins reacted with organolithium compounds to give a haloalkene in which a fluorine atom had been replaced by an alkyl or aryl group. No comparable reaction occurred between *unsym*-dichlorodifluoroethylene and trifluoroisopropenyllithium. Similarly, attempts to achieve nucleophilic substitution of fluorine in hexafluorobenzene with trifluoroisopropenyllithium were unsuccessful. Butyl bromide was obtained in good yield and hexafluorobenzene was recovered.

When trifluoroisopropenyllithium was prepared and treated with other compounds less reactive to Grignard and lithium reagents than those with carbonyl groups, *e.g.*, benzonitrile,[11] the usual result was that no useful products were observed, butyl bromide, lithium fluoride, difluoroallene, and the substrate being recovered. In these reactions, trifluoroisopropenyllithium was formed, as confirmed by the production of butyl bromide but obviously the reagent decomposed before the desired reaction could occur. This again demonstrates that it is necessary for trifluoroisopropenyllithium to attack the other reactant at temperatures below approximately −90°, otherwise decomposition of the lithium reagent takes place.

Attempts to prepare 3,3,3-trifluoroisopropenyllithium by reaction of butyllithium with trifluoroisoprene were unsuccessful. Addition of acetone to a mixture of these two reactants at −78° gave only butyldimethylcarbinol (89%) by reaction of unchanged butyllithium with the carbonyl compound. On allowing a mixture of butyllithium and trifluoroisopropene in ether solution to warm from −78° to room temperature three products were obtained. The first of these was 1,1-difluoroheptene resulting from addition of butyllithium to the double bond followed by lithium fluoride elimination (eq 7). The other two products

$$\begin{tikzcd} CF_3CH{=}CH_2 + C_4H_9Li \arrow[r] & CF_3CHLiCH_2C_4H_9 \arrow[d, "-LiF"] \\ & CF_2{=}CHC_5H_{11}\ (5\%) \end{tikzcd} \quad (7)$$

were inseparable by distillation or preparative-scale glpc and may have consisted of a mixture of 5-fluoroundecene-5 and 5-fluoroundecyne-5 resulting from further attack of butyllithium as shown in eq 8. This reaction has been described by Fontanelli and Sianesi[6] and a similar product mixture was obtained.

$$\begin{tikzcd} C_4H_9Li + CF_2{=}CHC_5H_{11} \arrow[r] & C_4H_9CF_2CHLiC_5H_{11} \arrow[d] \\ C_4H_9C{\equiv}CC_5H_{11} \arrow[r, "C_4H_9Li"] & C_4H_9CF{=}CHC_5H_{11} \end{tikzcd} \quad (8)$$

The next objective was to find a more stable fluorinated, unsaturated lithium reagent which might be of greater synthetic value than trifluoroisopropenyllithium. 3,3,3-Trifluoropropynyllithium was expected to be particularly stable since 1,1 or 1,2 elimination of lithium fluoride from the molecule was impossible.

A number of trifluoropropynylmetallic compounds have already been prepared, *e.g.*, $CF_3C{\equiv}CAg$, $CF_3C{\equiv}CCu$, $(CF_3C{\equiv}C)_2Hg$,[12] and $(CF_3C{\equiv}C)_2Zn$ (or $CF_3C{\equiv}CZn$ halide).[13] Trifluoropropynylmagnesium bromide has been made and treated with acetone to give, on hydrolysis, dimethyltrifluoropropynylcarbinol in high yield (75%).[14] Trifluoropropynylmagnesium iodide has also given the desired substituted compounds on reaction with various organometallic halides.[15] There is one report of the preparation of trifluoropropynyllithium *via* reaction of trifluoropropyne with lithium amide. The organolithium compound was then allowed to react with steroidal ketones to give biologically useful carbinols.[16]

We have prepared 3,3,3-trifluoropropynyllithium in high yield *via* exchange of the acidic terminal proton of 1,1,1-trifluoropropyne with butyllithium. The reaction conditions for this preparation were much less critical than those required in the preparation of trifluoroisopropenyllithium. A solution of butyllithium in ether was added to a similar solution of trifluoropropyne at −78°. The solution was stirred while warming to

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[8] C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, p 133.

[9] C. G. Krespan, in press.

[10] S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[11] C. G. Swain, *J. Am. Chem. Soc.*, **69**, 2306 (1947).

[12] R. N. Haszeldine, *J. Chem. Soc.*, 588 (1951).

[13] (a) W. P. Norris and W. G. Finnegan, *J. Org. Chem.*, **31**, 3292 (1966). (b) W. P. Norris and W. G. Finnegan, *ibid.*, **28**, 1139 (1963).

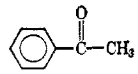
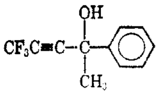
[14] A. L. Henne and M. Nager, *J. Am. Chem. Soc.*, **74**, 650 (1952).

[15] W. R. Cullen and W. R. Leeder, *Inorg. Chem.*, **5**, 1004 (1966).

[16] British Drug Houses Ltd.; *Chem. Abstr.*, **64**, 8266*b* (1966).

TABLE II

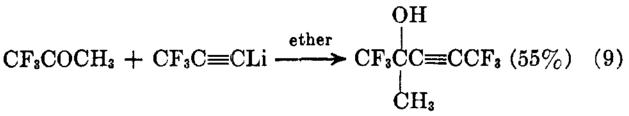
REACTIONS OF 3,3,3-TRIFLUOROPROPYNYLLITHIUM WITH VARIOUS CARBONYL COMPOUNDS AND TRIETHYLCHLOROSILANE

Reactant	Product[a]	Yield, %	Bp or (mp), °C	Refractive index	Formula	Calcd, % H	Calcd, % C	Calcd, % F	Found, % H	Found, % C	Found, % F
$(CH_3CH_2)_3SiCl$	$(CH_3CH_2)_3SiC\equiv CCF_3$	81	160	$n^{24}D$ 1.3542	$C_9H_{15}F_3Si$	7.25	51.92	27.34	7.22	51.71	27.10
CH_3COCH_3	$CF_3C\equiv C\overset{OH}{C}(CH_3)_2$	70	110–112[b]	$n^{27}D$ 1.3642[c]							
CH_3COCF_3	$CF_3C\equiv C\overset{OH}{C}(CH_3)CF_3$	55	96	$n^{24}D$ 1.3230	$C_6H_4F_6O$	1.94	34.95	55.34	1.98	34.72	55.51
CF_3COCF_3	$CF_3C\equiv C\overset{OH}{C}(CF_3)_2$	25	86	$n^{24}D$ <1.3000	C_6HF_9O	0.39	27.68	65.78	0.53	27.74	65.43
CH_3CH_2CHO	$CF_3C\equiv C-\overset{OH}{\underset{H}{C}}-CH_2CH_3$	54	118	$n^{24}D$ 1.3679	$C_6H_7F_3O$	4.60	47.37	37.50	4.82	47.29	37.27
		69	71–73		$C_{11}H_9F_3O$	4.21	61.68	26.63	4.49	61.90	26.32
$CH_3COOCH_2CH_3$	$(CF_3C\equiv C)_2-\overset{OH}{C}-CH_3$	25	130	$n^{24}D$ 1.3540	$C_8H_4F_6O$	1.74	41.47	49.57	1.87	41.55	49.87
CH_3COCl	$(CF_3C\equiv C)_2\overset{OH}{C}-CH_3$	54	130	$n^{24}D$ 1.3540	$C_8H_4F_6O$	1.74	41.47	49.57	1.87	41.55	49.87

[a] Infrared and ^1H and ^{19}F nmr spectra were consistent with these structures. [b] Lit.[14] bp 110–111°. [c] Reference 14; $n^{20}D$ 1.3629.

−40° and then chilled to −78° again before addition of any other reactants.

Trifluoropropynyllithium has been allowed to react with a number of aldehydes and ketones and excellent yields of the trifluoropropynyl-substituted carbinols were obtained. (The physical properties are shown in Table II.) Of particular interest was the reaction of fluorinated ketones which proved successful in forming acetylenic alcohols (eq 9).

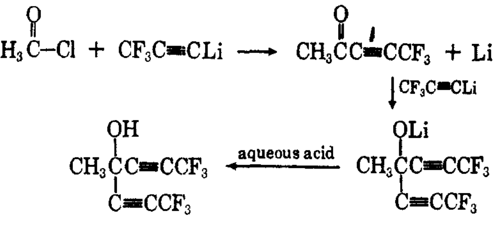


$$CF_3COCH_3 + CF_3C\equiv CLi \xrightarrow{\text{ether}} CF_3\overset{OH}{\underset{CH_3}{C}}C\equiv CCF_3 \ (55\%) \quad (9)$$

Reaction of trifluoroisopropenyllithium with trifluoroacetone gave Claisen condensation products resulting from attack on the acidic proton of trifluoroacetone rather than on the carbonyl function (see Scheme I).

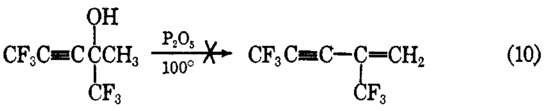
Acetyl chloride and ethyl acetate both reacted with 2 moles of trifluoropropynyllithium to give an interesting di(trifluoropropynyl)-substituted carbinol (see Scheme II).

SCHEME II



Reaction of triethylchlorosilane with the above lithium reagent gave triethyl trifluoropropynyl silane in 81% yield. No trace of triethylfluorosilane was observed. Again this was not unexpected since there was no β fluorine present in the molecule.

Although excellent yields of acetylenic carbinols were obtained, attempts to dehydrate these by heating with phosphorus pentoxide did not give the expected enynes, (see eq 10). Indeed no reaction at all took place on heating to 100–150°.



$$CF_3C\equiv C\overset{OH}{\underset{CF_3}{C}}CH_3 \xrightarrow[100^\circ]{P_2O_5} CF_3C\equiv C-\underset{CF_3}{C}=CH_2 \quad (10)$$

Attempted reactions of 3,3,3-trifluoropropynyllithium with hexafluorobenzene, benzonitrile, and fluoro olefins were unsuccessful. In each case, the starting material was recovered and a black insoluble solid was precipitated between 0° and room temperature. The latter presumably resulted from decomposition of trifluoropropynyllithium. It is interesting to note that decomposition did not take place below 0°. We have shown earlier that decomposition of trifluoroisopropenyllithium took place even at −90°. Most other known fluorine-containing unsaturated lithium reagents decompose also between −10 and 15° to give lithium fluoride and largely an intractable polymer.[17]

Experimental Section[18]

Preparation of Trifluoroisopropenyl Bromide.—Potassium hydroxide pellets (100 g) were placed in a three-necked flask fitted with a dropping funnel, stirrer, and distillation apparatus. Trifluorodibromopropane (100 g, 0.39 mole) was dropped onto the stirred potassium hydroxide which was cooled in an ice bath. When all the dibromide had been added, the ice bath was replaced by a water bath and the temperature increased until product began to distil out of the reaction vessel. Occasional immersion of the flask in the ice bath was required to control the rate of reaction.

The weight of product, $CF_3CBr{=}CH_2$, was 68 g (99% yield), bp 33° (lit.[5] bp 33°).

Reaction of Trifluoroisopropenyllithium with Benzaldehyde.—Trifluoroisopropenyl bromide (10 g, 0.057 mole) in dry diethyl ether (50 ml) was cooled to −95° under dry nitrogen. Butyllithium (0.057 mole) in mixed solvent (hexane (34.6 ml)–ether (50 ml)), precooled to −78°, and benzaldehyde (6.2 g, 0.057 mole) in ether (15 ml) were added alternatively in four aliquots each, the benzaldehyde solution being added immediately after the butyllithium solution. After the final addition, the temperature was maintained between −90° and −95° for 2 hr and then the reaction was allowed to warm very slowly to room

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

[18] Analyses by Galbraith Laboratories, Knoxville, Tenn.

temperature. Water (15 ml) was added, causing a dense white precipitate to form, followed by aqueous hydrochloric acid (1:1) (15 ml) which redissolved the solid to give a pale green solution. The organic layer was separated and dried ($CaSO_4$) and the solvent removed by distillation.

Fractionation at atmospheric pressure gave butyl bromide (2.6 g, 0.0190 mole, 33% yield), and at reduced pressure gave (a) 3.7 g (32% yield) of α-(trifluoroisopropenyl)benzyl alcohol, bp 122° (21 mm), $n^{22.5}$D 1.4746 (the infrared and ^1H and ^{19}F nmr spectra were consistent with this structure), and (b) 1.2 g (13% yield) of α-butyl benzyl alcohol, bp 95° (1.0 mm).

Anal. Calcd for $C_{10}H_9F_3O$: C, 59.41; H, 4.45; F, 28.21. Found: C, 59.65; H, 4.60; F, 27.96.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.49; H, 9.75. Found: C, 80.44; H, 8.70.

The Reaction with Acetone.—The use of the procedure described above with acetone gave the following compounds: butyl bromide, 43%, and dimethyl(trifluoroisopropenyl)carbinol, bp 116–117°, $n^{22.5}$D 1.3773.

Anal. Calcd for $C_6H_9F_3O$: C, 46.75; H, 5.85; F, 37.01. Found: C, 46.92; H, 6.00; F, 36.83.

The infrared and ^1H and ^{19}F nmr spectra were consistent with the assigned structure.

The Reaction with Acetaldehyde.—The products of the reaction, carried out in the usual manner, were separated by preparative-scale glpc (dinonyl phthalate, 100°). The carbinol, methyl (trifluoroisopropenyl)carbinol, bp 110–111°, $n^{22.5}$D 1.3646, was obtained in 44% yield.

Anal. Calcd for $C_5H_7F_3O$: C, 42.86; H, 5.00; F, 40.71. Found: C, 42.57; H, 4.93; F, 40.54.

The infrared spectrum was consistent with this structure.

The Reaction with Methyl Ethyl Ketone.—Trifluoroisopropenyl bromide (10 g, 0.057 mole) in diethyl ether (100 ml) was cooled to −90° under dry nitrogen. Butyllithium (0.057 mole) in hexane (34.6 ml)–ether (60 ml), precooled to −78°, and methyl ethyl ketone (4.16 g, 0.057 mole) in ether (50 ml) were alternately added in four aliquots each while the temperature was maintained for 3 hr. The products were processed in the way described above with fractional distillation giving butyl bromide (88.5%) and methylethyl(trifluoroisopropenyl)carbinol (42.5%), bp 130–131°, n^{25}D 1.3880.

Anal. Calcd for $C_7H_{11}F_3O$: C, 50.00; H, 6.55; F, 33.93. Found: C, 50.16; H, 6.70; F, 33.86.

The infrared ^1H and ^{19}F nmr spectra were consistent with the assigned structure.

Reaction with Acetophenone.—The reaction was carried out in the described manner for benzaldehyde. The products were separated by preparative-scale glpc (Carbowax, 200°) and consisted of butyl bromide (77%) recovered acetophenone (13%), and methylphenyl(trifluoroisopropenyl)carbinol (51%), bp 210–211°, n^{25}D 1.4785.

Anal. Calcd for $C_{11}H_{11}F_3O$: C, 61.11; H, 5.09; F, 26.39. Found: C, 61.06; H, 5.12; F, 26.63.

The infrared and ^1H and ^{19}F nmr spectra support the structure.

Reaction with Trifluoroacetone.—The reaction was carried out at −115° in the usual manner. Preparative-scale glpc was used to separate the products which were (a) butyl bromide (45%); (b) 1,1,1,5,5,5-hexafluoro-2-methyl-2-pentan-4-on-2-ol, (16%), bp 122–123°; (c) methylbutyltrifluoromethylcarbinol (10%), bp 135–136°, n^{25}D 1.3755; and (d) crude pyran derivative III (0.1 g) which on recrystallization from pentane gave mp 94–95° (lit.[7] 92–93°).

Anal. Calcd for $C_6H_6F_6O_2$: C, 32.14; H, 2.68; F, 50.89. Found: C, 32.38; H, 2.80; F, 50.68.

Anal. Calcd for $C_7H_{13}F_3O$: C, 49.41; H, 7.65; F, 33.53. Found: C, 49.18; H, 7.65; F, 33.20.

Anal. Calcd for $C_9H_9F_9O_3$: C, 32.15; H, 2.68; Found: C, 32.35; H, 2.80.

The infrared and ^1H and ^{19}F nmr spectra were in agreement with the assigned structures.

Preparation of 1,1-Difluoroallene.—Trifluoroisopropenyl bromide (10 g, 0.057 mole) in diethyl ether (30 ml) was cooled to −90° under dry nitrogen. Butyllithium (0.057 mole) in mixed solvent (hexane (34.6 ml)–ether (40 ml)), was added dropwise with stirring and the temperature maintained at −90 ± 2° for a further 30 min, before allowing the reaction to warm to room temperature. The overgases were condensed in an acetone–Dry Ice trap. The reaction mixture became dark colored at approximately −30° and precipitation of a solid material increased as the temperature rose.

At room temperature, water (40 ml) was added and the mixture filtered to give a solid (1.4 g) which was shown to be lithium fluoride (∼95%) together with some polymeric organic material.

The organic layer was separated and the aqueous layer extracted with ether. The ethereal extracts were combined and dried ($CaSO_4$). Glpc showed only the presence of ether, hexane, and butyl bromide. Fractional distillation gave butyl bromide (5.8 g, 74%).

The condensed overgases were distilled at low temperature to give difluoroallene with a boiling range of −20 to −21° (lit.[19] bp −20°), 3.1 g (72%).

The infrared spectrum of this compound was identical with that of an authentic sample of difluoroallene.[19]

Reaction of Trifluoroisopropenyllithium with Carbon Dioxide.—Trifluoroisopropenyl bromide (10 g, 0.057 mole) in diethyl ether (150 ml) was cooled to −110 ± 3° under dry nitrogen. Butyllithium (0.057 mole) in pentane (35 ml)–ether (40 ml), precooled to −78°, was added over 5 min while maintaining the temperature at −110 ± 3°. The reaction mixture was allowed to warm to −100° over 15 min and dry carbon dioxide was bubbled into the system. The introduction of carbon dioxide was continued until the temperature attained −78° and then the temperature was allowed to rise to that of the room. Hydrochloric acid (1:1) (40 ml) was added and the layers were separated. The aqueous layer was extracted three times with ether and the total ethereal solutions were combined and dried. Distillation gave butyl bromide 5.3 g, (68%) and a white crystalline residue of crude acid 4.5 g (56%). A pure sample of the acid was obtained by preparative-scale glpc (silicone elastomer, 140°) and shown to be 2-trifluoromethylacrylic acid, mp 50–51° (lit.[20] mp 50–52°).

The infrared ^1H and ^{19}F nmr spectra were consistent with this structure.

Reaction of Trifluoroisopropenyllithium and Triethylchlorosilane.—Trifluoroisopropenyl bromide (10 g, 0.057 mole) in diethyl ether (150 ml) was cooled to −110 ± 3° under nitrogen. Butyllithium (0.057 mole) in pentane (35 ml)–ether (45 ml), precooled to -78°, was added over 5 min while maintaining the temperature at −110 ± 3°. The mixture was allowed to warm to −100° over 20 min, and then triethylchlorosilane (8.58 g, 0.057 mole) in ether (40 ml) was added over 5 min, while maintaining the temperature at −100°. The reaction mixture was then allowed to attain room temperature. A dense white precipitate formed, was filtered, dried, and weighed (1.6 g). This solid was boiled with water and the insoluble component filtered, dried, and reweighed (0.9 g). This was shown to be lithium fluoride (61%); the aqueous solution contained lithium chloride (29%). The organic reaction mixture was fractionated to give (a) butyl bromide 5.9 g (76%), (b) impure product 0.8 g (∼11%), and unreacted triethylchlorosilane 5.9 g (69%).

A pure sample of the product was obtained by preparative-scale glpc (silicone gum rubber, 110°) and shown to be triethylfluorosilane, bp 109° (lit.[21] bp 109–110°). This compound had an infrared spectrum identical with that of an authentic sample of triethylfluorosilane. The ^1H and ^{19}F nmr spectra were consistent with this structure.

Dehydration of Carbinols.—The alcohol was dropped onto phosphorus pentoxide at 0° and the mixture warmed to 110–160°. The diene distilled normally from the flask and was purified by redistillation, usually from phosphorus pentoxide. Dehydration of phenylmethyl (trifluoroisopropenyl) carbinol was more difficult, requiring heating *in vacuo* to 160° for 30 min before distilling. This process was repeated three times to give pure 2-trifluoromethyl-3-phenyl-butadiene. The physical properties, yields, and analyses of the products are given in Table III.

Reaction of Trifluoropropene with Butyllithium Followed by Addition of Acetone.—Trifluoropropene (10 g, 0.104 mole) in diethyl ether (120 ml) was cooled to −90° under dry nitrogen. Butyllithium in pentane (60 ml)–ether (60 ml), precooled to −78°, was added over 10 min while the temperature was maintained at −95 ± 2° for one more hour. Acetone (5.8 g, 0.1 mole) in ether (50 ml) was added, and the mixture allowed to warm slowly to room temperature. Hydrochloric acid (1:1)

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(19) A. T. Blomquist and D. T. Longone, *J. Am. Chem. Soc.*, **79**, 4981 (1957).

(20) M. W. Buxton, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 366 (1954).

(21) M. G. Voronkov and Yu. I. Skorik, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1215 (1964); *Chem. Abstr.*, **61**, 12027 (1964).

TABLE III

PRODUCTS FROM DEHYDRATION OF ALCOHOLS USING PHOSPHORUS PENTOXIDE

Product[a]	Yield, %	Bp, °C	Formula	Calcd, %			Found, %		
				H	C	F	H	C	F
$CH_2{=}C(CF_3)C(CH_3){=}CH_2$	49	64–65	$C_6H_7F_3$	5.15	52.94	41.91	5.02	52.88	41.82
$CH_2{=}C(CF_3)CH{=}CH_2$	84	34–35[b]							
$CH_2{=}C(CF_3)C(CH_3){=}CHCH_3$	78	70–90	$C_7H_9F_3$	6.00	56.00	38.00	5.9	55.74	38.23
+		Mixture of isomers							
$CH_2{=}C(CF_3)C(C_2H_5){=}CH_2$									
$CH_2{=}C(CF_3)C(C_6H_5){=}CH_2$	82	~190 dec	$C_{11}H_9F_3$	4.55	66.67	28.78	4.70	66.58	29.05

[a] The infrared and ^1H and ^{19}F nmr spectra were consistent with these structures. [b] Lit. bp 35–35.5°: P. Tarrant and R. E. Taylor, *J. Org. Chem.*, **24**, 1888 (1959).

(40 ml) was added and the layers separated. The ethereal layer was dried and distilled to give only one product, butyl dimethyl carbinol, 8.0 g (69%) bp 141–142° (lit.[22] bp 139.4–140.4°). The infrared spectrum was consistent with this structure.

Reaction of Trifluoropropene and Butyllithium.—Trifluoropropene (9.6 g, 0.1 mole) in diethyl ether (100 ml) was cooled to −100° under dry nitrogen. Butyllithium (0.1 mole) in pentane (62 ml), precooled to −78°, was added over 10 min while the temperature was maintained at −100 ± 3°. The temperature was allowed to rise slowly to that of the room. A slight yellow coloration was observed and the mixture became gelatinous. A slow current of nitrogen was bubbled through the mixture and the effluent gas passed through a cold (−78°) trap. The contents of the trap were shown by infrared spectroscopy to consist only of diethyl ether, *i.e.*, no $CF_2{=}C{=}CH_2$ was present. The reaction mixture was treated with hydrochloric acid (1:1) (40 ml), and the organic layer was separated and dried, and the solvent removed by distillation. Analytical glpc showed the presence of a product of similar retention time to that of hexane, together with a much higher boiling component. The mixture was separated by preparative-scale glpc to give 1,1-difluoroheptene, bp 93–94° (lit.[6] bp 94–95°), 0.63 g (5%), and an inseparable mixture of two other compounds.

Reactions of 3,3,3-Trifluoropropynyllithium.—1,1,1-Trifluoropropyne was prepared in 80% yield by zinc dust dehalogenation of 1,1,2-trichloro-3,3,3-trifluoropropene-1.[13b]

Ether (120 ml) was added to a dry three-necked flask which had been previously flushed with nitrogen. 1,1,1-Trifluoropropyne (4.7 g, 0.05 mole) was condensed into the ether solution at −78°. A cooled (−78°) solution of butyllithium (0.05 mole) in a mixed solvent (pentane–ether (64 ml)) was then added dropwise over a 30-min period. The solution was stirred for 60 min more while being allowed to warm up to −30°. It was then cooled to −78° and the other reactant added (0.05 mole), usually[23] in ether solution (30 ml). The reaction mixture was then allowed to attain room temperature slowly (over 3 hr).

With carbonyl compounds as reactants the solutions become yellowish in color around room temperature. Water (20 ml) and 6 *N* hydrochloric acid (20 ml) were added. A white precipitate which formed on addition of water usually redissolved on stirring. The organic layer was separated and dried (Drierite), and the solvents were removed by distillation. Further distillation afforded a crude sample of the carbinol which was further purified by preparative-scale glpc. Yields and physical properties of the products are given in Table II.

On reaction of trifluoropropynyllithium with triethylchlorosilane a white precipitate of lithium chloride came out of solution at −20°. This was removed by filtration and the filtrate dried (Drierite) before solvent removal by distillation. Further distillation followed by preparative-scale glpc gave a pure sample of triethyltrifluoropropynylsilane (see Table II).

With unreactive substrates (C_6H_5CN, C_6F_6, and $(CH_3CH_2)_3SiCF{=}CF_2$) a black precipitate was formed between 0° and room temperature. No new products were formed as shown by glpc.

Registry No.—I, 14633-64-8; II, 649-65-0; α-(trifluoroisopropenyl)benzyl alcohol, 14633-65-9; α-butyl benzyl alcohol, 583-03-9; dimethyl(trifluoroisopropenyl)carbinol, 14633-66-0; methyl(trifluoroisopropenyl)carbinol, 14633-67-1; methylethyl(trifluoroisopropenyl)carbinol, 14629-72-2; methylphenyl(trifluoroisopropenyl)carbinol, 14856-83-8; $(CH_3CH_2)_3SiC{\equiv}CCF_3$, 14629-73-3; $CF_3C{\equiv}CC(OH)(CH_3)CF_3$, 14629-74-4; $CF_3C{\equiv}CC(OH)(CF_3)_2$, 14629-75-5; $CF_3C{\equiv}CCH(OH)CH_2CH_3$, 14629-76-6; $CF_3C{\equiv}CC(OH)(CH_3)C_6H_5$, 14629-77-7; $(CF_3C{\equiv}C)_2C(OH)CH_3$, 14629-78-8; $CH_2{=}C(CF_3)C(CH_3){=}CH_2$, 14629-79-9; $CH_2{=}C(CF_3)C(CH_3){=}CHCH_3$, 14629-80-2; $CH_2{=}C(CF_3)C(C_2H_5){=}CH_2$, 14856-84-9; $CH_2{=}C(CF_3)C(C_6H_5){=}CH_2$, 14629-81-3; 3,3,3-trifluoroisopropenyllithium, 14856-85-0; 3,3,3-trifluoropropynyllithium, 14856-86-1.

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[22] M. L. Henry, *Compt. Rend.*, **143**, 103 (1906).

[23] Trifluoroacetone and hexafluoroacetone were transferred directly (no solvent) from a flask containing phosphorus pentoxide.