A sample of the above solid was recrystallized twice from ether–petroleum ether (1:15); yellow crystals: m.p. 127–128°; $\lambda_{max}^{CHCl_3}$ 2.94, 6.13, 6.27 μ.

Anal. Calcd. for $C_{17}H_{11}N_2ClF_4$ (354.7): C, 57.6; H, 3.12; N, 7.90. Found: C, 57.4; H, 3.06; N, 8.06.

Reduction of 1-Chloro-2-carboxamidohexafluorocyclopentene-1 (III) with Lithium Aluminum Hydride.—(a) A solution of 1.27 g. (0.0050 mole) III in 5 ml. of tetrahydrofuran was added to 0.20 g. (0.0053 mole) of lithium aluminum hydride in 10 ml. of tetrahydrofuran held at 5°. The mixture was refluxed 16 hr. under nitrogen. The resultant black suspension was cooled in Dry Ice and decomposed by successive dropwise addition of 0.2 ml. of water, 0.6 ml. of 15 N sodium hydroxide solution, and 0.2 ml. of water. The mixture was then centrifuged. The supernatant liquid was boiled to 1 ml. volume and distilled in a 15-mm. tube at 5-mm. pressure.

The distillate was fractionated on a 10-ft. silicone-550 column at 190°. The three principal components were collected at indicated elution times.

1. 8 min.—m.p. 116–117°; wt. = 15 mg. starting material.

2. 16 min.—m.p. 139–141°; wt. = 15 mg. identified as XI by n.m.r.

3. 20 min.—m.p. 141–148°; wt. = 18 mg. identified as XII by n.m.r.

(b) Five grams of III (0.02 mole) was treated with 2.3 g. (0.06 mole) of lithium aluminum hydride in 50 ml. of tetrahydrofuran. After decomposition and centrifugation, the solvent was evaporated, leaving 6 g. of residue which was distilled (100°/140 mm.), giving 1.2 g. of clear liquid. Treatment with dry hydrogen chloride in ether afforded 1.0 g. of the hydrochloride of X (25% yield). A sample was recrystallized from methanol–ether.

Anal. Calcd. for $C_6F_4H_{10}NCl$ (207.6): C, 34.7; H, 4.85; Cl (ionic), 17.1. Found: C, 35.0; H, 4.64; Cl, 17.4.

The Preparation and Some Reactions of Trifluorovinyllithium[1]

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Trifluorovinyllithium has been prepared by an exchange reaction with trifluorovinyl bromide and an alkyllithium reagent. Its reaction with some aldehydes and ketones are described. An investigation of the stability of trifluorovinyllithium has been carried out.

Several workers[2-7] have made use of trifluorovinylmagnesium halides in the synthesis of derivatives of Groups II, III, IV, and V elements, as shown below for the mercury compound.

$$CF_2{=}CFMgI + HgCl_2 \longrightarrow (CF_2{=}CF)_2Hg$$
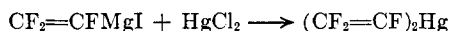
It thus seemed desirable to develop a practical method of synthesis of the corresponding lithium reagent and to study its properties.

Seyferth and co-workers[8] prepared trifluorovinyllithium by treating triphenyl(trifluorovinyl)tin with phenyllithium. Their primary objective was the determination of differences in the behavior of organometallic compounds and their synthesis of the lithium reagent is not a good preparative method.

Knunyants and his associates have reported[9] that trifluorovinyl iodide exchanged with phenylmagnesium bromide to give trifluorovinylmagnesium bromide and iodobenzene. Dixon,[10] however, reported that lithium reagents replaced fluorine atoms in a fluoroölefin. Therefore, it was of some interest to find that exchange rather than addition with loss of fluoride ion occurred when bromotrifluoroethylene reacted with methyl- or butyllithium. Yields of trifluorovinyllithium of at least 73% were realized.

The extent of exchange was determined by reaction with trifluoroacetone to give the corresponding alcohol (I).
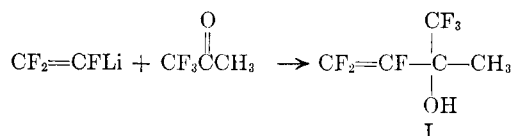
Side reactions gave small amounts of 2-trifluoromethyl-2-propanol (II) and a cyclic ether (III).
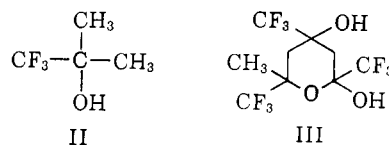
Compound III had been prepared previously[11] by reaction of trifluoroacetone with sodium. Compound II was obviously produced from the reaction of trifluoroacetone with methyllithium.

The alcohol (I) showed no tendency to rearrange under the reaction conditions employed, although previously workers[12] had found that similar compounds rearranged to α-fluoro-α,β-unsaturated acid fluorides.

This type of rearrangement has also been studied in our laboratories.[13] Here it was found that the presence

(1) Presented at the Second International Fluorine Symposium, Estes Park, Colo., July 17–20, 1962.

(2) I. L. Knunyants, R. N. Sterlin, R. D. Yatsenko, and L. N. Pinkina, *Chem. Abstr.*, **53**, 6987 (1959); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1345 (1958).

(3) H. D. Kaeze, S. L. Stafford, and F. G. A. Stone, *J. Am. Chem. Soc.*, **81**, 6336 (1959).

(4) R. N. Sterlin, V. Li, and I. L. Knunyants, *Chem. Abstr.*, **54**, 1273 (1960); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1506 (1959).

(5) R. N. Sterlin, L. N. Pinkina, R. D. Yatsenko, and I. L. Knunyants, *Chem. Abstr.*, **54**, 14103 (1960); *Khim. Nauka i Promy.*, **4**, 800 (1959).

(6) R. N. Sterlin, I. L. Knunyants, L. N. Pinkina, and R. D. Yatsenko, *Chem. Abstr.*, **54**, 1270 (1960); *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1492 (1959).

(7) R. N. Sterlin, R. D. Yatsenko, L. N. Pinkina, and I. L. Knunyants, *Chem. Abstr.*, **54**, 10838 (1960); *Khim. Nauka i Promy.*, **4**, 810 (1959).

(8) D. Seyferth, T. Wada, and G. Raab, *Tetrahedron Letters*, No. **22**, 20 (1960).

(9) 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).

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

(11) A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5148 (1954).

(12) R. N. Sterlin, R. D. Yatsenko, and I. L. Knunyants, *Khim. Nauka i Promy.*, **3**, 540 (1958); *Chem. Abstr.*, **53**, 4195 (1959).
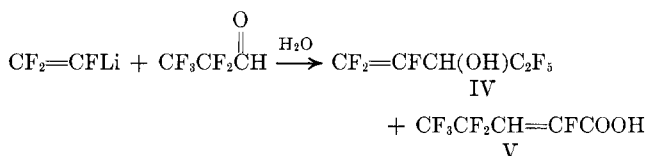
(13) P. Tarrant and R. D. Richardson, Abstract of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p. 17-M.
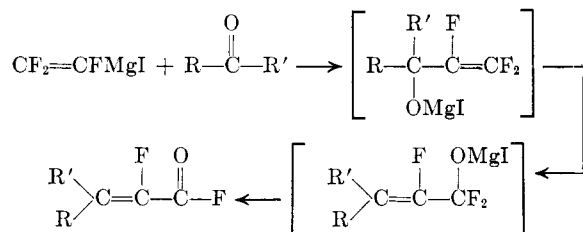
of a trifluoromethyl group adjacent to the carbonyl group primarily led to the alcohol rather than the rearranged acid derivative. Thus the present finding of the stability of compound I is in accordance with these studies.

Two techniques for treating trifluoroacetone with trifluorovinyllithium were applied. One involved addition of a methyllithium solution to a cooled solution of trifluorovinyl bromide followed by treatment of the resulting mixture with trifluoroacetone. In this case the side products II and III were formed. A better method was the alternate addition of aliquots of methyllithium and trifluoroacetone to the trifluorovinyl bromide solution; this operation produced no side products, and it was this method which was used in subsequent reactions.

Reaction of trifluorovinyllithium with other aldehydes and ketones gave good yields of alcohols or rearranged products. The presence of an electron-withdrawing group, as expected, retarded the rearrangement. Thus pentafluoropropionaldehyde gave a 28% yield of the corresponding alcohol (IV) with only 1.5% yield of the acid (V).

$$CF_2{=}CFLi + CF_3CF_2\overset{\overset{\displaystyle O}{\|}}{C}H \xrightarrow{H_2O} CF_2{=}CFCH(OH)C_2F_5$$
$$IV$$
$$+ CF_3CF_2CH{=}CFCOOH$$
$$V$$

These rearrangements generally occurred during the purification process and, therefore, it was possible to convert some of the less stable alcohols to other derivatives before rearrangement took place. 1-Trifluorovinylbenzyl alcohol (VI) prepared from trifluorovinylmagnesium bromide and benzaldehyde, has been shown to give α-fluorocinnamic acid upon heating or steam distillation.[13] However, treatment of the reaction product from trifluorovinyllithium and benzaldehyde with α-naphthyl isocyanate gave the urethane derivative of VI in 53% over-all yield.

It was anticipated that the rearrangement of 1-trifluorovinylcyclohexanol (VII) would be retarded, since formation of the acid fluoride involves the formation of an exocyclic double bond and the stability of the completely staggered cyclohexane conformation would be lost. VII was obtained in 80% yield from cyclohexanone and trifluorovinyllithium and could be distilled under reduced pressure. In one instance rearrangement occurred during distillation resulting in a mild explosion. The rearrangement is very probably acid-catalyzed and, since hydrogen fluoride is the other product of rearrangement, the catalytic effect would be cumulative. Thus refluxing VII with 6 N hydrochloric acid gave cyclohexylidenefluoroacetic acid (VIII) in 84% yield.

VII VIII
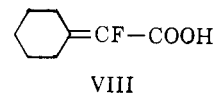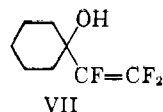
Reaction of mercuric chloride with trifluorovinyllithium at 0° gave bis(trifluorovinyl)mercury in 52.5% yield. We found that this was a much higher yield than that realized in our laboratories for the corresponding reaction between mercuric chloride and trifluorovinylmagnesium bromide.

Dixon[10] found that a number of fluoroölefins 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 dichlorodifluoroethylene and trifluorovinyllithium.

An attempt was made to convert the alcohol prepared from trifluoroacetone and trifluorovinyllithium into a butadiene. Pyrolysis of the acetate ester of this alcohol, however, gave only acetyl fluoride and α-fluoro-β-trifluoromethylcrotonoyl fluoride (IX). The reaction route may be via the intermediate shown below.

IX
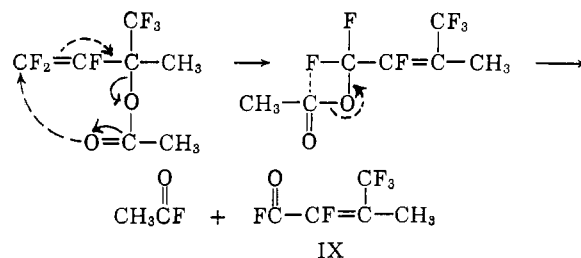
Perfluoroalkyllithium compounds are known to be unstable at ambient temperatures, decomposing to give the corresponding fluoroölefin.[14] Seyferth and his co-workers found that trifluorovinyllithium was stable in ether solution at −25° but unstable at 0°. In pentane the compound was stable at 0°.

In our present work a study was made of the thermal stability of the lithium reagent in ether at 0, −27, and −78° and in petroleum ether at −27°. The amount of lithium reagent present in solution was determined from the amount of sublimable acid isolated from the reaction with cyclohexanone, according to the reaction shown below.
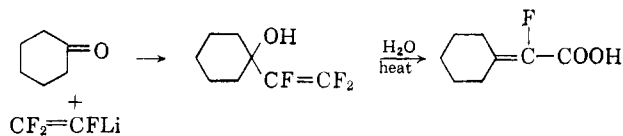
As indicated in the table, trifluorovinyllithium is stable for several hours at −78° but relatively unstable at −27° and higher temperatures. Experiments 6, 7, 13, and 14 show that trifluorovinyllithium can be a useful reagent in synthetic work at −27° and higher temperatures provided the proper technique is used. The effect of concentration on stability is demonstrated by experiments 8 and 9; a more dilute solution increases considerably the stability of the lithium reagent.

Only two products could be isolated from the decomposition of a pentane solution of trifluorovinyllithium. These were lithium fluoride (96% yield) and a
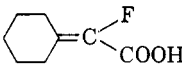
(14) O. R. Pierce, E. T. McBee, and G. F. Judd, J. Am. Chem. Soc., 76, 474 (1954); R. D. Chambers, W. K. R. Musgrave, and J. Savory, J. Chem. Soc., 1993 (1962).

high boiling, viscous oil. Elemental analysis of the latter gave an approximate C:H:F ratio of 2:2:1. Less than 1% bromine was present. An infrared spectrum clearly showed C—H double bond stretching frequencies. A 98% yield of butyl bromide was also obtained in the reaction thus indicating the extent of exchange between trifluorovinyl bromide and butyllithium in the preparation of trifluorovinyllithium.

Rate of decomposition of trifluorovinyllithium was shown to depend on concentration (experiments 8, 9), and it can therefore be presumed that such decomposition occurs *via* an intermolecular process. This rules out the intramolecular elimination of lithium fluoride to give difluoroacetylene as an intermediate for the formation of this polymeric material.

Previous reactions reported in Table I indicate that the exchange reaction is rapid even at −78° and thus the concentration of trifluorovinyl bromide would be low. We presume, therefore, that one step in the formation of the polymeric material is the elimination of lithium fluoride from separate molecules of trifluorovinyllithium. The amount of hydrogen present is surprising and can only be explained by the incorporation of solvent in the polymer. It is not yet possible to surmise how this was done.

TABLE I
STABILITY OF TRIFLUOROVINYLLITHIUM SOLUTIONS IN ETHER

Experiment	Time	Temp., °C.	Yield of	$\bigcirc$=C$\overset{F}{\underset{COOH}{}}$
1	30 sec.[a]	−78	66	72.5
2	30 min.[b]	−78	66	68.3
3	1 hr.[b]	−78	65	
4	6 hr.[b]	−78	55	56.3
5	24 hr.[b]	−78	44.8	46
6	Immediate add.[a]	−27	58	
7	30 sec.[a]	−27	56.3	55.8
8	2 min.[b]	−27	0	
9	2 min.[c]	−27	27.5	
10	5 min.[d]	−27	0	
11	30 sec.[e]	−27	39	
12	15 min.[f]	−27	0	
13	Immediate add.[a]	0	51.2	
14	30 sec.[a]	0	50.2	

[a] Five aliquots of methyllithium solution were added at 5-min. intervals each followed at the appropriate time by an aliquot of cyclohexanone solution. [b] The methyllithium solution was added over 2 min., then at the appropriate time the cyclohexanone solution was added over 2 min. [c] All solutions were six times as dilute as in [b]. [d] Five aliquots of methyllithium solution were added at 5-min. intervals, then 5 min. later the cyclohexanone solution was added over 2 min. [e] Five aliquots of n-butyllithium solution were added at 5-min. intervals, each followed after 30 sec. by an aliquot of the cyclohexanone solution. Pentane was used as solvent. [f] The n-butyllithium solution was added over 15 min., then 15 min. later the cyclohexanone solution was added over 2 min. Pentane was used as solvent.

Experimental[15]

Reactions of Trifluorovinyllithium. General Procedure.— These reactions were carried out under nitrogen in a flask fitted with two calibrated addition funnels, a mechanical stirrer, and a Dry Ice–acetone-cooled condenser. Unless otherwise stated, the reaction product was worked up as follows: It was hydrolyzed with 6 N hydrochloric acid (50 to 100 ml.) and the ethereal layer

separated and washed once with water. The combined aqueous layers were extracted twice with ether and the ethereal extracts combined, dried over magnesium sulfate, filtered, and distilled through a 9 in. by $^1/_2$ in. glass helices-packed column.

The yields quoted, unless pure products were isolated, were determined by conventional methods using vapor phase chromatography.

With Trifluoroacetone Using Successive Addition Method.— Methyllithium (227.5 ml., 0.603 N solution in ether, 0.137 mole) and trifluoroacetone (15.25 g., 0.136 mole) in ether (80 ml.) were added [first the methyllithium solution (20 ml.) followed 30 sec. later by ketone solution (10 ml.) at 5-min. intervals] to trifluorovinyl bromide (22.0 g., 0.137 mole) in ether (80 ml.) cooled in a Dry Ice–acetone bath. The bath was kept at −78° for 1 hr. and then allowed to reach room temperature after 4 hr. The reaction product was worked up, fractionated, and after removal of most of the solvent 28.5 g. of residue was obtained. 2-Methylhexafluoro-3-buten-2-ol (I) (19.2 g., 72.7% yield) was isolated from the latter by using preparative scale v.p.c.[16] and identified by its identical infrared spectrum to that of an authentic sample.[17]

Similarly, methyllithium (180 ml., 0.85 N solution in ether, 0.153 mole), trifluoroacetone (33.2 g., 0.296 mole), and trifluorovinyl bromide (24.6 g., 0.153 mole) in ether (70 ml.) when treated at −45° gave 7.04 g. (23% yield) of I and 1.21 g. (6.2% yield) of 2-trifluoromethyl-2-propanol.

With Trifluoroacetone Using Bulk Addition Method.—Methyllithium (280 ml., 0.810 N solution in ether, 0.226 mole) and trifluoroacetone (32.23 g., 0.288 mole) in ether (80 ml.) were added; (first the methyllithium solution then the ketone solution each over a period of 15 min.) to trifluorovinyl bromide (36.6 g., 0.227 mole) in ether (65 ml.) cooled in a bath at −50 to −40°. The reaction mixture was allowed to attain room temperature over 3 hr. Fractionation gave ether and other volatile material which was shown to contain 12.3 g. (28% yield) of I together with a small amount of 2-trifluoromethyl-2-propanol. A residue (10 g.) was distilled (b.p. 90–110° at ca. 20 mm.) and the partially solid distillate was recrystallized from a pentane–ether mixture giving crystalline material which was sublimed to give 0.9 g. of 1,3-dihydroxy-5-methyl-1,3,5-tris(trifluoromethyl)tetrahydropyran (m.p. 104–111°).

Anal. Calcd. for $C_9H_9F_9O_3$: C, 32.15; H, 2.68. Found: C, 32.36; H, 2.87.

The material showed strong infrared absorptions characteristic of —OH stretching frequency at 3367 and 3636 (sh), CH_2 asym. and CH_2 sym. stretching bands at 3012 (m) and 2976 (w) cm.$^{-1}$.

Similarly a reaction carried out at −78° gave a 15.7% yield of CF_3CCH_3—$(CF=CF_2)OH$ and 18.2% yield of $CF_3C(CH_3)_2OH$.

With Pentafluoropropionaldehyde.—This and subsequent reactions, unless otherwise stated, were carried out using the successive addition of methyllithium and carbonyl compound to the trifluorovinyl bromide.

Methyllithium (112 ml. 2.51 N solution in ether, 0.281 mole) and pentafluoropropionaldehyde (41.2 g., 0.278 mole) in ether (120 ml.) were treated with trifluorovinyl bromide (46.2 g., 0.287 mole) in ether (95 ml.) at −78°. Using distillation and preparative scale v.p.c., 18.0 g. (28% yield) of 2,2,3,3,3-pentafluoro-1-trifluorovinyl-1-propanol (b.p. 86–87°, n^{20}D 1.348) was obtained.

Anal. Calcd. for $C_5H_2F_8O$: C, 26.10; H, 0.87; F, 66.10. Found: C, 26.11; H, 1.02; F, 66.28.

Infrared absorptions at 3389 and 1795 cm.$^{-1}$ indicated bonded —OH and $CF_2=CF$ stretching frequencies, respectively. α-Fluoro-β-pentafluoroethylacrylic acid (0.8 g.) was also obtained, m.p. 67–70°.

This acid was characterized by its benzylthiuronium salt, m.p. 178–180.5°.

Anal. Calcd. for $C_{13}H_{10}F_6N_2O_2S$: C, 41.21; H, 3.01. Found: C, 41.70; H, 3.21.

With Benzaldehyde.—Methyllithium (220 ml., 0.586 N solution in ether, 0.129 mole) and benzaldehyde (13.7 g., 0.129 mole) in ether (150 ml.) were treated at −78° with trifluorovinyl bromide (20.8 g., 0.129 mole) in ether (80 ml.). After working up, ether was distilled and the residue shown to contain 12.9 g. (53% yield) of 1-trifluorovinylbenzyl alcohol which was characterized by its urethane derivative (m.p. 120.5–121.5°).

(15) Analysis by Galbraith Laboratories, Knoxville, Tenn.

(16) A preparative scale vapor phase chromatography unit for separating up to 10-g. quantities was constructed in the laboratory, involving a glass tube, 2.5 m. in length and 22-mm. i.d., containing dinonyl phthalate as the stationary phase supported on 80–100-mesh Chromosorb.

(17) R. D. Richardson, private communication.

Anal. Calcd. for $C_{20}H_{16}F_3NO_2$: C, 66.85; H, 4.45. Found: C, 67.13; H, 4.51.

An infrared spectrum in carbon tetrachloride solution showed C—H, N—H, CF=CF₂, C=O stretching and N—H deformation frequencies at 3484 (w), 3096 (w), 1786 (m), 1751 (s), and 1529 (s) cm.⁻¹, respectively.

With Cyclohexanone.—Cyclohexanone (30.7 g., 0.314 mole) in ether (120 ml.), trifluorovinyl bromide (50.4 g., 0.313 mole) in ether (100 ml.) and methyllithium (135 ml., 2.38 N solution in ether, 0.321 mole) were treated at −78° and 45.2 g. (80% yield) of 1-trifluorovinylcyclohexanol was obtained.

An infrared spectrum showed OH, CH₂ asym., CH₂ sym., CF= CF₂ stretching and CH₂ deformation absorptions at 3425 (s), 2967 (s), 2890 (s), 1776 (s), and 1451 (m) cm.⁻¹.

In one case rearrangement of this alcohol occurred during distillation causing an explosion. This rearrangement to cyclohexylidinefluoroacetic acid was controlled and carried out as follows: 1-Trifluorovinylcyclohexanol (6.1 g., 0.0339 mole) was refluxed with dilute hydrochloric acid for 4 hr., and the immiscible oil formed gave, on cooling, 4.5 g., (84% yield) of almost pure cyclohexylidinefluoroacetic acid. This was recrystallized from an acetone–heptane mixture and sublimed to give white crystals, (m.p. 109–110°).

Anal. Calcd. for $C_8H_{11}FO_2$: C, 60.75; H, 6.96. Found: C, 60.74; H, 7.10.

This compound showed absorption in the infrared at 3049 (s) 2950 (s), 2865 (s), 2800–2400, 1704 (s), 1692 (s), 1645 (s), 1451 (s), and 1427 (s) cm.⁻¹ indicating the presence of OH, C=O and C=C linkages.

This acid was further characterized by its benzylthiuronium derivative (m.p 193–193.5°).

Anal. Calcd. for $C_{16}H_{21}FN_2O_2S$: C, 59.27; H, 6.48. Found: C, 59.34; H, 6.32.

With Mercuric Chloride.—A solution of trifluorovinyl bromide (100 g., 0.62 mole) in ether (250 ml.), cooled in an ice–water bath, was treated over a period of 1 hr. simultaneously with methyllithium (270 ml., 1.84 N solution in ether, 0.50 mole) and a solution of mercuric chloride (63 g., 0.232 mole) in ether (1500 ml.). The dark brown reaction mixture was slowly allowed to attain room temperature and then treated with saturated ammonium chloride solution (250 ml.).

The two layers were separated and the ether layer dried over magnesium sulfate. The ether was removed under reduced pressure. Fractionation then gave 44 g. (52.5% yield) of bis(trifluorovinyl)mercury, boiling range 64–66° *ca.* 17 mm. (lit.,⁵ 65° *ca.* 17 mm.).

This compound showed strong absorptions in the infrared at 1718, 1295 (sh), 1279, 1160, 1133, 1111 (triplet), and 1011 cm.⁻¹ indicating the presence of a CF₂=CF— linkage.

Similarly a reaction carried out at −22° gave a 10.5% yield of the mercury derivative, and at −78° no (CF₂=CF)₂Hg was obtained.

With 1,1-Dichlorodifluoroethylene.—Trifluorovinyl bromide (45 g., 0.28 mole) in ether (25 ml.) was cooled in a bath at −78° and treated with n-butyllithium (180 ml., 1.556 N solution in ether, 0.28 mole) and then with 1,1-dichlorodifluoroethylene (37.3 g., 0.28 mole).

After being allowed to attain room temperature, the reaction was treated with 3 N hydrochloric acid and fractionated to give unchanged olefins and ether, boiling range 30–40° and 34 g. (89.5% yield) of n-butyl bromide. An investigation by analytical v.p.c. of all distillates and residue gave no indication of the presence of any 1,1-dichlorotetrafluorobutadiene.

Thermal Stability of Trifluorovinyllithium.—Trifluorovinyl bromide (10 g., 0.062 mole) in ether or pentane (50 ml.) was placed in a four-neck flask and cooled to the desired temperature. A 5% excess of methyllithium (34 ml., 1.9 N solution, 0.065 mole) in ether or a similar solution of n-butyllithium in pentane, and an equimolar amount of cyclohexanone in the desired solvent (25 ml.) were then added as described in the footnote to Table I. The reaction was continued at the bath temperature for 30 min., the bath removed, and after 1 hr. the reaction mixture was hydrolyzed with water (20 ml.) and 4 N hydrochloric acid (20 ml.). The solvent was distilled through a short glass helices-packed column and the residue refluxed for 6 hr. The water-insoluble acid was extracted with ether (3 × 20 ml.) and after the volatile material was removed, the acid was sublimed from the residue giving cyclohexylidinefluoroacetic acid characterized by its infrared spectrum being identical with that of an authentic sample.

Preparation and Decomposition of Trifluorovinyllithium.—Trifluorovinyl bromide (20.5 g., 0.127 mole) in pentane (100 ml.) was cooled in a bath at −78° and treated dropwise with n-butyllithium (82 ml., 1.55 N solution in hexane, 0.127 mole). The reaction was continued at −78° for 15 min. before being allowed slowly to attain room temperature. At −45° the almost clear solution started turning brown; this continued until at −25° the solution became dark brown and a dark precipitate was formed. Analytical v.p.c. showed that only a trace of trifluorovinyl bromide remained unchanged. The original reaction mixture was filtered and the precipitate was continuously extracted with pentane for 4 hr. and ether for 4 hr. before being dried. The white solid residue (3.25 g., 96% yield) was identified as lithium fluoride by the following: It was only slightly soluble in water but gave a solution which was shown to contain fluoride ion, it did not burn or decompose at 600°, it gave a red flame test of lithium. The combined pentane and ether solutions including extracts were fractionated to give 10.1 g. (88.5% yield) of n-butyl bromide which was identified by its infrared spectrum. The residue was then heated to 110° *ca.* 0.0001 mm. for 2 hr. when 7.0 g. of a dark brown viscous oil was obtained.

Anal. Found: C, 49.24; H, 4.01; F, 38.61; Br, 0.76.

Characteristic strong infrared absorption bands were 2960, 2940, 2875 (triplet), 1780, 1745, 1460, 1334–1150, 860, 830–790 cm.⁻¹.

An identical reaction was carried out up to the stage of attaining room temperature. Toluene (11.7 g., 0.127 mole) was added as a reference for analytical v.p.c. analysis. A comparison of the areas of peaks attributed to toluene and n-butyl bromide showed that 17.0 g. (98% yield) of the latter had been formed.

A similar reaction carried out in ether solution gave almost identical results. The polymer formed in this case gave the same elemental analysis and infrared spectrum as before; however, this polymer was a mixture of viscous oil and solid material.

Similar reactions carried out at −30° resulted in an 80% conversion of the trifluorovinyl bromide to give again a viscous oil from pentane solution and a hard black solid from ether solution.

Reactions carried out in the presence of n-butyl bromide (35 g., 0.256 mole) gave polymeric materials identical with those previously obtained.

Preparation of 3-Acetoxy-3-methylperfluorobutene-1.—Crude I prepared from trifluoroacetone (69.6 g., 0.622 mole), trifluorovinyl bromide (99 g., 0.615 mole) and methyllithium (260 mls., 2.397 N solution in ether, 0.623 mole), was refluxed for 6 hr. with acetyl chloride (110 g., 142 mole). Fractionation of the product gave 96 g. (66.2% yield) of CH₃CCF₃(CF=CF₂)OC(O)CH₃, b.p. 109°, n²⁰D 1.343.

Anal. Calcd. for $C_7H_6F_6O_2$: C, 35.60; H, 2.54. Found: C, 35.79; H, 2.73.

Characteristic infrared absorption bands were: 3021 (w), 2967 (w), 1456 (m), 1431 (m), 1385 (m), 1370 (m) 1783 (s) and 1767 (s) cm.⁻¹ indicating CH₃ and C=O stretching frequencies.

Pyrolysis of CF₃CCH₃(CF=CF₂)OC(O)CH₃.—CF₃CCH₃(CF= CF₂)OC(O)CH₃ (23 g., 0.0976 mole), in a stream of nitrogen, was passed, during a period of 65 min., through a Pyrex tube (16 in. × 1 in.) heated to 450°. Reaction products were collected in a trap cooled by Dry Ice–acetone and were fractionated through a glass helices-packed column to give (57% yield) of acetyl fluoride, b.p. 19–20° (lit.,¹⁸ 20.5°).

Anal. Calcd. for C_2FH_3O: mol. wt., 62. Found: mol. wt. 65.

An infrared spectrum showed strong C=O stretching absorption at 1873 cm.⁻¹; Bellamy¹⁹ gives the C=O stretching frequency in CH₃COF at 1872 cm.⁻¹.

The residue from the distillation was resolved by preparative-scale v.p.c. into 3.7 g. (84% conversion) of recovered CF₃CCH₃-(CF=CF₂)OC(O)CH₃, identified by its infrared spectrum, and 6.1 g. (42.5% yield) of α-fluoro-β-trifluoromethylcrotonoyl fluoride, b.p. 72–74°, n²⁰D 1.3386.

Anal. Calcd. for $C_5H_3F_5O$: C, 34.50, H, 1.72; mol. wt., 175. Found: C, 34.65; H, 1.85, mol. wt., 177.

Characteristic infrared absorption bands were: 1842 (s), 1667 (m), 1441 (m), 1357 (s), 1318 (m), 1277 (m), 1242 (vs), 1190 (vs), 1156 (vs), 1094 (s), and 1020 (s), cm.⁻¹.

This CH₃(CF₃)C=CFCOF was characterized further by hy-

(18) "Handbook of Chemistry and Physics," 36th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, p. 714.

(19) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc. New York, N. Y., 1958, p. 1900.

drolysis to the acid using sodium hydroxide solution, and isolation of the corresponding benzylthiouronium derivative. Recrystallization from aqueous alcohol gave pure $CH_3(CF_3)C=CFCOO^-$
$\overset{+}{N}H_2=C(OH_2)SCH_2C_6H_5$, 181–183°.

Anal. Calcd. for $C_{13}H_{14}F_4N_2O_2S$: C, 46.15; H, 4.14. Found: C, 45.85; H, 4.20.

Electrophilic Substitution at the Carbon–Lead Bond

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The rates of acetolysis of tetramethyllead, tetraethyllead, tetra-*n*-propyllead, tetra-*n*-butyllead, and tetra-isoamyllead were determined at 24.9, 49.8, and 60.0°. A reactivity series methyl > ethyl > *n*-propyl $\cong$ *n*-butyl $\cong$ isoamyl was found. The entropies and enthalpies of activation were very similar for all these compounds. The rate of acetolysis of tetra-*n*-butyllead was, surprisingly, almost identical with that of di-*n*-butylmercury. Perchloric acid cleavage in acetic acid solvent gave a reactivity series similar to that in acetolysis.

Few quantitative data on rates of electrophilic substitution at saturated carbon atoms are available. Data on cleavage by protonic acids of a metal–alkyl bond are particularly limited. We report here the rates of acetolysis at three temperatures of a series of tetra-*n*-alkyllead compounds.

$$R_4Pb + HOAc \longrightarrow RH + R_3PbOAc$$
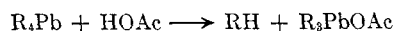
The rate of cleavage of these same compounds by perchloric acid in acetic acid solvent was also determined.

$$R_4Pb + HClO_4 \longrightarrow RH + R_3PbClO_4$$
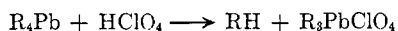
The only directly comparable data in the literature were obtained by Winstein and Traylor[1] on organomercury compounds. Dessy and his co-workers[2] have also studied rates of hydrogen chloride cleavage of organomercury compounds. This latter work was largely in mixed solvents, and the data obtained are not directly comparable to those in this paper.

Results

Table I summarizes the acetolysis data obtained during this work, together with the derived entropies and enthalpies of activation. Table II shows detailed data for a typical acetolysis run. In Table III are collected the data on rates of perchloric acid cleavage in acetic acid solvent. A typical perchloric acid cleavage run is presented in detail in Table IV. The required control experiments are described in the Experimental.

Discussion

We have used the kinetic data to calculate relative reactivities in electrophilic substitution at the primary carbon atoms in this series. The results are summarized in Table V. For these relative reactivities to be meaningful it must be shown that special steric effects due to the quaternary lead atom are not affecting the rate constants. It must be assumed also that the change in trialkyllead cation formed on cleavage as one proceeds through the series of tetraalkyllead compounds

does not substantially alter the reactivity of the lead–alkyl bonds.

Inspection of the enthalpies and entropies of activation in Table I makes it clear that no large steric effects are present, for the enthalpies and entropies of activation are all very similar. Such steric effects would not be expected *a priori* since a lead atom has twice the radius of a carbon atom. It is unlikely that variable inductive stabilization of the incipient trialkyllead cations affects our reactivity sequence; the large size of the lead atom should attenuate to insignificance this secondary inductive effect. Support for this view is obtained from recent work in silicon chemistry. Russel and Napgal have studied the rates of cleavage of alkyltrimethylsilanes with hydrogen bromide and aluminum bromide.[3] They find a reactivity sequence $CH_3 >> C_2H_5$ (1.0) $> n\text{-}C_3H_7$ (0.13) $\cong n\text{-}C_4H_9$- (0.17) with a constant trimethylsilyl leaving group. This reactivity series is similar to those reported in Table V and indicates that the reactivity order may be general in electrophilic substitution. A similar qualitative order was found by Whitmore and Bernstein[4] for the cleavage of alkyl groups from organomercury compounds.

The relative rate data from acetolysis at 25, 50, and 60° are self-consistent within the limits of error. The perchloric acid cleavage data show the same reactivity order as acetolysis but with a wider spread between methyl and ethyl. These reactivity orders are not those one would predict for simple inductive effects on S_E2 reactions.[5] In fact, the relative rates resemble those observed in S_N2 reactions.[6]

A point of similarity between S_N2 and S_E2 reactions is the presence of five-coördinate carbon in the transition state in each. The similar reactivities in S_N2 and S_E2 reactions may arise from some such general feature of the transition states. Russel and Napgal[3] consider that their relative rates of alkyltrimethylsilane cleavage are due to an undefined steric effect. This suggestion seems reasonable but we have no really specific and

(1) (a) S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **77**, 3747 (1955); (b) **78**, 2597 (1956).

(2) (a) R. E. Dessy and J. Y. Kim, *ibid.*, **83**, 1167 (1961); (b) R. E. Dessy, G. F. Reynolds, and J. Y. Kim, *ibid.*, **81**, 2683 9(159).

(3) G. A. Russel and K. L. Napgal, *Tetrahedron Letters*, 421 (1961).

(4) F. C. Whitmore and H. Bernstein, *J. Am. Chem. Soc.*, **60**, 2626 (1938).

(5) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

(6) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 154.