REACTIONS OF TRIFLUOROPROPYNE AND FLUORINATED ORGANOMETALLICS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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1955

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ACKNOWLEDGMENT

The author hereby expresses his appreciation to Dr. Albert L. Henne for his patience, encouragement and guidance throughout the course of this investigation. Financial assistance from the Union Carbide and Carbon Company, the Lubrizol Corporation and E. I. duPont de Nemours and Company is also gratefully acknowledged.
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1.0 INTRODUCTION, PURPOSE AND SCOPE

The study of the effects caused by electronegative groups on various functions in organic compounds with highly fluorinated alkyl groups as electronegative substituents has met with considerable success. The increased acidity of fluorinated acids and alcohols, the reversed direction of ionic addition to trifluoropropene and trifluoropropyne and the meta-directing influence of the trifluoromethyl group in aromatic substitution demonstrate the inductive effect of fluorine atoms. Attempts to demonstrate clearly an increased acidity of hydrogen atoms alpha to a trifluoromethyl group have, however, failed. Also, attempts to prepare fluorinated organometallics with their metal atoms separated from the fluorine atoms by only one methylene group have been defeated by elimination of fluorine ions from otherwise stable CF₃- and -CF₂- groups. 

The purpose of this investigation has been to continue the study of the effect of highly fluorinated alkyl groups on several adjacent functions. In scope, it covers a continued study of the reactions of trifluoropropyne (which had been synthesized and studied in part by Henne and Nager),\(^4\),\(^8\),\(^9\) attempts to demonstrate an increased acidity of hydrogen atoms alpha to fluorinated clusters and attempts to prepare fluorinated organometallic compounds containing only one methylene group.


\(^{(9)}\) Nager, M., Ph.D. dissertation, The Ohio State University, 1951.
2.0 RESULTS

2.1 Synthesis of 3,3,3-Trifluoropropyne

Henne and Nager⁸ have reported the synthesis of CF₃C≡CH from CCl₃CH₂CH₂Cl in a 73⁰/₀ overall yield as follows:

\[
\begin{align*}
\text{CCl₃CH₂CH₂Cl} & \xrightarrow{\text{SbF₃}} \text{CF₃CH₂CH₂Cl} \xrightarrow{\text{KOH}} \text{CF₃CH≡CH₂Br} \\
\text{CF₃CHBrCH₂Br} & \xrightarrow{\text{KOH}} \text{CF₃CBr₂CH₂Br} \xrightarrow{\text{KOH}} \text{CF₃C≡CH}
\end{align*}
\]

In the present work the starting material, CCl₃CH₂CH₂Cl, for the above sequence was prepared from carbon tetrachloride and ethylene in the presence of a peroxide essentially according to the procedure of Joyce.¹⁰ Additional amounts of it were made available by another group (Research Foundation Project 451).

The fluorination of CCl₃CH₂CH₂Cl to CF₃CH₂CH₂Cl by means of a mixture of SbF₃ and SbF₃Cl₂ (for a discussion of these attempts see Krehbiel)¹¹ or an excess of hydrogen fluoride (see Section 3.12) was very erratic and unsatisfactory. For this reason other sequences were investigated which might have led to intermediates from which CF₃C≡CH could have been prepared. The fluorination of


CClF₂CHClCH₂Br to CF₃CHClCH₂Br was successful but could not be used for lack of starting material. An attempted fluorination of CClF₂CH=CH₂ to CF₃CH=CH₂ by means of SbF₃Cl₂ gave only tars. The condensation of chloroform with CF₂=CCl₂ gave not the hoped for CClF₂CCl₂CHCl₂,¹² which might have been converted to CF₃C≡CH via CF₃CCl₂CHCl₂, but CCl₃CF₂CHCl₂.¹³,¹⁴

A sequence for the preparation of CF₃CH₂CH₂Cl was then developed by Krehbiel¹¹ in our laboratory, which proved quite practical:

\[
\begin{align*}
\text{CH₂ClCHClCH₃} & \xrightarrow{\text{Cl₂}} \text{CHCl₂CHClCH₃} \xrightarrow{\text{NaOH}} \\
\text{CCl₂=CHCH₃} & \xrightarrow{\text{HF/ SbF₃}} \text{CF₃CH₂CH₃} \xrightarrow{\text{Cl₂}} \text{CF₃CH₂CH₂Cl}.
\end{align*}
\]

CCl₂=CHCH₃ was prepared in yields comparable to those of Krehbiel,¹¹ and some CF₃CH₂CH₂Cl made by him became available; this was used to prepare CF₃C≡CH by the sequence outlined at the beginning of this discussion (page 3). The remaining steps of the synthesis proceeded substantially as indicated by Henne and Nager⁸ except for side reactions occurring in the preparation of CF₃CBr=CHBr. Treatment of CF₃CBr₂CH₂Br with alcoholic potassium hydroxide produced mostly the expected CF₃CBr=CHBr and recovered starting material, but also varying amounts of CF₃CBr=CBr₂ and CF₃CH₂COOC₂H₅ and

evidence for $\text{CF}_3\text{C}≡\text{CBr}$ and $\text{CF}_3\text{CBr}=\text{CH}_2$. The formula of the unexpected $\text{CF}_3\text{CBr}=\text{CBr}_2$ was established by bromine analysis and by oxidation to trifluoroacetic acid (see Section 3.114) and the presence of $\text{CF}_3\text{CH}_2\text{COOC}_2\text{H}_5$ was established by comparison of infrared spectra and hydrolysis to $\text{CF}_3\text{CH}_2\text{COOH}$ (see Section 3.113).

$\text{CF}_3\text{CBr}=\text{CBr}_2$ was used to prepare $\text{CF}_3\text{C}≡\text{CBr}$ (see Sections 3.224 and 3.242), another new compound. From the infrared spectra of $\text{CF}_3\text{C}≡\text{CBr}$ and $\text{CF}_3\text{CBr}=\text{CH}_2$, the presence of these two compounds as by-products in the preparation of $\text{CF}_3\text{CBr}=\text{CHBr}$ was inferred.

Further investigation of this reaction was, however, considered beyond the present scope and was not attempted.
2.2 Reactions and Derivatives of 3,3,3-Trifluoropropyne

2.21 Preparation of Trifluoromethyl-1,4-cyclohexadiene

Diels-Alder reactions have been reported with substances having isolated double or triple bonds; the reaction is facilitated when the dienophile is "activated", usually by alpha-beta unsaturation. Acetylenic aldehydes, ketones and nitriles have been used as dienophiles in Diels-Alder reactions but acetylenic acids and their derivatives, especially acetylene dicarboxylic acid and its methyl and ethyl esters have been studied more extensively.\(^{(15,16)}\)

Although the mechanism of the Diels-Alder reaction is disputed\(^{(15,17,18)}\) it appears that the more reactive dienophiles are those containing an electronegative group attached to the doubly bonded carbon atoms.\(^{(15)}\) In view of the demonstrated polarization of the triple bond by an adjacent CF\(_3\)-group\(^{(4)}\) it is not surprising that trifluoropropyne acted satisfactorily as a dienophile.

No reaction was observed between trifluoropropyne and butadiene up to 100\(^{\circ}\), but at 120\(^{\circ}\) (and more rapidly at higher temperatures)\(^{(15)}\)


\(^{(16)}\) Holmes, H. L., ibid. Chapter 2.


condensation occurred to give trifluoromethyl-1,4-cyclohexadiene, CF$_3$\!
\begin{center}
\begin{tikzpicture}
\node at (0,0) {
\begin{quiver}
\draw[double, double distance=1.5pt] (0,0) -- (1,0);
\draw[double, double distance=1.5pt] (1,0) -- (2,0);
\end{quiver}
\end{tikzpicture}
\end{center}
\text{,} \text{ in yields of 84\(^0\)0; the structure of this adduct was inferred from the following observations.}

(i) Aromatization of the adduct gave benzotrifluoride and complete reduction gave trifluoromethylcyclohexane, establishing the existence of a six-membered ring bearing a trifluoromethyl group.

(ii) Partial reduction of trifluoromethyl-1,4-cyclohexadiene gave a trifluoromethylcyclohexene which was oxidized by ozone to a keto-acid whose semicarbazone had an analysis and a neutralization equivalent consistent with the formula CF$_3$C(=NNHCONH$_2$)(CH$_2$)$_4$COOH. This also showed the six-membered ring structure and indicated that, barring rearrangement or 1,4-reduction of a conjugated dienic system (see iii), the original adduct had one of its double bonds alpha-beta to the CF$_3$-group.

(iii) The failure of the adduct to react further with maleic anhydride indicated that its two double bonds were not conjugated. Ozonolysis of the adduct, followed by oxidative cleavage with alkaline permanganate (see Section 3.215) produced trifluoroacetic and oxalic acids. A search for succinic acid proved negative. Since levulinic acid, malonic acid and acetoacetic ester are readily oxidized, their absence or that of their trifluoromethyl analogs
was considered meaningless; but the absence of succinic acid which resists alkaline permanganate was regarded as indicative that the adduct was not trifluoromethyl-1,5-cyclohexadiene. A repetition of the ozonolysis followed by oxidative cleavage of the ozonide with hydrogen peroxide yielded trifluoroacetone and carbon dioxide which were inferred to have been produced from trifluoroacetoacetic acid, which in turn had come from trifluoromethyl-1,4-cyclohexadiene. There was some evidence that trifluoroacetic acid had also been formed, and its presence was tentatively attributed to the oxidation of trifluoroacetoacetic acid or its precursors.

To substantiate the 1,4-cyclohexadiene structure of the adduct, its ultraviolet absorption spectrum was compared to that of CF₃CH=CHCH=CH₂, a 1,3-structure. The observed λ_max for 5,5,5-trifluoro-1,3-pentadiene was about 219 mµ which compares favorably with 217 mµ for butadiene¹⁹ and 223.5 mµ for 1,3-pentadiene.²⁰ With this trifluorinated conjugated diene as the only available basis for comparison, it seemed that the CF₃-group was not affecting the position of λ_max appreciably. For the adduct, however, no λ_max was observed in the range 215-320 mµ, but only a rising slope indicating the beginning of an absorption with a maximum somewhere below 215 mµ.


At greater concentrations, absorptions were resolved at 254, 260 and 266 m\(\mu\) with molar extinction coefficients of the order of 15. Since 1,3-cyclohexadiene, methyl-2,4-cyclohexadiene and other conjugated alkyl cyclohexadienes have a \(\lambda_{\text{max}}\) in the range of 256-265 m\(\mu\) with an average molar extinction coefficient of about 5500, it was concluded that the adduct did not contain a system of conjugated double bonds.

(iv) Since the adduct was a trifluoromethylcyclohexadiene with unconjugated double bonds, one of which was alpha-beta to the trifluoromethyl group, its formula was concluded to be \(\text{CF}_3\). Attempts to isomerize the cyclohexadiene to a conjugated form with mineral acids and with bases failed. A similar failure was reported by Lunt and Sondheimer who could not isomerize 2-methyl-1,4-cyclohexadiene-1-carboxaldehyde with either acid or base. They were, however, able to isomerize 2,4,6,6-tetramethyl-1,4-cyclohexadiene-1-carboxaldehyde to the corresponding isomer, and attributed this difference in ease of isomerization to the hyperconjugation effect of the methyl group in the 4-position.

---


(22) Lunt, J. C., and Sondheimer, F., ibid. 1950, 3361.
2.22 Attempted Preparation of \((\text{CF}_3\text{C} \equiv \text{C})_2\). Formation of \text{CF}_3\text{C} \equiv \text{CH Dimer, C}_6\text{H}_2\text{F}_6.\)

The cuprous derivatives of terminal acetylenes have been converted into diacetylenic compounds by the action of certain oxidizing agents such as oxygen, cupric chloride and bromide and potassium ferricyanide.\(^{23a,24,25}\)

\[
2\text{R} \equiv \text{C} \rightarrow \text{Cu} \xrightarrow{O} \text{R} \equiv \text{C} \equiv \text{C} \equiv \text{CR} + \text{CuO}
\]

The oxidation of halomagnesium derivatives of terminal acetylenes has also been reported to give diacetylenes.\(^{23a,24c}\)

Although the preparation of \(\text{CF}_3\text{C} \equiv \text{CCu}\) has been reported by Haszeldine,\(^{26}\) attempts to produce it in quantity from \(\text{CF}_3\text{C} \equiv \text{CH}\) with cuprous chloride, ammonium chloride and aqueous ammonia did not give more than trace amounts of a tan precipitate, assumed to be \(\text{CF}_3\text{C} \equiv \text{CCu}\). The main reaction product was, instead, a compound \(\text{C}_6\text{H}_2\text{F}_6\), the structure of which is discussed in the following


\(\textit{(25) Baeyer, A., and Landsberg, L., Ber. 15, 57, (1882); Baeyer, A., ibid. 18, 2269 (1885); Strauss, F., Ann. 342, 223 (1904); Strauss, F., and Kolleck, L., Ber. 59, 1664 (1926).}\)

section (2.23). This compound, C₆H₂F₆, formed very readily and when first observed was believed to be the desired (CF₃C=C)₂ formed by air or cupric ion oxidation of CF₃C≡CCu.²⁴

Bubbling air through a mixture of CF₃C≡CH, cuprous chloride, ammonium chloride and aqueous ammonia did not produce (CF₃C≡C)₂ but only C₆H₂F₆, transferred by entrainment to the surface of the Dry Ice reflux condenser from which it was later recovered. Dimerization of CF₃C≡CH occurs quite readily to give C₆H₂F₆ in fairly good yield.

Another attempt to prepare CF₃C≡CCu in cuprous hydroxide and oxidize it in situ with potassium ferricyanide failed to give any organic material besides recovered CF₃C≡CH.

An attempted preparation of (CF₃C≡C)₂ from CF₃CBr=CBr₂ and zinc in acetic anhydride produced CF₃C≡CBr in 37⁰/o yield, but a search for (CF₃C≡C)₂ in all fractions proved negative.

Treatment of CF₃C≡CBr with zinc and acetic anhydride was to be tried at somewhat elevated temperatures since CF₃C≡CBr had been isolated from a similar reaction medium at room temperature (see preceding paragraph). However, since reaction appeared to be occurring at room temperature and since lower temperatures are favored in the doubling up of fluorinated chains,²⁷ room temperature

was used for this reaction. Starting material was recovered in about 65\% yield and CF$_3$C≡CH in less than 5\% conversion. The presence of the trifluoropropyne could be explained by the reduction of CF$_3$C≡CZnBr. A search for (CF$_3$C≡C)$_2$ in fractions boiling below 90\° turned out negative.
2.23 Proof of Structure of the CF₃C≡CH Dimer, C₆H₂F₆

Acetylene has been polymerized to vinyl and divinyl acetylene by the action of cuprous chloride and ammonium chloride.²³b Indications for the polymerization of trifluoropropyne had been reported by Nager.⁹ Therefore, the isolation of a compound which proved to be a dimer of CF₃C≡CH in the action of ammoniacal cuprous and ammonium chlorides on trifluoropropyne was not surprising.

The structure of this compound is worthy of further discussion. The compound, by analysis, is (C₃HF₃)ₙ; its boiling point favors the consideration of n = 2, i.e., C₆H₂F₆.

The infrared spectrum of C₆H₂F₆ has one absorption in the 4.5μ region for C=C and another in the 6μ region for C=C as well as absorptions for CH and CF bonds at 3.3μ and 7-10μ respectively.

Addition of one mole of hydrogen gave a product presumed to be mostly C₆H₄F₆, which was probably a mixture. Oxidation of it produced trifluoroacetic and oxalic acids. The infrared spectrum of "C₆H₄F₆" had no absorption in the 4.5μ region for C≡C and two absorptions in the 6μ region for C=C. These absorptions were about 0.18μ apart and one was weaker than the other. Aliphatic conjugation usually produces absorption bands about
0.15 apart, with one usually weaker than the other.\textsuperscript{28}

Full reduction resulted in the absorption of three moles of hydrogen. Analysis of the reduced product proved consistent with the formula $C_6H_8F_6$, and not with the formula $C_9H_9F_7$, which would have been that of a partly reduced trimer. The infrared spectrum of $C_6H_8F_6$ showed no absorptions for either $C\equiv C$ or $C=C$.

During the course of this investigation $(CF_3CH=CH)_2$ and $CF_3(CH_2)_4CF_3$ were prepared in our laboratory by Groth.\textsuperscript{29} $C_6H_8F_6$ from the full reduction of $C_6H_2F_6$ proved to be identical with the synthetic $CF_3(CH_2)_4CF_3$ thus establishing its structure. The $''C_6H_4F_6''$ showed properties similar to, but not identical with, the synthetic $(CF_3CH=CH)_2$. The differences are tentatively attributed to the presence of cis-trans isomers in the mixture which are not present in the $(CF_3CH=CH)_2$ prepared by R. Groth who pyrolyzed the diacetate to obtain the diene.

The above evidence suggests the following sequence:

\[
\begin{align*}
2 \text{CF}_3\text{C} \equiv \text{CH} + \text{NH}_4\text{Cl} & \rightarrow \text{CF}_3\text{C} \equiv \text{CH} = \text{CHCF}_3 \quad \text{(C}_6\text{H}_2\text{F}_6) \\
\text{H}_2 & \rightarrow \text{CF}_3\text{CH} = \text{CHCH} = \text{CHCF}_3 \\
\text{3H}_2 & \rightarrow \text{CF}_3\text{CCH}_2\text{CH}_2\text{CCH}_2\text{CH}_2\text{CF}_3.
\end{align*}
\]


(29) Groth, R., Private communication.
However, neither C₆H₂F₆ nor "C₄H₄F₆" gave satisfactory results when treated with maleic anhydride. Although one attempted preparation of an adduct with maleic anhydride and C₆H₂F₆ gave a compound m. 136.5-7.5° (uncorr.) which gave a positive qualitative test for fluorine, its infrared spectrum was similar to that of maleic acid. This experiment was held to be inconclusive.

The evidence favors a linear structure for the dimer; the only possible cyclic compounds would be the bis(trifluoromethyl)-cyclobutadienes. The possibility of a cyclobutadiene structure for the dimer was examined because of the statement of Baker that cyclobutadiene might be prepared provided the reaction leading to its formation were not too strenuous, the observations that fluorinated olefins readily condense with certain other unsaturated compounds to give cyclobutane and cyclobutene derivatives and the formation of phenylcyclobutadienoquinone.


2.24 CF₃C≡CBr

It was during an attempted preparation of (CF₃C≡C)₂ from CF₃CBr=CBr₂ that CF₃C≡CBr was first isolated in a pure state (see Sections 2.22 and 3.22). The following alternate attempts to prepare it were unsuccessful. Treatment of CF₃CBr=CBr₂ with zinc in refluxing ethanol gave CF₃C≡CH in 58% yield; the formation of the propyne could be explained by the action of ethanol on the intermediate CF₃C≡CZnBr.³³ Substituting dry dioxane for ethanol as the solvent did result in the formation of the desired CF₃C≡CBr but only in traces. It had also been observed that the addition of alcoholic potassium hydroxide to CF₃CBr₂CH₂Br in the preparation of CF₃CBr=CHBr produced some CF₃C≡CBr (see Sections 2.1 and 3.1). An attempt to increase the yield by reversing the addition, i.e., dropping CF₃CBr₂CH₂Br into the caustic solution proved to be a mistake. No CF₃C≡CBr was obtained and CF₃CH₂COOC₂H₅ was again identified among the products as it had been in the preparation of CF₃CBr=CHBr. These observations and those of Grignard³⁴ that monosubstituted bromoacetylenes decompose in alcoholic potassium hydroxide from RC≡CBr to RC≡CH and ArC≡CBr to ArCH₂COOH point out the inadvisability of attempting to prepare CF₃C≡CBr in an excess of alcoholic alkali. Among the procedures used, the preparation of (33) Boord, C. E., J. Am. Chem. Soc. 74, 287 (1952).
CF$_3$C=CB from CF$_3$CB=CB$_2$ by means of zinc and acetic anhydride gave the most satisfactory results.

The structure of CF$_3$C=CBr was ascertained as follows. The infrared spectrum showed absorptions for C=C, CF, and none for =CH. Analysis was consistent with the empirical formula C$_3$BrF$_3$, and bromination with one mole of bromine gave CF$_3$CBr=CB$_2$.

CF$_3$C=CBr did not oxidize the iodide ion nor the ferrocyanide ion; it did not precipitate tribromophenol from a solution of phenol and hydrobromic acid$^{35}$ and it gave no precipitate with aqueous silver nitrate. With alcoholic silver nitrate it behaved as a primary alkyl bromide. It was therefore concluded that the bromine in CF$_3$C=CBr does not show marked positive character.

2.25 Attempted Addition of CH$_2$COOH/(CF$_3$CO)$_2$O to CF$_3$C=CH

1,3-Diketones have been prepared by the action of a mixed anhydride and an alkyne in trifluoroacetic anhydride$^{36}$ in yields of about 20\%. It seemed of interest to determine what effect a trifluoromethyl group adjacent to the triple bond would have on this reaction. No beta-carbonyl compound was formed even after a contact time of eleven days at 70-80°. Similar negative results had been noted in our laboratory by Greene$^{37}$ with olefinic compounds like allyl chloride and CF$_3$CCl=CClCF$_3$.

2.26 Attempted Michael Condensation of CF$_3$C=CH to Itself

Many examples of the use of acetylenic acids and their esters as acceptors in Michael condensations have been reported.$^{38}$ The use of propiolic ester as an addendum in a Michael condensation$^{39}$ led to the attempted addition of trifluoropropyne to itself. One attempt produced only recovered propyne (65\% yield), a fluorinated polymer, and fluoride ion.

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(37) Greene, P., Private communication.


2.27 Relative Acidity of CH$_3$C=CH and CF$_3$C=CH

That acetylenic hydrogen atoms have acidic character has been known for some time. The pK$_a$ of phenylacetylene has been reported as 21$^{40}$ and it is reasonable to assume that the acidity of most alkyl acetylenes is not too different from this value.

The determination of relative acidities of very weak acids by McEwen$^{40}$ and Conant and Wheland$^{41}$ consisted essentially of determining the equilibrium position when one weak acid was added to the metallic salt of another. This equilibrium position was estimated by colorimetric techniques, by carbonating the metallic salts, or from the change in optical rotation.

From a consideration of the reaction between trifluoropropyne and an alkynylmagnesium halide Henne and Nager$^4$ estimated the difference in acidity, if any, between trifluoropropyne and an alkyl acetylene at less than two pK units. A reconsideration of this question led to experiments designed to try to establish this relationship more firmly.

Both trifluoropropyne and propyne were added in separate experiments to an ether solution of indylsodium prepared from indene and triphenylmethylsodium. The addition of CF$_3$C=CH to indylsodium

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(41) Conant, J. B., and Wheland, G. W., ibid. 54, 1212 (1932).
produced an almost immediate blue color, which slowly disappeared with the formation of a dark brown polymeric substance. The blue color appeared only at low temperatures; an attempt to prepare and isolate the substance responsible for the blue color at room temperature gave only the dark brown polymeric substance. The addition of CH$_3$CSCH to indylsodium produced a slow color change indicating the establishment of an equilibrium involving propyne, indene and their sodium salts. However, since the addition of trifluoropropyne produced unidentified blue compounds instead of a similar equilibrium, further attempts to determine relative acidities by this method were abandoned.

In another method an attempt was made to establish an equilibrium between propyne, trifluoropropyne and their sodium salts in a closed system and to estimate by infrared analysis the position of this equilibrium by a quantitative determination of the amounts of the two propynes in the vapor phase. However, the solubility of the propynes in the solvent at low temperatures, and the decomposition of trifluoropropyne in the presence of its sodium salt at higher temperatures, defeated this procedure.
2.3 Acidity of Hydrogen Atoms Alpha to a Fluorinated Alkyl Group

In his study of the reactions of CF₃CH₂CH₃ and CF₃CH₂CF₃, Schmitz⁶ was unable to give a clear proof of the increased acidity of the hydrogen atoms. In the present investigation further attempts were made to evaluate the extent to which the acidity of a hydrogen atom alpha to a highly fluorinated alkyl group is increased.

CClF₂CH₃ was used because of its availability; it was reacted with ether solutions of phenyllithium and with ether or pentane solutions of n-butyllithium. Formaldehyde was then added to react with any CClF₂CH₂Li which might have been present, even though dehydrochlorination to yield CF₂=CH₂ was more likely to occur.

Only scant reaction was observed with these reagents: No CClF₂CH₂CH₂OH was found; traces of what appeared to be fluorostyrene were obtained from phenyllithium and CClF₂CH₃; a small scale reaction with triphenylmethyIsodium proved inconclusive. This is in contrast with the ready dehydrofluorination of CF₃CH₂CF₃ by ethyllithium⁶ and the easy reaction of CClF₂CH₃ with ethoxide ion.⁴²

Diazomethane had no effect on either CClF₂CH₃ or on CF₃CH₂CF₃.

---

2.4 Attempted Preparation of Fluorinated Organometallics

The formation and reactions of fluorinated organometallics proceed in the normal way when the fluorinated groups are separated from the reacting halogen by two or more methylene groups. For example, CF$_3$CH$_2$CH$_2$MgCl has been prepared from CF$_3$CH$_2$CH$_2$Cl and used in the usual way. However, if only one methylene group is present between the reacting halogen and the group of fluorine atoms, dehalogenation with the formation of an olefin becomes the main reaction. For example, the reaction of sodium and potassium on CHF$_2$CH$_2$I and CHF$_2$CH$_2$Br produced CHF=CH$_2$; magnesium and CHF$_2$CH$_2$I gave similar results while CHF$_2$CH$_2$Br was unaffected. CF$_3$CH$_2$Br failed to form a Grignard reagent but reacted with n-butyllithium to give CF$_2$=CH$_2$ and n-butyl bromide.

With perfluoroalkyl halides such as CF$_3$CF$_2$CF$_2$I both dehalogenation and the formation of an organometallic are observed; for


(44) Francis, W., Ph.D. dissertation, The Ohio State University, 1952.

(45) Ruh, R. P., Private communication to Dr. A. L. Henne.
example, CF₃CF₂CF₂I has been reacted with zinc,⁴⁶ magnesium⁴⁷ and lithium⁴⁸ to form both the olefin CF₃CF=CF₂ and the organo-metallic CF₃CF₂CF₂M in proportions which depend on the reaction conditions. The formation of CF₃MgI has been reported⁴⁹ and the attempted formation of CF₃Li led to CF₂=CF₂.⁴⁸ However, quite stable derivatives of mercury and CF₃I have been reported as well as compounds with antimony, arsenic, selenium, sulfur and phosphorus.⁵⁰,⁵¹

In the present investigation further attempts were made to prepare and characterize fluorinated organometallic compounds in which the metal and the fluorine atoms are separated by one methylene group.

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The attempted preparation of CHF₂CH₂Li from phenyllithium and CHF₂CH₂Br at room temperature resulted in the formation of vinyl fluoride, isolated as its dibromide CHBrFCH₂Br, and bromobenzene. Addition of phenyllithium and methyl ethyl ketone to CHF₂CH₂Br at -45° also gave vinyl fluoride and condensation products of phenyllithium with the ketone, but no 1,1-difluoro-3-methyl-3-pentanol.

These results are similar to those reported above for the reactions between CHF₂CH₂Br and sodium and potassium, and CF₃CH₂Br and n-butyllithium, and they led to the investigation of reactions with a less active metal.

CHF₂CF₂CH₂Br gave no reaction with metallic zinc in refluxing dioxane; this parallels the absence of reaction between CF₃CH₂Br and magnesium. Acetic anhydride has been used as a solvent with considerable success in promoting the doubling up of fluorinated organic halides; when it was added to a mixture of zinc, CHF₂CF₂CH₂Br and dioxane at 60° no doubled up molecule was found because elimination to give CHF₂CF=CH₂ had occurred instead.

Since reaction with zinc was presumably occurring through CHF₂CF₂CH₂ZnBr as an intermediate, the dioxane was replaced by acetophenone to give any CHF₂CF₂CH₂ZnBr formed an opportunity to condense with a carbonyl function rather than to react by elimination.
However, CHF₂CF=CH₂ was isolated in about 87\% yield from reaction of CHF₂CF₂CH₂Br with zinc in acetic anhydride and acetophenone. CHF₂CF=CH₂ (a new compound) was characterized by its infrared spectrum, by oxidation to CHF₂COOH, and by bromination to CHF₂CBrFCH₂Br.

Consideration of the facts that zinc alkyls are readily prepared from the corresponding mercury compounds\(^{52}\) and that fluorinated alkyl-mercury compounds had been prepared\(^{50,51}\) led to attempts to prepare CHF₂CF₂CH₂ZnX from the corresponding mercurial.

CHF₂CF₂CH₂HgI was prepared from CHF₂CF₂CH₂I and mercury in 71\% yield. It was characterized by reaction with iodine to give CHF₂CF₂CH₂I and mercuric iodide, and by analysis.

CHF₂CF₂CH₂HgI sublimes readily and is stable at temperatures below 150\°C, where it decomposes. One attempt to prepare the mercurial in the absence of ultraviolet light, by using heat only, led to mere recovery of the starting materials.

An attempted preparation of CHF₂CF₂CH₂ZnI from the mercurial and zinc at 150\°C led to the discovery of the instability of the mercurial at this temperature. Treatment of the mercurial with zinc and acetophenone at 50\°C and 100\°C produced CHF₂CF=CH₂ in 83\% and 73\% yields respectively. No ketone condensation products were detected.

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found. Thus the formation of CHF$_2$CF=CH$_2$ from the reaction of zinc on CHF$_2$CF$_2$CH$_2$Br and CHF$_2$CF$_2$CH$_2$HgI also parallels the results obtained with CHF$_2$CH$_2$I and CHF$_2$CH$_2$Br when reacted with the more active metals.

The same consideration which led to the postulation of the increased acidity of hydrogens alpha to a CF$_3$- group led to attempting the reaction of CHF$_2$CF$_2$CH$_2$HgI with acetyl chloride. No ketone was isolated. Similarly, attempted reaction with cyanogen bromide produced only recovered CHF$_2$CF$_2$CH$_2$HgI. These results are similar to those reported for unfluorinated organomercuric halides. 52
3.0 **EXPERIMENTAL**

3.1 **Synthesis of 3,3,3-Trifluoropropyne**

3.1.1 **Preparation of CCl₃CH₂CH₂Cl**

\[
\text{CCl}_4 + \text{CH}_2=\text{CH}_2 \xrightarrow{\text{peroxide}} \text{CCl}_3\text{CH}_2\text{CH}_2\text{Cl}
\]

The conditions were essentially those of Joyce.⁹ A 2.5 liter steel bomb equipped with a tee joint, pressure gage and valve was charged with freshly distilled carbon tetrachloride (150 ml., 1.56 moles) and t-butyl peroxide (14.5 ml., 0.08 mole), and placed in the heating jacket of a shaker. It was connected by a coil of copper tubing bearing a vent valve to an ethylene cylinder and flushed three times by adding ethylene to a gage pressure of 50 psi and releasing it through the vent valve.

Ethylene was then added to a pressure of 42 psig at 25°, and heating with agitation was begun. The temperature and pressure rose to 138° and 101 psig. More ethylene was added and at 140° and 117 psig a reaction started and the pressure began to decrease fairly rapidly. Ethylene was added intermittently to maintain the pressure between 117 and 128 psig; when ethylene absorption ceased and the pressure ceased to fall, the reaction was assumed to be complete. During this time the temperature rose from 140° to 154°. After cooling to room temperature the bomb contents were removed, the bomb was rinsed with carbon tetrachloride and the rinsings were added to the main fraction. This was then steam
distilled, dried over calcium chloride and distilled from a Claisen flask. Distillation gave recovered carbon tetrachloride and crude CCl$_3$CH$_2$CH$_2$Cl (93 g., 0.51 mole), b. 58-82° at 30 mm., n$^2$ 1.4777 (lit. 59° at 24 mm., n$^2$ 1.4794) and a residue (31 g.).

A number of successful runs which are summarized in Table I were made. Before these runs were begun, the bomb had been used to prepare SbF$_3$Cl$_2$. Therefore, when two consecutive runs failed to give any CCl$_3$CH$_2$CH$_2$Cl, the bomb was used to prepare another batch of SbF$_3$Cl$_2$ and the subsequent preparation of CCl$_3$CH$_2$CH$_2$Cl was again successful; the bomb was therefore, occasionally "reactivated" with SbF$_3$Cl$_2$. Eight successful runs gave 517 g. (2.84 moles) of CCl$_3$CH$_2$CH$_2$Cl, b. 59-63° at 25 mm., n$^3$ 1.4783, in a 23°/o average conversion.

A similar procedure was also worked out by A.C. Heidenreich.

3.12 Attempted Preparation of CF$_3$CH$_2$CH$_2$Cl from CCl$_3$CH$_2$CH$_2$Cl

The reaction

CCl$_3$CH$_2$CH$_2$Cl $\rightarrow$ CF$_3$CH$_2$CH$_2$Cl

was attempted by two slightly different procedures. In the first procedure, fluorination with SbF$_3$ and SbF$_3$Cl$_2$ according to the directions of Henne and Nager was attempted with D. Krehbiel in whose dissertation the subject is discussed thoroughly.

<table>
<thead>
<tr>
<th>No. of Run</th>
<th>Charge CCl₄ ml</th>
<th>Peroxide ml moles</th>
<th>Temp. Range °C</th>
<th>Press. Range psig</th>
<th>Crude Crude g moles</th>
<th>Grde CCl₃CH₂CH₂Cl b. 58-82°/30mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>96</td>
<td>1.0</td>
<td>9</td>
<td>0.049</td>
<td>140-160</td>
<td>100-110</td>
</tr>
<tr>
<td>2</td>
<td>150</td>
<td>1.56</td>
<td>14.5</td>
<td>0.079</td>
<td>140-154</td>
<td>117-128</td>
</tr>
<tr>
<td>3</td>
<td>154</td>
<td>1.60</td>
<td>20</td>
<td>0.109</td>
<td>140-156</td>
<td>156-185</td>
</tr>
<tr>
<td>4</td>
<td>123</td>
<td>1.28</td>
<td>17</td>
<td>0.092</td>
<td>140-156</td>
<td>160-175</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>1.56</td>
<td>16.5</td>
<td>0.090</td>
<td>140-150</td>
<td>116-156</td>
</tr>
<tr>
<td>6</td>
<td>151</td>
<td>1.57</td>
<td>15</td>
<td>0.082</td>
<td>140-170</td>
<td>121-193</td>
</tr>
<tr>
<td>7</td>
<td>150</td>
<td>1.56</td>
<td>15</td>
<td>0.082</td>
<td>140-177</td>
<td>140-150</td>
</tr>
<tr>
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<td>150</td>
<td>1.56</td>
<td>15.5</td>
<td>0.084</td>
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<tr>
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<td>15</td>
<td>0.082</td>
<td>140-177</td>
<td>140-150</td>
</tr>
</tbody>
</table>

(1) In runs 5 and 6 there was no pressure drop. Run 5 was not distilled. Run 6 was distilled but gave no product.

(2) Between runs 6 and 7 and between runs 10 and 11, SbF₃Cl₂ was prepared in the bomb, after which the bomb was cleaned and steam passed into it for 1 to 4 hours.

(3) After run 8 the bomb was rinsed with 10-15 ml. of SbF₃Cl₂, cleaned and steam was passed in for about one hour.

(4) Before run 10 the bomb received only a steam treatment for 2-1/2 hours.
In the second procedure, HF (approximately 80 g., 4 moles) SbF₃ (4 g., 0.022 mole) and CCl₃CH₂CH₂Cl (100 g., 0.57 mole) were placed in a 2.5 liter steel bomb connected to a caustic scrubber and a Dry Ice trap. The bomb was rocked at 100° and the pressure rose from 155 psig to 205 psig in four hours. The bomb was then cooled in ice and the gases bled off through the caustic scrubber. The remaining contents were poured on ice, neutralized with sodium hydroxide, just acidified with hydrochloric acid and steam distilled. After drying the organic material over calcium chloride, fractionation gave: 1.5 g., b. 45-7°; 2.5 g., b. 47-75°; 11 g., b. 75-85°; 5 g., b. 85-117°; 21 g., b. 117-23°; and 18 g. of residue. If it is assumed that the intermediate cuts are composed of about half the higher boiling fraction and half the lower boiling fraction then the composition of the distillate is approximately as follows: CF₃CH₂CH₂Cl b. 46°, 2.6°/o; CClF₂CH₂CH₂Cl b. 81°, 18°/o; CCl₂FCH₂CH₂Cl b. 120-1°, 27°/o. If the residue is assumed to be recovered starting material or 17.5°/o of the total, this represents a 65°/o material balance.

Two more runs were made, with reaction time lengthened to eight hours, and the generated hydrogen chloride was bled off in one of the runs; yet, at best, there was only a 35°/o yield of the monofluoride, CCl₂FCH₂CH₂Cl.
Another group (Research Foundation - Project No. 451) supplied additional CCl\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}Cl and also worked on the same problem with similar low results; this is also summarized in D. Krehbiel's dissertation.\textsuperscript{11}

3.13 Attempted Fluorination of CClF\textsubscript{2}CHClCH\textsubscript{2}Br

The reaction

\[
\text{CClF}_2\text{CHClCH}_2\text{Br} + \text{SbF}_3\text{Cl}_2 \rightarrow \text{CF}_3\text{CHClCH}_2\text{Br}
\]

was attempted in collaboration with D. Kraus. CClF\textsubscript{2}CHClCH\textsubscript{2}Br (114 g., 0.5 mole) was placed in a 500 ml. steel bomb with SbF\textsubscript{3}Cl\textsubscript{2} (80 g., 0.33 mole) at -78\textdegree. The bomb was closed and rocked at 100\textdegree for 66 hours. The contents were then steam distilled and dried. Fractionation gave 25 g., b. 76-90\textdegree; 45 g. CF\textsubscript{3}CHClCH\textsubscript{2}Br (42\% yield) b. 90-5\textdegree and 17 g. of residue.

3.14 Attempted Fluorination of CClF\textsubscript{2}CH=CH\textsubscript{2}

The attempted fluorination of CClF\textsubscript{2}CH=CH\textsubscript{2} was carried out in collaboration with D. Kraus. SbF\textsubscript{3}Cl\textsubscript{2} and CClF\textsubscript{2}CH=CH\textsubscript{2} were introduced into a one liter bomb. A violent reaction ensued. The bomb was rocked at 90\textdegree for 24 hours at the end of which time all gases were bled through two bromine traps and a Dry Ice trap. Much hydrogen fluoride had been produced and no organic material
was found either in the bromine traps after the bromine was
discharged or in the Dry Ice trap.

3.15 Condensation of Chloroform and \( CF_2=CCl_2 \)

\[
CHCl_3 + CF_2=CCl_2 \xrightarrow{AlCl_3} CClF_2CCl_2CHCl_2
\]

Technical grade chloroform was purified by shaking with
conzentrated sulfuric acid, washing with water, aqueous potassium
carbonate, and water, drying and distilling. The fraction boiling
60-1\(^\circ\) was used. Dry chloroform (478 g., 4 moles) and anhydrous
aluminum chloride (33 g., 0.25 mole) were placed in a one liter
three-necked flask equipped with a water jacketed dropping funnel,
a reflux condenser tailed by a Dry Ice trap, and a mercury sealed
stirrer. A salt brine cooling mixture was circulated through the
funnel jacket and the reflux condenser. CF\(_2=CCl_2\) (b. 19-20\(^\circ\),
133 g., 1 mole) was added to the well stirred mixture maintained at
43-7\(^\circ\) by an external oil bath over a period of one hour and 40
minutes. After five hours of additional stirring at 40-6\(^\circ\), the
mixture was cooled to 0-5\(^\circ\) and 90 ml. of hydrochloric acid (15\(^o/o\))
was added slowly with stirring. The entire mixture was then
steam distilled, the tail trap contents were added to the organic
phase, which was dried over calcium chloride. Fractionation gave
195 g., of C\(_3\)HCl\(_5\)F\(_2\) (78\(^o/o\) yield) b. 80-2\(^\circ\) at 38-40 mm.,
\(n^20\) 1.4634, (Analyses were by M. Renoll: Found, \(o/o\) F, 14.61,
14.71 (average 14.66); \(o/o\) Cl, 68.82, 70.01 (average 69.42).
Calculated for $\text{C}_3\text{HCl}_5\text{F}_2$, $\%\text{ F}$, 15.06; $\%\text{ Cl}$, 70.22, and 17 g.

b. 82° at 40 mm. to 102° at 5 mm. The literature indicates:

$\text{CHCl}_2\text{CCl}_2\text{CCIF}_2$, b. 168°, $n^{20}$ 1.4624; $^5\text{CHCl}_2\text{CF}_2\text{CCl}_3$, b. 174°, $n^{20}$ 1.4641.$^5$

3.16 Proof of Structure of $\text{C}_3\text{HCl}_5\text{F}_2$

(i) Attempted dehalogenation: $\text{C}_3\text{HCl}_5\text{F}_2 \xrightarrow{\text{metal}} \text{C}_3\text{HCl}_3\text{F}_2$

The compound was boiled with a metal (zinc or magnesium) in a solvent (ethanol, dioxane, phenetole or diphenyl ether) without success.

(ii) Attempted dehydrochlorination: $\text{C}_3\text{HCl}_5\text{F}_2 \xrightarrow{\text{KOH}} \text{C}_3\text{Cl}_4\text{F}_2$

$\text{C}_3\text{HCl}_5\text{F}_2$ (8.7 g., 0.034 mole) stirred with a solution of potassium hydroxide (2 g., 0.04 mole) in 15 ml. absolute ethanol gave no olefinic product.

(iii) Chlorination: $\text{C}_3\text{HCl}_5\text{F}_2 \xrightarrow{\text{Cl}_2} \text{C}_3\text{Cl}_6\text{F}_2$

$\text{C}_3\text{HCl}_5\text{F}_2$ (116 g., 0.46 mole) in a 500 ml. quartz flask was chlorinated under ultraviolet irradiation until a yellow color persisted for three hours after the chlorine flow had been stopped. The contents were then decolorized with aqueous potassium carbonate, dried and distilled. Distillation gave 110 g. of $\text{C}_3\text{Cl}_6\text{F}_2$.


$^5$(a) Henne, A. L., and Renoll, M., ibid., 59, 2434 (1937);
(83°/o yield) b. 93-6° at 35 mm., n20 1.4792, a middle portion of which had a normal boiling point of 193°, n20 1.4794 and a freezing point of -11 to -10° uncorrected.

The possible isomers of C3Cl6F2 are: CCl3CF2CCl3, m. -12.9°, b. 194°, n20 1.4800; CCl3CCl2CClF2, m. 51°, b. 193°; CCl2FCCl2CClF2, m. 30°, b. 194°, and CCl2FCCl2FCCl3, m. -55°, b. 196°, n20 1.4791. This proves that the chlorination product is CCl3CF2CCl3, and its parent is CHCl2CF2CCl3.

3.17 Preparation of CHCl2CHClCH3

\[ \text{Fe} \quad \begin{array}{c} \rightarrow \\ \text{Cl}_2 \end{array} \quad \text{CH}_{2}\text{ClCHClCH}_3 \rightarrow \text{CHCl}_2\text{CHClCH}_3 \]

CH2ClCHClCH3 was chlorinated in the dark at the boiling point according to the procedure of Levine and Cass. Seven runs varying in size from 8.65 moles to 17.7 moles gave yields of CHCl2CHClCH3 of from 35 to 57°/o. D. Krehbiel reported similar results for this reaction.


3.18 Preparation of $\text{CCl}_2=\text{CHCH}_3$

$$\text{CHCl}_2\text{CHClCH}_3 \xrightarrow{\text{NaOH}} \text{CCl}_2=\text{CHCH}_3$$

The procedure used was that of Cass.⁵⁹ Yields of $\text{CCl}_2=\text{CHCH}_3$ for three runs averaged 91°/o.

3.19 Preparation of $\text{CF}_3\text{CHBrCH}_2\text{Br}$

$$\text{CF}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{KOH}} \text{CF}_3\text{CH}=\text{CH}_2 \xrightarrow{\text{Br}_2} \text{CF}_3\text{CHBrCH}_2\text{Br}$$

The procedure was that of Henne and Nager.⁴,⁹ $\text{CF}_3\text{CHBrCH}_2\text{Br}$, b. 113-16⁰, n²¹ 1.4295, was obtained in 86°/o yield.

3.110 Preparation of $\text{CF}_3\text{CBr} = \text{CH}_2$

$$\text{CF}_3\text{CHBrCH}_2\text{Br} \xrightarrow{\text{KOH}} \text{CF}_3\text{CBr} = \text{CH}_2$$

$\text{CF}_3\text{CHBrCH}_2\text{Br}$ was dehydrobrominated according to the general procedure of Henne and Nager.⁴,⁹ $\text{CF}_3\text{CBr} = \text{CH}_2$, b. 33.5-5.0⁰ was obtained in 92°/o yield.

3.111 Preparation of $\text{CF}_3\text{CBr}_2\text{CH}_2\text{Br}$

$$\text{CF}_3\text{CBr} = \text{CH}_2 + \text{Br}_2 \rightarrow \text{CF}_3\text{CBr}_2\text{CH}_2\text{Br}$$

$\text{CF}_3\text{CBr} = \text{CH}_2$ was brominated under strong ultraviolet light by adding a very slight excess of bromine at a rate such as to maintain moderate reflux.⁴,⁹ $\text{CF}_3\text{CBr}_2\text{CH}_2\text{Br}$, b. 75.5-7.0⁰ at 45-7 mm., n²¹ 1.4830 was obtained in 91-3°/o yield.

3.112 Preparation of CF₃CBr=CHBr

\[ \text{CF}_3\text{CBr}_2\text{CH}_2\text{Br} \xrightarrow{\text{KOH}} \text{CF}_3\text{CBr}=\text{CHBr} \]

A slight excess (3-7\% of 6 N alcoholic potassium hydroxide was slowly dropped into stirred CF₃CBr₂CH₂Br at 0-5°; stirring was continued for one more hour. At this point two procedures were followed.

Procedure 1. A large excess of water was added, the reaction mixture was heated and the organic material was steam distilled out and washed to remove the alcohol. The material was lachrymatory (as was the original CF₃CBr₂CH₂Br) and turned yellow on standing. Nager⁹ reported that CF₃CBr₂CH₂Br decomposes with the evolution of bromine on standing at room temperature. In an effort to increase the yield of CF₃CBr=CHBr, this material was then recycled with one mole of potassium hydroxide dissolved in alcohol, and distilled from the reaction mixture as before, washed, dried and fractionated.

Two similar runs gave what was later shown to be the following:

1) A mixture, b. 26-37°, of CF₃C=CB₃ (b. 26°) and CF₃CBr=CH₂ (b. 33°) in 30-40\% conversion; 2) CF₃CBr=CHBr, b. 94-95°, in 40-50\% conversion; 3) a mixture, b. 99-105°, of CF₃CH₂COOC₂H₅ (b. 109°) and CF₃CBr=CHBr (b. 96°) in 6-7\% conversion; and 4) CF₃CBr=CBr₂, b. 154-5°, 70-2° at 45-7 mm., n²⁰ 1.4991, d₄²⁰ 2.517, in about 8\% conversion.
**Procedure 2.** A large excess of water was added, the mixture was allowed to settle and the organic layer was drawn off. The aqueous layer was then heated to boiling to recover residual organic material which amounted to about 2-5% of the total. The combined organic layers were then washed several times with water, dried and distilled. Two more runs gave the following compounds: 1) A mixture of CF$_3$C=CB$\text{r}$ and CF$_3$CB$\text{r}$=CH$_2$ in about 9-15% conversion; 2) CF$_3$CB$\text{r}$=CHBr in about 60-5% conversion; 3) CF$_3$CH$_2$COOC$_2$H$_5$ in an estimated 0-9% conversion; 4) CF$_3$CB$\text{r}$=CB$\text{r}$_2 in 0-5% conversion; and 5) CF$_3$CB$\text{r}$$_2$CH$_2$Br in about 5-12% recovery.

### 3.113 Proof of Structure of CF$_3$CH$_2$COOC$_2$H$_5$

The fraction b. 99-105° obtained from the dehydrobromination of CF$_3$CB$\text{r}$=CHBr was originally suspected of containing CF$_3$CH=CHOOC$_2$H$_5$ in CF$_3$CB$\text{r}$=CHBr. The first two experiments below were attempts to cleave the vinyl ether.

(i) CF$_3$CH=CHOOC$_2$H$_5$ + H$_2$ $\xrightarrow{\text{catalyst}}$ CF$_3$CH$_2$CHO + C$_2$H$_5$OH (9)

The mixture (8 g.) b. 99-105° was subjected to a hydrogen pressure of 50 psig in the presence of Raney nickel in a Parr hydrogenation apparatus for 18 hours. Since the pressure had dropped only two psig, platinum oxide was added and the material was shaken under 50 psig of hydrogen for five more hours. There was no pressure drop. It was assumed that no significant reduction had
occurred. Addition of the filtered mixture to a solution of 2,4-dinitrophenylhydrazine in 3 N hydrochloric acid gave no precipitate.

\[
(ii) \quad \text{CF}_3\text{C} \equiv \text{CHOC}_2\text{H}_5 + \text{HI} \quad \xrightarrow{\text{AcOH, pyridine}} \quad \text{CF}_3\text{CH}_2\text{CHO} + \text{C}_2\text{H}_5\text{I}
\]

This same mixture (10 g.) was refluxed with 40%/o hydrobromic acid (7.5 ml.), pyridine (one drop) and glacial acetic acid (30 ml.) for 24 hours. A sample removed gave no precipitate with a saturated solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid.

(iii) An infrared spectrum of the mixture b. 99-105° was compared with that of pure \(\text{CF}_3\text{CBr=CHBr} \), b. 96°, and that of pure \(\text{CF}_3\text{CH}_2\text{COOC}_2\text{H}_5 \), b. 109°, prepared by Hinkamp. When these two spectra were superimposed on that of the mixture it became apparent that the mixture very probably consisted of \(\text{CF}_3\text{CBr=CHBr} \) and \(\text{CF}_3\text{CH}_2\text{COOC}_2\text{H}_5 \).

The hydrolysis of the ester was carried out as follows. The mixture (26 g.) was refluxed with hydrochloric acid (60 ml. of 1:1) for 24 hours. Periodic tests with cerous nitrate for free fluoride ion were negative. The mixture was then neutralized.

(60) Hinkamp, P., Ph.D. dissertation, The Ohio State University, 1953.
with aqueous sodium hydroxide, extracted twice with ether, acidified with hydrochloric acid (60 ml. of 1:1) and extracted six times with ether. The ether was dried over calcium chloride and distilled. There was obtained an acid (1.5 g.), micro b.p. 141°, \(n^\circ 1.3330\) (\(\text{CF}_3\text{CH}_2\text{COOH b. 143-5°, }n^\circ 1.3317\)).

An authentic sample of \(\text{CF}_3\text{CH}_2\text{COOC}_2\text{H}_5\) was hydrated in the same manner. An infrared spectrum of the acid obtained was identical with that obtained from the mixture.

3.114 Proof of Structure of \(\text{CF}_3\text{CBr=CBr}_2\)

(i) Analysis by M. Renoll of the 154-5° material obtained from the dehydrobromination of \(\text{CF}_3\text{CBr}_2\text{CH}_2\text{Br}\) gave: \(\% \text{ Br, 71.97.}\) Calculated for \(\text{C}_3\text{Br}_3\text{F}_3\), \(\% \text{ Br, 72.0.}\)

(ii) Attempted reduction on platinum oxide in ether failed. The material did not decolorize a solution of bromine in carbon tetrachloride and decolorized aqueous potassium permanganate only on warming. The infrared spectrum showed no absorption in the 3-4\(\mu\) region for C-H but did show an absorption at 6.32\(\mu\) for C=C.

(iii) Oxidation of the double bond was attempted according to the equation

\[
3 \text{CF}_3\text{CBr=CBr}_2 + 4 \text{KMnO}_4 + 14 \text{KOH} \rightarrow 3 \text{CF}_3\text{COOK} + 3 \text{K}_2\text{CO}_3 + 9 \text{KBr} + 4 \text{MnO}_2 + 7 \text{H}_2\text{O}.
\]

CaBr\(^{Fg}\) (17 g., 0.051 mole) was dropped into a stirred refluxing solution of potassium permanganate (10.8 g., 0.068 mole), potassium hydroxide (13.3 g., 0.238 mole) and water (75 ml.). After six hours all the permanganate had been decolorized and some organic material still remained. A small sample of the clear upper layer gave a precipitate with aqueous calcium chloride; this precipitate did not decolorize two drops of a dilute sulfuric acid solution of potassium permanganate. The precipitate was assumed to be calcium fluoride since the solution gave a positive test for fluoride ion with cerous nitrate.

The mixture was acidified with dilute sulfuric acid (some bromine was liberated), and all the manganese dioxide and bromine were reduced with aqueous bisulfite. The mixture was then continuously extracted with ether for 65 hours, and the ether extract in turn was extracted three times with dilute aqueous sodium hydroxide. This basic solution was acidified and again continuously extracted with ether for 53 hours. The ether extract was distilled and there was obtained material (5-5.5 g.) b. 95-105°. This was in turn converted to the ester and the ester to the amide by the procedure of Henne and Kraus. Recrystallized amide (1.7 g.) was obtained m. 72-3°, mixed m. p. with authentic CF\(_3\)CONH\(_2\), 74-5°. This represents a 30°/o yield of amide based on CF\(_3\)CBr=CBr\(_2\). Titration of the aqueous washings from the ester
preparation showed the presence of more acid which, if CF$_3$COOH, represents another 25\% yield of CF$_3$COOH for a total yield of 55\%.

3.115 Preparation of CF$_3$C=CH

\[
\text{CF}_3\text{CBr}=\text{CHBr} + \text{Zn} \xrightarrow{\text{EtOH}} \text{CF}_3\text{C}=\text{CH} + \text{ZnBr}_2
\]

CF$_3$CBr=CHBr was dropped slowly into a 30\% excess of zinc dust in refluxing ethanol according to the procedure of Henne and Nager.\(^4,^9\) The CF$_3$C=CH was collected in a Dry Ice tail trap and rectified on a low temperature column. Yields of CF$_3$C=CH b. -48 \pm 3^\circ$ varied from 87-92\%.
3.2 Reactions and Derivatives of 3,3,3-Trifluoropropyne

3.21 Preparation of Trifluoromethyl-1,4-cyclohexadiene

\[ \text{CF}_3\text{C}≡\text{CH} + \text{CH}_2=\text{CHCH=CH}_2 \rightarrow \text{CF}_3\text{CECH} \]

\( \text{CF}_3\text{C}≡\text{CH} \) (20 g., 0.21 mole) and freshly distilled butadiene (11 g., 0.204 mole) b. -5.5 to -4\(^\circ\) were distilled into a 450 ml. steel bomb cooled to -78\(^\circ\). The bomb was heated to 125\(^\circ\), raising the pressure to 385 psig. In 2-1/2 days the pressure dropped to 150 psig; the temperature was raised to 140\(^\circ\) and kept there for 2-1/2 more days during which the pressure dropped to 70 psig. The bomb was cooled to -78\(^\circ\) and opened. By heating up to 50\(^\circ\), volatile materials were distilled into an ice trap tailed by a Dry Ice trap. The material was then distilled to give \( \text{C}_7\text{H}_7\text{F}_3 \) (23.7 g., 0.16 mole) b. 110-11.5\(^\circ\), \( n^\circ 1.4028 \), \( d_{20}^\circ 1.157 \) and holdup (2 g.) for a yield of 84\%/o. A middle fraction b. 110.5-10.8\(^\circ\) was submitted to Galbraith Laboratories for analysis: Found, \( \%\) C, 56.98; \( \%\) H, 4.63. Calculated for \( \text{C}_7\text{H}_7\text{F}_3 \): \( \%\) C, 56.75; \( \%\) H, 4.77). The infrared spectrum had two absorptions in the 6\( \mu \) region - one at 5.85\( \mu \) and the other (stronger) at 6.02\( \mu \). The AR\(_{TR}\) calculated for a trifluoromethylcyclohexadiene is 1.07. (Conjugated cyclohexadienes with less than two alkyl substituents show no exaltation of refractivity).\(^{62}\) Less than one gram of a mixture of \( \text{CF}_3\text{C}≡\text{CH} \)

and butadiene was recovered. Although the 84°/o yield was confirmed unexplained yields of only 55°/o and 65°/o were also encountered.

3.211 Reduction of $C_7H_7F_3$ to Trifluoromethylcyclohexane

$$\text{CF}_3\underset{\text{CF}}{\text{F}}\text{CF}_3 + H_2 \rightarrow \text{CF}_3\underset{\text{Ni}}{\text{CF}}\text{CF}_3$$

Trifluoromethyl-1-cyclohexene (3 g.) obtained by partial reduction of $C_7H_7F_3$ (see Section 3.213) was reduced with Raney nickel in ethanol at 1500 psig and 100° in high pressure hydrogenation apparatus. The alcohol solution was filtered, diluted with water and extracted with ether. The ether extract was washed three times with saturated aqueous calcium chloride, dried over calcium chloride and distilled. A fraction was obtained b. 103.5-5.0°, $n^\circ_{25} 1.3736$ and $d^2_{4} 1.029$. Trifluoromethylcyclohexane b. 106°, $n^\circ_{25} 1.3739$ and $d^2_{4} 1.077$. The infrared spectrum showed no absorption in the 6μ region for a carbon-carbon double bond but did show bands at 9.97μ and 9.65μ. Marrison states that two bands at 9.95-10.53μ and 9.47-10.00μ respectively are characteristic of cyclohexane derivatives.

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(64) Marrison, L. W., J. Chem. Soc. 1951, 1614.
3.212 Aromatization of \( \text{C}_7\text{H}_7\text{F}_3 \) to Benzotrifluoride

\[
\text{CF}_3\text{-} + (\text{O}) \rightarrow \text{CF}_3\text{-} 
\]

Two procedures were tried. First, the procedure of Braude\(^{65}\) was followed. Chromic anhydride (2.0 g.), concentrated sulfuric acid (1.8 ml.) and water (10 ml.) were added to \( \text{C}_7\text{H}_7\text{F}_3 \) (4 g.) in acetone (10 ml.) and stirred for 30 minutes at room temperature. It was then diluted with water to 100 ml., extracted four times with ether and the ether dried and distilled. There was obtained a substance b. about 107\(^{0}\) which by infrared analysis had some benzotrifluoride in it.

Next, \( \text{C}_7\text{H}_7\text{F}_3 \) (2.5 g. including the material from the first attempt), chloranil (6.0 g.) and \( \text{n-} \text{butyl ether (20 ml.} \) were stirred at reflux for 17 hours, filtered and distilled. There was obtained a substance (about 1 g.) b. 100-5\(^{0}\). Comparison of its infrared spectrum with those of benzotrifluoride and \( \text{n-} \text{butyl ether indicated that this material was almost entirely a mixture of these two compounds.}

3.213 Reduction of \( \text{C}_7\text{H}_7\text{F}_3 \) to Trifluoromethyl-l-cyclohexene

\[
\text{CF}_3\text{-} + \text{H}_2 \rightarrow \text{CF}_3\text{-} 
\]

The adduct $C_7H_7F_3$ (9 g., 0.061 mole) in dry ether (100 ml.) with platinum oxide (0.1 g.) was subjected to a hydrogen pressure of 40-50 psig. Total pressure drop was 23.5 psig in this range which was equivalent to about 0.055 mole of hydrogen, or about one equivalent. A similar reduction of the adduct (4.5 g., 0.030 mole) in glacial acetic acid resulted in the absorption of 0.025 mole of $H_2$.

Fractionation gave a compound b. 108-9°. A fraction b. 108.5-8.8°, $n^\circ 1.3860$, $d_4^{20} 1.096$, was submitted to Galbraith Laboratories for analysis: Found, °/o C, 56.53, 56.30, average 56.11; °/o H, 6.63, 6.42, average 6.52. Calculated for $C_7H_9F_3$: °/o C, 55.9; °/o H, 6.05. The infrared spectrum of the compound had a single absorption in the $6 \mu$ region at 5.92 $\mu$.

The constitution of this $C_7H_9F_3$ was proved by oxidation to be trifluoromethyl-1-cyclohexene.

\[
\begin{align*}
&CF_3 \overset{\text{1.03}}{\text{1,03}} \overset{2, H_2O_2}{\text{2, H}_2\text{O}_2} \\
&CF_3CO(CH_2)_4COOH
\end{align*}
\]

$C_7H_9F_3$ (4.0 g., 0.027 mole) in ethyl acetate (26 ml.) was ozonized at -78° until no more ozone was absorbed, as indicated by titration of the iodine liberated in an aqueous potassium iodide tail bubbler. (The ozonizer is described in Section 3.215). The ethyl acetate was replaced by glacial acetic acid and the ozonide was decomposed and worked up according to the procedure of
A fluorinated keto-acid (0.6 g.) m. 66-8° and over 0.3 g. of its recrystallized semicarbazone, m. 184-6° were obtained. (Analysis by Galbraith Laboratories of the semicarbazone gave: \(0\%/ C, 37.84\%; 0\%/ H, 4.80\). Calculated for \(C_8H_{12}F_3N_3O_3\), \(0\%/ C, 37.65\%; 0\%/ H, 4.75\).

A weighed sample of 0.0736 g. of this semicarbazone required 2.880 ml. of 0.1001 N NaOH to give a phenolphthalein end point, that is, a neutralization equivalent of 256; calculated for \(CF_3C(=NNHCONH_2)(CH_2)_4COOH\), N. E. = 255.

In addition a neutral substance (about 0.1 g.) with an aldehyde odor was isolated from the ozonolysis mixture.

The adduct \(C_7H_7F_3\) (2.0 g., 0.0135 mole) and maleic anhydride (1.3 g., 0.0135 mole) were heated at 100° for six hours, then at 130 ± 10° for 36 hours and let cool. Recrystallization gave only maleic anhydride. The mother liquid smelled strongly of the original butadiene adduct.

3.215 Ozonolysis of $C_7H_7F_3$

$$\text{CF}_3\left(\text{O}_3\rightarrow (\text{CF}_3\text{COCH}_2\text{COOH} + \text{HOOCCH}_2\text{COOH}) \rightarrow \text{CF}_3\text{COCH}_3 + \text{CH}_3\text{COOH} + 2 \text{CO}_2$$

An ozonizer was constructed as follows: Two Pyrex condensers each containing a 28 inch "cold finger" filled with mercury to serve as electrodes were mounted vertically on a ring stand. Each electrode was connected to one terminal of a 15,000 volt transformer; the condenser water completed the circuit between the two electrodes. The transformer was connected to a 110 volt source through a Variac set at 135. The oxygen supply passed through a flowmeter, then through the condensers which were mounted in parallel. The ozonizer was calibrated at several flowmeter settings by passing the effluent oxygen-ozone mixture through aqueous potassium iodide for a definite time interval and titrating the iodine liberated with standard sodium thiosulfate.

$C_7H_7F_3$ (15 g., 0.1 mole) in purified methylene chloride (150 ml.) was subjected to a stream of ozone for 30 hours at -78°. At this time one equivalent of ozone had been absorbed, the ozonide had precipitated out of solution and a small amount of iodoform (m. 121-2°, dec.) had formed in the aqueous potassium iodide tail bubbler. The methylene chloride-ozonide slurry was transferred to a larger flask, diluted to 750 ml. with more methyl-
ene chloride which dissolved some of the ozonide. Ozonolysis was continued until one more equivalent had been absorbed (about 72 hours). No more iodoform was found.

The methylene chloride-ozonide slurry was slowly dropped into a warm stirred solution of about half the theoretical amount of aqueous alkaline permanganate (sodium permanganate, 27.5 g., 0.14 mole; sodium hydroxide, 11.5 g., 0.28 mole; water, 90 ml.). When the original sodium permanganate had been decolorized the other half of the theoretical amount was slowly added plus about a 2/3 excess. The infrared spectrum of the off gas gave no evidence for fluoroform. The tail trap collected a very small amount of material which gave no precipitate when added to a sulfuric acid solution of 2,4-dinitrophenylhydrazine.

The alkaline solution was filtered of manganese dioxide and the clear filtrate extracted with methylene chloride. Evaporation of the solvent gave a gummy resin which was not investigated further. Acidification of the alkaline aqueous solution with hydrochloric acid liberated 0.066 mole of carbon dioxide. Ether extraction of this acid solution followed by distillation of the ether extract gave a material (5.2 g.) b. 105° which appeared to be the water azeotrope of CF₃COOH. The amide m. 74.0-5.5° was made through the ester in the manner of Henne and Kraus¹² (mixed m.p. with authentic CF₃CONH₂, 74.0-5.5°). No acetic acid was found.
The acidic aqueous solution was just neutralized and calcium chloride (5 g.) in water was added. Filtration gave a dry solid (3 g.) which decolorized a dilute sulfuric acid solution of potassium permanganate, and appeared to be calcium oxalate. Attempts to prepare the p-bromophenacyl ester, the p-nitrobenzyl ester, the anilide, and oxalyl chloride from a known sample of calcium oxalate failed. The infrared spectrum of a purified sample of the suspected calcium oxalate and that of known calcium oxalate were identical.

The aqueous portion from which the calcium oxalate had been filtered was reacidified and continuously extracted with ether for 15 days. Distillation of the extract left a gummy residue which gave a negative qualitative test for fluorine on sodium fusion and a negative qualitative test for succinic acid with a pine splinter.

Small scale oxidations were carried out with alkaline sodium permanganate on malonic, levulinic and succinic acids and acetoacetic ester because some of these acids or their CF₃ analogs were expected as oxidation products. Malonic and levulinic acids gave oxalic acid, and levulinic acid also apparently gave acetic acid (as shown by the addition of ferric ion to a neutral sample). Acetoacetic ester was oxidized fairly rapidly but products were not identified. Succinic acid seemed to be oxidized only slowly if at all,
In the second attempted ozonolysis the adduct $C_7H_7F_3$ (15 g., 0.1 mole) was dissolved in C. P. carbon tetrachloride (570 ml.) and ozonized at $-15 \pm 3^\circ$. After about 13 hours one equivalent of ozone had been absorbed and the ozonide separated as a gum. Addition of more ozone resulted in no absorption even when the mixture was stirred, and iodoform formed as before (m. $121-2^\circ$, dec.). About half the carbon tetrachloride was replaced by glacial acetic acid (by adding the acid and evaporating off the carbon tetrachloride under reduced pressure at room temperature) and the resulting homogeneous mixture was ozonized at $0^\circ$ until an additional 1.2 equivalents had been absorbed. Most of the remainder of the carbon tetrachloride was then removed under reduced pressure as before and the diozonide was decomposed by dropping it into a mixture of 30%/o hydrogen peroxide (45 g.) and water (80 ml.) with an arrangement to remove any carbon tetrachloride and/or lower boiling material as formed. The mixture was slowly raised to reflux (about $64^\circ$) and distillate was slowly removed until the temperature rose to $97^\circ$. It was then refluxed at $97^\circ$ for one hour and 45 minutes during which time more distillate was slowly removed. The reaction mixture was then allowed to cool to room temperature. About 0.11 mole of carbon dioxide was absorbed on ascarite during this process.
The collected distillate was then redistilled and the portion up to 45° collected, combined with the tail trap contents from the decomposition of the ozonide and again redistilled. There was collected a material (1.8-2.0 g.) b. 20-30° which gave a 2,4-dinitrophenylhydrazone m. 136.5-7.0° and a semicarbazone m. 127-8°. (The 2,4-dinitrophenylhydrazone of CF$_3$COCH$_3$ m. 139°$^67$ and an authentic sample of the semicarbazone of CF$_3$COCH$_3$ m. 127-8°). A mixed melting point of the semicarbazone with a sample of the authentic semicarbazone of CF$_3$COCH$_3$ was 127.5-8.5°. CF$_3$COCH$_3$ was therefore obtained, and in about 15-18°/o yield.

The main reaction mixture was then treated with aqueous sodium bisulfite until a sample removed gave no color with acidified aqueous potassium iodide as evidence of the absence of peroxides. The mixture was heated to reflux and distillate collected up to 105°. This was combined with the other distillates from which CF$_3$COCH$_3$ had been removed and the entire mixture was redistilled. The portion boiling 101-5° gave a positive test for fluorine on fusion but was not further characterized; it was assumed to be the CF$_3$COOH-water azeotrope.

In view of the large amount of acetic acid present no further
characterization of the reaction mixture was attempted.

3.216 Interpretation of Ultraviolet Spectra

CF₃CH=CHCH=CHCF₃ prepared by Hinkamp⁶⁰ was redistilled,
b. 45°. A solution of this in absolute methanol (0.00026 g/100 ml.,
2.13 x 10⁻⁵ molar) was used to determine the ultraviolet spectrum
from 208 mμ to 270 mμ on a Beckman Quartz Spectrophotometer
(see Figure 1). The cell corrections for this range were first
determined for the solvent. The curve showed a \( \lambda_{\text{max}} \) at
219+ mμ with a molar extinction coefficient of about 19,900.
(A second determination at 5.33 x 10⁻⁶ molar gave the same \( \lambda_{\text{max}} \),
but a molar extinction coefficient of about 35,000. This second
determination appears anomalous since acyclic dienes have reported
molar extinction coefficients of about 22,000.)²¹

Similar determinations were made for trifluoromethyl-1,4-
cyclohexadiene (see Figure 2) at concentrations of 1.01 x 10⁻⁴ molar
(0.001495 g/100 ml.) and 1.01 x 10⁻² molar (0.1495 g/100 ml.) and
for trifluoromethyl-1-cyclohexene (see Figure 3) at 0.97 x 10⁻⁴
molar (0.001452 g/100 ml.) and 0.97 x 10⁻² molar (0.1452 g /
100 ml.). For both compounds the curves at 10⁻⁴ molar showed
no \( \lambda_{\text{max}} \) from 210-320 mμ but indicated by a rising slope
that an absorption maximum lay somewhere below 210 mμ. The
ULTRAVIOLET ABSORPTION SPECTRA OF 5,5,5-TRIFLUORO-1,3-PENTADIENE IN ABSOLUTE METHANOL

- 2.13 x 10^-5 MOLAR
- 5.33 x 10^-6 MOLAR

FIGURE I
ULTRAVIOLET ABSORPTION SPECTRA OF TRIFLUOROMETHYL-1,4-CYCLOHEXADIENE IN ABSOLUTE METHANOL

- 1.01 x 10^{-4} MOLAR
- 1.01 x 10^{-2} MOLAR

FIGURE 2
ULTRAVIOLET ABSORPTION SPECTRA OF TRIFLUOROMETHYL-1-CYCLOHEXENE IN ABSOLUTE METHANOL

---

FIGURE 3

WAVELENGTH, mp

OPTICAL DENSITY

---

0.300

0.200

0.100

0.000

0.97 \times 10^{-4} \text{ MOLAR}

0.97 \times 10^{-2} \text{ MOLAR}

---

210 220 230 240 250 260 270 280 290

---
spectra at $10^{-2}$ molar brought out three peaks at about 254, 260 and 266 m$\mu$ for both compounds with molar extinction coefficients about 14, 17, and 14, respectively, for the cyclohexadiene, and 18, 25 and 19, respectively, for the cyclohexene.

There was also the beginning of a strong absorption whose maximum again appeared to be below 215 m$\mu$.

3.217 Attempted Rearrangement of Trifluoromethyl-1,4-cyclohexadiene

\[
\begin{align*}
\text{CF}_3 & \quad \text{acids or bases} \quad \text{CF}_3 & \quad \text{and/or CF}_3 \\
& \quad \text{or bases} \\
\end{align*}
\]

Since the adduct of butadiene and CF$_3$C=CH had been shown to be trifluoromethyl-1,4-cyclohexadiene, the following attempts were made to rearrange it to a conjugated diene.

(i) The diene (5.5 g.) and 85/o phosphoric acid (15 ml.) were heated with stirring at 50-80$^\circ$ for 45 minutes, diluted with water, extracted with ether and the extract distilled. The distillate was recovered starting material as shown by comparison of infrared spectra.

(ii) Aqueous sulfuric acid (15 ml., 50/o) and the material from (i) (5.2 g.) were refluxed for seven hours, let stand for 16 hours more, diluted with water, extracted, and the extract distilled after washing with aqueous sodium carbonate and drying over calcium
chloride. The distillate was again recovered diene. What appeared to be polymeric resin was present in the residue.

(iii) The distillate from (ii) (4.0 g.) was stirred with aqueous sodium hydroxide (15 ml., 10°/o) for 1-1/2 hours at room temperature. Again no isomerization was observed as indicated by infrared spectra.

(iv) The material from (iii) was heated with aqueous sodium hydroxide (15 ml., 10°/o) at 90-8° for two hours with stirring. Again no difference in the infrared spectrum was observed. No fluoride ion was found in the reaction mixture.

(v) The material from (iv) was refluxed with aqueous sodium hydroxide (18 ml., 16°/o) for eight hours, cooled, extracted and the extract distilled. The distillate had the same infrared spectrum as the original starting material in (i) above.
Attempted Preparation of \((\text{CF}_3\text{C}≡\text{C})_2\)

Reaction of \(\text{CF}_3\text{C}≡\text{CH}\) with Cuprous and Ammonium Chlorides

\[
\begin{align*}
\text{CF}_3\text{C}≡\text{CH} + \text{Cu}(\text{NH}_3)_2\text{Cl} & \rightarrow \text{CF}_3\text{C}≡\text{CCu} + \text{NH}_3 + \text{NH}_4\text{Cl} \\
2 \text{CF}_3\text{C}≡\text{CCu} + \text{O}_2 & \rightarrow (\text{CF}_3\text{C}≡\text{C})_2 + 2 \text{CuO}
\end{align*}
\]

The procedures used were adapted from those of Jones,\(^{24}\) Baeyer\(^{25}\) and Strauss.\(^{25}\) Ammonium chloride (16 g., 0.33 mole) was stirred with water (40 ml.) until an approximately saturated solution was obtained. Cuprous chloride (9 g., 0.09 mole, prepared according to the procedure of Lucas and Pressman,\(^{68}\) washed and dried according to Keller and Wycoff\(^{69}\)) was added with enough concentrated ammonium hydroxide to give a clear solution. This solution was then placed in a flask bearing a Dry Ice filled reflux condenser tailed by a receiver cooled in Dry Ice, and \(\text{CF}_3\text{C}≡\text{CH}\) (5 g., 0.053 mole) was distilled into the solution. After about one hour a small amount of a tan precipitate was noticed which later disappeared and was replaced by an oil. Believing that air or cupric ion oxidation of the \(\text{CF}_3\text{C}≡\text{CCu}\) was producing \((\text{CF}_3\text{C}≡\text{C})_2\),\(^{24}\) the mixture was warmed to 50-60° after completing the addition of

---


CF₃C≡CH and a slow current of air was passed through the mixture until the oil disappeared. The mixture was then allowed to cool to room temperature after which the air flow was stopped and the Dry Ice reflux condenser was replaced by an air condenser.

The Dry Ice reflux condenser was warmed to room temperature and an oil (1.7 g.) was recovered which was distilled from Drierite, b. 58°. An infrared spectrum showed absorptions at about 3.3 μ, 4.6 μ and 6.05 μ.

Filtration of the main reaction mixture gave a very small amount of a tan precipitate, presumably CF₃C≡CCu. Extraction of the filtrate with toluene and distillation of the extract produced only material boiling above 104°. No CF₃C≡CH was recovered in any of the tail traps.

Several other attempts were made to prepare the compound produced above (b. 58°), and yields varied from 40 to 68°/o. The most successful procedure is given below.

CF₃C≡CH (11 g., 0.117 mole) was slowly distilled over a period of 45 minutes into a stirred aqueous solution of Cu(NH₃)₂Cl and ammonium chloride (prepared by using twice the quantities above) contained in a one liter flask equipped with an inlet tube, mercury sealed stirrer, and a Dry Ice cooled reflux condenser leading to a Dry Ice trap. The solution warmed somewhat during the addition
and was cooled externally by an ice bath. Fifteen minutes after the addition was complete refluxing had practically stopped, and an oil was visible on the surface of the reaction mixture. The Dry Ice was removed from the reflux condenser and replaced with water. The mixture was stirred at room temperature for one hour, at the end of which no material was found in the tail trap. After replacing the condenser by a takeoff, the mixture was heated and the oil was steam distilled out. It was washed with dilute hydrochloric acid, dilute aqueous sodium carbonate and dried over anhydrous sodium carbonate. Only ammonia was found in the tail trap. Distillation of the oil from Drierite gave a product (7.5 g.) b. 58.0-8.8° and a residue (0.6 g.). A fraction b. 58.5°, n_20^20 1.3242, d_4^20 1.286, was sent to Galbraith Laboratories for analysis: Found, °/o C, 38.05; °/o H, 1.08. Calculated for (C_3HF_3)_n, °/o C, 38.31; °/o H, 1.07. The yield was 68°/o.

The infrared spectrum of this material had, in addition to other bands, absorptions at 3.25-3.30 μ, 4.55-4.60 μ and 6.05 μ. There was no band in the 3μ region for acetylenic hydrogen.

In every case filtration gave only traces of a tan precipitate which could have been CF_3=C=CCu. In one run, boiling the reaction mixture with strong acid gave no CF_3C=CH.
3.222 Attempted Reaction of CF₃C=CH with Cuprous Hydroxide

\[
\begin{align*}
\text{CF}_3\text{C}=\text{CH} + \text{CuOH} & \rightarrow \text{CF}_3\text{C}=\text{CCu} + \text{H}_2\text{O} \\
2 \text{CF}_3\text{C}=\text{CCu} + 3 \text{K}_3\text{Fe(CN)}_6 & \rightarrow (\text{CF}_3\text{C}=\text{C})_2 + 3 \text{K}_4\text{Fe(CN)}_6 + \\
& \quad \text{Cu}_2\text{Fe(CN)}_6
\end{align*}
\]

The procedure was adapted from Baeyer. Cuprous chloride (12 g., 0.12 mole) was dissolved in concentrated hydrochloric acid (60 ml.) and dropped slowly into an excess of cooled cold 5 N sodium hydroxide with stirring. The orange precipitate was allowed to settle, decanted and washed twice by decantation. The resulting slurry was transferred to a 500 ml. three-necked flask equipped with a mercury sealed stirrer, a Dry Ice cooled reflux condenser connected to a tail trap cooled in Dry Ice, and a Y-tube with a dropping funnel and an acetylene inlet tube. Sodium hydroxide (20 g., 0.5 mole) in water (100 ml.) was added, stirring was begun, and CF₃C=CH (10 g., 0.10 mole) was distilled in, and the mixture was let stir at room temperature for seven hours, then let stand overnight. Most of the orange-colored solid was still present with traces of a green precipitate. Potassium ferricyanide (66 g., 0.204 mole) as a saturated aqueous solution was added, the mixture was stirred for one hour and an excess of dilute sulfuric acid was added. The only organic material isolated was some of the original CF₃C=CH (2 g.) along with much hydrogen cyanide. 

(70) Baeyer, A., Ber. 18, 2269 (1885).
3.223 Reaction of $\text{CF}_3\text{CBr}=\text{CBr}_2$ with Zinc in Acetic Anhydride

$$2\text{CF}_3\text{CBr}=\text{CBr}_2 + 3 \text{Zn} \xrightarrow{\text{Ac}_2\text{O}} (\text{CF}_3\text{C}≡\text{C})_2 + 3 \text{ZnBr}_2$$

Granular zinc (24.5 g., 0.375 mole), redistilled Skellysolve C (100 ml., b. 93-7°) and acetic anhydride (100 ml.) were placed in a 500 ml. three-necked flask equipped with a thermometer dipping into the liquid, an equilibrated dropping funnel, a mercury sealed stirrer and a reflux condenser leading to a tail trap cooled in Dry Ice. $\text{CF}_3\text{CBr}=\text{CBr}_2$ (83 g., 0.25 mole) was slowly dropped in at such a rate as to keep the reaction temperature below 41°. The reaction mixture was then stirred at room temperature for four hours and at 40-5° for four hours. Water (50 ml.) was added with cooling to the thick white slurry giving two layers. The cold mixture was decanted from the zinc (3.8-4.0 g. recovered or 16°/o) and the two layers were separated. No material had collected in the tail trap at this point. The organic phase was neutralized with aqueous sodium carbonate in the original flask; some material collected in the tail trap. Although excess carbonate was used, the organic phase was still acidic; it was dried over anhydrous sodium sulfate.

The aqueous hydrolysate from the main reaction mixture was also neutralized and a small amount of material collected in the tail trap. All trap contents were added to the main organic portion drying over
sodium sulfate. Fractionation from Drierite gave material b. 25-8° (14 g.), an intermediate cut b. 28-86° (4 g.), recovered Skellysolve C, and a residue (4.2 g.). The residue appeared to contain Skellysolve, CF\textsubscript{3}CBr\textsubscript{2} and acetic acid and was not further investigated. Assuming the intermediate cut to be half CF\textsubscript{3}C\equiv CBr and ignoring the residue, the crude yield of CF\textsubscript{3}C\equiv CBr was 37°/o.

The 25-8° fraction was redistilled from Drierite and there was obtained a fraction (12.9 g.) b. 25.2-6.5°, n\textsuperscript{D} 1.3518, d\textsubscript{4} 1.716. (Part of a middle portion b. 25.5-5.8°, n\textsuperscript{D} 1.3515 was submitted to Galbraith Laboratories for analysis: Found, °/o C, 21.02; °/o H, 0.18. Calculated for C\textsubscript{3}BrF\textsubscript{3}, °/o C, 20.83; °/o H, 0.00). An infrared spectrum showed no absorptions at 2-4\textmu, a strong peak at about 4.6\textmu and none around 6\textmu.

This material was fused with sodium and qualitative tests for fluorine with cerous nitrate, and for bromine with silver nitrate and nitric acid, and chloroform and chlorine water were positive.

3.224 Attempted Reaction of CF\textsubscript{3}C\equiv CBr with Zinc in Acetic Anhydride

\[
CF\textsubscript{3}C\equiv CBr + Zn \xrightarrow{Ac\textsubscript{2}O} (CF\textsubscript{3}C\equiv C)_2 + ZnBr_2
\]

A mixture (24 g.) of CF\textsubscript{3}C\equiv CBr and CF\textsubscript{3}CBr=CH\textsubscript{2} b. 26.0-8.5°, and pure CF\textsubscript{3}C\equiv CBr (2 g.) in redistilled Skellysolve C (25 ml., b. 93-7°) were dropped into a stirred mixture of granular zinc.
(10.8 g., 0.165 mole), acetic anhydride (40 ml.) and redistilled Skellysolve C (25 ml.). Since reaction appeared to be occurring at room temperature the mixture was stirred at room temperature for 15-1/2 hours. It was hydrolyzed with cooling with 100 ml. of water, decanted off the zinc (7.6 g. was recovered or 70°/o) and the organic material was separated from the aqueous. The organic material was returned to the flask and neutralized with aqueous sodium carbonate, and some material was collected in the trap. After separating the two phases the organic phase was combined with the trap contents and distilled. Fractionation gave a mixture (14 g., 54°/o) of CF₃C≡CBr and CF₃CBr=CH₂ b. 26-30°, an intermediate cut (2 g.) b. 30-89° and a residue assumed to be Skellysolve C which was not investigated further. In the tail trap from the distillation was a mixture (about 1.5 g., 6-8°/o) which appeared to contain CF₃C≡CH, CF₃C≡CBr and CF₃CBr=CH₂ as indicated by infrared spectra. The infrared spectrum of the recovered mixture of CF₃C≡CBr and CF₃CBr=CH₂ was identical with that of the starting mixture and the spectrum of the material b. 30-89° indicated that it was a mixture of CF₃C≡CBr, CF₃CBr=CH₂ and Skellysolve C, with traces of a carbonyl compound, presumably acetic acid.
3.23 Proof of Structure of the CF$_3$C=CCH Dimer, C$_6$H$_2$F$_6$

3.231 Reduction of C$_6$H$_2$F$_6$ to C$_6$H$_4$F$_6$

$$C_6H_2F_6 + H_2 \rightarrow C_6H_4F_6$$

C$_6$H$_2$F$_6$ (10 g., 0.053 mole) from 3.221 above was reduced at 40-50 psig with palladized charcoal in ethanol until approximately one equivalent of hydrogen had been absorbed. The filtered material was poured into an aqueous calcium chloride solution with the resultant formation of an emulsion which was very difficult to break. The organic material obtained was washed with water, dried over calcium chloride and distilled. There was obtained a fraction b. 87-90$^\circ$ which behaved as a mixture and which was redistilled. Distillation then gave 2.5 g. b. 70-87$^\circ$, $n^\circ$ 1.3302; 2.0 g. b. 86.5-8.5$^\circ$, $n^\circ$ 1.3295, $d^\circ_4$ 1.286; 0.7 g. b. 88.5-90.0$^\circ$, $n^\circ$ 1.3270, $d^\circ_4$ 1.284 and 1.2 g. of residue $n^\circ$ 1.3421. The infrared spectra of the two middle fractions which were almost identical showed absorptions at about 3.45 $\mu$, none in the region 4-5 $\mu$, and two in the 6$\mu$ region at about 5.90-5.95 $\mu$ and 6.05 to 6.1 $\mu$ respectively. The spectra were similar to, but not identical with, that of CF$_3$CH=CH-CH=CHCF$_3$, b. 85.5-6.5$^\circ$, $n^\circ_{25}$ 1.3403, $d^\circ_{25}$ 1.286, prepared by Groth.$^{29}$

An attempt was made to prepare the maleic anhydride adduct of C$_6$H$_4$F$_6$ as follows: C$_6$H$_4$F$_6$ (1.0 g., 0.0052 mole) and maleic anhydride (0.5 g., 0.0051 mole) sealed in an ampoule at 0$^\circ$ were
heated in a boiling water bath for 21 hours. No color had developed and the material appeared unchanged. It was then heated at 160 ± 3° for 27 hours during which a slight brown color developed, and finally at 190° for 10 hours. At this time the contents were quite dark. When the ampoule was opened at 0° a gas was liberated and the remaining material was resinous.

3.232 Oxidation of C₆H₄F₆

\[
3 \text{CF}_3\text{CH} = \text{CH}_2 + 16 \text{KMnO}_4 \rightarrow 6 \text{CF}_3\text{COOK} + 3 \text{(COOK)}_2 + 16 \text{MnO}_2 + 4 \text{KOH} + 4 \text{H}_2\text{O}
\]

C₆H₄F₆ (4.0 g., 0.021 mole), potassium permanganate (17.8 g., 0.112 mole), sodium hydroxide (0.5 g.) and water (150 ml.) were refluxed for seven hours, the remaining permanganate was removed with a small amount of hydrogen peroxide and the mixture was cooled and filtered. The filtrate was neutralized and aqueous calcium chloride was added. The precipitate composed of calcium fluoride and calcium oxalate was filtered off and added to hydrochloric acid (30 ml., 3 N). After filtration to remove the calcium fluoride the calcium oxalate (0.5 g., 15°/o yield) was reprecipitated by the urea method, and identified by its infrared spectrum and

the fact that it decolorized a dilute sulfuric acid solution of potassium permanganate.

The filtrate from which the calcium salts had been removed was reacidified and continuously extracted with ethyl ether for 36 hours. The ether extract was distilled and a fraction (3.5 g.) b. about 100° was collected. Two grams of this was converted to the amide m. 73.5-5.5° by the procedure of Henne and Kraus. A mixed m. p. with authentic CF₃CONH₂ was 73.5-5.5°. An aliquot of the fraction b. 100° was titrated with 0.10 N sodium hydroxide. On the basis that this acid was all CF₃COOH, a yield of 55°/o on oxidation was realized.

3.233 Reduction of C₆H₂F₆ to C₆H₆F₆

\[ C₆H₂F₆ + 3 H₂ \rightarrow C₆H₆F₆ \]

C₆H₂F₆ (7.2 g., 0.038 mole) was hydrogenated at 40-50 psig in dry ether with palladized charcoal. When the rate of hydrogen absorption appeared to be decreasing, platinum oxide (0.1 g.) was added. Total hydrogen absorbed was 33 psig. Since 4.17 g. (0.0424 mole) of 99.8 mole °/o trans-2-heptene required 11.5 psig of hydrogen under the same conditions, one equivalent of the compound absorbed three equivalents of hydrogen. The mixture of reduced compound and ether was filtered of catalysts and distilled. Fractionation gave 1.5 g. b. 70-98°, 4.5 g. b. 98-100° and 1.4 g. of holdup.
A middle portion of the main fraction b. 99.5-100°, n\(^{20}\) 1.3103, 
d\(^{20}\) 1.231, was submitted to Galbraith Laboratories for analysis:

Found, o/o C, 37.09, 37.23, average 37.16; o/o H, 4.52, 4.56,
average 4.54. Calculated for C\(_6\)H\(_2\)F\(_6\), o/o C, 37.12; o/o H, 4.15.

The infrared spectrum showed no absorption in the region 3.5-
6.7 μ, and was identical with that of CF\(_3\)(CH\(_2\))\(_4\)CF\(_3\), b. 97.5-
9.5°, n\(^{25}\) 1.3105, d\(^{25}\) 1.236, prepared by Groth.\(^{29}\)

3.234 Attempted Reaction of C\(_6\)H\(_2\)F\(_6\) with Maleic Anhydride

\[
\text{CF}_3\text{C}≡\text{CCH=CHCF}_3(?) + \text{CH}≡\text{C}=\text{O} → \begin{array}{c}
\text{CH}≡\text{C}=\text{O} \\
\text{CH}≡\text{C}=\text{O}
\end{array}
\] (?)

C\(_6\)H\(_2\)F\(_6\) (2.0 g., 0.01 mole) and maleic anhydride (1.0 g.,
0.01 mole) were sealed in an ampoule at 0° and heated in a boiling
water bath for 17 hours. About 0.8 g. of doubly recrystallized
material m. 52.0-3.5° mixed m.p. with maleic anhydride 54-5°
was obtained. However, qualitative analysis showed the presence
of fluorine.

In a second attempt C\(_6\)H\(_2\)F\(_6\) (1.0 g., 0.005 mole) and maleic
anhydride (0.5 g., 0.005 mole) were heated in a boiling water bath
for 8 hours then let stand for six days. There was obtained a
material which on recrystallization from a mixture of benzene and
petroleum ether melted at 136.5-7.5°, which had an infrared spectrum
very similar to that of maleic acid (m. 131°, dec. 135°) but which
contained fluorine.
3.24 CF$_3$C=CBr

3.241 Attempted Alternate Syntheses of CF$_3$C=CBr

CF$_3$C=CBr had been synthesized as shown in Section 3.223; alternate syntheses were tried as follows.

(i) CF$_3$C=CB$_r$_2 + Zn $\xrightarrow{\text{EtOH}}$ CF$_3$C=CBr + ZnBr$_2$

CF$_3$C=CB$_r$_2 (33 g, 0.1 mole), zinc dust (8.5 g, 0.13 mole) and ethanol (55 ml) were refluxed for four hours. CF$_3$C=CH (3.5-4.0 g, approx. 0.4 mole) identified by its infrared spectrum was collected in the Dry Ice tail trap in 58% yield. The reaction mixture was cooled, and filtered, and three g. of zinc or 35% of the original amount was recovered. Water and enough 15% sulfuric acid to dissolve any precipitate of zinc was added to the filtrate and the organic material was steam distilled out, to recover the original CF$_3$C=CB$_r$_2 (about 10 g. or 30%o), then a small, unidentified fraction (1.5 g.) b. 52$^\circ$ at 200 mm. to 64$^\circ$ at 46 mm. No other product was obtained.

(ii) CF$_3$CBr=CB$_r$_2 + Zn $\xrightarrow{\text{dioxane}}$ CF$_3$C=CBr + ZnBr$_2$

A 500 ml. three-necked flask was equipped with a mercury sealed stirrer, a takeoff condenser connected to a receiver, both of which were connected through a tee joint to a tail trap in Dry Ice, and a dropping funnel.

The dropping funnel was equipped with a stirrer to keep the zinc dust dispersed in dry dioxane. Dioxane (about 250 ml.) which
had been dried according to the method of Feiser\(^{72}\) and

\[ \text{CF}_3\text{CBr}=\text{CBr}_2 \] (37 g., 0.11 mole) were added to the flask. Zinc dust (6.5 g., 0.1 mole) was placed in the funnel with dry dioxane (75 ml.) and stirred. The reaction mixture was heated to 50\(^\circ\) by means of an oil bath and half of the zinc dust was added in portions over a six hour period as the temperature was slowly raised to a mild reflux. The remainder of the zinc was added and refluxing material removed until the reflux temperature remained at 100\(^\circ\). The mixture was allowed to cool overnight. Filtration recovered 4.0-4.3 g. (67\%/o) of the zinc. The main reaction mixture was heated on a fractionating column and material again collected up to 100\(^\circ\). This was combined with the original distillate obtained during reaction and redistilled. There was obtained less than one g. boiling below 50\(^\circ\). This appeared to be largely dioxane with some acetylenic material present.

All residues were combined and after separation, the organic phase was diluted with water, washed with dilute acid and then twice with water and distilled. About 50-55\%/o (18.3 g.) of the original \[ \text{CF}_3\text{CBr}=\text{CBr}_2 \] contaminated with dioxane was recovered. No other material was isolated.

(iii) \[ \text{CF}_3\text{CBr}_2\text{CH}_2\text{Br} + \text{KOH} \xrightarrow{\text{EtOH}} \text{CF}_3\text{C}≡\text{CBr} + \text{other products} \]

(See Section 3.112)

\[ \text{CF}_3\text{CBr}_2\text{CH}_2\text{Br} \] (133 g., 0.41 mole) was slowly dropped into a cold stirred solution of potassium hydroxide (33 g., 0.85⁰/o, 0.5 mole) in ethanol at 0-5⁰, and stirred for 18 hours. A large excess of water was added and organic material was distilled out until the temperature began to rise above 80⁰. Water was added to the distillate and to the reaction flask and the organic phases were separated from the water phases, combined, washed, dried and distilled. Only 6 g. boiled below 103⁰. The remainder (86 g.) boiling above that temperature seemed from a comparison of infrared spectra to be composed of \[ \text{CF}_3\text{CH}_2\text{COOC}_2\text{H}_5, \text{CF}_3\text{CBr}=\text{CBr}_2 \] and \[ \text{CF}_3\text{CBr}_2\text{CH}_2\text{Br} \] but was not investigated further.

3.242 Proof of Structure and Properties of \( \text{CF}_3\text{C}≡\text{CBr} \)

To measure the unsaturation, \( \text{CF}_3\text{C}≡\text{CBr} \) (3 g., 0.017 mole) was treated with bromine (3 g., 0.019 mole). The initial reaction was very exothermic and luminiferous and had to be cooled. The excess bromine was discharged with aqueous sodium bisulfite and the organic material was extracted with ether. The ether extract was washed twice with water, dried and distilled giving material (3.2 g.) b. about 50⁰ at 8-10 mm., the infrared spectrum of which was identical with that of \( \text{CF}_3\text{CBr}=\text{CBr}_2 \).
The following tests were carried out to determine if the bromine in CF$_3$C=CBBr had much positive character.

(i) Aqueous silver nitrate gave no precipitate within half an hour.

(ii) Alcoholic silver nitrate affected it much as it does n-butyl bromide. Both precipitated AgBr at a rate such that equal volumes of solution turned completely opaque in four to six minutes. With ethyl iodide the silver nitrate solution turned opaque in a matter of seconds.

(iii) Neutral or basic aqueous starch iodide paper remained colorless in contact with CF$_3$C=CBBr at room temperature in a closed vial overnight.

(iv) CF$_3$C=CBBr (1 g.), potassium ferrocyanide (0.5 g.) and water (15 ml.) gave no apparent difference in color when equal volumes of this mixture and a blank of potassium ferrocyanide (0.5 g.) in water (15 ml.) were treated with two drops of freshly prepared ferrous sulfate solution, even after one to two days. However, the CF$_3$C=CBBr solution did darken slightly on standing.

(v) CF$_3$C=CH (1 g.), phenol (0.2 g.), concentrated hydrobromic acid (0.5 ml.) and water (20 ml.) gave no precipitate after four hours.

(vi) CF$_3$C=CBBr and aqueous hydriodic acid (1:1) showed no difference in color when compared with aqueous hydriodic acid (1:1) alone after several hours.
3.25 Attempted Addition of CH$_3$COOH/(CF$_3$CO)$_2$O to CF$_3$C≡CH

\[
\text{CF}_3\text{C≡CH} + \text{CH}_3\text{COOH} + (\text{CF}_3\text{CO})_2\text{O} \rightarrow \text{CF}_3\text{C} (\text{COCH}_3) = \text{CHOOCF}_3 + \text{CF}_3\text{COOH}
\]

\[
\text{CF}_3\text{C} (\text{COCH}_3) = \text{CHOOCF}_3 + \text{CH}_3\text{OH} \rightarrow \text{CF}_3\text{CH} (\text{COCH}_3) \text{CHO} + \text{CF}_3\text{COOCH}_3
\]

(CF$_3$CO)$_2$O (10.5 g., 0.05 mole), glacial acetic acid (3 g., 0.05 mole) and CF$_3$C≡CH (4.7 g., 0.05 mole) were sealed in a Carius type ampoule at -78° and warmed to room temperature. The mixture was kept at room temperature for three days, then cooled to -78°. The ampoule was opened and allowed to warm to room temperature all volatile material being collected in a Dry Ice trap. The reaction mixture was transferred to a 50 ml. round bottom flask equipped with a funnel and a reflux condenser leading to a Dry Ice trap. Methanol (14 ml.) was added and the contents were refluxed for one hour. Distillation gave only methanol, methyl trifluoroacetate and traces of water. All cuts gave negative tests with 2,4-dinitrophenylhydrazine in sulfuric acid and with aqueous copper acetate. The CF$_3$C≡CH recovered amounted to about 4.2 g. or 85-90°/o. 

An identical run heated at 70-80° for eleven days gave the same results with 89°/o of the acetylene recovered.
3.26 Attempted Michael Condensation of $\text{CF}_3\text{C}≡\text{CH}$ to Itself

$$2 \text{CF}_3\text{C}≡\text{CH} \xrightarrow{\text{Na, ether}} \text{CF}_3\text{C}≡\text{CCH}=\text{CHCF}_3$$

The method was adapted from Ingold. Freshly cut sodium (2.3 g., 0.1 mole) and dry toluene (100 ml.) were placed in a three-necked, 500 ml. flask equipped with a mercury sealed stirrer and a reflux condenser connected to a tail trap cooled in Dry Ice. The toluene was heated to reflux and stirred very rapidly. When the sodium appeared to be very finely divided, the rapidly stirring mixture was cooled, the stirrer was stopped, and the sodium allowed to settle. The toluene was decanted off and the sodium sand was washed three times with dry ether and covered with dry ether (175 ml.). After the water cooled reflux condenser was replaced by a Dry Ice cooled reflux condenser, $\text{CF}_3\text{C}≡\text{CH}$ (22 g., 0.23 mole) was distilled into the reaction flask. The mixture was permitted to stand at room temperature for about 14 hours, and during the last four hours the Dry Ice condenser was permitted to warm to room temperature. A small amount of water was added slowly to the mixture followed by 20% sulfuric acid (100 ml.) and the mixture was refluxed gently to distill off the $\text{CF}_3\text{C}≡\text{CH}$ which was collected in the tail trap.
The two phases were then separated but a considerable quantity of dark brown fluorine containing polymer made separation difficult. Distillation of the ether phase gave only ether and a small amount of fluorinated residue. A sample of the aqueous phase gave a copious precipitate with cerous nitrate indicating the presence of much fluoride ion. Rectification of the cold trap contents produced $\text{CF}_3\text{C}:=\text{CH}$ (14 g., 0.15 mole) in 65$^\circ$/o recovery.
3.27 Relative Acidity of CH₃C≡CH and CF₃C≡CH

3.271 Attempted Determination of Relative Acidity by a Colorimetric Method

The method used was essentially that of Conant⁴¹ and McEwen⁴⁰ modified for the convenient handling of gases.

\[
\begin{align*}
(C_6H_5)_3CCl + 2 Na/Hg & \rightarrow (C_6H_5)_3CNa + NaCl + Hg \\
(C_6H_5)_3CNa + \text{yellow-orange} & \rightarrow (C_6H_5)_3CH + \text{(colorless)}
\end{align*}
\]

3.2711 Description of the apparatus

The reaction flask was a 50 ml. flat bottomed flask with three necks. Two necks had standard taper joints, one connected the flask to the apparatus, the other held a standard taper glass plug. The third neck bore a stopcock and a turned down stopper from a serum bottle. Stirring was effected by a Teflon covered stirring bar and a magnetic stirrer.

The apparatus consisted of a horizontal Pyrex glass tube to which were attached 1) a three way stopcock leading to a vacuum pump, 2) a three way stopcock leading to a dry nitrogen source, 3) a stopcock connected by a short piece of Tygon tubing to a 100 ml. soft glass gas buret which, in turn, was connected by Tygon tubing
to a mercury leveling bulb, 4) a stopcock with the outer half of a ball joint pair to which the acetylene ampoule could be attached, 5) a stopcock connected to an open end manometer and 6) a stopcock leading to the reaction flask.

3.2.1.2 Reagents

Dry oxygen-free nitrogen was prepared by passing cylinder nitrogen through Fieser's solution, lead acetate solution, concentrated sulfuric acid, a xylene solution of benzophenone ketyl, and liquid paraffin. 73

Commercial indene was distilled, b. 180-3.5°. Methylmagnesium bromide (50 ml., about 2 N) was added to the fraction b. 182,1-3.0°, and this mixture was fractionated. Indene was removed at a constant index of refraction of 1.5744 at 20° (n19°s 1.5767)74 b. 182.5°.

CF₃C≡CH was redistilled b. -46.5 ± 0.5° under a dry nitrogen atmosphere into a storage ampoule containing the inner half of a ball joint pair, and a stopcock.

CH₃C≡CH was prepared from propylene bromide according to the procedure of Heisig,75 redistilled under dry nitrogen, (b. -23.3 to

---


-23.0\(^\circ\) C, \(\text{CH}_3\text{C}≡\text{CH}_2\), b. -23.3\(^\circ\),\(^{76}\) and placed in a storage ampoule.

Dry ether (b. 35\(^\circ\)) was prepared by drying commercial ether over calcium chloride and sodium wire and distilling from sodium wire. It was stored over sodium wire.

Triphenylmethyl chloride, m. 112-13\(^\circ\), recrystallized from a mixture of five parts Skellysolve C (b. 90-7\(^\circ\)) and one part acetyl chloride and sodium amalgam (about 3\%o) were used to prepare triphenylmethylnsodium in ether by the procedure of Renfrow and Hauser.\(^{77}\)

The triphenylmethylnsodium solution was stored in a 500 ml. two-necked flask bearing a turned down rubber stopper from a serum bottle and a three way stopcock bearing a nitrogen filled rubber balloon. A source of dry nitrogen could be attached to the stopcock and the balloon filled as needed.

The triphenylmethylnsodium solution was standardized in the following way: A 10 ml. hypodermic syringe was inserted into the solution through the turned down rubber stopper and 10 ml. of solution was withdrawn. This was added to 25 ml. of distilled water and titrated with standard hydrochloric acid using phenolphthalein as

---


an indicator. The volumes of 0.1004 N hydrochloric acid required for two 10 ml. portions of triphenylmethylysodium were 11.75 ml. and 11.70 ml. respectively. The normality was calculated to be 0.1180 and 0.1175, average 0.118.

3.2713 General Procedure

The reaction flask and the ampoule containing the acetylene to be used were attached to the system. A Dry Ice cooling bath kept the acetylene cold so that pressure would not cause the closed stopcock to slip. The system was flushed with dry nitrogen for several hours. It was then alternately evacuated and filled with dry nitrogen three times. Between evacuations, the gas buret was flushed with dry nitrogen by alternately raising and lowering the mercury filled leveling bulb. With dry nitrogen passing through the system, the Teflon covered stirring bar and a weighed sample of indene in a glass capsule were added against a countercurrent flow of nitrogen. The nitrogen flow was stopped and the reaction flask closed to the atmosphere. The indene capsule was opened with the stirring bar or, if necessary, with a partial vacuum. Triphenylmethylsodium (10 ml.) was added through the turn down rubber stopper with a hypodermic syringe and a color change from red to yellow-orange was observed. The reaction flask was isolated from the rest of the system, which in turn was closed to the nitrogen source. When the mercury leveling bulb had been adjusted so that
the manometer indicated atmospheric pressure within the system, the mercury level in the gas buret and the temperature and atmospheric pressure were recorded. The propyne was admitted into the system by removing the cooling bath surrounding the ampoule, opening the stopcock on the ampoule and letting the propyne vaporize into the system. It was found advisable, however, after the first run to let the ampoule warm up somewhat with the stopcock closed since upon cooling to $-78^\circ$ a partial vacuum developed in the ampoule. When approximately the predetermined volume of propyne was in the system as indicated by the mercury level in the gas buret and the manometer, the stopcock of the ampoule was closed and the ampoule was reimmersed in the cooling bath.

The system was then allowed to stand for 20-40 minutes to permit temperature equilibrium to take place, the mercury leveling bulb was adjusted so that the manometer indicated atmospheric pressure in the system, and again the mercury level in the gas buret and the temperature and atmospheric pressure were recorded. From the difference in gas buret readings and the temperature and pressure the number of moles of the propyne was calculated.

The reaction flask was opened to the system, stirring was begun and the pressure in the system was increased by raising the mercury leveling bulb. This was done in order to increase the solution rate of the propyne into the reaction mixture; simultaneous cooling of the
reaction flask was also done to serve the same purpose. After the reaction appeared to be complete as indicated by a color change, or after the reaction was stopped, the flask was removed, cleaned and dried, and the rest of the system flushed of any remaining propyne before the next run.

Additional propyne was added as seemed advisable by isolating the reaction flask and proceeding as before.

3.2714 Attempted Determination of Relative Acidity

(i) Indene (0.1504 g., 0.00129 mole), triphenylmethylsodium (10 ml. of 0.118 N, 0.00118 mole) in ether and CH₂C=CH (85.30 ml. at 25.5° and 740 mm., 0.00338 mole) were reacted as outlined in the general procedure (Section 3.2713). A slight color change was noticed after 40 minutes, and in two hours and 40 minutes the color of the solution was yellow. A mixture of indene and triphenylmethylsodium in ether was yellow-orange.

A second determination with similar quantities produced a yellow-green color in three hours and 40 minutes. When this mixture was added to water it turned yellow.

(ii) Indene (0.1503 g., 0.00129 mole), triphenylmethylsodium (10 ml. of 0.118 N, 0.00118 mole) in ether and CF₃C≡CH (60.65 ml. at 25° and 741 mm., 0.00241 mole) were reacted as outlined in the general procedure (Section 3.2713). Addition of the CF₃C≡CH produced a color change from pale yellow to a deep blue in five or ten seconds.
On standing for a few minutes the blue color slowly faded and a dark brown polymer was formed.

The reaction was repeated with similar quantities of reagents with similar results.

(iii) Finally, as a blank test, indene (0.1565 g., 0.00135 mole) and triphenylmethylsodium (10 ml., 0.118 N3, 0.00118 mole) in ether were reacted as above but no propyne was added. After four hours and 30 minutes only a questionable change in color was observed.

3,272 Attempted Determination of Relative Acidity by Infrared Analysis

An attempt was made to establish an equilibrium between propyne, trifluoropropyne, and their sodium salts in a closed system and to estimate the position of this equilibrium by a quantitative determination of the amounts of the two propynes in the vapor phase by infrared analysis.

3,2721 Description of the Apparatus

Infrared spectra were recorded with a Perkin-Elmer Model 21 Recording Infrared Spectrophotometer.

The reaction flask was a single-necked 500 ml. cylindrical flask with a thermometer well. A tee bearing an inlet tube which reached almost to the bottom of the flask was attached to the neck of the flask by standard taper joints. One arm of the tee led to the dry
nitrogen source and was also used to admit both of the propynes. The second arm of the tee led to a three way stopcock; this was attached by a ball joint pair to a gas sample holder, and by rubber tubing to a mercury manometer. Temperature was measured by a potentiometer connected to a thermocouple inserted in the thermometer well.

The gas sample holder was a Pyrex tube containing a stopcock on one end and a two way stopcock on the other. The apparatus used for transferring a sample of gas from the sample holder to the ten cm. gas cell which was used for determining the spectra was as follows: A 100 ml. gas buret containing mercury was mounted vertically and attached by rubber tubing to a leveling bulb and to a two way stopcock. One arm of the stopcock was connected by ball joints to the two way stopcock of the gas sample holder and the other arm to the ten cm. gas cell by a pair of ball joints. The gas cell, in turn, was connected by ball joints to a three way stopcock leading to a vacuum pump and to a manometer.

3.2722 Reagents

Triphenylmethylsodium was prepared and standardized as in Section 3.2712. Propyne (obtained from Research Foundation, Project 451) was redistilled, b. -23.0°; trifluoropropyne was distilled twice and a fraction b. -47.0° ± 0.5° was used. Ether was
dried over calcium chloride, sodium wire and stored over fresh sodium wire prior to use. Dry oxygen-free nitrogen was prepared as in Section 3.2712.

3.2723 Procedure

Curves of optical density versus partial pressure were first made for both propyne and trifluoropropyne. Each propyne was transferred in turn from its ampoule to the gas sample holder by alternately evacuating the gas sample holder and filling it with the propyne at least five times to assure complete removal of nitrogen and air. The gas sample holder was then attached to the gas buret of the transferring device and the space between the gas buret and the gas sample holder was evacuated. A portion of the propyne was then drawn into the gas buret by lowering the mercury leveling bulb and, after evacuating the ten cm. gas cell, propyne was admitted into the gas cell to a predetermined pressure as indicated by the manometer. The gas buret was then flushed out with nitrogen three times to remove any residual propyne and filled with nitrogen. Enough nitrogen was admitted into the ten cm. gas cell to give a total pressure of 100 ± 3 mm. The cell was then removed and the infrared spectrum was taken.

The system in which the equilibrium between the two propynes and their sodium salts was to be established was flushed with dry oxygen-free nitrogen for three hours. An ether solution (305 ± 3 ml.)
of triphenylmethylsodium (0.308 ± 0.004 mole) was added to the reaction flask and cooled to -78° under a cover of nitrogen. Propyne (1.187 g., 0.0296 mole) and trifluoropropyne (3.462 g., 0.0370 mole) were distilled in, the system was closed and allowed to warm to -10°. After 15 minutes at this temperature a sample of the vapor was removed by evacuating the gas sample holder and then opening it into the system. A sample of this vapor transferred to the ten cm. gas cell (16 mm. partial pressure, total pressure to 103 mm. with nitrogen) showed no absorptions in the infrared for acetylenic or fluorinated compounds. A second sample taken one-half hour later (55 mm. partial pressure, total pressure to 101 mm. with nitrogen), showed only a trace of acetylenic material, insufficient for quantitative determination. By this time a very noticeable darkening of the solution had occurred; it was apparent that the trifluoropropyne was decomposing or polymerizing. After rapidly raising the temperature to 20° and withdrawing a sample of the vapor, the solution was black. The spectrum of the vapor (79 mm. partial pressure, total pressure to 101 mm. with nitrogen) showed the presence of small amounts of acetylenic material, again insufficient for quantitative estimation.

It was therefore concluded that at temperatures of 20° or below both propynes are too soluble in ether to make this method of value, and at temperatures of -10° or above trifluoropropyne decomposes or polymerizes in the presence of a strong base.
3.3 Acidity of Hydrogen Atoms Alpha to Highly Fluorinated Alkyl Groups

3.3.1 Attempted Reaction of CClF₂CH₃ with Organolithium Compounds

In order to prepare CClF₂CH₃, the directed chlorination of CHF₂CH₃ was relied upon according to the equation

\[
\text{CHF}_2\text{CH}_3 + \text{Cl}_2 \xrightarrow{\text{u. v.}} \text{CClF}_2\text{CH}_3 (70\% \text{ yield}) + \text{CClF}_2\text{CH}_2\text{Cl} (6\% \text{ yield})^{78}.
\]

A typical chlorination of CHF₂CH₃ (60 g, 0.91 mole, b. -23°) under ultraviolet light produced recovered CHF₂CH₃ (31 g, 0.48 mole) and CClF₂CH₃ (37 g, 0.37 mole, b. -10 to -9°) for an 86°/o yield.

The following sequence was attempted in efforts to react one of the hydrogen atoms of CClF₂CH₃:

\[
\text{CClF}_2\text{CH}_3 + \text{RLi} \longrightarrow \text{CClF}_2\text{CH}_2\text{Li} + \text{RH}
\]

\[
\text{CClF}_2\text{CH}_2\text{Li} + \text{HCHO} \longrightarrow \text{CClF}_2\text{CH}_2\text{CH}_2\text{OLi}
\]

\[
\text{CClF}_2\text{CH}_2\text{CH}_2\text{OLi} \xrightarrow{\text{H}^+} \text{CClF}_2\text{CH}_2\text{CH}_2\text{OH}
\]

The reactions studied are summarized in Table II. Phenyl-lithium was prepared by adding dry redistilled bromobenzene, dry ether, and lithium particles to a flask containing a reflux condenser leading to a tail trap cooled in Dry Ice, and refluxing until reaction was complete. n-Butyllithium was prepared by adding dry

## ATTEMPTED REACTIONS BETWEEN ORGANOLITHIUM COMPOUNDS AND CClF₂CH₃

<table>
<thead>
<tr>
<th>Organometallic</th>
<th>Solvent, volume, ml.</th>
<th>Weight of CClF₂CH₃, g</th>
<th>Exchange Time</th>
<th>Temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>moles</td>
<td></td>
<td>moles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. C₆H₅Li, 0.5</td>
<td>Ether, 500</td>
<td>46</td>
<td>23 hrs. (2)</td>
<td>0 (3)</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. C₆H₅Li, ca. 0.15</td>
<td>Ether, ca. 30</td>
<td>18</td>
<td>13 days</td>
<td>R. T.</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. C₆H₅Li, 0.75</td>
<td>Ether, 300</td>
<td>80</td>
<td>6.3/4 days (2)</td>
<td>21±3 (3)</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. n-C₄H₉Li, 0.35</td>
<td>Ether, 400</td>
<td>35</td>
<td>16 hrs. (2)</td>
<td>R. T.</td>
</tr>
<tr>
<td>(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. n-C₄H₉Li, 0.13</td>
<td>Pentane, 400</td>
<td>15</td>
<td>8 hrs. (2)</td>
<td>23±3</td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Recovered Recovered RH Other Fluorinated |
|-----------------------------------------|-----------------|----------------|----------------|
| CClF₂CH₃, moles                         | C₆H₅Br, moles   | Produced       | Product        | Product |
| Recovered C₆H₅Br, moles                 | C₆H₆, 0.35      |               | (C₆H₅)₂        | Traces  |
| Recovered CH₃(CH₂)₄OH                   |                 |               |                |         |
| 1. 0.09 (20°/o)                         | 0.09            |               | (C₆H₅)₂        | Traces  |
| 2. (6)                                  |                 |               |                |         |
| 3. 0.17 (21°/o)                         | 0.16            |               | (C₆H₅)₂        | Traces (4) |
| 4. 0.31 (89°/o)                         |                 |               |                | none    |
| 5. 0.065 (23°/o)                        |                 |               | CH₃(CH₂)₄OH    | 70-90°/o |
| (1) Assuming RBr + 2Li → RLi + LiBr to be essentially complete, unfiltered. |
| (2) Including addition time, about 3 hours per mole of CClF₂CH₃. |
| (3) Temperature of cooling bath. |
| (4) The material had a b.p. 59-62, 5° at 40 mm., contained fluorine and bromine, reacted with sodium, absorbed bromine rapidly, formed no 3, 5-dinitrobenzoate, and appeared to polymerize on standing. Oxidation gave benzoic acid, and analysis showed 0°/o F 0.29, 0°/o Br 50.0 (M. Renoll). (C₆H₅Br b. 67-70° at 40 mm., calculated for Br, 50.9°/o). |
| (5) Filtered and an aliquot titrated. |
| (6) After 13 days the opened Carius type ampoule in which the reaction had been run was connected to a bromine trap to collect any CF₂=CH₂. The bromine was sucked into the ampoule destroying any CClF₂CH₂Li which might have been present. About half the CClF₂CH₃ was recovered, no other attempts were made to isolate any products. |
redistilled n-butyl bromide dropwise to lithium particles in dry ether with stirring at -20°. When dry pentane was used as the solvent, n-butyllithium was prepared as was phenyllithium above. Filtration of the organometallic solutions was effected under nitrogen with a sintered glass filter stick or with a glass wool plug held in a piece of glass tubing. Formaldehyde was generated by heating paraformaldehyde which had been previously dried over phosphorous pentoxide for ten days or more.

Reactions one, four and five (see Table II) were carried out in a three-necked flask equipped with a Dry Ice cooled reflux condenser leading to a tail trap cooled in Dry Ice, a mercury sealed stirrer and inlet tubes for CCIF₂CH₃ and nitrogen. A solution of the corresponding lithium compound was added to the dry system and CCIF₂CH₃ was distilled into the solution. The mixture was allowed to stand to permit reaction to occur, and then formaldehyde was added to react with any CCIF₂CH₂Li present. When this reaction was complete (as indicated by the absence of the characteristic blue color when a sample was added to Michler's ketone in dry benzene followed by the addition of water and a drop of a solution of iodine in glacial acetic acid), the lithium compounds were decomposed by adding a 150-300°/o excess of 20-30°/o sulfuric acid. The solution was then steam distilled to hydrolyze any formal produced, and the organic phase was fractionated.

Reaction three (see Table II) was carried out in essentially
the same manner but with the following modifications. The mercury
sealed stirrer was replaced with a stirrer assembly capable of
withstanding pressure of one-half to three-quarters of an atmos-
phere patterned after that used by Hinkamp. $^{60}$ CClF$_2$CH$_3$ was
added to a solution of the lithium compound, the solution was
cooled and the Dry Ice reflux condenser was replaced by a water
reflux condenser. The system was closed by a mercury manometer
and allowed to warm to room temperature during which period the
pressure rose to about three-quarters of an atmosphere. The
pressure was reduced to about one-quarter atmosphere by
temporarily opening the system to the tail trap, and the flask was
surrounded by a large water bath. After standing for almost seven
days the reaction mixture was treated as before.

Recovery of CClF$_2$CH$_3$ varied from 20-89\%o. An undetermined
amount of CClF$_2$CH$_3$ remained dissolved in the ether from which it
was later partially removed by long refluxing. No CClF$_2$CH$_2$CH$_2$OH
was isolated in any of the reactions. There was no evidence for any
reaction between n-butyllithium and CClF$_2$CH$_3$. However, traces of
a fluorinated product were detected in a fraction isolated from the
reaction of phenyllithium and CClF$_2$CH$_3$. Its properties (see Table
II, run 3, footnote 4) were consistent with a fluorostyrene which
could have been formed as follows:
\[
\begin{align*}
\text{C}_6\text{H}_5\text{Li} + \text{CClF}_2\text{CH}_3 & \quad \rightarrow \quad \text{C}_6\text{H}_6 + \text{CClF}_2\text{CH}_2\text{Li} \\
\text{CClF}_2\text{CH}_2\text{Li} & \quad \rightarrow \quad \text{CF}_2=\text{CH}_2 + \text{LiCl} \\
\text{C}_6\text{H}_5\text{Li} + \text{CF}_2=\text{CH}_2 & \quad \rightarrow \quad \text{C}_6\text{H}_5\text{CF}_2\text{CH}_2\text{Li} \\
\text{C}_6\text{H}_5\text{CHFCH}_2\text{Li} & \quad \rightarrow \quad \text{C}_6\text{H}_5\text{CF}=\text{CH}_2 + \text{LiF}
\end{align*}
\]

3.32 Attempted Reaction of \(\text{CClF}_2\text{CH}_3\) with Triphenylmethylsodium

\[
(\text{C}_6\text{H}_5)_3\text{CNa} + \text{CClF}_2\text{CH}_3, \quad \rightarrow \quad (\text{C}_6\text{H}_5)_3\text{CH} + \text{CClF}_2\text{CH}_2\text{Na}
\]

A solution of triphenylmethylsodium (0.006 mole, max.) in ether was transferred under nitrogen to a 100 ml. two-necked flask containing an inlet tube and a Dry Ice cooled reflux condenser leading to a trap cooled in Dry Ice and thence to a bubbler containing a very dilute solution of bromine in carbon tetrachloride. \(\text{CClF}_2\text{CH}_3\) (3 g., 0.03 mole) was distilled into the flask and a very slow stream of nitrogen passed through the system.

After four hours the color had changed from red to orange; after standing overnight the color was yellow. The bromine-carbon tetrachloride bubbler decolorized several times during this time, more rapidly at first (about every 25 minutes). No attempt was made to isolate any products. The removal of \(\text{CF}_2=\text{CH}_2\) formed from \(\text{CClF}_2\text{CH}_2\text{Na}\) would explain the observations. However, a closed system was not used so the results are not necessarily conclusive because the removal of \(\text{CF}_2=\text{CH}_2\) would displace any equilibrium involving \(\text{CClF}_2\text{CH}_2\text{Na}\) and triphenylmethylsodium.
### Attempted Reaction of CClF₂CH₃ and CF₃CH₂CF₃ with Diazomethane

This sequence of reactions was carried out in collaboration with R. Groth who was interested in reactions using diazomethane.

(i) \[ \text{CClF}_2\text{CH}_3 + \text{CH}_2\text{N}_2 \rightarrow \text{CClF}_2\text{CH}_2\text{CH}_3 + \text{N}_2 \]

An ethereal solution (40 ml.) of diazomethane (0.025 mole) was placed in a flask with a Dry Ice reflux condenser leading to a Dry Ice trap and CClF₂CH₃ (3.5 g., 0.035 mole) was added. After four hours no color change was observed. A small portion was placed in a Carius type ampoule, sealed, and heated to 100°. No change was observed in five minutes. It was assumed that no reaction had occurred.

(ii) \[ \text{CF}_3\text{CH}_2\text{CF}_3 + \text{CH}_2\text{N}_2 \rightarrow \text{CF}_3\text{CH(CH}_3\text{)}\text{CF}_3 + \text{N}_2 \]

CF₃CH₂CF₃ was prepared in collaboration with R. Brown. A solution (220 ml.) of diazomethane (0.055 mole) in cyclohexane was added to a flask equipped with a Y-joint, a Dry Ice cooled reflux condenser and a tail trap cooled in Dry Ice. The tail trap was connected by a calcium chloride tube to a three liter flask filled with water which was used to measure nitrogen evolution. CF₃CH₂CF₃ (9.7 g., 0.064 mole, b. 1.5 ± 1.0°) was distilled in and the mixture was allowed to sit at room temperature for five hours. Water was displaced from the three liter flask during this time indicating gas evolution. The mixture was heated at 40° for three hours, then at 63° for eight hours.

---

and finally at 85° for two hours after which it stood at room
temperature overnight. A definite color change had occurred and
a white precipitate had formed. Benzoic acid (about 5 g.) was
added to discharge the remaining color and the Dry Ice reflux con-
denser was replaced with a takeoff. Distillate was collected up to
80°, then 35 ml. more. Redistillation of this gave only recovered
$\text{CF}_3\text{CH}_2\text{CF}_3$ and no $\text{CF}_3\text{CH(CH}_3\text{)CF}_3$ (b. 21.5°).

(iii) A solution of diazomethane in cyclohexane of the same
concentration as used above was divided into two parts. Each part
was sealed in a Carius type ampoule and one ampoule was kept
cold in Dry Ice. The second was heated at 50-80° for 24 hours at
which time it had completely decolorized and a white precipitate
had formed; the contents of the cold ampoule were still yellow.
It was concluded from these experiments that no reaction had
occurred between $\text{CF}_3\text{CH}_2\text{CF}_3$ or $\text{CCIF}_2\text{CH}_3$ and diazomethane, and
that color changes observed were due to thermal decomposition of
the diazomethane.
3.4 **Attempted Preparation of Fluorinated Organometallics**

In view of the unsuccessful attempts to prepare an organometallic compound from CClF₂CH₃ (see Section 3.31) attention was turned to attempts to prepare similar fluorinated organometallic compounds from the corresponding fluorinated organic halides.

3.4.1 **Attempted Preparation of CHF₂CH₂Li**

When treatment of CHF₂CH₂Br with lithium in ether failed to give any evidence of reaction attempts were made to prepare CHF₂CH₂Li according to the reaction

\[ \text{CHF}_2\text{CH}_2\text{Br} + \text{C}_6\text{H}_5\text{Li} \rightarrow \text{CHF}_2\text{CH}_2\text{Li} + \text{C}_6\text{H}_5\text{Br} \].

An ether solution (370 ml.) of phenyllithium (0.24 mole, prepared as in Section 3.31) was filtered under nitrogen into a dry one liter three-necked flask equipped with a nitrogen inlet, a mercury sealed stirrer, an equilibrated dropping funnel, a thermometer and a reflux condenser leading to a tail trap cooled in Dry Ice, which in turn led to a bromine trap. CHF₂CH₂Br (36 g., 0.25 mole, redistilled from phosphorus pentoxide, b. 56-7°) dissolved in ether (40 ml.) was placed in the funnel and a slow flow of nitrogen was begun. The CHF₂CH₂Br was added slowly over a period of about one-half hour during which heat was evolved, the mixture refluxed and the bromine bubbler bubbled. When addition was complete, refluxing stopped and the temperature dropped to about 25°. After stirring at this temperature for a few hours, a test with Michler's ketone for organo-
metallics proved negative. Therefore, a solution of 10% sulfuric acid (0.60 mole) was added to the solution and the two phases were separated. The organic phase was dried and distilled. Fractionation gave \( \text{CHF}_2\text{CH}_2\text{Br} \) (about 3 g., 0.02 mole, 80% recovery) b. 51-60°C, \( \text{C}_6\text{H}_5\text{Br} \) (about 25 g., 0.16 mole, 67% yield) b. 67-70°C at 40 mm., \( n_2^1 \) 1.5588, and a residue (2 g.) which was not investigated further. A sample of the aqueous layer gave a positive test for fluoride ion when treated with cerous nitrate.

The liquid which had collected in the tail trap was bubbled through the bromine trap which unfortunately was not adequate; some material was lost. However, distillation of the organic material obtained after the bromine had been discharged with aqueous sodium bisulfite gave a material (7 g.) b. 119-21°C, which appeared to be \( \text{CHBrFCH}_2\text{Br} \), b. 122°C. It thus appears that elimination had occurred to give \( \text{CHF} = \text{CH}_2 \).

The success of McBee in reacting perfluoroalkyllithium compounds by a technique of simultaneous addition at lowered temperatures led to the following experiment.

A one liter three-necked flask was fitted with a mercury sealed stirrer and two Y-joints. To one Y-joint was added a thermometer.

---

well and an equilibrated dropping funnel, to the other a similar funnel and a reflux condenser leading to a trap cooled in Dry Ice. The temperature was observed by a potentiometer connected to a thermocouple inserted in the thermowell.

A filtered solution (300 ml.) of phenyllithium (0.23 equivalents) in ether prepared as before was placed in one funnel, and an ether solution (95 ml.) of methyl ethyl ketone (16 g., 0.22 mole, b. 79°) was added to the other. A consideration of the probable boiling points of the anticipated products led to the choice of this ketone. CHF₂CH₂Br (distilled from phosphorus pentoxide, b. 56-70°, 32 g., 0.22 mole) was placed in the dry flask with dry ether (100 ml.), a slow nitrogen flow was begun and the solution was cooled to -50°. Both the phenyllithium and ketone solutions were dropped simultaneously into the rapidly stirred solution at rates such that about equimolar amounts of both entered the solution in the same time interval. The addition was completed in one hour and 15 minutes at a temperature of -43 to -51°. The solution was allowed to warm up to room temperature, and refluxed for about 45 minutes. A solution of 10°/o sulfuric acid (0.13 mole) was then added, the two layers were separated, the water layer was washed three times with ether and all ether portions were combined. After washing the ether phase with a small amount of aqueous sodium carbonate and drying
it over anhydrous sodium carbonate it was distilled. Fractionation
gave: 1) a forecut (7 g.) b. 40-53°, 2) recovered CHF₂CH₂Br
(11 g.) b. 53-60°, 3) a fraction (9.5 g.) b. 60-75°, 4) an intermediate
fraction (2.5 g.) b. 75-175° and 5) 24 g. b. 66° at 40 mm. to 73°
at 10 mm.

Fraction 3) (9.5 g.) which, by analogy with C₂H₅(CH₃)C=CHCH₃
(b. 65.7°) and (C₂H₅)₂C=CH₂ (b. 66.2°), would have contained
some of the dehydration products of CHF₂CH₂C(OH)(CH₃)CH₂CH₃
gave a negative test for unsaturation with potassium permanganate.
Positive tests with 2,4-dinitrophenylhydrazine, and aluminum
chloride and chloroform, indicated the presence of methyl ethyl
ketone and either benzene or bromobenzene or both. The probable
presence of CHF₂CH₂Br in this fraction made any qualitative tests
for fluorine or bromine superfluous.

Fraction 4) (2.5 g.), which by analogy with CH₃CH₂C(OH)-(CH₃)CH₂CH₃
(b. 122°), would have contained CHF₂CH₂C(OH)-(CH₃)CH₂CH₃
was obviously an intermediate cut between fraction 3)
(discussed in the preceding paragraph) and fraction 5) which appeared
to be C₆H₅C(OH)(CH₃)CH₂CH₃ or its dehydration products.

The tail trap contents were passed into bromine and
CHBrFCH₂Br (3 g.) was again obtained. The amount of the starting

material, CHF₂CH₂Br, accounted for was estimated at 55-60°/o.

It was therefore concluded that CHF₂CH₂C(OH)(CH₃)CH₂CH₃ or its dehydration products were produced in negligible amounts and that reaction between phenyllithium and methyl ethyl ketone probably occurred producing 2-phenyl-2-propanol or 2-phenyl-propene. What reaction did occur between CHF₂CH₂Br and phenyllithium apparently produced CHF=CH₂.

3.42 Attempted Preparation of CHF₂CF₂CH₂ZnBr from CHF₂CF₂CH₂Br

\[
\text{CHF}_2\text{CF}_2\text{CH}_2\text{Br} + \text{Zn} \rightarrow \text{CHF}_2\text{CF}_2\text{CH}_2\text{ZnBr}
\]

CHF₂CF₂CH₂OH⁸⁴ was converted to CHF₂CF₂CH₂Br, b. 73.0°, n₂₀ 1.3580, d₂⁰ 1.819 (Analysis by Galbraith Laboratories: Found, °/o C, 18.52; °/o H, 1.52. Calculated for C₃H₃BrF₄, °/o C, 18.48; °/o H, 1.55) by the procedure of Tiers⁸⁵ in 85°/o yield.

(i) Granular zinc (7.2 g., 0.11 mole) and dry dioxane (20 ml.)<sup>72</sup> were placed in a 250 ml. three-necked flask equipped with a dropping funnel, a mercury sealed stirrer and a reflux condenser in which was hung a thermometer. The condenser led to a trap cooled in Dry Ice. After flushing the system thoroughly with nitrogen, CHF₂CF₂CH₂Br

---

(84) Courtesy of W. B. McCormack, Jackson Laboratory, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

(19.5 g., 0.1 mole) in dry dioxane (20 ml.) was placed in the funnel and added slowly with stirring. As no reaction was apparent the reaction was slowly refluxed overnight. The mixture was cooled and the zinc (7.2 g., 100%o) recovered. It was assumed that no reaction had occurred.

(ii) In a second attempt in the same dry apparatus CHF₂CF₂CH₂Br (19.5 g., 0.1 mole), 90/o zinc dust (8.0 g., 0.11 mole zinc) and dry dioxane (10 ml.) were stirred at 40-70° for two hours. When no apparent reaction had occurred, a mixture of dioxane (20 ml.) and acetic anhydride (30 ml.) was slowly added to the reaction mixture which was then maintained at 60 ± 5° (internal temperature) overnight. The next morning a copious white precipitate had formed, and a small amount of material was in the tail trap. The acetic anhydride was hydrolyzed with water (60 ml.) containing a trace of sulfuric acid. The reaction mixture was filtered (the main reaction at this point was assumed to be a doubling up of the molecules) and the zinc (3 g., or 38%o) was recovered. The mixture was extracted with ether and the ether distilled. Only a gummy fluorinated residue was obtained.

The original aqueous portion gave a positive test for halide ion with silver nitrate and for fluoride ion with cerous nitrate. Titration of an aliquot with silver nitrate accounted for 80%o of the bromine as bromide ion.
The low boiling material in the trap had an approximate boiling point of 5^\circ; it gave a slowly positive test for unsaturation with bromine in carbon tetrachloride and with aqueous potassium permanganate. Its properties were the same as those of CHF_2CF=CH_2 which was later characterized. Most of it was lost on filtration.

(iii) In a third attempt granular zinc (20 mesh, 16.5 g., 0.28 mole), acetic anhydride (47 ml., 0.43 mole) and acetophenone (47 ml., 0.4 mole) were placed in the flask and a mixture of CHF_2CF_2CH_2Br (36 g., 0.185 mole) and acetophenone (40 ml., 0.37 mole) was slowly added over a period of 45 minutes. The reaction was stirred at room temperature for 57 hours, after which the reflux condenser water was disconnected. The mixture was heated to 80-95^\circ for one hour to remove any CHF_2CF=CH_2, which collected in the tail trap. Hydrolysis of the acetic anhydride was effected with water containing a trace of sulfuric acid. The reflux condenser was replaced by a takeoff, the mixture was made just basic with sodium hydroxide, heated to boiling and organic material was distilled out, some material being collected in the tail trap. This distillate was washed and distilled giving only CHF_2CF_2CH_2Br (7 g., 19^\circ/o) b. 63-76^\circ, n^20 1.3558. The material left in the reaction flask was extracted with ether and the ether distilled. The only fluorinated material obtained was about one and a half grams of material collected in the tail trap.
The various trap contents were combined and distilled giving \( \text{CHF}_2\text{CF} = \text{CH}_2 \), b. 4.0-4.5° in 85% yield. It thus appears that reaction of \( \text{CHF}_2\text{CF}_2\text{CH}_2\text{Br} \) with zinc in acetic anhydride and acetophenone produced only \( \text{CHF}_2\text{CF} = \text{CH}_2 \) which was characterized as follows:

\[ \text{CHF}_2\text{CF} = \text{CH}_2 \ (4.5 \text{ g.}, \ 0.047 \text{ mole}) \] was passed into a hot stirred solution of potassium permanganate (20 g., 0.127 mole), potassium hydroxide (4 g., 0.071 mole) and water (160 ml.) in a three-necked flask equipped with a mercury sealed stirrer and a short reflux condenser capped by a Dry Ice reflux condenser leading to a tail trap cooled in Dry Ice. After refluxing for eight hours, the excess permanganate was reduced to manganese dioxide with aqueous sodium bisulfite. The cold reaction was filtered, acidified with concentrated hydrochloric acid (50 ml.) and continuously extracted with ether for 74 hours. The ether was distilled from the extract, and the residue distilled under reduced pressure. There was obtained 3.6 g. of crude \( \text{CHF}_2\text{COOH} \).

The acid (1 g., 0.0104 mole) was mixed with ethanol (1.2 g., 0.25 mole) and concentrated sulfuric acid (1.5 g., 0.015 mole) in a small distilling flask. When the mixture cooled, two layers separated. The ester was distilled out, a portion (0.5 g., 0.004 mole) was dissolved in ether (6 ml.) and saturated with gaseous ammonia. The ether was
removed leaving an oil; benzene (3 ml.) was added and after cooling in ice the amide crystallized, m. 49.5-51.5°. The yield of amide from olefin was 43°/o. A mixed melting point with CHF₂CONH₂ (m. 51.5-2.0°) prepared from CHF₂COOCH₃ was 51.5-2.0°.

CHF₂CF=CH₂ was brominated under ultraviolet light to CHF₂CBrFCH₂Br, b. 124.0-5.0°, n° 1.4450, d° 2.160 in 77°/o yield. (Analysis by Galbraith Laboratories: Found, °/o C, 14.15; °/o H, 1.45. Calculated for C₃H₃Br₂F₃, °/o C, 14.08; °/o H, 1.21).

### 3.43 Preparation of CHF₂CF₂CH₂HgI

$$\text{CHF}_2\text{CF}_2\text{CH}_2\text{I} + \text{Hg} \xrightarrow{\text{u.v.}} \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI}$$

CHF₂CF₂CH₂OH was converted to CHF₂CF₂CH₂I, b. 98.5-9.0°, n° 1.4149, d° 2.123 in 81°/o yield using the procedure of Tiers. (Analysis by Galbraith Laboratories: Found, °/o C, 14.82; °/o H, 1.20. Calculated for C₃H₃F₄I, °/o C, 14.89; °/o H, 1.25).

The procedure found to give satisfactory yields of the mercurial is the following:

Three indentations to serve as baffles were put in the side of a one liter Pyrex suction flask and a 19/38 standard taper outer joint was attached to the side arm. The mercury sealed stirrer was glass and just fit the bottom of the flask. Mercury (500 g., 2.5 moles) and

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(86) Courtesy of Caribou Chemical Company, 716 Rose Ave., Columbus 19, Ohio.
CHF₂CF₂CH₂I (100 g., 0.41 mole) were added to the flask and a reflux condenser leading to a trap cooled in Dry Ice was attached. Rapid stirring was begun (vigorous stirring is apparently quite essential) and the flask and contents were irradiated with ultraviolet light at room temperature for three days. The system was partially evacuated and CHF₂CF₂CH₂I (46 g., 0.19 mole or 46.5⁰/o) b. 95-9⁰ was recovered. The solid was extracted with a mixture of ether and carbon tetrachloride, the ether was removed by evaporation, and CHF₂CF₂CH₂HgI crystallized out when the carbon tetrachloride solution was cooled. Crude yield, 69 g. (0.149 mole) or 71⁰/o on a 37⁰/o conversion.

Analyses of a sample of CHF₂CF₂CH₂HgI, m. 140-1⁰, for mercury according to the procedure in Fuller⁸⁷ and for iodine according to Rupp and Lemke⁸⁸ as modified by D'Alcontres⁸⁹ gave the following minimum percentages: Hg, 43.7⁰/o; I, 27.9⁰/o. Calculated for C₃H₅F₄HgI: Hg, 45.3⁰/o; I, 28.7⁰/o. A great deal of difficulty was encountered in both analyses in obtaining complete decomposition and in the iodine analysis with loss of iodine. Accordingly, a sample of

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CHF₂CF₂CH₂HgI was repurified by two sublimations, m. 139.5-40.0°, and submitted to Galbraith Laboratories for analysis: Found, °/o C, 8.13; °/o H, 0.62. Calculated for C₃H₃F₄HgI: °/o C, 8.14; °/o H, 0.68.

An attempted preparation of the mercurial in the absence of ultraviolet light from CHF₂CF₂CH₂I (20 g., 0.1 mole) and mercury (40 g., 0.2 mole) at 80° resulted in the complete recovery of all the starting materials.

3.44 Attempted Preparation of CHF₂CF₂CH₂ZnI from CHF₂CF₂CH₂HgI

CHF₂CF₂CH₂HgI + Zn → CHF₂CF₂CH₂ZnI + Hg

(i) CHF₂CF₂CH₂HgI (15 g., 0.034 mole) and zinc (6 g., 0.09 mole) were sealed in a Carius type ampoule at -78° and heated to 150° for two days. Some decomposition occurred. The ampoule was opened at -78°, connected to a trap cooled in Dry Ice and warmed in a hot water bath. CHF₂CF=CH₂ (1.6 g., 0.017 mole) was collected in 50°/o yield and identified by its infrared spectrum.

The solid remaining in the tube was extracted three times with water, the water was diluted to 200 ml. and an aliquot was titrated. Iodide ion (0.018 equivalents) was found in about 53°/o yield.

(ii) In an attempt to react any CHF₂CF₂CH₂ZnI as soon as formed, CHF₂CF₂CH₂HgI (15 g., 0.034 mole), zinc (4.5 g., 0.069 mole) and acetophenone (12 g., 0.1 mole) were sealed in a Carius type ampoule at -78° and heated to 100° for 69 hours. The ampoule
was opened at -78°C, connected to a trap cooled in Dry Ice and heated in a boiling water bath for one and a half hours. CHF₂CF=CH₂ (3 g., 0.031 mole) was collected in 91.0/o yield. The residue was extracted with water, the water was diluted to 200 ml. and titrated with standard silver nitrate. Halide ion was found in 83.0/o yield. A sample of the acetophenone portion from the above aqueous extraction gave a negative qualitative test for fluorine.

(iii) A similar experiment with CHF₂CF₂CH₂HgI (13 g., 0.029 mole), zinc (6 g., 0.09 mole) and acetophenone (12 g., 0.1 mole) at 50°C produced CHF₂CF=CH₂ (2.0 g., 0.021 mole) in 73.0/o yield.

3.45 Attempted Reactions with CHF₂CF₂CH₂HgI

3.451 Attempted Reaction of CHF₂CF₂CH₂HgI and Silver

\[
2 \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} + 2 \text{Ag} + 2 \text{CH}_3\text{COCl} \rightarrow 2 \text{CHF}_2\text{CF}_2\text{CH}_2\text{COCH}_3 + \text{Hg}_2\text{I}_2 + 2 \text{AgCl}
\]

CHF₂CF₂CH₂HgI (20 g., 0.045 mole), finely divided metallic silver (6 g., 0.055 mole), acetyl chloride (8 g., 0.1 mole) and dry decalin (70 ml.) were stirred at room temperature for one month in a three-necked flask equipped with a reflux condenser leading to a trap cooled in Dry Ice. The mixture was then heated to 100°C for two hours during which a material (1.5 g.) b. 5-15°C had collected in the tail trap; it was not further characterized.

The reaction mixture was diluted with ether, filtered, and the filtrate was washed twice with dilute sodium hydroxide and three times
with water. Addition of cerous nitrate to the aqueous phase gave no precipitate for fluoride ion. Addition of alkaline aqueous iodine to the aqueous phase gave no iodoform. The ether from the organic phase was removed by distillation and the residue was cooled. Tests on this residue for a methyl ketone with aqueous alkaline iodine solution, with 2,4-dinitrophenylhydrazine in sulfuric acid, and with hydroxylamine hydrochloride were negative. Addition of sulfuric acid to the aqueous washings above gave a copious white precipitate which was filtered, dried, and weighed (9 g.); it was assumed to be a mercurial but was not investigated further.

Since no fluoride ion was found in the aqueous washings above it appeared that elimination to form CHF₂CF=CH₂ had not occurred. The failure to demonstrate the presence of any ketonic material would seem to imply the absence of any CHF₂CF₂CH₂Ag. This behavior is similar to that of unfluorinated organomercuric halides and silver. ⁵²

3.452 Reaction of CHF₂CF₂CH₂Hgl and Iodine

\[
\text{CHF}_2\text{CF}_2\text{CH}_2\text{Hgl} + \text{I}_2 \rightarrow \text{CHF}_2\text{CF}_2\text{CH}_2\text{I} + \text{Hgl}_2
\]

CHF₂CF₂CH₂Hgl (15 g., 0.029 mole) was dissolved in a minimum of ethanol and placed in a two-necked flask equipped with a funnel and a reflux condenser leading to a trap cooled in Dry Ice. A solution of iodine (7.5 g., 0.029 mole) in warm ethanol (50 ml.) was dropped into the refluxing mixture as rapidly as the reaction
decolorized. After about 80% of the iodine-alcohol solution had been added, no further decolorizing occurred even after further refluxing for one hour. The mixture was cooled; after the precipitate had settled, the liquid was decanted from the solid \( \text{HgI}_2 \), decolorized with sodium thiosulfate and steam distilled. \( \text{CHF}_2\text{CF}_2\text{CH}_2\text{I} \) (3 g., 0.012 mole) b. 98.5°, \( n^\circ \) 1.4109 was obtained in 42% yield. The \( \text{HgI}_2 \) (8 g., 0.018 mole) was obtained in 62% yield and identified by the fact that treatment with concentrated sulfuric acid produced purple vapors of iodine, and that the color changed from red to yellow on heating and back to red again on cooling. (Red mercuric oxide turns black on heating).

3.453 Attempted Reaction of \( \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} \) and \( \text{BrCN} \)

\[
\text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} + \text{BrCN} \rightarrow \text{CHF}_2\text{CF}_2\text{CH}_2\text{CN} + \text{HgBrI}
\]

Cyanogen bromide was prepared according to the procedure of Hartman and Dreger\(^{90}\) in 60-65% yield.

\( \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} \) (24 g., 0.054 mole) was dissolved in methanol (70 ml.) and to it was added cyanogen bromide (7.0 g., 0.066 mole) in methanol (25 ml.). After standing at room temperature for 20 hours the mixture was heated to 50-60° for two days and cooled.

The mixture was divided into two equal parts; one part was diluted

with water and filtered. \( \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} \) (12 g.), m. 141-2°, was obtained in 100°/o recovery, so the reaction was not investigated further.

3.454 Attempted Reaction of \( \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} \) and Acetyl Chloride

\[
\text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} + \text{CH}_3\text{COCI} \rightarrow \text{CHF}_2\text{CF}_2\text{CH}_2\text{COCH}_3 + \text{HgClI}
\]

\( \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} \) (15 g., 0.034 mole) and acetyl chloride (20 ml., 0.28 mole) were refluxed for three days in a flask tailed by a trap cooled in Dry Ice. During this time no material had collected in the tail trap. The reaction mixture was then transferred to a distilling flask; as much of the liquid as possible was distilled over at atmospheric pressure, then the receiver was cooled in ice water and the remainder of the liquid was distilled over at reduced pressure. The trap contents were added to the distillate which was hydrolyzed with water and made slightly basic with sodium hydroxide. Sodium chloride was added to saturate the solution and it was extracted four times with ether. Distillation of the ether extract produced only ether (b. 35-6°); no ketone was found.

From the distillation residue was obtained crude \( \text{CHF}_2\text{CF}_2\text{CH}_2\text{HgI} \) (8 g., 0.018 mole) and an undetermined amount of a dark red substance assumed to contain mercury salts but which was not further investigated.
3.455 Stability of CHF₂CF₂CH₂HgI

CHF₂CF₂CH₂HgI (10 g., 0.023 mole) was heated in a sealed Carius type ampoule at 100° for 69 hours. No visible change in appearance had taken place so the ampoule was heated at 150° for two days. The contents of the tube were black when the tube was cooled to -78° and opened, gases rushed out with violence. The tube was connected to a trap cooled in Dry Ice and heated on a water bath. A small amount of fluorinated liquid with a b.p. of about 45°, n₂₀ 1.3335 was obtained which was not further characterized. The black residue gave only a faint qualitative test for fluorine when a sample was fused with sodium.
4.0 SUMMARY

3,3,3-Trifluoropropyne was synthesized for the purpose of studying the effect of a trifluoromethyl group on the adjacent triple bond and the acetylenic hydrogen. Several attempts were made to prepare intermediates from which trifluoropropyne could be synthesized. After the synthesis of CF₃CH₂CH₂Cl from CH₂ClCHClCH₃ had been developed by Krehbiel¹¹ this compound was converted to trifluoropropyne according to the procedure of Henne and Nager.⁸ In the sequence of reactions converting CF₃CH₂CH₂Cl to trifluoropropyne treatment of CF₃CBr₂CH₂Br with alcoholic potassium hydroxide produced, in addition to the expected CF₃CBr=CHBr, varying amounts of CF₃CH₂COOC₂H₅ and CF₃CBr=CBr₂, as well as evidence for CF₃CBr=CH₂ and CF₃C≡CBr.

Trifluoropropyne was condensed with butadiene to give trifluoromethyl-1,4-cyclohexadiene. The structure of this compound was established by reduction to trifluoromethylcyclohexane, aromatization to benzotrifluoride, ozonolysis (yielding trifluoroacetone), and comparison of ultraviolet spectra. This diene failed to rearrange when treated with aqueous acid or base. Partial reduction of trifluoromethyl-1,4-cyclohexadiene produced trifluoromethyl-1-cyclohexene which, on ozonolysis, gave 7,7,7-trifluoro-6-oxoheptanoic acid.
Treatment of trifluoropropyne with ammoniacal cuprous and ammonium chlorides produced not \( \text{CF}_3\text{C} \equiv \text{CCu} \) but a dimer, \( \text{C}_6\text{H}_2\text{F}_6 \).

Reduction of \( \text{C}_6\text{H}_2\text{F}_6 \) to \( \text{CF}_3(\text{CH}_2)_4\text{CF}_3 \), and partial reduction to \( \text{C}_6\text{H}_4\text{F}_6 \) which on oxidation gave oxalic and trifluoroacetic acids support the linear structure, \( \text{CF}_3\text{C} \equiv \text{CCH} = \text{CHCF}_3 \), for the dimer.

No reaction was observed between \( \text{CF}_3\text{C} \equiv \text{CH} \) and cuprous hydroxide.

Treatment of \( \text{CF}_3\text{CBr} = \text{CBr}_2 \) with zinc in acetic anhydride produced not \( (\text{CF}_3\text{C} \equiv \text{C})_2 \) but \( \text{CF}_3\text{C} \equiv \text{CBr} \) which was brominated to \( \text{CF}_3\text{CBr} = \text{CBr}_2 \). Tests on \( \text{CF}_3\text{C} \equiv \text{CBr} \) showed that the bromine atom was, unexpectedly, devoid of positive character. An attempted reaction of \( \text{CF}_3\text{C} \equiv \text{CBr} \) with zinc and acetic anhydride failed to yield any \( (\text{CF}_3\text{C} \equiv \text{C})_2 \).

Attempts to react trifluoropropyne with a mixed anhydride in the presence of trifluoroacetic anhydride gave no 1,3-dicarbonyl compound.

An attempted use of trifluoropropyne as both acceptor and addendum in a Michael condensation produced only a polymeric material.

Attempted estimation of the relative acidity of trifluoropropyne and propyne by a colorimetric method failed when trifluoropropyne and indylsodium produced an unidentified blue compound instead of trifluoropropynylsodium. The quantitative estimation by infrared
analysis of the ratio of propyne and trifluoropropyne in the vapor over an equilibrium solution of the two propynes and their sodium salts in ether was not possible because of the solubility of both propynes in the ether at low temperatures, and because of the decomposition of trifluoropropyne in the presence of base at higher temperatures.

Attempted reaction of CClF₂CH₃ with organolithium compounds and with triphenylmethysodium and reaction of CClF₂CH₃ and CF₃CH₂CF₃ with diazomethane failed to demonstrate any increased acidity caused by the electronegative induction of the fluorine atoms.

Attempts were also made to prepare fluorinated organometallic compounds having one methylene group between the fluorinated group and the metal atom. No reaction was observed between CHF₂CH₂Br and lithium in ether or between CHF₂CF₂CH₂Br and zinc in dioxane. Treatment of CHF₂CH₂Br with phenyllithium, even at -45° in the presence of a methyl ketone to accept the organometallic as formed, produced only CHF=CH₂. Addition of acetic anhydride to CHF₂CF₂CH₂Br, zinc and acetophenone similarly produced only CHF₂CF=CH₂.

Irradiation of a stirred mixture of CHF₂CF₂CH₂I and mercury produced CHF₂CF₂CH₂HgI. This mercurial was thermally stable below 150°, reacted with iodine to give CHF₂CF₂CH₂I and mercuric
iodide, reacted with zinc in acetophenone to give only \( \text{CH}_2\text{CF} = \text{CH}_2 \), and failed to react with cyanogen bromide or acetyl chloride.
### TABLE III

**PHYSICAL CONSTANTS OF NEW COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Analyses</th>
<th>m.p.</th>
<th>b.p.</th>
<th>n°</th>
<th>d°</th>
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<tbody>
<tr>
<td>CF₃-C</td>
<td>p. 42</td>
<td>110-11.5°</td>
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<td>NNHCONH₂</td>
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<td>C₆H₂F₆</td>
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<td>99.5-100°</td>
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<td>p. 63</td>
<td>25.5-6.0°</td>
<td>1.3515(at 9°)</td>
<td>1.716(at 9°)</td>
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<tr>
<td>CHF₂CF₂CH₂Br</td>
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<td>73.0°</td>
<td>1.3580</td>
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<td>CHF₂CF=CH₂</td>
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<tr>
<td>CHF₂CBrFCH₂Br</td>
<td>p. 101</td>
<td>124-5°</td>
<td>1.4450</td>
<td>2.160</td>
<td></td>
</tr>
<tr>
<td>CHF₂CF₂CH₂HgI</td>
<td>p. 103</td>
<td>139.5-40.0°</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>CF₃CBr=CBR₂</td>
<td>p. 39</td>
<td></td>
<td>154-5°</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>70-2°/45-7mm</td>
<td>1.4991</td>
<td>2.517</td>
</tr>
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</table>
AUTOBIOGRAPHY

I, Russell Leo Kenneth Carr, was born in Wakefield, Michigan, April 26, 1926. I received my secondary school education in the public schools of Green Bay, Wisconsin, and Dayton, Ohio. My undergraduate training was obtained at the University of Dayton and at The Ohio State University from which I received the degree Bachelor of Science in 1951. In October, 1951, I received an appointment as Assistant in the Department of Chemistry. I subsequently held appointments as Assistant Instructor, Union Carbide and Carbon Company Fellow, Lubrizol Corporation Fellow, and Research Assistant while completing the requirements for the degree Doctor of Philosophy.