RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS

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INTRODUCTION

The purpose of this project is to conduct the necessary research for the preparation of unsaturated organic compounds containing fluorine, and, when synthetic methods have been developed, to prepare various fluoroölefins which may give elastomers which are oil and fuel resistant and which retain their elasticity at low temperatures.

It is estimated that 100% of the work has been completed to date and that 98% of the estimated costs have been incurred to date.

This research is authorized under Contract Number DA-19-129-AMC-79(N) and is a further continuation of the work initiated under DA-44-109-QM-522 and continued under DA-44-109-QM-1469 and DA-19-129-QM-500.

This is the 6th report under the contract but the 53rd since the project was initiated in 1951.

II. SUMMARY OF CURRENT PROGRESS

Work has continued on some aluminum chloride catalyzed additions of polyhaloalkanes to haloölefins. Additional work has been done using perfluoroallyl systems.

Nitrosyl chloride has been allowed to react with some fluorodienes to give a nitroso derivative in one case (but to give a suspected Diels-Alder adduct when the diene was conjugated).

Free radical additions of haloalkanes to various olefins have been attempted and in some cases reactions of the products investigated.

The free radical addition of haloalkanes to aromatic nuclei has been continued and terminated.

Some Diels-Alder additions between cyclopentadiene and some haloölefins has been effected, and the preparation of some fluoronorbornadienes from the products has been attempted.

III. DISCUSSION

Aluminum Chloride Catalyzed Additions of Polyhaloalkanes to Haloolefins

Further work has been done on the addition of $CFCl_3$ to CFCl=CFCl* in an effort to elucidate the possible mechanism involved. It was shown that pure CFCl=CFCl did not rearrange to $CF_2=CCl_2$ under the influence of $AlCl_3$. Neither were any other olefins formed by replacement of fluorine atoms by chlorine.

Addition of $CFCl_3$ to pure CFCl=CFCl gave a 72% yield of the expected adduct, $C_3Cl_5F_3$. N.m.r. spectroscopy has shown this to consist of $CF_2ClCFClCCl_3$ (81%), $CFCl_2CFClCFCl_2$ (18%), and $CF_3CCl_2CCl_3$ (1%). Isomerization of this material by $AlCl_3$ in CCl_4 gave chiefly the replacement product, $C_3Cl_6F_2$, although enough rearranged $C_3Cl_5F_3$ was recovered for n.m.r. analysis. The latter material consisted of

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*CFCl=CFCl, prepared from zinc dehalogenation of crude Freon 112, was found to contain ca. 3% $CF_2=CCl_2$. This arose from the presence of ca. 3% CF_2ClCCl_3 in the crude Freon 112. Pure CFCl=CFCl was obtained by subjecting the crude olefin mixture to the action of sodium ethoxide in ethanol. This selectively removed the $CF_2=CCl_2$ to give pure CFCl=CFCl.

$CF_2ClCFClCCl_3$ (95%) and $CF_3CCl_2CCl_3$ (5%). Hence, the $CFCl_2CFClCFCl_2$ was completely rearranged to the $CF_2ClCFClCCl_3$. This type of $AlCl_3$ catalyzed rearrangement also occurred with the $C_3Cl_6F_2$ fraction formed in this addition reaction. The initially formed material consisted of $CF_2ClCCl_2CCl_3$ (46%) and $CFCl_2CFClCCl_3$ (54%). The $C_3Cl_6F_2$ isolated as the major product from isomerization of $C_3Cl_5F_3$ consisted of only $CF_2ClCCl_2CCl_3$.

The following scheme is proposed to account for these data:

$$CFCl_3 + AlCl_3 \rightleftharpoons CCl_3^{\oplus} + AlCl_3F^{\ominus} \qquad (1)$$

$$CCl_3^{\oplus} + CFCl{=}CFCl \rightleftharpoons CCl_3CFClCFCl^{\oplus} \qquad (2)$$

$$CCl_3CFClCFCl^{\oplus} + AlCl_3F^{\ominus} \rightleftharpoons CCl_3CFClCF_2Cl + AlCl_3 \qquad (3)$$

$$CFCl_3 + AlCl_3 \rightleftharpoons CFCl_2^{\oplus} + AlCl_4^{\ominus} \qquad (4)$$

$$CFCl_2^{\oplus} + CFCl{=}CFCl \rightleftharpoons CFCl_2CFClCFCl^{\oplus} \qquad (5)$$

$$CFCl_2CFClCFCl^{\oplus} + AlCl_4^{\ominus} \rightleftharpoons CFCl_2CFClCFCl_2 + AlCl_3 \qquad (6)$$

$$CFCl_2CFClCFCl_2 \xrightarrow{AlCl_3} CF_2ClCFClCCl_3 \qquad (7)$$

From the fact that (7) is an irreversible rearrangement it is concluded that (4) (followed by (5) and (6)) must be operative to some extent since there was produced initially 18% $CFCl_2CFClCFCl_2$, which can only arise in this manner. An attempt was made to detect the $CFCl_2^{\oplus}$ cation using F^{19} n.m.r., but scanning a mixture of $CFCl_3$ and $AlCl_3$ at both high and low fields gave no evidence for anything other than $CFCl_3$. This however is not proof of the total absence of this ion.

Previously (1) the addition of $CFCl_3$ to $CF_2=CFBr$ was shown to give $CF_3CFBrCCl_3$ (56%) and $CF_2BrCF_2CCl_3$ (44%) in 5 hrs. In an effort to determine the effect of the reaction time on possible isomerization of these isomers, another run was made (70 hrs.) and the product consisted of these isomers in 57 and 43%, respectively. It was concluded that in this case essentially no further change in the isomer distribution occurred in the presence of $AlCl_3$. Hence, it appears that each reaction must be considered separately as the mechanism apparently differs with the olefin used.

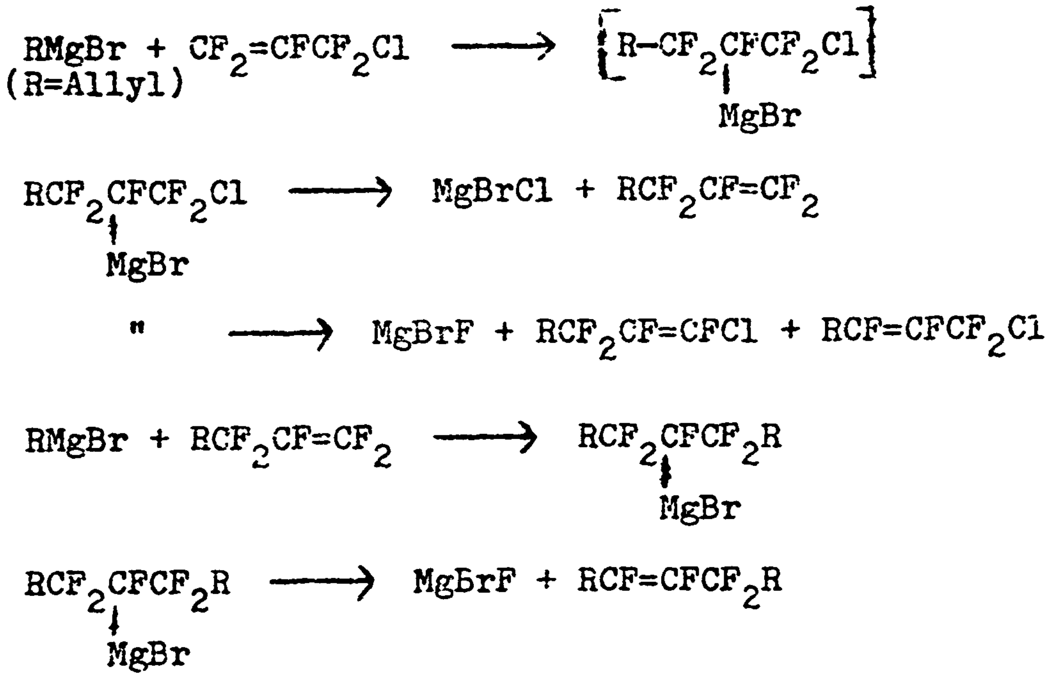
Further attempts to extend this type of addition reaction to alkanes other than $CFCl_3$ and $CHFCl_2$ were still unsuccessful (2). Treatment of CF_2Br_2 and $CF_2=CCl_2$ with $AlCl_3$ gave no reaction. A repeat of the attempted addition (3) of $CF_2ClCFCl_2$ to $CFCl=CFCl$ was run to check the possibility of alkane rearrangement. Previous workers (4-7) have shown that $CF_2ClCFCl_2$ readily rearranges to CF_3CCl_3 or undergoes replacement reactions, but these were all done at reflux (47°). Under carefully controlled temperature conditions (24-7°) it was found that neither addition nor rearrangement (as determined by n.m.r.) occurred. A very small amount of CF_2ClCCl_3 was obtained.

Perfluoroallyl Systems

As part of the continuing study of reactions of the 3-halopentafluoropropene system, further work was done in an attempt to improve the yield of the ether,

$CH_2{=}CHCH_2OCF_2CF{=}CF_2$, which was formed when $CF_2{=}CFCF_2Cl$ was treated with KOH in allyl alcohol. It was previously (8) shown that this was only 19% of the product mixture. It was felt that reaction of sodium allyloxide in the absence of a hydrogen donor would give this desired ether in much better yield. However, reaction in dioxane and acetone gave no product at all. Apparently the sodium allyloxide was too insoluble in these solvents. Attempts to find a solvent for this salt which did not contain labile hydrogens were unsuccessful. These included methyl ethyl ketone, N,N-dimethylformamide, dimethylsulfoxide, and t-butanol.

The reaction of $CF_2{=}CFCF_2Cl$ with allylmagnesium bromide was successfully carried out to give two new materials: $C_6H_5ClF_4$, probably a mixture of $CH_2{=}CHCH_2CF_2CF{=}CFCl$ and $CH_2{=}CHCH_2CF{=}CFCF_2Cl$, and $C_9H_{10}F_4$, $CH_2{=}CHCH_2CF{=}CFCF_2CH_2CH{=}CH_2$. No $CH_2{=}CHCH_2CF_2CF{=}CF_2$ was detected. The following scheme is proposed to account for these products:



$$\underset{(R{=}Allyl)}{RMgBr} + CF_2{=}CFCF_2Cl \longrightarrow \left[R{-}CF_2\underset{\substack{|\\ MgBr}}{C}FCF_2Cl\right] \tag{1}$$

$$RCF_2\underset{\substack{|\\ MgBr}}{C}FCF_2Cl \longrightarrow MgBrCl + RCF_2CF{=}CF_2 \tag{2}$$

$$'' \longrightarrow MgBrF + RCF_2CF{=}CFCl + RCF{=}CFCF_2Cl \tag{3}$$

$$RMgBr + RCF_2CF{=}CF_2 \longrightarrow RCF_2\underset{\substack{|\\ MgBr}}{C}FCF_2R \tag{4}$$

$$RCF_2\underset{\substack{|\\ MgBr}}{C}FCF_2R \longrightarrow MgBrF + RCF{=}CFCF_2R \tag{5}$$

This high reactivity of the trifluorovinyl group was also apparent in the reactions of alkoxide systems with $CF_2{=}CFCF_2Cl$.

In the previous report (10) the adduct formed by addition of $CHFCl_2$ to $CFCl{=}CFCl$ was given as $CF_2ClCFClCHCl_2$ (70%), $CF_2ClCHFCCl_3$ (25%), and $CF_3CCl_2CHCl_2$ (5%). On the basis of more careful n.m.r. calculations, the assignments for this second isomer more closely fit CF_2ClCCl_2CHFCl (F^{19}, relative to TFA, had doublet doubled at -19.6 ppm, J=14.6, 9.2 cps, rel. area 2.6, and a triplet doubled at +54.9 ppm, J=49.2, 15.3 cps, rel. area 1.5; H: relative to TMS, had doublet at ca. 3.47, J=48.3 cps).

Preparation of Fluoronitroso Compounds

In the present work an attempt was made to prepare a series of nitroso compounds containing another functional group. Therefore, the reaction of $CF_2{=}CFCH_2CH{=}CH_2$ and nitrosyl chloride was effected to yield $CF_2ClCF(NO){\cdot}CH_2CH{=}CH_2$.

The diene was prepared by the known route (11) of addition of $CF_2BrCFClBr$ to allyl chloride, followed by dehalogenation By the usual procedure (12) the addition of nitrosyl chloride to the diene was predominantly at the $CF_2{=}CF-$ grouping. The yield of nitroso compound was poor and nearly 30% of the starting diene was recovered when equimolar proportions of nitrosyl chloride and diene were used, but if an excess of nitrosyl chloride was used several unidentified high boiling products were formed. The infrared spectrum of the high boiling products showed absorption at

5.55μ and 5.78μ, compared to N-O and -HC=CH- absorption of the nitroso adduct at 6.31μ and 6.1μ (weak) respectively. The nitroso adduct was decomposed by air and heat from a blue liquid through green and yellow to give finally a dark brown viscous liquid. The compound was sufficiently stable to allow gas chromatographic separation at 50-60°.

The reaction of $CF_2=CFCH=CH_2$ with nitrosyl chloride has been studied in this laboratory before and a very small amount of blue liquid was obtained, but no further work was done. In the present work the addition was attempted using aluminum chloride and D.M.F. as solvent as before. Orange or light green colored reaction mixtures were obtained depending on conditions used, but in both cases the low boiling nitroso compound was a minor product, the major product (>95%) being a colorless high boiling compound. This main product showed absorption in the infrared spectrum of 5.78μ and 6.05μ but the structure is still under investigation.

The reaction of $CF_2=CFCH=CHCF_3$ with nitrosyl chloride also gave a high boiling colorless product rather than a low boiling blue nitroso compound. The main product had absorption peaks in the infrared spectrum at 5.80μ and 6.05μ, respectively.

The Free Radical Reactions of Haloalkanes with Olefins

$CCl_3CF_2CF_2Br$, prepared by addition of CCl_3Br to tetrafluoroethylene in the presence of benzoyl peroxide, is to be treated with ethylene in the presence of benzoyl peroxide.

1,2-Dibromohexafluorocyclobutane and $CF_2BrCFHBr$ did not react with ethylene in the presence of benzoyl peroxide.

Ethylene was bubbled through CF_2ICF_2I and benzoyl peroxide at 100°, but no higher boiling product was detected. An attempted reaction of the same mixture at 100° in an autoclave gave less than 1% higher boiling product. An autoclave reaction at 220° gave a polymeric solid which gave no liquid product on attempted dehydrohalogenation. This is in contrast to the literature, when ethylene and CF_2ICF_2I in the presence of benzoyl peroxide at 220° gave $CF_2ICF_2CH_2CH_2I$ in 80% yield (13)

A series of compounds, CF_2BrCF_2Br, $CF_3CFBrCF_2Br$, and $CF_3CFBrCFBrCF_3$ were treated with ethylene in the presence of benzoyl peroxide. Reaction of the first dibromo-compound gave a 30% yield of $CF_2BrCF_2CH_2CH_2Br$. $CF_3CFBrCF_2Br$ gave a 51% yield of 1:1 adduct which was identified as $CH_2BrCH_2CF(CF_3)CF_2Br$ rather than $CF_3CFBrCF_2CH_2CH_2Br$. The last dibromide, $CF_3CFBrCFBrCF_3$ gave no reaction with ethylene in the presence of a 0.01 molar proportion of benzoyl peroxide. When the proportion of benzoyl peroxide was increased to greater than a 0.04 molar proportion, perfluorobutene-2 and CH_2BrCH_2Br were isolated in 29% and 21% yield respectively. This result is somewhat similar to the reaction of CFClBrCFClBr with ethylene under free radical conditions when CFCl=CFCl was isolated in 20% yield (14).

The addition of $CF_3CFBrCF_2Br$ and CF_2ICF_2I to allyl chloride in the presence of benzoyl peroxide gave no higher boiling products. Similar results were obtained previously when $CF_3CF_2CCl_3$ and $CF_2ClCF_2CCl_3$ were allowed to react with allyl chloride (14). In contrast allyl chloride was allowed to react with CCl_3Br and $CF_2BrCFClBr$ under free radical conditions to produce $CCl_3CH_2CHBrCH_2Cl$ (15) and $CF_2BrCFClCH_2CHBrCH_2Cl$, respectively.

$CF_3CFBrCFClBr$ and CF_2BrCF_2Br do not react with allyl ethyl ether, in the presence of benzoyl peroxide under the conditions employed. This is in contrast to the reported reaction of CCl_3Br and $CF_2BrCFClBr$ with the unsaturated ether under free radical conditions (16) to produce $CCl_3CH_2CHBrCH_2OC_2H_5$ and $CF_2BrCFClCH_2CHBrCH_2OC_2H_5$, respectively.

Addition of 1,3-butadiene to 1,2-dibromohexafluorocyclobutane and iodotrifluoromethane were attempted under free radical conditions. In the former reaction no high boiling products were formed, and in the latter reaction a polymeric solid, iodine and a low boiling gas only were detected.

Vinyl iodide was prepared by addition of iodine to ethylene followed by dehydroiodination. The product and tetrafluoroethylene were exposed to sunlight, but most of the tetrafluoroethylene was recovered. The only other product isolated was a very high boiling viscous mixture. No simple 1:1 adduct was formed.

Allyl iodide was allowed to react with tetrafluoroethylene in the presence of benzoyl peroxide to yield four main products which have been identified as CH_3CHICH_3, $CH_2=CHCH_2CF_2CF_2I$, CF_2ICF_2I, and suspected

$CH_2{=}CHCH_2CF_2CF_2CH_2CH{=}CH_2$. The yield of 1:1 adduct was increased from 20% to 40% when the reaction time was halved.

Addition of a haloalkane to an olefin was attempted via a Grignard reagent. Thus vinyl magnesium chloride and allylmagnesium bromide were allowed to react with 1,2-diiodotetrafluoroethane. The former reaction gave one product which is consistent with vinyl iodide. The latter reaction also gave a single product, which appears to be allyl iodide, but further confirmation is in progress.

The preparation of nitroso compounds of dehydrohalogenation products of two of the adducts previously prepared was attempted. No nitroso compound was formed when $BrCF_2CF_2CH{=}CH_2$ (17) was treated with nitric oxide in the presence of mercury and sunlight. A reaction under similar conditions using $CF_2ICF_2CH_2CH{=}CH_2$ gave a blue color indicative of a nitroso compound, which was discharged when the product was brought to ambient in the presence of oxygen. The reaction is to be repeated and the product purified under a nitrogen atmosphere.

Octene-1 has been reacted with $CF_3CF_2CCl_3$ under free radical conditions to give two high boiling products which are being identified.

Dehydrohalogenation of $CCl_3CF_2CFClCH_2CH_2Br$ (14) gave only one product which was identified as $CCl_3CF_2CFClCH{=}CH_2$.

Attempted Formation of Radicals from $CF_2ClCFClI$ and $CF_2BrCFClBr$ and Their Reaction *in situ* with Aromatic Nuclei

Since the previous report the only aromatic compounds used have been benzene and pentafluorobenzene. The former was used in attempts to increase yields of products and the latter in attempts to prepare perfluorostyrene. All experiments were carried out in Fischer-Porter tubes heated on an oil bath.

There was no detectable reaction between benzene and $CF_2BrCFClBr$ when heated alone, therefore, an experiment was carried out in the presence of a 1/10 molar proportion of benzoyl peroxide as an initiator. Two high boiling products were detected by v.p.c. which corresponded to bromobenzene and suspected $C_6H_5CFClCF_2Br$ (as isolated from a previous experiment). They formed 9% and 5% of the volatile products respectively. Non-volatile products, which may include derivatives of benzoic acid, were not examined.

It has been shown previously that reaction of benzene with $CF_2ClCFClI$ gives yields of $C_6H_5CFClCF_2Cl$ up to 24%. As benzoyl peroxide seems to assist the reaction of benzene and $CF_2ClCFClBr$, it was used in a comparison experiment in an attempt to increase the yield of $C_6H_5CFClCF_2Cl$ from benzene and $CF_2ClCFClI$. A blank experiment in which only benzene and $CF_2ClCFClI$ were heated was run under identical conditions. The former experiment showed an 18% conversion to higher boiling products compared to the conversion in the latter which was only 2%. The higher boiling product from the former experiment was a single peak on a silicon gum packed gas chromatography column at 180°, but on the same packing at 100° it separated into two peaks in the ratio of 18:82. The minor component was identified as iodobenzene and the major component was identified as $C_6H_5CFClCF_2Cl$ by gas chromatographic retention time. Therefore, the overall conversion to $C_6H_5CFClCF_2Cl$ was 14.8% in the benzoyl peroxide initiated reaction but in the blank experiment the conversion to $C_6H_5CFClCF_2Cl$ was only 2%.

An experiment to compare the reactivity of benzene and iodobenzene (i.e. ease of removal of hydrogen and iodine atoms from an aromatic nuclei) with $CF_2ClCFClI$ was attempted, but conditions were too mild to detect any reaction in either case.

A different approach was next used in an attempt to increase the yield of $C_6H_5CFClCF_2Cl$ from benzene and $CF_2ClCFClI$. Rather than use a free radical source as an initiator, the reaction was carried out in the presence of a metal which would easily take up the liberated iodine atoms (viz. mercury and copper dust). A blank experiment was again run under identical conditions for comparison. The blank experiment showed a 2.3% conversion to $C_6H_5CFClCF_2Cl$, whereas the experiment in the presence of mercury showed a 9.3% conversion to a higher boiling product corresponding to $C_6H_5CFClCF_2Cl$. The experiment, in the presence of electrolytic copper dust, could not be compared directly as the organic liquid formed a slurry with the dust.

In the previous report it has been shown that pentafluorobenzene and $CF_2ClCFClI$ did not react alone. In a preliminary reaction of pentafluorobenzene and $CF_2ClCFClI$ in the presence of benzoyl peroxide there was a 6% conversion to a higher boiling product. Therefore, three comparison reactions were set up under identical conditions. The first tube (1) contained pentafluorobenzene, $CF_2ClCFClI$ in equimolar proportions and 0.425 molar proportion of benzoyl peroxide. The second tube (2) contained pentafluorobenzene and $CF_2ClCFClI$ in equimolar proportions and a 0.2 molar proportion of benzoyl peroxide. The third tube (3) contained pentafluorobenzene and $CF_2BrCFClBr$ in equimolar proportions and 0.2 molar proportion of benzoyl peroxide. The percentages of high boiling products from gas chromatographic peak areas were (1) 27%, (2) 8%, (3) 23%. The high boiling product was isolated from (1) by gas chromatography and was shown to be iodobenzene by infrared spectroscopy. The major high boiling product from (3) had the same gas chromatographic retention time as bromobenzene. The minor product of slightly longer retention time than bromobenzene was in insufficient quantity for identification. Only volatile products were investigated.

As this whole series of experiments, using $CF_2BrCFClBr$ and $CF_2ClCFClI$ as sources of radicals to react with aromatic nuclei to form ethyl benzenes, gave poor yields, this route to styrenes has been abondoned.

Additions of Cyclopentadiene to Various Fluoroölefins

In the previous report cyclopentadiene was allowed to react with CFCl=CFCl but no product could be isolated. In order to test the procedure the previously known Diels-Alder addition of cyclopentadiene and perfluoropropene (18) was attempted and the adduct isolated in 19% yield. Similarly, perfluorobutene-2 was allowed to react with cyclopentadiene and the adduct was formed in 88% yield. The adduct gave a consistent infrared, and ^{19}F n.m.r. spectra and elemental analysis; decolorised a bromine solution and was oxidized by potassium permanganate. The proton n.m.r. spectrum showed a Diels-Alder (1,4-) adduct rather than a 1,2- adduct (19).

Dehalogenation of the Diels-Alder adduct, 5,6-difluoro-5,6-bis(trifluoromethyl)-norborn-2-ene was attempted using zinc in isopropanol, but only starting material was detected. Dehydrohalogenation was attempted by dropping the adduct on to molten potassium hydroxide. It was thought that if the bridge-head carbonium ion could be formed that it might rearrange, but only starting material was recovered in 84% yield.

As the Diels-Alder adduct from perfluorobutene-2 could not be dehalogenated, a Diels-Alder addition between cyclopentadiene and 2,3-dichlorohexafluorobutene-2 was attempted. The reaction mixture showed starting materials, dicyclopentadiene (trace) and adduct by gas chromatography. The product was isolated (33% conversion) as a white waxy solid which easily was oxidized by potassium permanganate and decolorised a bromine solution. A consistent infrared spectrum and elemental analysis were obtained for an adduct, which from the proton n.m.r. spectrum was shown to be a Diels-Alder adduct, 5,6-dichloro-5,6-bis(trifluoromethyl)-norborn-2-ene (19). The pure product gave an unsymmetrical gas chromatographic peak.

Dechlorination of the adduct was attempted by two methods. The hydrocarbon nornornadiene has been prepared by addition of cyclopentadiene to sym-dichloroethylene followed by dechlorination by magnesium iodide in ether (20). Dechlorination of 5,6-dichloro-5,6-bis(trifluoromethyl)-norborn-2-ene was attempted under identical conditions, but only trace quantities of product were detected by gas chromatography and a quantitative yield of starting material was recovered. The second dechlorination route attempted was using activated zinc in isopropanol. The dechlorination product was formed in at least 86% yield and was identified by infrared spectroscopy as 2,3-bis(trifluoromethyl)norbornadiene. This product was also obtained from addition of cyclopentadiene to hexafluorobutyne-2.

Hexafluorobutyne was prepared by a known route (21). The addition between cyclopentadiene and hexafluorobutyne was facile and the adduct was formed in 84% yield, the remainder being low boiling starting material and a trace of dicyclopentadiene. The pure adduct was oxidized by potassium permanganate and decolorized bromine. The adduct had a consistent infrared spectrum, particularly the medium intensity absorption at 5.92μ attributable to $CF_3-\overset{\diagup}{C}=\overset{\diagdown}{C}-CF_3$.

The elemental analysis was consistent for the adduct. The proton n.m.r. spectrum was consistent for a Diels-Alder adduct, 2,3-bis(trifluoromethyl)norbornadiene.

The addition of cyclopentadiene to sym-dichlorodifluoroethylene was attempted at 150° on a small scale. A shoulder was noticed on the dicyclopentadiene peak. The reaction was therefore repeated at 170°, at which temperature dicyclopentadiene cleaves to give the monomer. This reaction increased the yield of the shoulder so that it became larger than the dicyclopentadiene peak. An autoclave reaction of the 0.5 molar scale gave an 11.5% conversion to the adduct, the major product being a highly viscous high boiling liquid, which crystallised on standing. Identification of the latter product has not been attempted, although from the similarity of its infrared spectrum to the Diels-Alder adduct and from previous literature, it is suspected to be the product of further addition of cyclopentadiene.

The product formed in 11.5% yield, which was a low melting solid, which was oxidized by potassium permanganate solution and decolorized bromine. It gave a consistent infrared spectrum and elemental analysis for an adduct. The proton n.m.r. spectrum was consistent for the 1,4-adduct, 5,6-dichloro-5,6-difluoronorborn-2-ene (19). The ^{19}F n.m.r. spectrum was inconclusive.

As dechlorination of 5,6-dichloro-5,6-bis(trifluoromethyl)norborn-2-ene was easily effected by activated zinc in isopropanol, the same system was used in an attempt to dechlorinate 5,6-dichloro-5,6-difluoronorborn-2-ene. The starting material was recovered in 95.5% yield.

The addition of cyclopentadiene to trifluoroethylene was attempted, as dehydrofluorination of the adduct should give the same product as the dechlorination attempted on 5.6-dichloro-5,6-difluoronorborn-2-ene. Initial attempts at the addition on a small scale gave recovered olefin in from 92-76% yield. It was noted in these experiments that there was always a minor product of suitable gas chromatographic retention time for an adduct. Also an increase in reaction temperature gave a decrease in the percentage of unchanged olefin recovered. In this whole series of experiments it was found that the autoclave reaction where the whole vessel was heated gave superior yields to the small scale experiments in Fischer-Porter tubes where only part of the vessel was heated. Also additions that had to be effected at higher temperatures gave poor yields of simple adduct accompanied by higher boiling products.

An autoclave addition of cyclopentadiene and trifluoroethylene was carried out at 165° and 53% of the unchanged olefin was recovered. The adduct, which was a waxy solid, was formed in 33% yield based on unrecovered olefin, the major product being a high boiling liquid which was not identified. The purified simple adduct was oxidized by potassium permanganate and decolorized bromine. It gave consistent infrared spectrum and elemental analysis for an adduct. The ^{19}F n.m.r. spectrum indicated a mixture of two isomers of 5,5,6-trifluoronotborn-2-ene, but the proton n.m.r. spectrum was inconclusive.

Dehydrofluorination of the adduct was attempted using aqueous and alcoholic aqueous potassium hydroxide but no product was detected, the yield of starting material being quantitative in both cases.

Small scale addition of cyclopentadiene to chlorotrifluoroethylene gave a 44% recovery of starting olefin, but an autoclave reaction gave a negligible amount of low boiling product. A large amount of brown viscous liquid of low volatility was formed. The adduct, which was a liquid, was formed in 26% yield. It easily was oxidized by potassium permanganate and decolorized bromine solution. The adduct gave a consistent infrared spectrum and elemental analysis. The proton and ^{19}F n.m.r. spectra indicated at least four components which seemed to be isomers of both the 1,4- and 1,2- adducts.

The last addition attempted used isopropenylacetylene as a diene. It was allowed to react with octafluorobutene-2 as this olefin gave a facile reaction with cyclopentadiene. Under the conditions used no adduct was detected and a very good recovery of starting material was obtained.

IV. EXPERIMENTAL

Aluminum Chloride Catalyzed Additions of Polyhaloalkanes to Haloölefins

Preparation and Purification of CFCl=CFCl

$CFCl_2CFCl_2$ (566 g., 2.77 mole) was added dropwise to zinc dust (200 g., 3.07 mole) in absolute ethanol (300 ml.) at reflux over 4.5 hr. After refluxing for 1.5 hr. a total of 337 g. crude olefin was collected. Distillation gave material (307 g. 84%), b.p. 22.5-23.5°, having infrared bands at 5.73μ (CF_2=) and 5.86μ(*cis*-CF=CF-).

Removal of the $CF_2=CCl_2$ was accomplished by adding the crude olefin mixture (192 g.) from dropping funnel over 0.75 hr. to a solution of sodium (0.5 g.) in absolute ethanol (200 ml.) at 18-24°. After stirring for 2.5 hr., distillation gave pure CFCl=CFCl (172 g., 90% recovery), b.p. 22-3°, with no infrared band at 5.73μ.

Attempted Isomerization of CFCl=CFCl using $AlCl_3$

Pure CFCl=CFCl (21.2 g., 0.159 mole) and $AlCl_3$ (1.0 g.) were combined at 0° in a Fischer-Porter tube and rocked for 20 min. More $AlCl_3$ (1.5 g.) was added and after 1 hr. another 1.5 g. were added. After 4 hr. at room temperature the mixture was worked up in the normal manner to give a liquid (14.9 g.) which contained no $CF_2=CCl_2$ (by infrared) and no higher boiling material - only unchanged CFCl=CFCl.

Addition of $CFCl_3$ to $CFCl=CFCl$ using $AlCl_3$

$CFCl_3$ (281 g., 2.04 mole) and pure $CFCl=CFCl$ (200 g., 1.50 mole) were combined in a flask at 0°, $AlCl_3$ (15 g.) was added and the ice bath was removed. After 18 min. $AlCl_3$ (15 g.) was added as the first batch had adhered to the side of the flask. After 22 min. another 15 g. $AlCl_3$ were added then the mixture was stirred for 3 hr. $AlCl_3$ (10 g.) was added and the mixture stirred at room temperature for 2.5 hr. The total $AlCl_3$ used was 55 g. (0.42 mole) and the total time was 6.25 hr. Normal work-up gave material (467 g.) which on distillation gave CCl_4 (78 g.), $C_3Cl_4F_4$ (3.3 g.), $CCl_2=CCl_2$ (14.2 g.), $C_3Cl_5F_3$ (294 g., 72%), $C_3Cl_6F_2$ (43 g., 10%), and higher boiling material (3 g.).

Isomerization of $C_3Cl_5F_3$ by $AlCl_3$ in CCl_4

$C_3Cl_5F_3$ (24.0 g., 0.089 mole), CCl_4 (56 g.), and $AlCl_3$ (4 g., 0.03 mole) were combined in a Fischer-Porter tube at room temperature and rocked occasionally for 61 hr. Work-up gave material (66 g.), which after removal of the CCl_4 (35 g.), gave a residue (30 g.) containing CCl_4 (33%, 9.9 g.), $CCl_2=CCl_2$ (25%, 7.5 g.), $C_3Cl_5F_3$ (15%, 4.5 g.), and $C_3Cl_6F_2$ (27%, 8.1 g.). Distillation gave the latter two in pure state for n.m.r. analyses.

Addition of $CFCl_3$ to $CF_2=CFBr$ using $AlCl_3$

$CFCl_3$ (308 g., 2.24 mole) and $AlCl_3$ (10 g.) were combined in a flask at -52°, then $CF_2=CFBr$ (44 g., 0.273 mole) was bubbled through the mixture at -40° to -6° during 0.75 hr.

The mixture was cooled to -20°, then stirred for 3 hr. whilst attaining room temperature. $AlCl_3$ (6 g.) was added and the mixture was stirred for 1.5 hr., then left in a stoppered flask for 60 hr. The total $AlCl_3$ used was 16 g. (0.12 mole). Work-up gave $C_3BrCl_3F_4$ (61 g., 75%), b.p. 125-7°.

Attempted Addition of CF_2Br_2 to $CF_2{=}CCl_2$ using $AlCl_3$

CF_2Br_2 (79 g., 0.376 mole), $CF_2{=}CCl_2$ (21 g., 0.158 mole), and $AlCl_3$ (6 g., 0.045 mole) were combined at 0° in a Fischer -Porter tube and rocked at room temperature for 5.25 hr. Only unreacted starting materials were present.

Attempted Addition of $CF_2ClCFCl_2$ to $CFCl{=}CFCl$ using $AlCl_3$

$CF_2ClCFCl_2$ (76.5 g., 0.409 mole), $CFCl{=}CFCl$ (27.6 g., 0.208 mole), and $AlCl_3$ (8 g., 0.06 mole) were combined in a flask equipped with thermometer, magnetic stirrer, and ice water reflux condenser. After stirring at 25.5-27.0° for 1 hr., the $AlCl_3$ had coagulated so the liquid was decanted into clean flask with fresh $AlCl_3$ (8 g.). The mixture was stirred for 5 hr. at 24.5-27.0° then stoppered and left at room temperature for 60 hr. Work-up gave a liquid (81.5 g.) which was chiefly unreacted alkane. Distillation gave $C_2Cl_3F_3$ (4.5 g.), b.p. 47.0-47.5°, $n_D^{21.5}$ 1.3599 and a material, b.p. 88-94°, m.p. 37.5-38.5°, identified as CF_2ClCCl_3. N.m.r. analysis of the $C_2Cl_3F_3$ showed it to be entirely $CF_2ClCFCl_2$.

Preparation of Sodium Allyloxide

Allyl alcohol (60 g., 1.03 mole) was placed in a flask equipped with magnetic stirrer, then sodium (14.7 g., 0.64 mole) was added slowly in small pieces. After about one-third of the sodium had been added the reaction became sluggish so more allyl alcohol (52 g., 0.90 mole) was added and the mixture was heated while the rest of the sodium was added. The solution turned from colorless to deep orange. The excess alcohol was removed in vacuo to give a tan solid which was pulverized and stored under nitrogen.

Attempted Reaction of Sodium Allyloxide with $CF_2=CFCF_2Cl$ in Dioxane

A suspension of sodium allyloxide (8.0 g., 0.10 mole) in dry dioxane (50 ml.) was cooled in an ice bath and $CF_2=CFCF_2Cl$ (16.8 g., 0.10 mole) was added over 0.5 hr. The mixture was stirred up to room temperature over 1.5 hr. but gas chromatography showed no reaction had occurred.

Attempted Reaction of Sodium Allyloxide with $CF_2=CFCF_2Cl$ in Acetone

A suspension of sodium allyloxide (8.0 g., 0.10 mole) in dry acetone (130 ml.) was cooled to 0° then $CF_2=CFCF_2Cl$ (14.2 g., 0.085 mole) was added in 40 min. The mixture was stirred to room temperature for 4 hr. but none of the expected product was formed.

Reaction of Allylmagnesium Bromide with $CF_2=CFCF_2Cl$

Magnesium (8.5 g., 0.352 mole) and dry ether (120 ml.) were combined in a dry flask under nitrogen. The magnesium was activated by adding a few drops of CH_2BrCH_2Br and stirring at room temperature for 18 min. The flask was then cooled in an ice bath and allyl bromide (18.0 g., 0.149 mole) in dry ether (20 ml.) was added dropwise during 20 min. The resulting mixture was stirred for 6 min. then filtered into a dry dropping funnel. The solid residue was also washed with ether and the ether was combined with the Grignard solution.

Dry ether (20 ml.) and $CF_2=CFCF_2Cl$ (13.0 g., 0.078 mole) were combined at 0°. The Grignard solution was added dropwise to give an immediate white precipitate. After 0.25 hr. (ca. one-fourth the Grignard had been added) a gray sludge had formed which made stirring difficult. The remaining Grignard was added during 0.5 hr. After stirring to room temperature for 7 min. water was added and the mixture was left overnight. The ether layer was washed with dilute sulfuric acid, then dried over Drierite. The aqueous layer gave positive tests for chloride and fluoride ions. Distillation gave a residue (12.5 g.) containing some ether, a small amount of allyl bromide and compounds I and II. Further distillation gave ether (4.2 g.), allyl bromide (0.4 g.), I (1.7 g.), and a residue (5.0 g.). This latter contained I (34%, 1.7 g.), II (40%, 2.0 g.), and three higher boiling components (26%, 1.3 g.). Preparative gas chromatographic separation (silicon elastomer, 110°) gave pure I, b.p. 96-8° (micro), $n_D^{20.5}$ 1.3787, with a strong infrared band at 5.94μ and a weaker band at 6.08μ and pure II, b.p. 139-40° (micro), $n_D^{20.5}$ 1.3970, with medium infrared bands at 5.78 and 6.08μ. Anal. for I calc'd. for $C_6H_5ClF_4$: C, 18.81; F, 40.32. Found: Cl, 16.93; F, 37.14, identified as $CH_2=CHCH_2CF_2CF=CFCl$. Anal. for II calc'd. for $C_9H_{10}F_4$: C, 55.64; H, 5.20; F, 39.16. Found: C, 55.77; H, 5.20; F, 39.45, identified as $CH_2=CHCH_2CF=CFCF_2CH_2CH=CH_2$.

Fluoronitroso Compounds

Preparation of $CF_2=CFCH_2CH=CH_2$ and its Reaction with NOCl

$CH_2=CHCH_2Cl$ (114 g., 1.5 mole) and benzoyl peroxide (24 g., 0.092 mole) were added to a refluxing solution of $CF_2BrCFClBr$ (1100 g., 4.0 mole). Reaction was continued for another 7 hr. Excess $CF_2BrCFClBr$ was distilled off and the residue was washed with sodium carbonate solution and H_2O and dried. Distillation gave the adduct $CF_2BrCFClCH_2CHBrCH_2Cl$ (146 g., 28.2%), b.p. 90°/6 mm. (lit. b.p. 90°/6 mm.). Dehalogenation of the adduct was carried out as usual by zinc in ethanol. Fractional distillation gave the diene $CF_2=CFCH_2CH=CH_2$ (23 g., 45.8%), b.p. 38° (lit. 38°/870 mm.).

Nitrosyl chloride (3.3 g., 0.05 mole) was added to a stirred mixture of $CF_2=CFCH_2CH=CH_2$ (6.2 g., 0.05 mole), $AlCl_3$ (6.7 g., 0.05 mole) and DMF (100 ml.) at 0°, and the reaction continued for 3 hr. The color of the solution changed from yellow to greenish brown. Water was added slowly to a reaction mixture and a blue organic liquid (2.1 g.) was obtained. Gas chromatographic analysis of the product showed $CF_2{=}CFCH_2CH{=}CH_2$ (1.8 g.), $CF_2ClCF(NO)CH_2CH{=}CH_2$ (0.3 g.) and a trace of high boiling material. $CF_2ClCF(NO)CH_2CH{=}CH_2$, which was purified by preparative gas chromatography . had the following properties: No definite boiling point at normal pressures, color changed slowly to green at ca. 100°, to greenish yellow at ca. 110°, to yellowish brown at ca. 115°, to dark brown at ca. 120°. Anal. calc'd. for $C_5H_5ClF_3NO$: C, 32.02; H, 2.68. Found: C, 32.22; H, 2.76.

Preparation of $CF_2{=}CFCH{=}CH_2$ and its Reaction with NOCl

$CF_2BrCFClCH{=}CH_2$ (135 g., 0.5 mole), which was prepared by addition of $CF_2BrCFClBr$ to $CH_2{=}CH_2$, followed by dehydrobromination, was added to a stirred refluxing suspension of Zn (60 g., 0.7 mole), $ZnCl_2$ (2.0 g.) and in EtOH (200 ml.) over a period of two hours and the reaction was continued for another two hours. The product which was collected in a cold trap (-78°) was distilled to give $CF_2{=}CFCH{=}CH_2$ (48 g., 89%), b.p. 8°.

$CF_2{=}CFCH{=}CH_2$(10.8 g., 0.1 mole) was condensed into a stirred mixture of $AlCl_3$ (13.4 g., 0.1 mole), NOCl (9.8 g., 0.15 mole) and DMF (100 ml.) at 0°. The color of the solution changed from orange to greenish yellow shortly after the addition of the diene and then changed to orange again. After five hours, water was added and the organic layer was separated and dried.

The crude light yellow product (13 g.), which consisted of one major component (over 95%), was separated by preparative gas chromatography to yield the major product as a colorless liquid, b.p. 177-178° (micro), n_D^{26} 1.3975. The infrared absorption peaks at 5.70 and 6.05 are characteristic of $-CF{=}CH-$, and $CH_2{=}CH-$, respectively. When the reaction was carried out with $CF_2{=}CFCH{=}CH_2$ (7.8 g., 0.07 mole), NOCl (5.9 g., 0.09 mole), $AlCl_3$ (6.7 g., 0.05 mole) and DMF (80 ml.), the color of the reaction mixture was light green, which after treatment with water, yielded a blue liquid (6.9 g.).

Though the main product was the same, a trace of a blue compound, probably a nitroso compound, was obtained.

Further attempts at making the nitroso compound will be continued.

Preparation of $CF_2{=}CFCH{=}CHCF_3$ and its Reaction with NOCl

$CF_2ClCFClI$ (279 g., 1.0 mole), $CF_3CH{=}CH_2$ (28.8 g., 0.03 mole) and benzoyl peroxide (2 g.) were allowed to react in an autoclave at 100° for four hours. Excess $CF_2ClCFClI$ was distilled off and the residue was fractionated to give $CF_2ClCFClCH_2CHICF_3$ (90 g., 77.5%), b.p. 61°/18 mm. Dehydroiodination was effected by aqueous potassium hydroxide (100 g. in 60 ml.) and $CF_2ClCFClCH{=}CHCF_3$ (40 g., 67.4%) was obtained. Dechlorination by zinc dust in ethanol gave $CF_2{=}CFCH{=}CHCF_3$ (15.8 g., 56%), b.p. 49°.

$CF_2=CFCH=CHCF_3$ (13.8 g., 0.08 mole), NOCl (9.8 g., 0.15 mole), $AlCl_3$ (6.7 g., 0.05 mole), and DMF (100 ml.) were allowed to react at 0°. After two hours, the mixture was treated with H_2O and a light yellow product (17.3 g.) was obtained. The main product was a colorless liquid rather than a blue nitroso compound. A sample has been submitted for elemental analysis.

Free Radical Reactions of Haloalkanes with Olefins

Preparation of $CCl_3CF_2CF_2Br$

CCl_3Br (396 g., 2 moles), Bz_2O_2 (3 g.), and $CF_2=CF_2$ (78.5 g., 0.78 mole) were heated in an autoclave at 100° for 8 hr. The autoclave was vented and gaseous material (1 g.), which was mainly $CF_2=CF_2$, was condensed out. A liquid mixture (448.5 g.) which contained 29.6% adduct (44.5% yield based on $CF_2=CF_2$ used) was obtained. On distillation almost pure $CCl_3CF_2CF_2Br$ (135 g.) was obtained from the reaction mixture. This product is to be allowed to react with ethylene under free radical conditions.

Preparation of 1,2-Dibromohexafluorocyclobutane

$CF_2=CFBr$ (297 g.) was heated in an autoclave for 12 hr. at 190°. Unchanged $CF_2=CFBr$ (1.5 g.) was condensed out of the autoclave. On distillation, the residual liquid yielded 1,2-dibromohexafluorocyclobutane (86 g., 30% yield).

Addition of 1,2-Dibromohexafluorocyclobutane to Ethylene

1,2-Dibromohexafluorocyclobutane (83 g.), ethylene (5 g.), and benzoyl peroxide (1 g.) were heated in an autoclave at 100° for 12 hr. On venting the autoclave an almost quantitative yield of ethylene was condensed out. A gas chromatogram of the residual liquid indicated two higher boiling products, as less than 1% of the mixture, which could not be isolated.

Addition of CF_2ICF_2I to Ethylene

(a) Ethylene was passed into CF_2ICF_2I at 100° and in the presence of Bz_2O_2 for 4 hr. Gas chromatography indicated the absence of any higher boiling material in the reaction mixture.

(b) CF_2ICF_2I (352 g.), Bz_2O_2 (1.5 g.), and ethylene (16.2 g.) were heated in an autoclave at 100° for 12 hr. Highly volatile material (20 g.) was condensed out of the autoclave. It was mostly ethylene. The residual liquid showed one high boiling product in less than 2% yield (by gas chromatography). Most of the CF_2ICF_2I was distilled off and the residue treated directly with alcoholic potassium hydroxide. A dehydrohalogenation product was indicated by gas chromatography, but it was in insufficient quantity to be isolated.

(c) When the above reaction was repeated at 220° and in the absence of Bz_2O_2, only solid material was obtained. No liquid product was obtained when this solid material was heated with alcoholic potassium hydroxide.

Addition of $CF_2BrCFHBr$ to Ethylene

$CF_2BrCFHBr$ (297 g.), Bz_2O_2 (1.5 g.), and ethylene (9 g.) were heated in an autoclave at 100° for 12 hr. An almost quantitative recovery of ethylene was obtained on venting the autoclave. A gas chromatogram indicated the absence of any higher boiling material in the residual mixture.

Addition of $CF_3CFBrCFBrCF_3$ to Ethylene

(a) $CF_3CFBrCFBrCF_3$ was made by passing perfluorobutene-2 into bromine. $CF_3CFBrCFBrCF_3$ (82 g.), Bz_2O_2 (1 g.) and ethylene (6 g.) were heated in an autoclave at 100° for 12 hr. The gaseous material was collected in a cooled trap. The residual liquid contained one higher boiling material as less than 3% of the mixture.

(b) $CF_3CFBrCFBrCF_3$ (346 g.), benzoyl peroxide (10 g.), and ethylene (14.5 g.) were heated in an autoclave at 100° for 8 hr. Gaseous material (30 g.) was condensed out on venting the autoclave. From the gas chromatogram this was shown to be a mixture of very low boiling material (8.5 g.) and octafluorobutene-2 (21.5 g.). The residual liquid (317 g.) was a mixture containing the three main components, octafluorobutene-2, $CF_3CFBrCFBrCF_3$ and CH_2BrCH_2Br. Distillation gave octafluorobutene-2 to give a total yield of 29% from distillate and low boilers. Distillation also yielded $CF_3CFBrCFBrCF_3$ (201.5 g.) and CH_2BrCH_2Br in 21% yield.

Addition of $CF_3CFBrCF_2Br$ to Allyl Chloride

$CF_3CFBrCF_2Br$ (254 g.), benzoyl peroxide (1 g.), and allyl chloride (38.5 g.) were heated in an autoclave at 100° for 12 hr. The reaction mixture was examined by gas chromatography. No higher boiling product was indicated.

Addition of CF_2ICF_2I to Allyl Chloride

Allyl chloride (7.65 g.), CF_2ICF_2I (70.6 g.), and benzoyl peroxide (0.5 g.) were heated in a Fischer-Porter tube at 100° for 8 hr. The reaction mixture was examined by gas chromatography which indicated no high boiling products.

Addition of $CF_3CFBrCF_2Br$ and CF_2BrCF_2Br to $C_2H_5-OCH_2-CH=CH_2$

Additions were attempted as in the previous two experiments but in both cases gas chromatography showed no higher boiling products.

Addition of 1,2-Dibromohexafluorocyclobutane to 1,3-Butadiene

1,2-Dibromohexafluorocyclobutane (68 g.), benzoyl peroxide (1 g.), and 1,3-butadiene (9 g.) were heated in an autoclave at 100° for 12 hr. The autoclave was vented and the gaseous material was collected in a cold trap. Most of the 1,3-butadiene was recovered while gas chromatography indicated the absence of any higher boiling material in the residual mixture.

Addition of Iodotrifluoromethane to 1,3-Butadiene

Iodotrifluoromethane (101 g.) and 1,3-butadiene (14 g.) were heated in an autoclave at 200° for 8 hr. Gaseous material (83 g.) was collected of which 23.5 g. was material boiling in the range -70 to -80°. The residual product was a solid material and iodine. It appeared that the 1,3-butadiene polymerized. No 1:1 or 1:2 adducts were detected.

Addition of Vinyl Iodide to Tetrafluoroethylene

Vinyl iodide (28.5 g.) and tetrafluoroethylene (23 g.) were exposed to sunlight in a 22 lt. flask for 16 hr. The contents of the flask were vacuum transferred to a cold trap to yield a liquid (41.5 g.) which consisted of tetrafluoroethylene (21 g.) and vinyl iodide (20.5 g.) but no higher boiling material. A high boiling material (10 g.) remaining in the flask showed several high boiling components by gas chromatography. No simple one to one addition product appeared to be formed.

Addition of Allyl Iodide to Tetrafluoroethylene

Allyl iodide (108 g.), tetrafluoroethylene (38 g.), and benzoyl peroxide (1 g.) were heated in an autoclave at 100° for 8 hr. On venting the autoclave gaseous material (17 g.) was condensed out which was almost pure tetrafluoroethylene. The residual liquid (90.5 g.) and some solid product were recovered from the autoclave. A gas chromatogram of the liquid showed six components in the following proportions:

	% of Residual Liquid by Peak Areas	Component	Estimated Wt.	% Yield*
I	1%	Low boiling (probably $CF_2=CF_2$)	0.75 g.	
II	14%	CH_3CHICH_3	10.5 g.	28
III	37.5%	$CH_2=CHCH_2I$	28.0 g.	
IV	3.5%	$CH_2=CH-CH_2CF_2CF_2CH_2-CH=CH_2$	2.6 g.	6
V	26%	$CH_2=CH-CH_2CF_2CF_2I$	19.5 g.	34
VI	18.2%	CF_2ICF_2I	13.7 g.	17.5

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* Based on $CF_2=CF_2$ used.

The liquid mixture was distilled, to yield components II through VI, and a residue (15 g.). The compounds were further purified by gas chromatography to show the following properties:

II identified as CH_3CHICH_3; n_D^{20} 1.4996; d^{21} 1.666 (lit. b.p. 89.5°, n_D^{20} 1.4996; d^{20} 1.703). Analysis calc'd. for C_3H_7I: C, 21.09; H, 4.12; I, 74.8. Found: C, 21.43, H, 4.29, I, 73.11%.

IV identified as $CH_2=CH-CH_2CF_2CF_2CH_2-CH=CH_2$; b.p. 118°; n_D^{20} 1.3721. Analysis calc'd. for $C_8H_{10}F_4$: C, 52.75; H, 5.49; F, 41.76. Found: C, 52.33; H, 5.31; F, (by difference) 42.36%. No iodine was found in this compound.

V identified as $CH_2=CH-CH_2-CF_2CF_2I$; b.p. 114°; n_D^{20} 1.4388. Analysis calc'd. for $C_5H_5F_4I$: C, 22.39; H, 1.87; I, 47.78. Found: C, 22.93; H, 1.99; I, 48.88%.

VI identified as CF_2ICF_2I; b.p. 108.5°, $n_D^{20.5}$ 1.4892; d^{21} 2.581 (lit. b.p. 112-3°; n_D^{25} 1.4895; d_4^{25} 2.6293). Analysis calc'd. for CF_2ICF_2I: C, 6.91; H, 0.0; I, 71.80. Found: C, 7.81; H, 0.22; I, 70.24%.

Reaction of CH_2=CHMgCl with CF_2ICF_2I

CH_2=CHMgCl (0.05 mole) in T.H.F. was added dropwise to a stirred mixture of CF_2ICF_2I (0.05 mole) in T.H.F. The reaction mixture was added to dilute hydrochloric acid, the organic layer was washed several times with water and dried. A gas chromatogram showed only one lower boiling product as a minor component together with unreacted CF_2ICF_2I and T.H.F. The low boiling product was isolated by preparative gas chromatography. The proton and ^{19}F n.m.r. spectra indicate only vinyl protons and the absence of fluorine. It has the same gas chromatographic retention time, infrared and n.m.r. spectra as CH_2=CHI. Elemental analysis calc'd. for C_2H_3I: C, 15.5; H, 1.95; I, 82.47. Found: C, 17.76; H, 2.58; I, 79.62%.

Reaction of CH_2=CH-CH_2MgBr with CF_2ICF_2I

CH_2=$CHCH_2$MgBr (0.1 mole) in ether was added dropwise to a stirred solution of CF_2ICF_2I (30 g.) in ether (100 ml.) The reaction mixture was refluxed for 0.5 hr., then cooled and hydrolyzed with dilute hydrochloric acid. The organic layer was separated, washed with water and dried. Gas chromatography indicated only one lower boiling product which had the same gas chromatographic retention time as allyl iodide. This will be separated and its properties will be compared with allyl iodide.

Reaction of $CF_2BrCF_2CH=CH_2$ with Nitric Oxide

A 3 lt. flask was charged with mercury (70 ml.), evacuated, and $CF_2BrCF_2CH=CH_2$ (2.9 g.) added to give a pressure of 83 mm. Nitric oxide was added to increase the pressure to 185 mm. The flask was irradiated with sunlight for 12 hr. The volatile material was collected in a trap. The absence of blue color indicated that no nitroso compound was formed.

Reaction of $ICF_2CF_2CH_2-CH=CH_2$ with Nitric Oxide

A 5 lt. flask was charged with mercury (70 ml.), evacuated, and $CH_2=CHCH_2CF_2CF_2I$ (7.8 g.) condensed in. Nitric oxide was added to a pressure of 245 mm. The flask was irradiated with sunlight for 12 hr. There was a reduction of pressure of 117 mm. The product, which had blue color, was collected in a cold trap, but when this was brought to room temperature the blue color discharged to leave a yellow viscous liquid.

Reaction of $CF_3CF_2CCl_3$ with 1-Octene

$CF_3CF_2CCl_3$ (262 g.), benzoyl peroxide (5 g.), and 1-octene (46 g.) were refluxed for 18 hr. Most of 1-octene was consumed and gas chromatography indicated two higher boiling materials, which will be identified in the future.

Preparation of $CCl_3CF_2CFClCH=CH_2$ from $CCl_3CF_2CFClCH_2CH_2Br$

$CCl_3CF_2CFClBr$ (172 g.), benzoyl peroxide (1 g.), and ethylene (8 g.) were heated in an autoclave at 100° for 8 hr. On opening the autoclave ethylene (5 g.) condensed out.

The residual mixture was distilled to remove most of the $CCl_3CF_2CFClBr$. The residue was refluxed with potassium hydroxide (8 g.), methanol (15 ml.) for 0.5 hr. The reaction mixture was poured into water, the organic layer was washed with water and dried. The organic liquid (11.5 g.) obtained showed one main component by gas chromatography. This was purified by preparative gas chromatography to yield a liquid: b.p. 182°, n_D^{21} 1.4504, d^{21} 1.6357. Analysis calc'd. for $C_5H_3Cl_4F_3$: MR_D, 44.3; Cl, 54.1. Found: MR_D, 43.1; Cl, 53.90%.

Attempted Formation of Radicals from $CF_2ClCFClI$ and $CF_2BrCFClBr$ and Their Reaction *in situ* with Aromatic Nuclei

Reaction of Benzene with $CF_2BrCFClBr$ in the Presence of Benzoyl Peroxide

Benzene (0.78 g., 0.01 M), $CF_2BrCFClBr$ (2.76 g., 0.01 M) and benzoyl peroxide (0.26 g., 0.001 M) were heated in a sealed Fischer-Porter tube on an oil bath at 155° for 96 hours. Gas chromatographic examination of the products showed peaks corresponding to starting materials, bromobenzene and suspected $C_6H_5CFClCF_2Br$. The latter two components were 9% and 5% by peak areas respectively.

Benzene (0.78 g., 0.01 M) and $CF_2BrCFClBr$ (4.48 g., 0.0165 M) were sealed in a Fischer-Porter tube and heated on an oil bath at 181-188° for 78 hours. The product on gas chromatographic examination showed no long retained materials.

The Effect of Benzoyl Peroxide on the Reaction of Benzene with $CF_2ClCFClI$

A Fischer-Porter tube was charged with benzene (2.34 g., 0.03 M), $CF_2ClCFClI$ (4.19 g., 0.015 M) and benzoyl peroxide (0.38 g., 0.0015 M). A similar tube was charged with benzene (2.34 g.) and $CF_2ClCFClI$ (4.19 g.) only. The tubes were sealed and heated together on an oil bath at 170° for 89 hours.

A gas chromatogram of the products showed that long retained material (pure $C_6H_5CFClCF_2Cl$) formed 2% of the volatile products when benzoyl peroxide was absent (98% unchanged starting materials). In the presence of benzoyl peroxide long retained material (one peak on Si gum at 180°) formed 18% of the volatile products (82% unchanged starting material).Re-examination of the gas chromatogram on Silicon gum at 100° and 130° showed that the long retained material was 18% iodobenzene and 82% $C_6H_5CFClCF_2Cl$: overall yield of $C_6H_5CFClCF_2Cl$ in benzoyl peroxide initiated reaction was 14.8%.

Comparison of the Reaction of Iodobenzene and Benzene with $CF_2ClCFClI$

Iodobenzene (2.04 g., 0.01 M) and $CF_2ClCFClI$ (2.79 g., 0.1 M) were sealed in a Fischer-Porter tube. In a similar tube benzene (0.8 g., 0.01 M) and $CF_2ClCFClI$ (2.79 g., 0.01M) were sealed. The tubes were heated together on an oil bath at 140-4° for 88 hours.

There was insufficient reaction to measure gas chromatographic peak areas to obtain a comparison.

Reaction of Benzene and $CF_2ClCFClI$ in the Presence of Mercury or Copper

A Fischer-Porter tube was charged with benzene (0.78 g., 0.01 M), $CF_2ClCFClI$ (2.79 g., 0.1 M) and clean dry mercury (7.5 g., 0.0375 M). A similar tube was charged with benzene (0.78 g., 0.01 M), $CF_2ClCFClI$ (2.79 g., 0.01 M) and electrolytic copper dust (1.92 g., 0.0303 M). Another tube was charged with benzene (0.78 g., 0.01 M) and $CF_2ClCFClI$ (2.79 g., 0.01 M) only. The tubes were sealed and heated together, with occasional shaking, on an oil bath at 170° for 88 hours.

The organic liquid of the first (Hg) and last tubes (blank) were examined by gas chromatography. In the second tube (Cu) the organic liquid and copper powder formed a solid mass and therefore a direct gas chromatographic examination could not be made with the two other reactions. The reaction in the presence of mercury showed a 9.3% conversion to $C_6H_5CFClCF_2Cl$ (free from C_6H_5I) whereas in the blank experiment the conversion was 2.3%.

The Reaction of Pentafluorobenzene with $CF_2ClCFClI$ in the Presence of Benzoyl Peroxide

Pentafluorobenzene (2.79 g., 0.0166 M), $CF_2ClCFClI$ (4.19 g., 0.015 M) and benzoyl peroxide (0.36 g., 0.0015 M) were sealed in a Fischer-Porter tube and heated on an oil bath at $171\text{-}8^{\circ}$ for 84 hours. A long retained peak formed 6% of the volatile products (by gas chromatography).

Reaction of Pentafluorobenzene with $CF_2ClCFClI$ and $CF_2BrCFClBr$ in the Presence of Benzoyl Peroxide (A Comparison Experiment).

Pentafluorobenzene (1.70 g., 0.01 M), $CF_2ClCFClI$ (2.79 g., 0.01 M) and benzoyl peroxide (1.03 g., 0.00425 M) were sealed in a Fischer-Porter tube (tube 1). Pentafluorobenzene (1.74 g.), $CF_2ClCFClI$ (2.79 g.) and benzoyl peroxide (0.5 g., 0.002 M) were sealed in a Fischer-Porter tube (tube 2). Pentafluorobenzene (1.71 g.), $CF_2BrCFClBr$ (2.77 g., 0.01 M) and benzoyl peroxide (0.5 g., 0.002 M) were sealed in a similar tube (tube 3). The three tubes were heated together on an oil bath at 168-172° for 114 hours.

The products were examined by gas chromatography to show the following percentages of long retained products: Tube 1, 26.8%; Tube 2, 8.4%; Tube 3, 22.8%. The remaining 73.2% and 81.6% in tubes 1 and 2 were starting materials and very minor short retained products. In tube 3, in addition to starting materials, there was also 2.6% of a long retained product.

The product in tube 1 was separated by preparative gas chromatography (Si gum 110°) to yield the long retained product (0.29 g.) which was shown by infrared spectroscopy to be iodobenzene containing a minor impurity. The major long retained product in tube 3 corresponded by v.p.c. to bromobenzene.

Additions of Cyclopentadiene to Various Fluoroöolefins

Diels-Alder Addition of Cyclopentadiene and Perfluoropropene

A Fischer-Porter tube was charged with freshly distilled cyclopentadiene (2.06 g., 0.031 M) and hydroquinone (0.1 g.). Perfluoropropene (5.2 g., 0.035 M) was condensed into the tube under vacuum and the tube was heated at 170° for 117 hours. Unchanged perfluoropropene (1.5 g., 29%) was recovered and the residual liquid examined by gas chromatography to show ca. 91% Diels-Alder adduct, the other components being perfluoropropene and dicyclopentadiene (trace). The liquid was separated by gas chromatography (Si gum 100°) to give 5-trifluoromethyl-5,6-difluoronorborn-2-ene (1.0 g., 19%, based on unrecovered olefin) b.p. 140°; n_D^{20} 1.3774 (lit. b.p. 141°; n_D^{20} 1.3741), which was oxidized by an acetone solution of potassium permanganate and decolorised 3% bromine in carbon tetrachloride. The low recovery of Diels-Alder adduct may be due to poor gas chromatographic recovery but probably is due to the presence of a high percentage of involatile material in the product, such as the products of further Diels-Alder additions.

The proton n.m.r. spectrum of the simple adduct was typical of a 1,4-adduct (19).

Diels-Alder Addition of Cyclopentadiene and Perfluorobutene-2

A Fischer-Porter tube was charged with freshly distilled cyclopentadiene (2.0 g., 0.0303 M) and hydroquinone (0.1 g.). Perfluorobutene-2 (6.3 g., 0.0315 M) was condensed into the tube under vacuum and the mixture was heated on an oil bath at 146-156° for 69 hours. The Fischer-Porter tube leaked during the reaction and 1.0 g. of material was lost. Unchanged perfluorobutene-2 (0.05 g.) was recovered on opening the tube. The residual crude product (6.0 g.), which contained perfluorobutene-2 and traces of cyclopentadiene in addition to a main product of the suspected Diels-Alder adduct, was separated by gas chromatography (Si gum 100°) to yield 5,6-bis(trifluoromethyl)-5,6-difluoro-norborn-2-ene (4.0 g., 50% based on cyclopentadiene), $n_D^{22.5}$ 1.3655. Analysis calc'd. for $C_9H_6F_8$: C, 40.62; H, 2.27; F, 57.11. Found: C, 40.46; H, 2.26; F (by difference), 57.28%. The norbornene was oxidized by an acetone solution of potassium permanganate and decolorised a 3% bromine solution in carbon tetrachloride. It gave consistent infrared and ^{19}F n.m.r. spectra. The proton n.m.r. spectrum proved the adduct to be a Diels-Alder adduct rather than a 1,2-adduct (19).

A large scale experiment in a 300 ml. autoclave at 150° for 17 hr. gave an estimated 88% yield of product.

Attempted Dehalogenation of 5,6-Difluoro-5,6-bis(trifluoromethyl)norbornene

The norborn-2-ene (30.0 g.) was added dropwise over a period of 15 min. to a stirred suspension of zinc (12 g.) and zinc chloride (0.1 g.) in isopropanol (40 ml.). The refluxing was continued for a further 4 hr. No reaction was indicated by gas chromatography. A further 10 g. of zinc was added and the stirred mixture refluxed for 1.75 hr.

There was no apparent reaction. The zinc was filtered off and the filtrate fractionated to remove most of the isopropanol. The residue was separated by gas chromatography (Si gum 100°) to yield the norbornene (21.9 g., 73% recovery), as indicated by infrared spectroscopy.

Attempted Dehydrohalogenation of 5,6-Difluoro-5,6-bis(trifluoromethyl)norbornene

The norborn-2-ene (2.75 g.) was dropped on to molten potassium hydroxide (10 g.) at 220°. After refluxing for 1 min. the mixture was cooled, water was added and the organic layer separated to yield unchanged starting material (2.3 g., 84% recovery) as shown by gas chromatography and infrared spectroscopy.

Dechlorination of $CF_3CCl_2CCl_2CF_3$

A stirred suspension of zinc dust (150 g.) and zinc chloride (2-5 g.) in reagent grade dioxane (150 ml.) was brought to reflux in a 3-necked flask fitted with a 1 ft. fractionation column and head. The outlet of the fractionation head lead to a trap cooled at -78°.

A saturated solution of 2,2,3,3-tetrachlorohexafluorobutane (304 g.) in dioxane was added dropwise to the suspension at such a rate to give a steady reflux at the fractionation head, where the fraction boiling up to 72° was collected. Fractionation was continued after the chlorofluoroalkane had been added and the fraction up to b.p. 95° was collected.

The experiment was repeated with 196 g. of alkane and proportionate amounts of zinc, etc.

The distillates were combined and fractionated to give: $CF_3CCl{=}CClCF_3$ (368 g., 96% yield) containing small traces of a low boiling component and dioxane. 101.

Only traces of material condensed in the cooled (-78°) trap.

Addition of Cyclopentadiene to 2,3-Dichlorohexafluorobutene-2

Freshly distilled cyclopentadiene (19.8 g., 0.3 mole), 2,3-dichlorohexafluorobutene-2 (78.4 g., 0.336 mole) and hydroquinone (1.0 g.) were rocked in a 300 ml. autoclave at 145° for 16 hr.

The product was steam distilled. The distillate was an immiscible liquid at first, but soon a solid condensed. The condenser was changed to an air condenser which extended under iced water. The total organic distillate in ether (65.19 g.) contained 53% of the adduct by gas chromatographic peak area. Therefore estimated yield of adduct based on cyclopentadiene was 38.6%.

A sample was purified by gas chromatography (Si gum 110°) and dried by sublimation at 125° under reduced pressure to yield 5,6-dichloro-5,6-bis(trifluoromethyl)norborn-2-ene. Analysis for $C_9H_6Cl_2F_6$: C, 36.15; H, 2.02. Found: C, 35.91; H, 1.89%. The sublimate was easily oxidized by an acetone solution of potassium permanganate and slowly decolorised 3% bromine in carbon tetrachloride. The infrared spectrum showed very weak C-H absorption and C=C absorption could not be detected above the background noise. There was absorption at 7.7μ - 9.1μ attributable to C-F.

The proton n.m.r. spectrum in $CFCl_3$ solution was consistent with a 1,4 adduct. The ^{19}F n.m.r. spectral analysis is in progress.

Dechlorination of 5,6-Dichloro-5,6-bis(trifluoromethyl)-norborn-2-ene

(a) Magnesium Iodide

Iodine was dried by sublimation under reduced pressure. The norbornene (53% solution in ether) was dried over Drierite.

Iodine (0.41 g.), magnesium (1.94 g.) and dry ether (100 ml.) were refluxed for 0.5 hr. 5,6-Dichloro-5,6-bis(trifluoromethyl)norbone-2-ene (30 g. of a 53% solution in ether $\equiv$ 15.9 g. norbornene) was added to the refluxing mixture over a period of 5 min. Refluxing was continued for 8 hr. The magnesium turnings (2.07 g.) were filtered off and washed, but remained dull after repeated washings with ether.

The filtrate was distilled using a 6" Vigreux column to remove most of the ether. A gas chromatogram of the residue (27.22 g.) showed a trace of the dechlorination product, but starting material formed 59.7% of the mixture (from gas chromatogram peak area). This is equivalent to 16.2 g., therefore recovery of norbornene was quantitative.

(b)

Zinc powder was activated prior to use by washing with dilute hydrochloric acid, water, and acetone and drying on a vacuum line.

5,6-Dichloro-5,6-bis(trifluoromethyl)norborn-2-ene (30.0 g. of a 53% solution in ether $\equiv$ 15.9 g. norbornene) was added to a refluxing stirred suspension of activated zinc dust (5.0 g.) in isopropanol (50 ml.) over a period of 15 min. There was an apparent increase in reflux rate, but this may have been due to ether present. Refluxing and stirring were continued for a further 2 hr., when more activated zinc (4.0 g.) was added and the reaction continued for a further 3 hr.

A gas chromatogram of the filtered product showed a main peak corresponding to 2,3-bis(trifluoromethyl)norbornadiene. The product was fractionated (1' column) to yield a distillate (17.71 g.) containing 12.4% of the product. The residual liquid (52.64 g.) contained an estimated 10.95% of the dechlorination product.

A sample (3.30 g.) of the residual liquid was separated by gas chromatography (Si gum, 90°) to yield the dechlorination product 2,3-bis(trifluoromethyl)norbornadiene (0.51 g.) which had an identical infrared spectrum to an authentic sample (see later). Estimated yield of norbornadiene: 0.51 g. in 3.30 g. Therefore, residual liquid contains <u>ca</u>. 8.15 g. Distillate contains 12.4% ($\equiv$ 2.2 g.). Therefore, estimated yield = 10.35 g. = 86%.

Dechlorination of 2,3-Dichlorohexafluorobutene-2

2,3-Dichlorohexafluorobutene-2 (233 g., 1.0 mole) was dried over Drierite and added dropwise over a period of 3 hr. to a stirred refluxing suspension of zinc (85 g.) and zinc chloride (1 g.) in glacial acetic acid (200 ml.). The acetylene was collected through the top of the water condenser in an acetone/dry ice cooled trap. The reaction was continued for 2 hr. when more zinc (20 g.) was added and the reaction continued for a further 2 hr.

The material in the acetone/dry ice trap was distilled into another trap to yield hexafluorobutyne-2 (17.6 g., 35% yield based on unreacted olefin), which gave an infrared spectrum consistent with an authentic specimen.

The zinc dust was filtered from the liquid in the flask and the filtrate fractionated to yield 2,3-dichlorohexafluorobutene-2 (160.9 g.), which was contaminated with a small quantity of low boiling compound (probably a reduction product).

<u>Addition of Cyclopentadiene to Hexafluorobutyne-2</u>

Hydroquinone (0.2 g.) and freshly distilled cyclopentadiene (5.62 g., 0.085 mole) were weighed into a hard glass tube (<u>ca</u>. 100 ml. capacity). Hexafluorobutyne (17.6 g.) was condensed in, the tube sealed under vacuum and heated at 130° for 15 hr.

On opening the tube hexafluorobutyne (1.3 g.) distilled out and was identified by its infrared spectrum. A gas chromatogram of the residual liquid (22.71 g.) showed low boiling components, a main peak with a small shoulder and a trace of dicyclopentadiene.

Separation of 20.7 g. by gas chromatography (Si gum 104°) yielded (1) low boilers + (4) dicyclopentadiene, (3.37 g.) (2) main peak, 2,3-bis(trifluoromethyl)norbornadiene (14.48 g.). Analysis calc'd. for $C_9H_6F_6$: C, 47.38; H, 2.65; F, 49.97. Found: C, 47.43; H, 2.75; F (by difference), 49.82%. The pure product was easily oxidized by a potassium permanganate solution in acetone and decolorized a 3% bromine solution in carbon tetrachloride. The infrared spectrum showed moderate intensity absorption at 5.92µ which is consistent with $CF_3C{=}C{-}CF_3$, and C–H and C–F absorptions. The proton n.m.r. was completely consistent with a Diels-Alder adduct, (3) main peak residue + shoulder (0.41 g.), contained 77% of the norbornadiene. Total yield norbornadiene: 14.8 g., 76% (based on cyclopentadiene).

Addition of Cyclopentadiene to sym-Dichlorodifluoroethylene

A 300 ml. autoclave was charged with hydroquinone (1 g.), freshly distilled cyclopentadiene (33 g., 0.5 mole) and CFCl=CFCl (68 g., 0.51 mole) and heated at 165-170° for 65 hr. No low boiling products distilled out on opening the autoclave.

The black liquid product (96.7 g.) was steam distilled. The organic material (11.3 g.), distilling over after several hours, was a pure high boiling viscous liquid, which showed C–H, weak C=C and C–F absorptions in the infrared spectrum. This material partially solidified on standing.

The first part of the steam distillate was distilled under high vacuum to yield (1) a liquid (10.29 g.) containing 61.8% adduct, (2) pure adduct (3.27 g.), (3) a residue (21.62 g.) which contained only a trace of simple adduct. Therefore, estimated yield of simple adduct = 6.35 g. (from fraction 1) + 3.27 g. = 9.62 g. = 9.7% based on cyclopentadiene. Total yield of high boiling viscous products was 32.96 g.

A sample of the simple adduct was purified by gas chromatography to yield 5,6-dichloro-5,6-difluoronorborn-2-ene.

Analysis calc'd. for $C_7H_6Cl_2F_2$: C, 42.24; H, 3.04. Found: C, 42.54; H, 3.29%.

The infrared spectrum showed relatively strong C–H absorption and absorption attributable to C–F and C–Cl. The pure product was easily oxidized by an acetone solution of potassium permanganate and decolorized a 3% solution of bromine in carbon tetrachloride. The proton n.m.r. spectrum was completely consistent with a 1,4-(Diels-Alder) adduct. The ^{19}F n.m.r. spectrum was inconclusive.

Attempted Dehalogenation of 5,6-Dichloro-5,6-Difluoronorborn-2-ene

5,6-Dichloro-5,6-difluoronorborn-2-ene (12.5 g. of a 65% solution in ether $\equiv$ 8.1 g. norbornene) was added dropwise over a period of 10 min. to a stirred refluxing suspension of activated zinc (5 g.) in isopropanol (30 ml.). The reaction was continued for 1.5 hr. when additional activated zinc (5 g.) was added and the reaction continued for a further 3 hr. A chromatogram of the product showed only starting material and isopropanol. The product was filtered and fractionated. The first 1 ml. of distillate was pure isopropanol as was the remaining distillate. Most of the isopropanol was fractionated off to leave a residue (26.10 g.) of 45.6% norbornene in isopropanol. This is equivalent to 11.9 g. norbornene = 95% recovery of starting material.

Addition of Cyclopentadiene to Trifluoroethylene

A 300 ml. autoclave was charged with freshly distilled cyclopentadiene (33 g., 0.5 mole) and hydroquinone (1.0 g.).

Trifluoroethylene (44 g., 0.537 mole) was condensed under vacuum into the autoclave which was heated at 165° for 17 hr. On opening the autoclave trifluoroethylene (23.4 g., 53%) distilled out.

The residual liquid and ether washings were steam distilled to give an initial organic steam distillate (37.1 g.) and a later organic distillate which was a high boiling viscous liquid (8.25 g.) of at least three components. The initial steam distillate was distilled to give (1) ether + trace of adduct (5.54 g.), (2) adduct (3.58 g.) > 95% pure, (3) 4.68 g. containing 73.6% adduct, (4) 17.84 g. containing 28.6% adduct, (5) 2.38 g. of high boiling material containing trace of the simple adduct, (6) a small brown tarry residue. Estimated yield of simple adduct: 12.1 g. = 33% based on unrecovered olefin.

A sample of the adduct was separated by preparative gas chromatography (Si gum 95°) to yield 5,5,6-trifluoronorborn-2-ene. Analysis calc'd. for $C_7H_7F_3$: C, 56.75; H, 4.77; F, 38.48. Found: C, 56.91; H, 4.68%; F (by difference), 38.41%. The proton n.m.r. spectrum was inconclusive but the ^{19}F n.m.r. spectrum indicated a mixture of two isomers of the Diels-Alder adduct.

Attempted Dehydrofluorination of 5,5,6-Trifluoronorborn-2-ene

(a) Aqueous Potassium Hydroxide

The norbornene (ca. 8.52 g. in high boiling material, total wt. 22.54 g.) was refluxed for 4 hr. with aqueous potassium hydroxide (13 g. in 40 ml. H_2O). A gas chromatogram of the organic phase (20.98 g.) showed only starting materials.

(b) Aqueous Alcoholic Potassium Hydroxide

The norbornene mixture (19.46 g.) was added over a period of 20 min. to a refluxing solution of potassium hydroxide (10 g.) in ethanol (20 ml.) - water (5 ml.) solution. The mixture was refluxed for 7 hr. There was a considerable darkening of both phases. After normal work-up, an organic product (18.78 g.) containing 46% of the norbornene was recovered. Therefore recovery of starting material was quantitative. A gas chromatogram showed no dehydrofluorination product.

Addition of Cyclopentadiene to Chlorotrifluoroethylene

A 300 ml. autoclave was charged with hydroquinone (1.0 g.) and freshly distilled cyclopentadiene (41.96 g., 0.635 mole). Chlorotrifluoroethylene (76.5 g., 0.657 mole) was condensed under vacuum into the autoclave which was heated at 170° for 16 hr. On opening the autoclave low boiling material (0.4 g.) distilled out. The residual liquid (112.6 g.) was steam distilled to yield an organic distillate (68.7 g.), which was dried, and a residual brown viscous liquid (32.9 g.)

A sample (10.8 g.) of the steam distillate was separated by gas chromatography (Si gum 110°) to yield (1) low boiling components (not collected), (2) the adduct (4.56 g.). Therefore, yield of adduct is 26% based on cyclopentadiene, n_D^{23} 1.430 ± 0.001. Analysis calc'd. for $C_7H_6ClF_3$: C, 46.05; H, 3.31. Found: C, 46.26; H, 3.28%. The infrared spectrum showed medium C–H absorption, weak C=C absorption and absorption attributable to C–F and C–Cl. The proton and ^{19}F n.m.r. spectra suggested a mixture of at least four isomers, which were probably the isomers of the 1,4- and 1,2-adducts. On standing the adduct darkened.

Attempted Addition of Octafluorobutene-2 to Isopropenylacetylene

A 300 ml. autoclave was charged with hydroquinone (0.6 g.). Isopropenylacetylene (10.0 g.) was vacuum distilled into the autoclave followed by octafluorobutene-2 (42.3 g.). The autoclave was sealed under vacuum and heated at 120° for 16 hr.

On opening the autoclave, volatile material (44.8 g.) distilled out to leave a residual liquid which was greater than 95% isopropenylacetylene with a trace of higher boiling material. The isopropenylacetylene was allowed to evaporate to leave a small brown viscous liquid residue. Total recovery of starting material was 90%.

V. FUTURE WORK

The reaction of $CH_2=CBrCF_3$ with butyllithium to give $CH_2=CLiCF_3$ will be carried out. The organometallic reagent will be transformed into $CH_2=C=CF_2$ for U. S. Rubber and Peninsular ChemResearch, Inc. The reagent will also be used in further syntheses of various molecules containing the $CH_2=C(CF_3)-$ group.

Free radical reactions of allyl iodides with tetrafluoroethylene will be studied as a possible route for obtaining $CH_2=CHCH_2CF_2CF_2I$. It is hoped that the iodide will react with NO to give the corresponding nitroso compound.

The reaction of nitrosyl chloride with $CH_2=CHCH_2CF=CFCl$, $CH_2=CHCH_2CF=CFBr$ and $CF_2=CFCF_2CF=CF_2$ will be studied.

APPENDIX

The following compounds were prepared and shipped to U. S. Rubber:

α-Trifluoromethylstyrene (23 g.)

1,1,1-Trifluoropentadiene-2,4 (10 g.)

3-Acetoxy-3-trifluoromethylbutene-1 (43 g.)

5,6-Difluoro-5,6-bi (trifluoromethyl)norborn-2-ene (15 g.)

Crude 5,6-dichloro-5,6-difluoronorborn-2-ene (0 g.).

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Department of Chemistry, University of Florida, Gainesville, Florida. RESEARCH ON SYNTHESIS OF UNSATURATED FLUOROCARBON COMPOUNDS - Paul Tarrant, Doug Perry, Jai Tandon, Alan Wright, Susumu Misaki. March 31, 1966, 52 pp. (Semiannual Report 6) Unclassified Report. Work has continued on some aluminum chloride catalyzed additions of polyhaloalkanes to haloolefins. Additional work has been done using perfluoroallyl systems. Nitrosyl chloride has been allowed to react with some fluorodienes to give a nitroso derivative in one case (but to give a suspected Diels-Alder adduct when the diene was conjugated). Free radical additions of haloalkanes to various olefins have been attempted and in some cases reactions of the products investigated. The free radical addition of haloalkanes to aromatic nuclei has been continued and terminated. Some Diels-Alder additions between cyclopentadiene and some haloölefins has been effected, and the preparation of some fluoronorbornadienes from the products has been attempted.

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2. Elastomers

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14. KEY WORDS						
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Fluorochemicals	1,2					
Elastomers	2					
Nitroso rubber	2					
Unsaturated	0					

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13. ABSTRACT

Work has continued on some aluminum chloride catalyzed additions of polyhaloalkanes to haloolefins. Additional work has been done using perfluoroalkyl systems.

Nitrosyl chloride has been allowed to react with some fluorodienes to give a nitroso derivative in one case (but to give a suspected Diels-Alder adduct when the diene was conjugated).

Free radical additions of haloalkanes to various olefins have been attempted and in some cases reactions of the products investigated.

The free radical addition of haloalkanes to aromatic nuclei has been continued and terminated.

Some Diels-Alder additions between cyclopentadiene and some haloolefins have been effected, and the preparation of some fluoronorbornadienes from the products has been attempted.

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