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Perfluoroalkyl(aryl)acetylenes

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ABSTRACT. Methods of preparing perfluoroalkyl(aryl)acetylenes, their physical properties, and chemical reactivity have been reviewed. Synthetic routes to aliphatic, alicyclic, aromatic and heterocyclic compounds from perfluoroalkyl(aryl)acetylenes have also been examined.

The bibliography contains 361 references.

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I. Introduction

The study of fluorine-containing compounds is a key aspect of modern laboratory and industrial chemistry. Such compounds are placed in prominent position in the economies of the developing nations, and their varied structural types and unique properties are evident in the synthesis of such materials as fluorinated polymers, Freons, herbicides, drugs and dyes. The physiological activity of fluorine-containing compounds is so broad that they are used both medicinally and as highly toxic agents.

An enormous amount of data is available on fluorine-containing compounds, which has been reviewed in many well-known monograph series as well as in the journal literature.[1–4]

The chemistry of perfluoroalkyl(aryl)acetylenes has developed only in the last 40 years. Only the literature up to 1977 has been adequately reviewed,[5–7] while coverage of more recent information has been rather fragmentary.[8–10] This new field of organic chemistry has not been reviewed as an isolated topic.

In the present article we have sought to cover this field of chemistry with particular reference to the last ten years, which, as yet, has not been adequately studied as a review topic in the literature. We have excluded those properties of perfluoroalkyl-(aryl)-substituted acetylenes, such as oxidation and hydrogenation, which have already been analysed in depth in earlier reviews, and concentrated only on recent developments in this area; this review also excludes routine functional group interconversions involving this structural type. Information on the physical properties of the individual perfluoroalkyl(aryl)acetylenes, of which more than 300 are known to date, can be obtained from those references where synthetic details are reported.

II. Methods of preparation

Most synthetic routes to perfluoroalkyl(aryl)acetylenes are based on perfluoroalkyl(aryl) iodides which in many countries are commercially available and frequently used. Direct fluorination methods have been used to a lesser extent.

There are two classical multi-step routes to perfluoroalkyl-acetylenes. The first step in these methods is the addition of perfluoroalkyl iodides to olefins or acetylenes. The final step in the first method is dehalogenation of an intermediate perfluoro-dibromoalkene, which is normally carried out with zinc in ethanol or dimethyl sulfoxide.[11–13]

$$R_FCH_2CH_2Hal \xrightarrow{KOH,\ C_2H_5OH} R_FCH{=}CH_2 \xrightarrow{Br_2,\ h\nu}$$

$$\longrightarrow R_FCHBrCH_2Br \xrightarrow{KOH,\ C_2H_5OH} R_FCBr{=}CH_2 \xrightarrow{Br_2,\ h\nu}$$

$$\longrightarrow R_FCBr_2CH_2Br \xrightarrow{KOH,\ C_2H_5OH} R_FCBr{=}CHBr \xrightarrow{Zn} R_FC{\equiv}CH,$$

$R_F = CF_3,\ C_4F_9,\ C_6F_{13},\ C_8F_{17}.$

In certain countries perfluoroalkylethylenes are currently commercially available. They may be converted to perfluoroalkyl-acetylenes by an alternative scheme.[14,15]

$$\left.\begin{array}{l} R_FCH{=}CH_2 \xrightarrow{Cl_2,\ h\nu} R_FCCl_2CCl_3 \\ CCl_3CCl{=}CCl_2 \xrightarrow{SbF_3/SbF_5} CF_3CCl{=}CCl_2 \end{array}\right| \xrightarrow{Zn}$$

$$\longrightarrow [R_FC{\equiv}CZnCl + (R_FC{\equiv}C)_2Zn] \xrightarrow[H^+]{H_2O,} R_FC{\equiv}CH,$$

$R_F = CF_3,\ C_4F_9,\ C_6F_{13},\ C_8F_{17}.$

The debromination with zinc may be accompanied by partial prototropic isomerisation.[16]

Debromination of 1,3,3,3-tetrafluoro-1,2-dibromopropene with zinc in dioxane or with copper at 260 °C affords perfluoro-propyne.[17–19]

Dehalogenation is also the final step in the synthesis of perfluoro-2-butyne and other symmetrically substituted perfluoroacetylenes.[20–24]

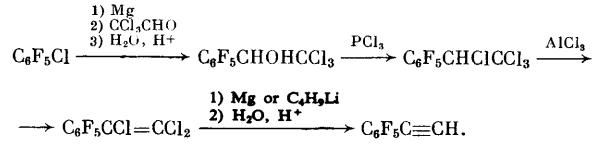
Trifluoromethylperfluoroalkoxyacetylenes have been prepared via elimination of BrCl with Zn/Cu couple in adiponitrile.[25]

$$F_3CC{\equiv}CCl \xrightarrow[H^+]{RCOF,\ AgF} \begin{array}{c} F_3C \quad\quad OCF_2R \\ \diagdown \quad / \\ C{=}C \\ / \quad \diagdown \\ H \quad\quad Cl \end{array} \xrightarrow{Br_2}$$

$$\longrightarrow F_3CCHBrCClBrOCF_2R \xrightarrow{(C_2H_5)_3N} F_3CCBr{=}CClOCF_2R \xrightarrow{Zn/Cu}$$

$$\longrightarrow F_3CC{\equiv}COCF_2R,\ R = F,\ C_2F_5.$$

Dehalogenation is also a key step in the synthesis of pentafluorophenylacetylene.[26,27]

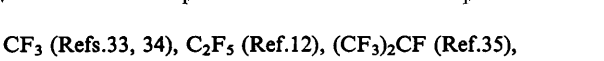


Chloropentafluorophenylacetylene is obtained if one equivalent of butyllithium is used in the last step instead of two equivalents.[27] A mixture of pentafluoro- and 2,3,5,6-tetrafluoro-phenylacetylene was obtained from the product formed by treatment of acetophenone with PCl_5.[28]

Reaction of pentafluorophenyllithium with alkenyl halides affords chloropentafluorophenylacetylenes (from CFCl=CFCl or CF_2=CHCl) and decafluorotolan (from CF_2=CFH or CF_2=CFBr). In this case, dehalogenation is accompanied by nucleophilic substitution of fluorine in the *p*-position, as a result of which tolan derivatives are formed with either one or two 2,3,5,6-tetrafluorophenyl rings.[29]

Treatment of pentafluorophenylcopper with iodotrifluoroethylene to give decafluorotolan is also accompanied by dehalogenation,[30] as well as by action of copper on pentafluorophenyltribromomethane at 570 °C (70% yield).[31]

Methods of preparing fluorine-containing alkynes by dehydrohalogenation of (a) (perfluoroalkyl)alkenyl halides, obtained normally by radical addition of perfluoroalkyl iodides to alkynes, or (b) dihalogenated perfluoroalkanes, obtained from the corresponding alkenes, are limited by the nature of the perfluoroalkyl (or perfluoroaryl) substituent.[32] Thus, in spite of the fact that the number of steps is normally smaller, such dehydrohalogenative methods are not always preferred to the dehalogenative routes described above. Anhydrous base or ethanolic base (with cooling) or trialkylamines have been used as dehalogenating agent.[13,33–35]



R_F=CF_3 (Refs.33, 34), C_2F_5 (Ref.12), $(CF_3)_2CF$ (Ref.35),

C_nF_{2n+1} (n=4, 6, 8) (Ref.13).

There was no increase in the yield of perfluoroalkylacetylenes with KF/18-crown-6-ether as dehydroiodinating agent.[36]

Dehydroiodination of 4,4,4-trifluoro-2-iodo-1-butene with alcoholic KOH gives a 1:2 mixture of the corresponding acetylene and allene.[37] Hexafluoro-2-butyne,[38,39] perfluoro-2,5-dimethyl-3-hexyne,[40] perfluoroalkylated acetylene-alcohols[41–43] and -thioethers,[44] and α-halogenoperfluoroalkylacetylenes[18,45] have all been prepared by dehydrohalogenation with alcoholic KOH or anhydrous base.

Perfluoroacetylenic tertiary alcohols, $R_2C(OH)C{\equiv}CR_F$ (R_F = C_4F_9, C_6F_{13}, C_8F_{17}), have been prepared by dehydroiodination of the corresponding iodides and converted to the corresponding perfluoroalkylacetylenes by Favorskii cleavage.[42,46,47]

Aryltrifluoromethylacetylenes[48] have been isolated in 65–78% yield by 2-step dehydrobromination of 3,3,3-trifluoro-1,2-dibromo-1-arylpropanes, and *bis*(trifluoromethyl)trifluoropropynylamine has been prepared by 2-step dehydrobromination of *N,N-bis*(trifluoromethyl)-3,3,3-trifluoro-1,2-dibromopropylamine.[49]

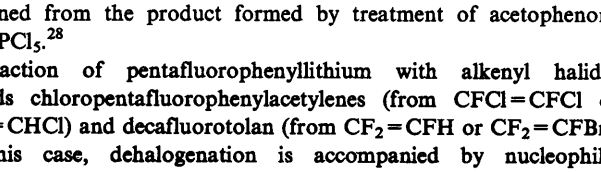
Aryltrifluoromethylacetylenes with a variety of substituents in the benzene ring have been synthesised under mild conditions. The dehydrochlorination in the second step has been carried out with $NaNH_2$ in *tert*-butanol/benzene at room temperature.[50,51]



R=X-C_6H_4, X=4-Cl, 2-Cl, 4-OCH_3, 4-NH_2, 4-C_6H_5; 3-pyridyl, 1-naphthyl and others.

In certain cases, dehydrohalogenation is accompanied by decarboxylation. Treatment of perfluoroalkylacetyl chlorides with strong base leads to perfluoroalkylacetylenes.[52]

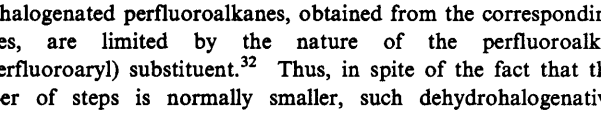
In an alternative synthesis, treatment of perfluorocarboxylic acid chlorides with triethyl phosphite leads to perfluoroalkylacetylenes with the same number of carbon atoms (60–66% yield).[53]



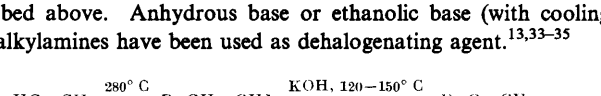
R_F = C_2F_5, C_6F_{13}, C_8F_{17}, $HCF_2(CF_2)_8$.

Aldol-type adducts are formed if the dephosphonylation is carried out in the presence of aldehydes[53] or their trimethylsilyl enol ethers.[54]

A new route to perfluoroalkylacetylenes is based on radical addition of perfluoroalkyl iodides to trimethylethynylsilanes in the presence of *tert*-butyl peroxide at 120 °C, followed by dehydroiodination and desilylation with potassium *tert*-butoxide at –20 °C. The yield exceeds 90%.[55]



Non-conjugated perfluorodiacetylenes are obtained by this method if the starting material is a diiodoperfluoroalkane:[55]

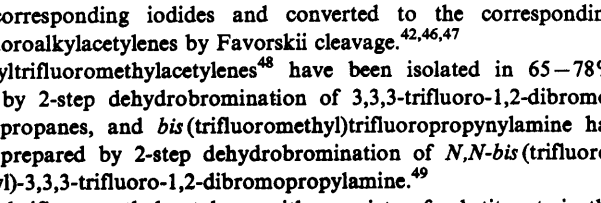


n = 2, 4, 6, 8, 10, 12.

The same products are obtainable from *bis*(trimethylsilyl)acetylene.

Organometallic compounds have also been widely used in the synthesis of perfluoroalkyl(aryl)acetylenes. There are two possible routes: one based on perfluoroalkyl(aryl) halides with intermediate formation of organometallic compounds, and the other based on alkylation of non-fluorinated acetylides with perfluoroalkyl(aryl) halides. Substituted and functionalised perfluoroalkyl(aryl)acetylenes are often obtained from perfluoroalkyl(aryl)acetylides. Such routes differ in the choice of the starting metal and the conditions. Organo-magnesium or -lithium compounds are normally used, although in certain cases the best results are obtained with organocopper, -zinc or -tin compounds.

Thus, perfluoroalkylacetylenes are prepared in up to 70% yield by the following scheme:[56,57]



R_F=C_4F_9, C_6F_{13}; R=C_2H_5, C_4H_9, C_8H_{17}, C_6H_5, *o*-$CH_3C_6H_4$, $CH_2CH{=}CH_2$.

The somewhat unexpected initial stages of this reaction, as proposed by the authors, was confirmed by the ultimate formation of $R_FCF=CHF$ on hydrolytic work-up.

Perfluorotolan was obtained in 56% yield by reaction of pentafluorophenylmagnesium bromide with diiodoacetylene in the presence of $CoCl_2$.[58]

Treatment of α-halogenoacetylenes with perfluoroalkyl(aryl)-copper reagents affords the corresponding perfluoroalkyl(aryl)-acetylenes.[59–61]

The interaction of hexafluorobenzene with lithium or magnesium acetylides proceeds with replacement of one or two fluorine atoms to give a mixture of perfluorophenylacetylenes.[61–63] Such reactions are facilitated by the addition of cerium and ytterbium salts.[63] *p-Bis*-(ethynyl)tetrafluorobenzene, for example, is obtained as follows:[61]

$$(C_2H_5)_3SiC\equiv CH \xrightarrow{C_6F_6} p\text{-}(C_2H_5)_3SiC\equiv CC_6F_4C\equiv CSi(C_2H_5)_3 \xrightarrow[H_2O/CH_3OH]{NaOH} \rightarrow p\text{-}HC\equiv CC_6F_4C\equiv CH.$$

The same product is formed by treatment of trimethylsilylacetylene with bromo(iodo)pentafluorobenzene in the presence of Pd(0) and Cu(I).[64]

$PdCl_2-CuI$ may be used effectively in the reaction of iodoperfluorobenzene with terminal acetylenes.[65,66]

$$p\text{-}RC_6F_4X + HC\equiv CR' \xrightarrow{PdCl_2[(C_6H_5)_3P]_2,\ CuI} p\text{-}RC_6F_4C\equiv CR'$$

X = I, Br; R = F, OCH_3, $N(CH_3)_2$ etc.;
R' = C_6H_4X', X' = H, *p*-CO_2CH_3, *p*-NO_2;
$Si(C_2H_5)_3$; $(CH_2)_nCH_3$, $n=2-5$, etc.

Treatment of pentafluorochlorobenzene with lithium alkyl- or phenylacetylides affords the corresponding *p*-chlorotetrafluorophenylacetylenes.[67] Thus, reaction takes place by preferential replacement of fluorine not chlorine.

Coupling of lithium and magnesium acetylides may proceed with perfluoroalkyl(phenyl)iodonium triflates in place of perfluoroalkyl halides.[68] The highest yield was recorded for n = 8.

$$RC\equiv CM \xrightarrow[-78 \text{ to } -30\ ^\circ C,\ THF]{R_FI(C_6H_5)OSO_2CF_3} RC\equiv CR_F,\ M = Li,\ MgX;\ R_F = C_nF_{2n+1},$$

n = 2, 3, 6, 8; R = C_6H_5, C_6H_{13-n}.

The interaction of pentafluoroiodobenzene and 4-substituted tetrafluoroiodobenzenes with cuprous 3-(tetrahydropyran-2-yloxy)-prop-1-ynide in pyridine affords the corresponding fluorophenyl-substituted propargyl alcohols which are converted to the corresponding terminal acetylene derivatives on oxidation with NiO_2.[69]

$$p\text{-}RC_6F_4I + CuC\equiv CCH_2-O-\text{(THP)} \longrightarrow \rightarrow p\text{-}RC_6F_4C\equiv CCH_2OH \rightarrow p\text{-}RC_6F_4C\equiv CH,$$

R = F, H, CH_3, CF_3, OCH_3, NH_2, $N(CH_3)_2$.

Reaction of perfluoroalkyl iodides with trimethylstannylacetylenes proceeds on UV irradiation in the presence of azodiisobutyronitrile or transition metal complexes to give perfluoroalkylacetylenes.[70–73]

$$R_FI + (CH_3)_3SnC\equiv CR \rightarrow R_FC\equiv CR,$$
$$R_F = CF_3,\ C_3F_7,\ CF(CF_3)_2,\ C_4F_9,\ C_6F_{13};$$
$$R = C(CH_3)_3,\ C_6H_{13},\ C_6H_5,\ Sn(CH_3)_3,\ C\equiv CSn(CH_3)_3.$$

Iotsich reagents prepared from perfluoroalkyl(aryl)acetylenes have been used in the synthesis of allyltrifluoromethylacetylenes,[74] propargyltrifluoromethylacetylenes,[75,76] pentafluorophenyl-*tert*-butylacetylene,[77] acetylenic alcohols[78,79] and α-halogenoacetylenes,[80] as well as a number of elementoorganic compounds.[77,81–85] for example:

$$R_FC\equiv CMgX + R_nEX \rightarrow R_FC\equiv CER_n,$$

$R_F = CF_3$, C_6F_5; E = Si, Ge, Sn, As; R = CH_3, C_2H_5, C_3H_7, C_4H_9.

Lithium perfluoroalkylacetylides are more effective than the corresponding magnesium acetylides in certain cases.[86–89] Thus, lithium perfluoroalkylacetylides have been used for the preparation of a number of primary, secondary and tertiary acetylenic[27,42,86,87] and non-conjugated diacetylenic alcohols,[87] as well as certain perfluoroalkyl(aryl)acetylenic acids or esters[27,88,89,90] and the corresponding phosphine and arsine derivatives.[91]

Zinc perfluoroalkylacetylides[15,92] may also be used for the synthesis of perfluoroalkyl compounds, notably aryltrifluoromethylacetylenes,[92] α-halogenotrifluoromethylacetylenes,[25,93] vinylperfluoroalkylacetylenes,[94] and *bis*(trifluoromethyl)diacetylenes.[93]

Perfluoroalkyl(aryl)alkynylstannanes have been used to prepare perfluoroalkyl(aryl)alkynyl-silanes and -germanes in >90% yield.[95–97]

$$R_FC\equiv CSnR_3 + R'_3EX \xrightarrow[HMPT]{80\ ^\circ C} R_FC\equiv CER'_3 - R_3SnX,$$

E = Si, Ge; X = Cl, Br.

Reaction does not take place in the absence of solvent.[98] Specific solvating effects are responsible for polarisation of the E–X and Sn–C bonds in the starting materials.[96,99,100]

A similar reaction has been used for the replacement of one acetylenic stannyl group by another (trans-stannylation),[101,103] and for the synthesis of α-halogenoacetylenes.[104]

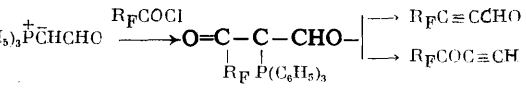
Trifluoromethylacetylene was prepared as long ago as 1959 by treatment of propiolic acid with SF_4 (60% yield).[105] Hexafluoro-2-butyne was obtained similarly by treatment of acetylenedicarboxylic acid with SF_4.[106] However extension of this method to other perfluoroalkylacetylenes is limited since the corresponding acetylenic acids are not readily available.

The intramolecular Wittig reaction, which is a well-known route to a variety of acetylenes,[107,108] has been applied to the synthesis of perfluoroalkyl(aryl)acetylenes as well as a number of functionalised derivatives: aryltrifluoromethylacetylenes,[109,110] perfluoroalkylpentafluorophenylacetylenes,[111] *bis*(pentafluorophenyl)acetylene,[112] aryloxyperfluoroalkylacetylenes,[113] arylthiotrifluoromethylacetylenes,[114] α-thienylperfluoroalkylacetylene,[115] perfluoroalkylacetylenic aldehydes and ketones,[116,117] esters,[118] thioesters,[119] and nitriles,[120] perfluoroalkylacetylenic acids and perfluoroalkylacetylenic phosphonates.[121] This is illustrated by the synthesis of thioester derivatives:[119]

$$(C_6H_5)_3P + BrCH_2CSCH_3 \longrightarrow [(C_6H_5)_3\overset{+}{P}CH_2CSCH_3]Br^- \xrightarrow{NaOH} \rightarrow (C_6H_5)_3\overset{+}{P}\overset{-}{C}HCSCH_3 \xrightarrow{R_FCOCl} (C_6H_5)_3\overset{+}{P}-C(-O-C(=O)-R_F)=C(-SCH_3)=O \xrightarrow[-(C_6H_5)_3PO]{180-220\ ^\circ C} \rightarrow R_FC\equiv CC(=O)SCH_3$$

$R_F = C_2F_5$, C_3F_7, C_7F_{15} etc.

On hydrolysis of C-perfluoroacylformylmethylenetriphenylphosphoranes, the corresponding aldehydes and ketones are obtained in approximately equal amounts. In this case, the reaction proceeds in two directions as a result of charge delocalisation.[116]



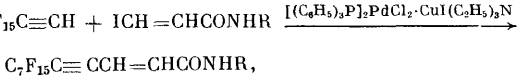
$R_F = CF_3$, C_2F_5, n-C_3H_7.

Perfluoroalkyl(aryl)acetylenes are also formed on hydrolysis of perfluoroalkyl(aryl)-substituted triazines[122] and pyridazines.[123,124] The latter are obtained by a multistep route from readily available tetrafluoropyridazine.[125] Yields are not high by this route, but it is interesting in that a variety of perfluoroalkyl groups can be introduced from accessible starting materials.

There is also reference in the literature to the formation of perfluoroalkylacetylenes by pyrolytic processes. For example, hexafluoro-2-butyne is obtained in high yield by pyrolysis of perfluorocyclobutene in a flow system over CsF or KF at 510–590 °C.[126] Perfluoroalkynes are formed by pyrolysis of various sodium perfluoroalkenoates,[127,128] as well as by pyrolysis or photolysis of certain sulphur-containing three- and five-membered heterocyclics.[129]

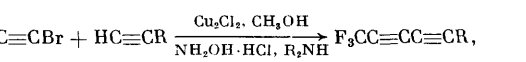
Trifluoromethylarylacetylenes may also be prepared by replacement of halogen by fluorine in trihalogenomethylacetylenes.[130]

Catalysts play an important role in the conversion of terminal acetylene derivatives to acetylenes containing two conjugated or non-conjugated multiple bonds. Conjugated enynes were thus obtained in the presence of a palladium catalyst:[47]



$R = CH_2CH(CH_3)_2$.

In recent years the Cadiot-Chodkiewicz reaction has been generally applied to the synthesis of conjugated trifluoromethyldiynes, as illustrated in the following variant:[131,133]



$R = CH(CH_3)_2$, $C(CH_3)_3$, $C(OH)(CH_3)_2$.

The yield (around 35%) is lower than in the preparation of simple, non-fluorinated, diynes since the resulting fluorinated diyne reacts to some extent with the nucleophiles (amines, methanol) which are present in the medium. Attempts to conduct this reaction under different conditions, notably by using alkylbromoacetylenes and trifluoropropynes, have been unsuccessful.

The first member of this class of perfluoroalkyldiyne—hexafluoro-2,4-hexadiyne—has been prepared by oxidative dimerisation of zinctrifluoromethylacetylide with $CuCl_2$ in dimethylformamide.[93]

A number of *bis*(perfluoroaryl)-1,3-butadiynes (including *p*-substituted derivatives) has been obtained by oxidative dimerisation in the presence of $CuCl_2$ or NiO_2.[61,66,69,134]

III. Characteristic physical properties

Many of the physical properties of perfluoroalkyl(aryl)acetylenes are typical of fluorine-containing compounds in general. By comparison with non-fluorinated acetylenes having the same number of carbon atoms, the boiling points and refractive indices are lower and the density is somewhat higher.[16,17,24,74,91,93,131–133]

The stereochemistry of certain perfluoroalkyl(aryl)acetylenes has been determined by gas-phase electron diffraction, microwave spectroscopy[135–145] and X-ray analysis.[146] The calculated C–C and C≡C bond lengths are in no way anomalous by comparison with those of simple alkynes.

The high polarity of unsymmetrically substituted perfluoroalkyl-(aryl)acetylenes is a result of the high electron-accepting property of the perfluoroalkyl and perfluoroaryl groups.[77,104,132,133,147–149] Perfluoroalkyldicetylenes have an unusually high polarity by comparison with non-fluorinated analogues (~3.8 D).[132,133,149]

The UV spectra of several perfluoroalkyl(aryl)acetylenes have been recorded.[29,58,62,93,112,150,151]

By comparing the IR spectra of perfluoroalkyl(aryl)acetylenes with those of non-fluorinated analogues, it is notable that the triple bond absorption in the former compounds is very high as a consequence of the high polarity.[17,25,35,48,55,61,74,93,123,131–133,143,151–158] The value of this absorption is shifted some 20–40 cm^{-1} into the short-wavelength region. By comparing the IR spectra of α-halogenotrifluoromethylacetylenes, the absorption of the triple bond is shifted into the long-wavelength region on passing from chlorine to iodine. The force constants for these compounds have been calculated.[156,157] The Δν(OH) shift values for phenol on complex formation with the triple bond of $Me_3MC{\equiv}CC_6H_5$ and $Me_3MC{\equiv}CC_6F_5$ increase in each case in the order M = C, Si, Ge, Sn, although the spectral shift in the spectra of the latter compounds is approximately half.[159]

Microwave[5,135,143,160] and infrared[143,155–157] spectral data have also been obtained for a number of trifluoromethylacetylenes.

In the ^{19}F NMR spectra the signals of the ^{19}F atoms in the trifluoromethyl group depend on the position of fluorine in the molecule. In the spectra of trifluoroalkanes, the signals are in the region 2–6 p.p.m.; for trifluoromethylethylenes they are in the region 10–15 p.p.m., and for trifluoromethylacetylenes in the region 25–29 p.p.m. (using CF_3COOH as standard).[161] Thus in acetylene derivatives the fluorine atom is least shielded.[5,15,17,18,35,74,93,123,131–133,143] The change in the chemical shift of the fluorine nucleus in the α-position relative to the triple bond is around 1.8 p.p.m. and is dependent on the polarity of the solvent.[162,163]

By comparing the ^{19}F NMR spectra of stannanes substituted with one to four $C{\equiv}C{-}C_6F_5$ groups, the chemical shift of the ^{19}F nucleus decreases with increase in the number of $C{\equiv}C{-}C_6F_5$ groups with a corresponding increase in the coupling constant from 2.4 to 3.5 Hz. This is in accord with the distribution of the electron density in the benzene ring.[84,164]

In the ^1H NMR spectra the signals of the hydrogen atom at the acetylene terminus are almost identical with those of non-fluorinated analogues. The signals from the protons of the CH_3 and CH_2 groups in the α-position relative to the triple bond are split (~4 Hz) as a result of remote interaction of the fluorine atoms through the triple bond; for the protons of the methine group in the spectra of 1,1,1-trifluoro-6-methyl-2,4-heptadiyne the value is ~1.2 Hz.[5,35,74,75,132,165]

In studying the chemistry of perfluoroalkyl(aryl)acetylenes, particular attention has been paid to their ^{13}C NMR spectra since the position of the signals from the carbon atoms is an indication of the distribution of electron-density in the molecule. The shielding of the carbon atoms of the triple bond is quite the reverse when a trifluoromethyl group is appended, by comparison with the shielding in the non-fluorinated analogue. This is an indication of an increase

in the polarisation of the triple bond in perfluorinated acetylenes.[149,165] Replacement of hydrogen in 3,3,3-trifluoropropyne by chlorine significantly affects the distribution of electron density. In unsymmetrical diynes the polarisation of a non-trifluoromethylated triple bond is the same as in the corresponding non-fluorinated diyne.[149]

The values of the spin-spin coupling constants for the C–F bond in the spectra of trifluoromethylacetylenes are as follows: $J_{CF}(CF_3)$ 256.9 Hz, $J_{C(1)F}$ 53–55 Hz, $J_{C(2)F}$ 6.5–7 Hz.[17,18,149,165,166]

The ^{13}C chemical shifts and spin-spin coupling constants have also been determined for perfluoropentylacetylene[167] and β-substituted trimethylethynyl-stannanes and -silanes containing CF_3 and C_6F_5 groups.[168,169]

A study has also been made of the photo-electron spectra of a number of trifluoromethylacetylenes, $CF_3C{\equiv}CX$ (where X = H, CF_3, $C{\equiv}CF$, Br, I, CN, SF_5,[170–173] $C(CH_3)_3$, $Si(CH_3)_3$ and $Ge(CH_3)_3$,[150,174,175] and of the X-ray spectrum of hexafluoro-2-butyne (300–800 eV).[176]

Electron-impact mass spectra have been recorded for many perfluoroalkyl(aryl)acetylenes and perfluorinated diynes.[17,19,30,89,91,132,143,153,155,177–183] Characteristically, the intensity of the molecular ion is less than that of non-fluorinated alkynes and alkadiynes. In most spectra the $[M-CF_3]^+$ ion is the most intense. The $[M-F]^+$ ion is also characteristic. ΔHf(g.) values (found or calculated) for the ion $[CF_3C{\equiv}CE(CH_3)_2]^+$ (E = C, Si, Ge, Sn) have been derived from the energy of the $[M-CF_3]^+$ ion as recorded by photoionisation mass-spectrometry. It has been shown that the CF_3 group has a similar stabilising effect to the cyano group in the analogous cation.[182] The introduction of a CF_3 group into the molecule increases the π-orbital ionisation potential (9.59 eV for 2-butyne and 12.36 eV for hexafluoro-2-butyne).[183]

Studies have also been made of the mass spectrum of negative ions from hexafluorobutyne.[184,185]

Quantum chemical calculations are also available for perfluoroalkyl(aryl)acetylenes and perfluorinated diynes.[109,144,147,149,186–191] Although independently computed data for σ- and π-charge density are not entirely consistent from one study to another, the calculations do confirm the charge distribution as determined from the $\delta(C^{13})$ chemical shift values.[149]

For complexes formed between acetylene derivatives of the type $R_FC{\equiv}CSnMe_3$ (R_F = CF_3, C_6F_5) and electron-donating solvents the stability constants decrease in the order: hexamethylphosphoramide > methyl tetramethylphosphorodiamidate > dimethyl sulfoxide > pyridine > acetonitrile > acetone.[85,192,193]

IV. Chemical properties

Normally, a mechanistic criterion is used as the basis for the classification of the chemical conversions of organic compounds. However, with perfluoroalkyl(aryl)acetylenes, reaction mechanisms have only been established with certainty in a few cases. Thus, in the present article, we have based the classification on the most likely mechanism, taking account of the nature of the reagent and the reaction conditions.

The polarisation of the triple bond by the perfluoro-alkyl or -aryl group largely determines the reactivity of perfluoroalkyl(aryl)-acetylenes. These groups are strong electron acceptors, primarily as a consequence of their inductive effect. The effect of the CF_3 group is readily transmitted through double and triple bonds, the $CF_3C{\equiv}C$ group being a stronger electron acceptor than the $CF_3CH{=}CH$ group and significantly greater in this respect than the CF_3 group.[8] By comparing the orientation of addition of nucleophiles to the system $CF_3CH{=}CHX$ where X is also an electron-accepting group), the relative electron-accepting effect of the CF_3 group is in the order: 2 × CF_3 > COOH > CF_3.[194] A comparison of the electron-accepting effect of the CF_3 group with that of other groups has been made elsewhere.[195] The CH-acidity of terminal acetylenes substituted by perfluoroalkyl groups is clearly greater (by a factor of *ca.* 2) than that of non-fluorinated terminal acetylenes.[78]

1. Electrophilic addition

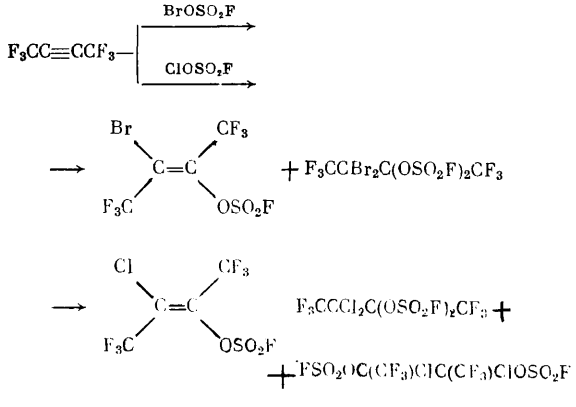
In their addition reactions, alkynes are less nucleophilic than alkenes,[196] and with perfluoroalkyl or perfluoroaryl substitution the nucleophilicity of the triple bond is even lower. Thus, electrophilic reagents do not readily react with perfluoroalkyl(aryl)acetylenes.

There are several reports on the interaction of perfluoroalkyl-(aryl)acetylenes with halogens in the absence of radical initiators or irradiation. However, strictly speaking, such reactions cannot be classified as electrophilic additions.[26,33,58,93,197]

Quite recently, information was published on the conjugate electrophilic addition of I_2 and mixed halides and pseudohalides—ClI, BrI, and ICN—to terminal perfluoroalkylacetylenes. Here, there is a sharp contrast with the results obtained on the interaction of other electrophiles to such compounds.[198] Electrophilic iodine attacks the terminal carbon atom. This fact is very important to the theory of addition to multiple bonds and can only be explained by a different mechanism of addition (via a carbenium or onium ion). Thus, in such polarised compounds hydrogen and halogen may attack different carbon atoms. There have been a few reports in the literature which substantiate this fact.[199]

Bromine adds to propargyltrifluoromethylacetylene at the mono-substituted acetylene group, while addition to the non-fluorinated analogue—propargylmethylacetylene takes place at the disubstituted acetylene group.[75] Allyltrifluoromethylacetylene and its homologues are brominated at the double bond (at –15 °C), as would be expected.[74]

Below –20 °C hexafluoro-2-butyne reacts with chlorine and bromine fluorosulphate to give the corresponding *trans*-monoadducts (in 38.8 and 34.9% yield) together with products formed as a result of addition of two molecules of the fluorosulphate: with $ClOSO_2F$ the di-adduct is a 3:2 mixture of regioisomers while that formed from two molecules of $BrOSO_2F$ is a single regioisomer:[200]



Trifluoromethylacetylene is more reactive towards hydrogen halides than trifluoromethylethylene,[78,201] just as non-fluorinated acetylenes react more smoothly than ethylenes. Trifluoromethyl-acetylene adds hydrogen halides under comparatively mild conditions

in accordance with the polarisation of the multiple bond, i.e. in the same manner as hydrogen halides add to the analogous perfluoromethylethylenes.[78,202]

The rate of addition of HBr and HI is significantly enhanced in the presence of aluminium halides as catalyst, under which conditions an electrophilic mechanism clearly obtains.

Hydrogen chloride adds to 1,1,1-trifluoro-2-butyne in the presence of $AlCl_3$ to give 1,1,1-trifluoro-2-chloro-2-butene.[16]

The addition of hydrogen halides to hexafluoro-2-butyne is considerably slower and requires (except with HF) a catalyst which promotes electrophilic addition, such as an aluminium halide.[24,202]

Hydrobromination of $CF_3C{\equiv}CN(CF_3)_2$ in the presence of $AlBr_3$ in the dark gives [*Z*]-2-bromo-3,3,3-trifluoroprop-1-enyl-*N*,*N*-*bis*-(trifluoromethyl)amine together with 7% of the regioisomer as an impurity.[197] The regioselectivity of the addition of HBr is explained by the fact that the amine forms with $AlBr_3$ a stable complex in which the polarisation of the triple bond is in the reverse direction by comparison with the uncomplexed amine.

Both geometrical isomers of $F_3CCBr{=}CHSF_5$ are formed by addition of $BrSF_5$ to 3,3,3-trifluoropropyne at 100 °C. However, the mechanism of this reaction has not been established.[44,203]

In the presence of a catalyst, substituted allyltrifluoromethylacetylenes add HBr only across the double bond, the regioselectivity of the reaction depending on the structure of substrate in such a way that the more stable carbonium ion is formed in the initial step.[204]

$$F_3CC{\equiv}CCH_2C(CH_3){=}CH_2 \xrightarrow{HBr} F_3CC{\equiv}CCH_2CBr(CH_3)_2,$$

$$F_3CC{\equiv}CCH_2CH{=}C(CH_3)_2 \xrightarrow{HBr} F_3CC{\equiv}CCH_2CH_2CBr(CH_3)_2$$

3,3,3-Trifluoropropyne is not hydrated with dilute H_2SO_4 at 100 °C. Trifluoroacetone is formed in low yield (19%) on treatment with $HgSO_4$ in water at 130 °C. Under the conditions of the Kucherov reaction (in the presence of $HgSO_4$ and H_2SO_4) a 1:2 mixture of the corresponding aldehyde and ketone is obtained at room temperature.[12] Under similar conditions 1,1,1-trifluorobutyne affords 4,4,4-trifluoro-2-butanone,[16] while perfluorohexylacetylene gives $C_6F_{13}COCH_3$.[205]

Hexafluoro-2-butyne is hydrated without a catalyst in sulfolane at 110 °C to give 1,1,1,4,4,4-hexafluorobutanone in high yield.[206]

Pentafluorophenylacetylene is hydrated very slowly under the Kucherov conditions with the formation of pentafluoroacetophenone (8% yield over 8 days).[26] *p*-amino-β,β,β-trifluoropropiophenone is obtained by hydrolysis of *p*-(trifluoropropynyl)phenyl isocyanate.[48]

Catalytic hydration can only be considered as an electrophilic process in a formal sense.

2. Reactions with nucleophilic reagents

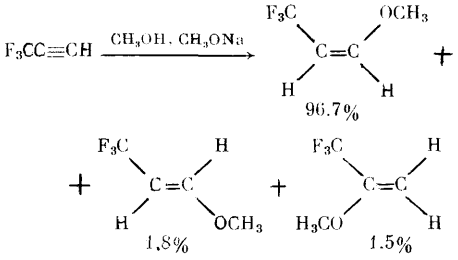
Nucleophilic addition is more characteristic of perfluoroalkylacetylenes since the R_F group significantly enhances the electrophilic character of the triple bond.

a) Addition of *O*-nucleophiles

Studies have been made of the addition of alcohols, phenol and organic acids of perfluoroalkylacetylenes. Non-fluorinated alkynes add such *O*-nucleophiles only in the presence of a catalyst on prolonged heating.[196] Perfluoroalkyl(aryl)acetylenes react with *O*-nucleophiles in the absence of catalyst on moderate heating or at room temperature in the presence of a catalyst.

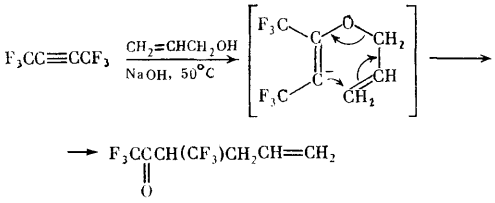
3,3,3-Trifluoropropyne does not add water either in the presence or absence of base. However, hexafluoro-2-butyne adds water in the presence of trimethylamine at room temperature with the predominant formation of *bis*(hexafluoro-2-butenyl) ether.[207]

Alcohols are added to 3,3,3-trifluoropropyne only in the presence of alkoxide or triethylamine at room temperature or lower to give the corresponding *Z*-propenyl ethers.[78,202,208]



In contrast to 3,3,3-trifluoropropyne, hexafluoro-2-butyne adds alcohols in the absence of catalyst at 95–100 °C. The proportion of (*Z*)- and (*E*)-enol ethers which are formed depends significantly on the nature of the solvent: without solvent the (*Z*)-isomers predominate, while in ether or sulfolane the (*E*)-isomers are principally formed (independent of the nature of the alcohol).[206] The (*Z*)-isomers are obtained almost exclusively on treatment with base, independent of the temperature and the nature of the solvent. On increasing the molecular weight of the alcohol, the proportion of (*E*)-isomer increases slightly.[206] There is a detailed discussion in the literature on the effect of the reaction conditions on the mechanism of this reaction.[206,208]

Allyl alcohol adds to hexafluoro-2-butyne with allyl rearrangement:[209]



Bis(pentafluorophenyl)actylene does not add methanol in the presence of NaOH: reaction proceeds by replacement of both *p*-fluoro atoms by an alkoxy group.[58] Such substitution by nucleophilic reagents is characteristic of perfluoroarylacetylenes.[66,69,190]

The addition of phenol to trifluoromethylacetylene in the presence of potassium *tert*-butoxide in alcoholic media at 25 °C (under kinetic control), or on heating at 150 °C (under thermodynamic control) leads to the exclusive formation of the corresponding (*Z*)-enol ether, as would be expected on the groups of polarisation of the triple bond.[210,211]

Acetic acids adds to hexafluoro-2-butyne in the same way as alcohols on heating at 60–100 °C (in the presence of sodium acetate as catalyst) to give the corresponding mono- and di-esters.[212] Dialkyl phosphites and thiophosphites also add to a variety of perfluoroalkylacetylenes at 50–100 °C:[213–214]

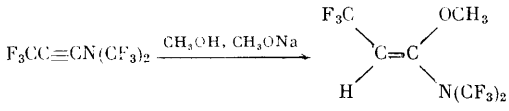
$$F_3CC{\equiv}CX \xrightarrow{(RO)_2PYH}$$

$$\longrightarrow F_3CCH{=}CXYP(OR)_2 \rightarrow F_3CCH{=}CXP(Y)(OR)_2,$$

X = H, Cl, Br, CF_3;

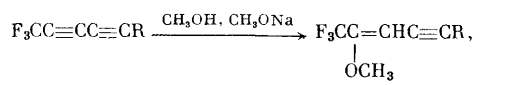
Y = O, S; R = C_2H_5, $CH(CH_3)_2$, CH_2CH_2Cl.

Methanol does not add to $CF_3C{\equiv}CN(CF_3)_2$ in neutral or acidic media. However, even at room temperature, treatent with alkoxide affords the corresponding (*Z*)-aminoacetal in 96% yield with 4% of the regioisomer.[197]



Stabilisation of the intermediate carbanion is facilitated by the inductive effect of the trifluoromethyl groups, as would be anticipated.

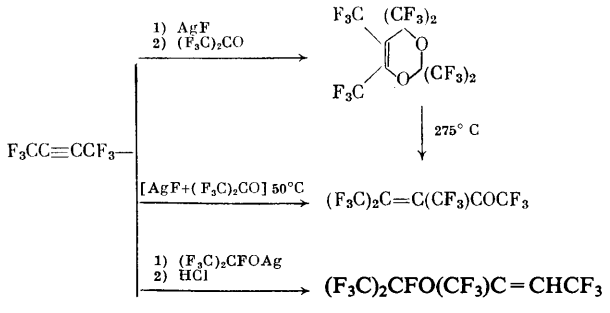
Recently, a study was made of the addition of methanol to isopropyltrifluoromethyldiacetylene in the presence of sodium methoxide at 55–60 °C.[132,133] In this case, the methoxy group is added to the acetylenic carbon substituted by the trifluoromethyl group, i.e. not in accordance with the polarisation of the system (see Section III). In a similar way, under still milder conditions (at room temperature with evolution of heat), alcohols add to trifluoromethyl-substituted diacetylenic alcohols.[133] The regioselectivity is the same as that observed for the addition of other nucleophiles to trifluoromethyldiacetylenes.



$$R = CH(CH_3)_2,\ C(OH)(CH_3)_2.$$

The regioselectivity of addition of alcohols to keto derivatives and to esters of trifluoroalkyl-substituted acetylenic acids is determined by the mesomeric effect of the carbonyl group.[80,118]

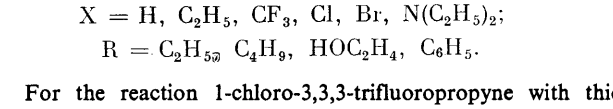
Typically, perfluoroalkylacetylenes react with perfluoro substituted carbonyl compounds—perfluoroanhydrides and perfluoroacetone—in the presence of metal fluorides (AgF). In the case of fluoroanhydrides, the anion $R_FCF_2O^-$ adds across the triple bond (see above).[25] Depending on the conditions, the reaction between hexafluoro-2-butyne and hexafluoroacetone in the presence of AgF (with intermediate formation of the anion $(CF_3)_2CFO^-$) leads to various products (see Ref. 6, Vol. 3, p. 124).



b) Addition of *S*-nucleophiles

The addition of *S*-nucleophiles to acetylenes is more characteristic than addition of *O*-nucleophiles. The rate of addition of *S*-nucleophiles to perfluoroalkylacetylenes is also greater than the rate of addition of *O*-nucleophiles.

Trifluoromethylacetylenes readily add thiols and thiophenols at room temperature (using sodium alkoxide or triethylamine as catalyst) as would be anticipated from the polarisation of the triple bond:[210,211215,216]



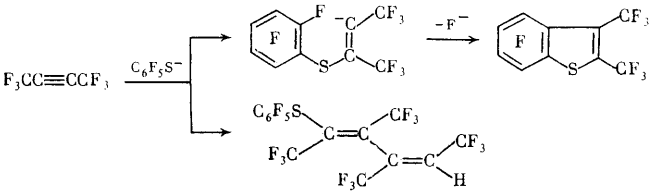
For the reaction 1-chloro-3,3,3-trifluoropropyne with thiols in the presence of alkoxide, 1,1-*bis*(alkylthio)-3,3,3-trifluoropropenes are formed as by-product.[215]

The addition of mercaptopurines in the presence of sodium methoxide leads exclusively to the formation of the corresponding (*Z*)-thioenolethers which rearrange to the (*E*)-isomers on UV-irradiation.[216]

The addition of alkyl mercaptans to allyltrifluoromethylacetylenes proceeds across the triple bond to give, initially, $CF_3CH=C(SR)CH_2CR=CR_2$ which isomerises to the corresponding 1-alkylthio-1,3-dienes, $CF_3CH_2C(SR)=CHCR=CR_2$ under the conditions of the reaction.[217]

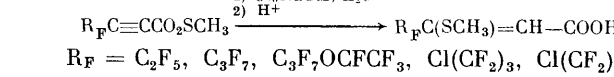
The addition of thiophenol to phenyltrifluoromethylacetylene under kinetic control (at 25 °C with sodium *tert*-butoxide as catalyst) leads to the (*Z*)-thioenolether, while a 23:64 mixture of (*Z*) and (*E*)-isomers is formed under thermodynamic control (at 150 °C). The geometry of the phenol and thiophenol adducts is different since with phenol the (*Z*)-isomer is stabilised by orbital interaction of the aryloxy group with the trifluoromethyl group.[211]

The reaction of lithium pentafluorophenylthiolate with hexafluoro-2-butyne at –70 °C gives a complex mixture of products, from which 4,5,6,7-tetrafluoro-2,3-*bis*(trifluoromethyl)benzo[*b*]thiophene and *trans,trans*-1-pentafluorphenylthio1,2,3,4-tetrakis(trifluoromethyl)butadiene have been isolated in 11% and 2% yield, respectively.[218]



Thiophosphites and esters of thio- and dithio-phosphoric acids add to trifluoromethylacetylene and hexafluoro-2-butyne in the same manner as mercaptans.[213,219]

A study has also been made of the addition of methyl mercaptan to esters of perfluoroalkylacetylenic acids in the presence of NaOH. (Z)-Adducts are formed, and methyl mercaptan is liberated as a result of hydrolysis of the corresponding thioester.[220]

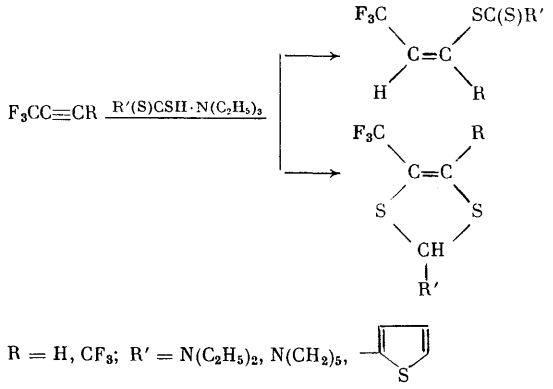


$$R_F = C_2F_5,\ C_3F_7,\ C_3F_7OCFCF_3,\ Cl(CF_2)_3,\ Cl(CF_2)_5.$$

Thus, the orientation of addition, as in other related examples, is determined by the mesomeric effect of the carbonyl group.

Trifluoromethylacetylenes and hexafluoro-2-butyne react with salts of dithiocarboxylic acids to give, depending on their structure, products arising by nucleophilic addition or 1,3-anionic cycloaddition.[221,222] Only the linear (*Z*)-adducts are obtained by addition of *N,N*-diethyl- and *N*-pentamethylene-dithiocarbamic acids salts,

while salts of 2-thienyldithiocarboxylic acid form 1,3-cycloadducts (see below) or a mixture of both linear and cyclic adducts.[221,222]



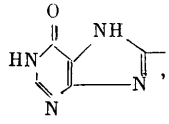
R = H, CF_3; R′ = $N(C_2H_5)_2$, $N(CH_2)_5$,

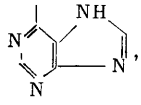
The nucleophilic addition of thiols and thioacids to trifluoromethyldiacetylenes has been studied during the last ten years. The reaction proceeds at room temperature with the same regioselectivity as the addition of alcohols, i.e. not in the same manner as the addition to perfluoroalkylacetylenes.[131–133,216,222] With diacetylenic alcohols it is necessary to perform the reaction in the cold (–20 °C), the product being formed in a matter of minutes.[133]

$$F_3CC{\equiv}CC{\equiv}CR \xrightarrow{R^1SH} F_3CC(SR^1){=}CHC{\equiv}CR,$$

R = $CH(CH_3)_2$, $C(CH_3)_3$, C(OH) $(CH_3)_2$;

$R^1 = C_2H_5$,





R^2(S)C; $R^2 = N(C_2H_5)_2$, $N(CH_2)_5$.

Molecular sulphur also serves as nucleophile in its addition to hexafluoro-2-butyne (at 110 °C in sulpholane) and to decafluorotolan (at 190 °C in benzene). The respective products are *tetrakis*-(trifluoromethyl)- and *tetrakis*(pentafluorophenyl)-thiophene.[58,206]

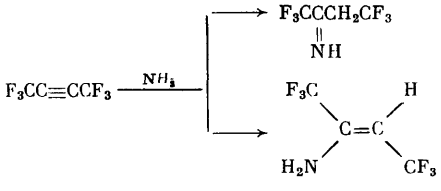
c) Addition of *N*-nucleophiles

The reaction of perfluoroalkylacetylenes with *N*-nucleophiles (ammonia, primary and secondary amines, and *N*-heterocyclics with an NH group) have been studied quite extensively, as well as the addition of secondary phosphines and arsines.

Trifluoromethylchloroacetylene reacts with ammonia at –78 °C to give 2,2,2-trifluoropropionitrile, while excess of ammonia at 50–60 °C yields malononitrile.[223]

$$F_3CC{\equiv}CCl \xrightarrow{NH_3} [F_3CCH{=}CClNH_2 \rightleftarrows F_3CCH_2CCl{=}NH] \longrightarrow F_3CCH_2CN.$$

Ammonia adds to hexafluor-2-butyne in ether at 0 °C to give a 3:5 mixture of the corresponding imine and (*Z*)-enamine.[224]



A study has also been made of the addition of ammonia to trifluoromethyl-substituted acetylenic ketones.[225]

Ethylamine and aniline add to 3,3,3-trifluoropropyne at –70 °C to give a mixture of the corresponding imine and enamine.[210]

The addition of primary amines to other perfluoroalkylacetylenes at 0 °C is accompanied by dehydrofluorination. The enamines thus obtained are hydrolysed to the corresponding enaminoketones:[226]

$$R_FCF_2C{\equiv}CH \xrightarrow[-HF]{RNH_2} R_FCF{=}CHCH{=}NR \xrightarrow{H_3O^+} R_FCOCH{=}CHNHR,$$

$R_F = C_5F_{11}$, C_7F_{15}; R = C_3H_7, C_4H_9.

Secondary amines, such as aromatic nitrogen-containing heterocyclics—pyrazole, benzimidazole, pyrimidine, and purine—add to perfluoroalkylacetylenes at room temperature or on cooling in a number of different solvents to give the corresponding (*E*)-enamines.[202,227–229]

$$R_FC{\equiv}CR \xrightarrow{R_2'NH} R_FCH{=}CRNR_2', \quad R_F = CF_3,\ C_5F_{11},\ C_7F_{15};$$

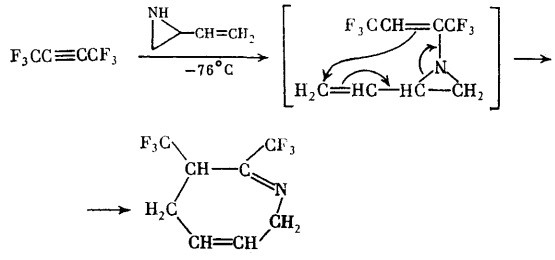
R = H, CF_3.

The rate of reaction is determined by the basicity of the amine and decreases in the order:[227]

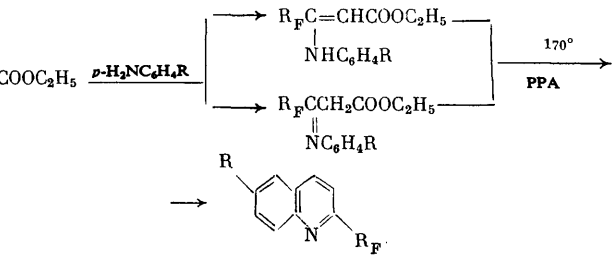
$(C_2H_5)_2NH$ > $(iso\text{-}C_4H_9)_2NH$ > HN > HN >

> ≫ $NH(CH_2C_6H_5)_2$ (Ref.227).

The addition of vinylaziridine to hexafluoro-2-butyne is accompanied by opening of the 3-membered ring with the formation of a 7-membered ring.[230]



Primary aromatic amines add to perfluoroalkylacetylenecarboxylic acid esters at 40 °C (30 h) to give the expected mixture of enamine and imine. The regioselectivity of addition is the same as that resulting on addition of amines to non-fluorinated acetylenic esters.[88]



$R_F = C_4F_9$, C_6F_{13}, C_8F_{17}; R = H, OCH_3, Cl.

Secondary phosphines and arsines add to trifluoromethylacetylene and hexafluoro-2-butyne at 20 °C with the same regioselectivity as in the addition of amines. The product contains a mixture of (*Z*)- and (*E*)-isomers in varying proportion.[207,228,231]

There is an isolated example of the addition of dimethylamine to a mono-substituted perfluoroalkyldiacetylene. At –30 to –40 °C in ether, addition takes place only at the terminal triple bond, the

regioselectivity being in accord with the polarisation of the bond, as is the case with the addition of such secondary amines to perfluoroalkylacetylenes.[232]

$$C_3F_7C{\equiv}C-C{\equiv}CH \xrightarrow{(CH_3)_2NH} C_3F_7C{\equiv}CCH{-}CHN(CH_3)_2$$

However, in the case of di-substituted alkyl(trifluoromethyl)diacetylenes, secondary amines attack exclusively the carbon atom bearing the trifluoromethyl group, i.e. not in accord with the charge distribution in the compounds.[132,133]

$$F_3CC{\equiv}CC{\equiv}CR \xrightarrow{R_2'NH} F_3CC{=}CHC{\equiv}CR, \quad \begin{matrix} | \\ NR_2' \end{matrix}$$

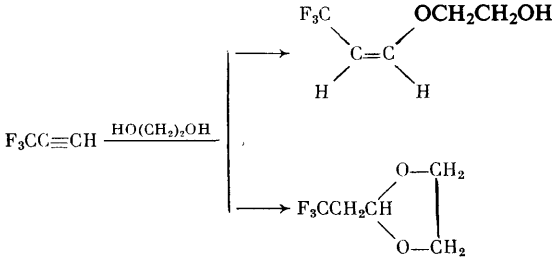
R = $CH(CH_3)_2$, $C(CH_3)_3$, $C(OH)(CH_3)_2$; R′ = CH_3, C_2H_5

Where the orientation of addition *O*-, *S*- and *N*-nucleophiles to trifluoromethyldiacetylenes is not in accord with the polarisation of such molecules, it is assumed that the regioselectivity is a function of increased stabilisation in the transition state (and intermediate) since it is only by such an orientation of addition that the entire conjugated system can participate and exert a stabilising effect.[149] If such shifts in electron density arise by a mesomeric effect, and not by an inductive effect, as is the case, for example, with diacetylenic acids[233] or phosphates,[149] the most stable transition state results by attack of the nucleophile at the terminal carbon atom furthest from the polarising group.[149]

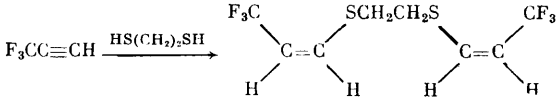
d) Addition of *O*, *S*- and *N*-dinucleophiles

The reactions of perfluoroalkylacetylenes with dinucleophiles is potentially interesting from the view-point of preparing perfluoroalkyl-substituted heterocyclics with high biological activity. Studies have been made of the reactions of perfluoroalkylacetylenes and perfluoroalkyldiacetylenes with compounds containing two hydroxyl groups, two sulfhydryl and two amino groups, as well as with compounds containing either a hydroxyl and a sulfhydryl group or a hydroxyl group and an amino group. The regioselectivity of these reactions is determined by the nature of the nucleophile.

Glycols react with trifluoromethylacetylene at –78 to 80 °C (in the presence of KOH) to give a 4:1 mixture of the corresponding (*Z*)-enolether and 1,3-dioxalane.[210]

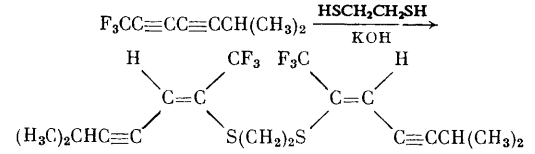


Under the same condition 1,2-dithiols react by a different pathway. (*Z*,*Z*)-1,2-*Bis*(vinylthio)ethanes are formed predominantly, together with small amounts of the corresponding dithiolane if the reaction is carried out in a non-polar solvent.[210]



The contrasting mode of addition of glycols and 1,2-dithiols to diacetylenes is because the activity of the triple bond of the second diyne molecule is significiantly greater than the activity of the double bond arising as a result of the initial addition of the 1,2-dithiol molecule.

Trifluoromethyldiacetylenes react with ethanedithiol, irrespective of the conditions, to give linear (*Z*,*Z*)-*bis*-adducts. However, the orientation of addition of ethanedithiol is the reverse of that observed with perfluoroalkylacetylenes.[165]



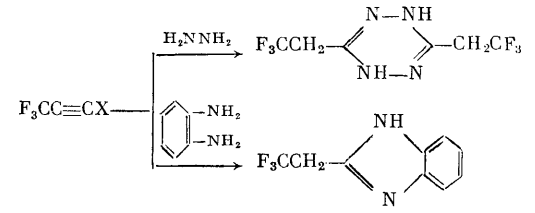
Monothioglycol adds to trifluoromethylacetylene to give only the corresponding thioenolether as a 7:1 mixture of (*Z*)- and (*F*)-isomers.[210]

The reactions of perfluoroalkylacetylenes with nitrogen-containing binucleophiles (e.g. hydrazine and its derivatives, ethylenediamine, phenylenediamine, guanidine and hydroxylamine) have been studied quite extensively.

Hydrazine reacts with trifluoromethylacetylene at –70 °C to give 3,3,3-trifluoropropanal hydrozone (as a 10:1 mixture of (*Z*)- and (*E*)-isomers), which is converted to the corresponding azine in the presence of an excess of trifluoromethylacetylene.[210]

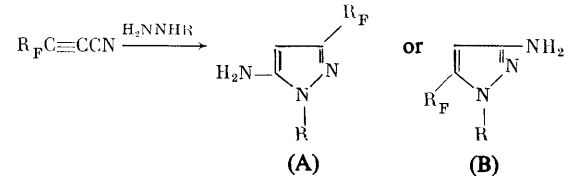
Treatment of hexafluoro-2-butyne with hydrazine affords 1,1,1,4,4,4-hexafluoro-2-butanone hydrazone.[224]

α-Halogenotrifluoromethylacetylenes interact with hydrazine at –60 °C with participation of both the triple bond and α-halogen to give 3,6-*bis*(2,2,2-trifluoroethyl)-1,4-dihydro-*s*-tetrazine. *o*-Phenylenediamine reacts in a similar way to give 2-(2,2,2-trifluoroethyl)benzimidazole.[234]



X = Cl, Br.

Perfluoroalkylacetylenes react with hydrazine, methylhydrazine and phenylhydrazine on heating in methanol according to the following scheme:[235,236]



(A) (B)

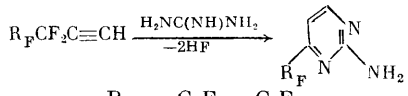
$R_F = C_7F_{15}$; R = H, CH_3 (A), C_6H_5 (B).

Ethylenediamine adds to trifluoromethylacetylene at –70 °C to give the corresponding imidazole exclusively. Total replacement of fluorine takes place at a higher temperature to give the hydrofluoride salt of ethylenediamine and tarring.[210]

The reaction of trifluoromethylacetylene with *o*-phenylenediamine proceeds at room temperature during 5 days to give the corresponding substituted benzimidazole as the main product. This is accompanied by small amounts of isomeric enamines,

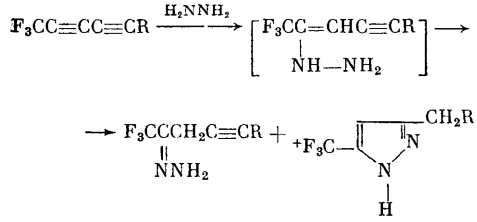
$CF_3CH=CHNHC_6H_4NH_2$ and $CF_3C(NHC_6H_4NH_2)=CH_2$, in 8:1 proportion.[210]

The addition of guanidine to perfluoroalkylacetylenes at 0 °C in THF/water leads to perfluoroalkylaminopyrimidines. The atoms of fluorine of the CF_2-group participate in the reaction.[237]



$R_F = C_5F_{11}$, C_7F_{15}.

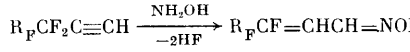
Trifluoromethyldiacetylenes react with hydrazine at −10 to −20 °C to give, initially, an enehydrazine which readily isomerises to the corresponding non-conjugated hydrazone or cyclises to a pyrazole derivative.[132,133]



The proportion of hydrazone and pyrazole depends on the nature of the radical, R, which affects the electrophilicity of the triple bond. The hydrazone:pyrazole ratio is 2:1 for R = Pr-*i*, and 1:10 for R = $Me_2C(OH)$.

The reaction of trifluoromethyldiacetylenes with ethylenediamine, the basicity of which is greater than that of hydrazine, proceeds in the absence of solvent at −60 °C with the formation of the corresponding trifluoromethyldiazepine exclusively. Both linear and cyclic products are formed in THF.[238]

The reaction of perfluoroalkylacetylenes with *N,O*-dinucleophiles has only been studied with hydroxylamine.[237] At 35 °C in ether/ethanol containing Et_3N, an oxime is formed during 20 h by elimination of HF.[237]

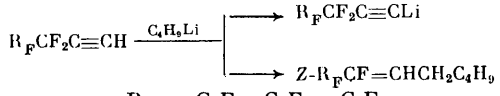


d) Addition of *C*-nucleophiles

Reactions with *C*-nucleophiles are not as well defined as those with *O*-, *S*- and *N*-nucleophiles since in the majority of cases there are no mechanistic details.

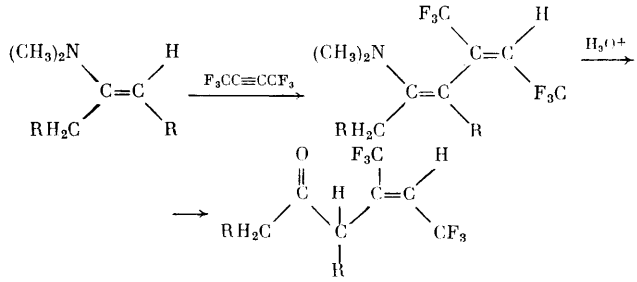
Alkyllithiums are normally selected for studies involving the interaction of unsaturated compounds with *C*-nucleophiles.

Treatment of terminally unsubstituted perfluoroalkylacetylenes with butyllithium in THF at −60 °C leads to replacement of the acidic hydrogen by lithium or addition to the triple bond to give an anomalous by-product:[89]



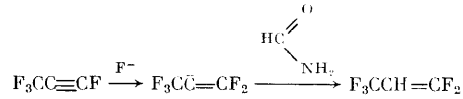
$R_F = C_3F_7$, C_5F_{11}, C_7F_{15}.

Certain enamines serve as *C*-nucleophiles in their reactions with perfluoroalkylacetylenes. Reaction is exothermic and proceeds by attack of the carbon atom at the β-position relative to nitrogen.[239]

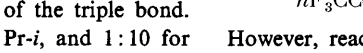


R, R = $(CH_2)_3$; R = CH_3.

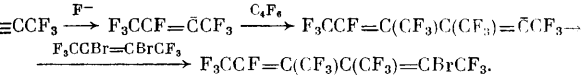
The fluoride ion of certain metallic fluorides (AgF, CsF, HgF_2) adds to perfluoroalkylacetylenes to give *C*-nucleophilic species. In the presence of a proton donor these are quenched to effect nucleophilic hydrofluorination, as shown below with perfluoropropyne.[18]



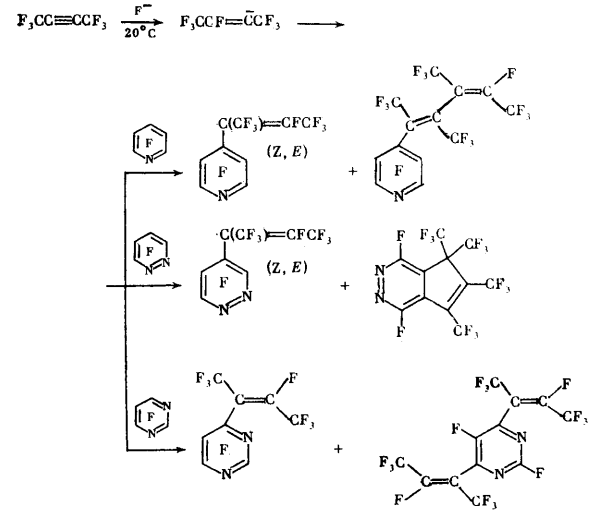
If there are no added reagents to intercept the formed carbanion, hexafluoro-2-butyne polymerises in sulpholane on treatment with CsF.[240–242]



However, reaction can be stopped at the stage of dimerisation if a suitable electrophile, e.g. $F_3CBr=CBrCF_3$, is present:[240,243]



The intermediate obtained by reaction of hexafluoro-2-butyne with fluoride ion is an extremely reactive nucleophile, which participates in nucleophilic substitution with a number of *N*-heterocyclics—perfluoro-pyridine, -pyridazine and -pyrimidine.[240,244]



Anionic telomerisation (*n* = 2,3) also takes place with perfluoropyridine, while in the case of perfluoro-pyridazine and -pyrimidine

an additional product arises as a result of nucleophilic attack at two electrophilic ring positions.

1-Chloro-3,3,3-trifluoropropyne reacts smoothly with perfluoroisobutylene in the presence of fluoride ion. The latter initiates the formation of perfluoro-*tert*-butyl anion which readily displaces chlorine.[245]

$$(F_3C)_2C{=}CF_2 \xrightarrow{F^-} (F_3C)_3C^- \xrightarrow[-Cl^-]{F_3CC\equiv CCl} F_3CC\equiv C\dot{C}(CF_3)_3.$$

The reaction of HCN with 3,3,3-trifluoropropyne in the presence of KCN and Cu_2Cl_2 at 110–120 °C possibly involves nucleophilic addition.[202]

$$F_3CC\equiv CH \xrightarrow{HCN} F_3CCH{=}CHCN \xrightarrow{10\%NaOH,\ H_2O} F_3CCH{=}CHCOONa.$$

3. Radical polymerisation and addition

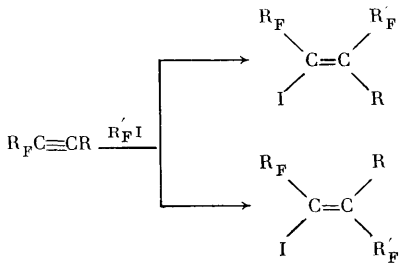
Various polymeric products—linear, cyclic (including benzene derivatives by trimerisation) and tetramers—are formed from perfluoroalkyl(aryl)acetylenes on photochemical activation, heating, or on treatment with peroxides or complex metal catalysts.[246–256]

UV-irradiation of hexafluoro-2-butyne affords tetramers of different structural type, amongst which perfluoro-octamethylcubane, perfluoro-octamethylsemibulvalene and perfluoro-octamethyloctatetraene have been identified.[252] It is thought that all of these products arise via UV-irradiation of the two geoisomeric forms of the simple tetramer, perfluoro-octamethylcyclo[4.2.0.$0^{2,5}$]-3,7-octadiene, or the dimer, perfluorotetramethylcyclobutadiene. It is possible that reaction proceeds via other cyclic systems.[243,252,253]

Certain linear fluoro-polymers and -copolymers with other monomers have been used as stable plastic materials, although they are not as useful as Teflon.[25] Polymers based on fluorine-containing diacetylenes have been used in the manufacture of heat-sensitive materials with improved surface characteristics. These have been applied domestically and scientifically in the design of electronic and optical probes.[256–268]

Examples of radical halogenation[24,34,38,48,259] and hydrobromination[197,202,260] of perfluoroalkylacetylenes have been reported. In the latter reaction, the regioselectivity of addition is the same as that of electrophilic hydrobromination.[197]

Perfluoroalkyl iodides add to perfluoroalkylacetylenes under photochemical or thermal activation as follows:[22,40,261–266]



$R_F = CF_3,\ C_3F_7,\ C_6F_{13},\ C_8F_{17};$
$R = H,\ CF_3;\ R'_F = CF_3,\ C_2F_5,\ C_3F_7,\ CF(CF_3)_2.$

Hydrolysis of the resulting perfluoroiodoalkenes in the presence of freshly precipitated copper leads to perfluoroallenes.[263] Iodotrichloromethane reacts with trifluoromethylacetylenes in the same way as iodotrifluoromethane.[266]

The addition of $I(CH_2)_2O(CF_2)_2SO_2F$ to 3,3,3-trifluoropropyne in the presence of benzoyl peroxide at 195 °C leads to a 3 : 1 mixture of the corresponding (*Z*)- and (*E*)-iodoethylenesulfonyl fluorides.[267]

In the photochemical reaction of perfluoropropyne with trichlorosilane, the Cl_3Si radical attacks primarily the C_2 atom, whereas in the reaction with trimethylsilane attack is predominantly at the C_1 atom. In the case of 3,3,3-trifluoropropyne, both radicals attack primarily the terminal carbon atom.[268]

Trifluoronitrosomethane interacts with 3,3,3-trifluoro-1-propynyl-*N,N-bis*(trifluoromethyl)amine at 95 °C to give a 97% yield of 1 : 1 adduct as follows:[269]

$$F_3CC\equiv CN(CF_3)_2 + F_3CN{=}O \longrightarrow \underset{96\%}{F_3CN{=}C(CF_3)CN(CF_3)_2} + \underset{4\%}{F_3CCC{=}NCF_3}$$
(O; O; O N(CF$_3$)$_2$)

The stable *bis*(trifluoromethyl)nitroxyl adds to perfluoroalkylacetylenes at 85 °C with the formation predominantly of the corresponding perfluorinated carbonyl and dicarbonyl compounds.[270]

$$R_FC\equiv CR \xrightarrow{(F_3C)_2NO} R_FC{=}CR \begin{cases} \longrightarrow R_FCOCOR \\ \longrightarrow R_FCOC[ON(CF_3)_2]_2R \end{cases}$$
((F$_3$C)$_2$NO; ON(CF$_3$)$_2$)

$R_F = CF_3,\ C_6H_5;\ R = H,\ F,\ CF_3,\ C_6H_5.$

N-Chlorodimethylamine adds to hexafluoro-2-butyne by a radical mechanism.[207] Several products are obtained by radical addition of *N*-bromo-*bis*(trifluoromethyl)amine to 3,3,3-trifluoropropyne: (*Z*)-2-bromo-3,3,3-trifluoro-1-propenyl-*N,N-bis*-(trifluoromethyl)amine is the main product (52%), formed together with 21% of the corresponding (*E*)-isomer and a mixture of (*E*)- and (*Z*)-regioisomers in 3% and 11% yield, respectively.[197]

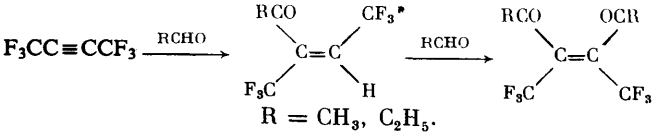
Perfluoroalkylacetylenes add perfluorohydrazine by a radical mechanism to give *N,N*-perfluorodiamines which rearrange on heating to imines:[271,272]

$$F_3CCCF(NF_2)R \text{ (NF)} \quad \text{and} \quad F_3CCF(NF_2)CR \text{ (NF)}$$

Hexfluoro-2-butyne reacts similarly with tetraphenyldiphosphine.[207]

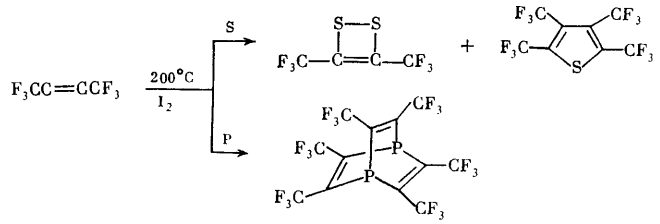
The reaction of 3,3,3-trifluoropropyne with atomic oxygen has also been studied.[273] Radical addition of methanol and 2,2,2-trifluoroethanol to hexafluoro-2-butyne under γ-irradiation affords *trans*-4,4,4-trifluoro-2-trifluoromethyl-2-buten-1-ol (12%) with the former alcohol and, with the latter, a 1 : 1 mixture of *cis*- and *trans*-1,1,1,5,5,5-hexafluoro-3-trifluoromethyl-3-penten-2-ol.[174]

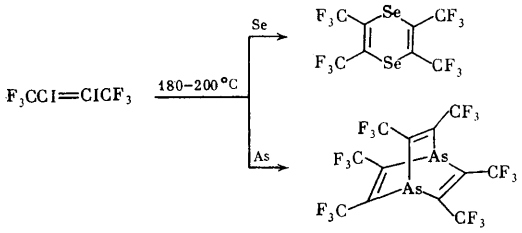
The radical addition of acetaldehyde and propionaldehyde to hexafluoro-2-butyne has also been studied (under γ-irradiation or in the presence of benzoyl peroxide). Reaction proceeds with the formation of adducts in 1 : 1 and 1 : 2 proportion.[274]



$R = CH_3,\ C_2H_5.$

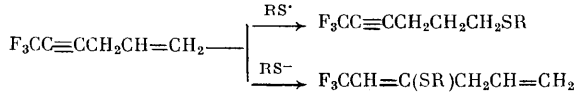
Sulphur and phosphorus react with hexafluoro-2-butyne in the presence of iodine to give heterocyclic compounds. Selenium and arsenic only form heterocyclic compounds with 2,3-diiodohexafluoro-2-butene.[259,275,276]





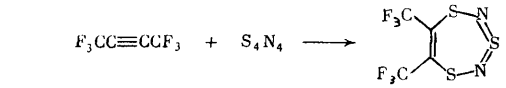
Hydrogen sulphide reacts with 3,3,3-trifluoropropyne and hexafluoro-2-butyne on irradiation to give stable enethiols, $F_3CCH=CHSH$ and $F_3CCH=C(SH)CF_3$.[277] On UV-irradiation of these same perfluoroalkyacetylenes with methyl mercaptan, 1:2 adducts of the type, $CF_3CH(SCH_3)CH_2SCH_3$, are formed.[278]

The addition of alkyl mercaptans to allyltrifluoromethylacetylene and its homologues in the presence of *tert*-butyl peroxide takes place across the double bond. The thiiyl radical thus attacks the terminal carbon atom, while nucleophilic addition of mercaptide anion takes place across the triple bond:[217]

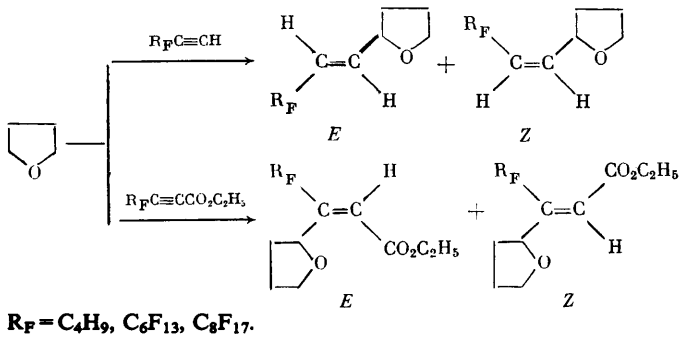


Dimethyl disulphide reacts with hexafluoro-2 butyne on UV-irradiation at 100 °C to give a high yield of 2,3-*bis*-(methylthio)hexafluoro-2-butene as a mixture of (*Z*)- and (*E*)-isomers.[279]

Hexafluoro-2-butyne condenses with tetrasulphur tetranitride to give *bis*(trifluoromethyl) derivatives of a trithiadiazepine. However, the mechanism of this reaction has not been established.[280]



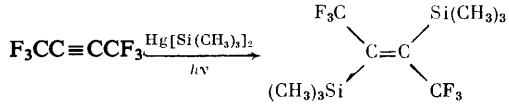
Perfluoroalkylacetylenes and esters of perfluoroalkylpropiolic acid add tetrahydrofuran (on heating) according to the following scheme:[281]



$R_F = C_4H_9$, C_6F_{13}, C_8F_{17}.

The regioselectivity of the reaction between tetrahydrofuran and perfluoroalkylpropiolic acid esters is a consequence of the mesomeric effect of the carboxyl group. In both cases, (*E*)-isomers are formed (80 and 70% yield, respectively).

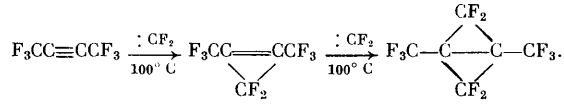
The possibility of silylating perfluoroalkylacetylenes has also been investigated. This is exemplified by the following scheme:[282]



Flash-photolysis of 3,3,3-trifluoropropyne is reported to give HF.[283]

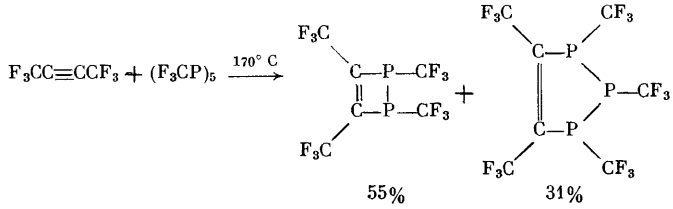
4. Reactions with carbenes and related compounds

Difluorocarbene, obtained by pyrolysis of $(CF_3)_3PF_2$ at 100 °C adds to hexafluoro-2-butyne in the gas phase as follows:[284]

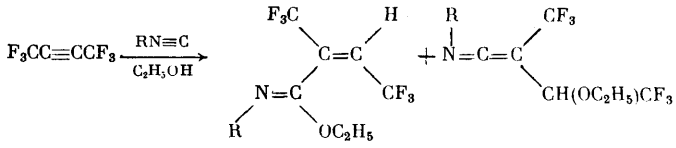


3,3,4,4-Tetrafluoro-3-trifluoromethyl-1-butyne, $CF_3C\equiv CH$ and $C_2F_5C\equiv CH$ react with difluorocarbene, obtained by heating $(CH_3)_3SnCF_3$ at 150 °C, to give the corresponding cyclopropenes in low yield.[35] Hexafluoro-2-butyne reacts with dichlorocarbene, generated by thermal decomposition of CCl_3SiF_3, to give a mixture of 3,3-dichloro*bis*(trifluoromethyl)- and 1,3-dichloro*bis*(trifluoromethyl)-cyclopropene.[285]

A mixture of four- and five-membered phosphorus-containing heterocyclics is obtained by reaction of hexafluoro-2-butyne with phosphenes.[286]

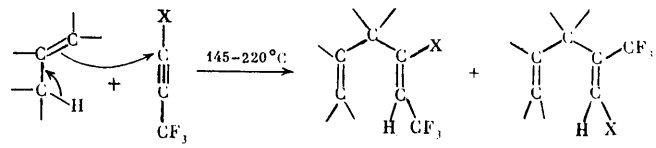


Treatment of hexafluoro-2-butyne with isonitriles in ethanol affords a mixture of iminoesters and ketenimines. The proportion of each depends on the nature of the isonitrile (see Ref. 6, Vol. 3, p. 121).



5. Condensation with alkenes

The high electrophilicity of the triple bond of perfluoroalkylacetylenes and the high nucleophilicity of the double bond of alkenes favour interaction between these compounds:[287]

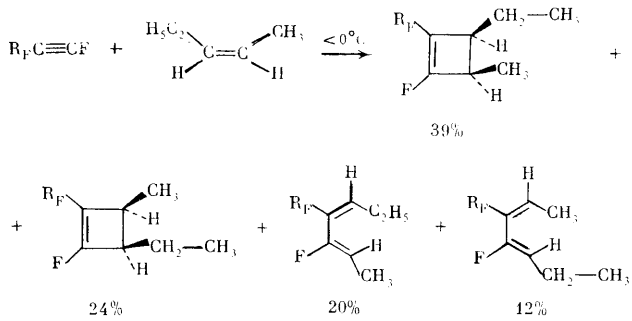


X = H, CF_3.

Thus, reaction of 3,3,3-trifluoropropyne with alkenes leads to a regioisomeric mixture of two non-conjugated 1,4-alkadienes. With substitution of the alkene at C_1 and C_2, several isomeric adducts may be formed.

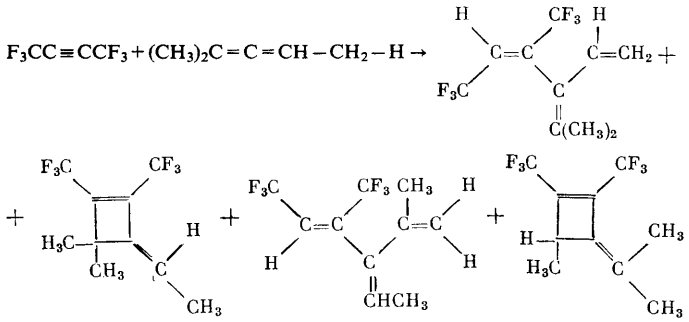
A 1:1 and 1:2 adduct are obtained by reaction of hexafluoro-2-butyne with isobutene.[287]

The interaction of perfluoro-3-methyl-1-butyne with the (*Z*)- and (*E*)-isomers of 2-pentene affords a [2+2]-cycloadduct together with lesser amounts of acyclic compounds formed as a result of ring cleavage of a σ-bond.[122]

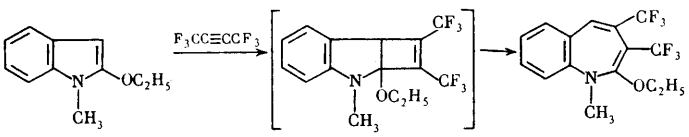


Phenylperfluorohexylacetylene reacts similarly with tetrafluoroethylene. Ring opening of the intermediate cycloadduct yields 1,1,4,4-tetrafluoro-2-perfluorohexyl-3-phenyl-1,3-butadiene.[32]

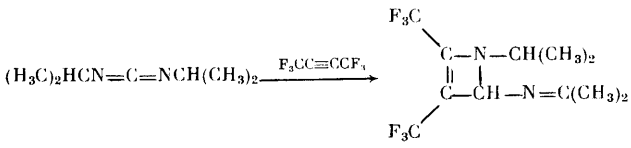
The direction of the related reaction of hexafluoro-2-butyne with allenes depends on the substitution of the latter.[288] Thus, reaction of 3-methyl-1,2-butadiene with hexafluoro-2-butyne affords only a [2+2]-cycloadduct,[289] while trimethylallene gives a mixture of products as follows:[290]



Hexafluoro-2-butyne condenses with *N*-methyl-2-ethoxyindole to give a 1-benzazepine via transannular cyclobutene ring opening.[291]



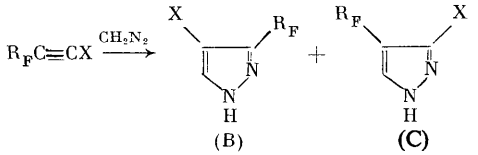
Heterocumulenes, such as diisopropylcarbodiimide, also participate in [2+2]-cycloaddition (see Ref. 6, Vol. 4, p. 121), e.g.



6. 1,3-Dipolar and anionic cycloaddition

Perfluoroalkyl(aryl)acetylenes have been widely used as active dipolarophiles in their reactions with such octet-stabilised dipoles as diazoalkanes, alkyl or aryl azides, nitrile oxides, nitrilimines, sydnones and nitrones. In this way a variety of perfluoroalkyl-substituted heterocyclics have been prepared, primarily with a view to studying the effect of perfluoroalkyl substitution on the biological activity of heterocyclics. Such 1,3-dipolar cycloadditions proceed under much milder conditions than the corresponding reactions with non-fluorinated acetylenes or perfluoroalkylethylenes.[1,6,196,201]

The reaction of perfluoroalkylacetylenes with diazomethane proceeds regioselectively at room temperature to give only one of the two possible cycloadducts. Isomer (B) is formed where X = H, and isomer (C) where X = COOEt. Thus, in the former, the perfluoroalkyl group determines the regioselectivity, while in the latter it is the carbethoxy group.[292,293]



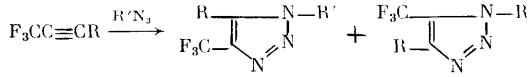
$R_F = CF_3, C_4H_9, C_6H_{13}, C_8H_{17}$; X = H, *n*-$CH_3OC_6H_4$, *n*-$NO_2C_6H_4$, $COOC_2H_5$.

Treatment of aryltrifluoromethylacetylenes with one equivalent of diazomethane gives a 19:1 mixture of the corresponding pyrazoles (B) and (C). Thus, condensation proceeds in accordance with the polarisation of the reactants. The regioselectivity of the reaction is not affected by electron-donating (e.g. OMe) or electron-accepting (e.g. NO_2) substituents in the benzene ring, but the yield of adduct is higher in the latter case.[109]

3,3,3-Trifluoropropyne react with trifluoromethyldiazomethane to give 3,5-*bis*(trifluoromethyl)pyrazole (and a trace of regioisomer in 6% yield), while hexafluoro-2-butyne affords 3,4,5-*tris*(trifluoromethyl)pyrazole.[294]

The addition of diphenyldiazomethane to perfluoropropyne proceeds non-selectively: a 1:1 mixture of isomeric pyrazoles is obtained.[295] The addition of diazocyclohexane,[296] tetraphenyldiazocyclopentadiene[297] and diazofluorene[298] to hexafluoro-2-butyne has also been studied.

Normally, organic azides interact with substituted acetylenes to give a mixture of regioisomeric triazoles. Activation of the triple bond by electron-accepting substituents facilitates this process.[299] Thus, the addition of aliphatic and aromatic azides to trifluoromethylacetylenes proceeds with the predominant formation of 4-trifluoromethyl-1,2,3-triazoles, the permitted R and R′ values being shown below.[109,300–302]



R = H, CF_3, C_6H_5, 4-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$, Br, $CH(OH)_2C_2H_5$, $C{\equiv}CC(CH_3)_3$, $C \equiv CC(OH)(CH_3)_2$;
R′ = CH_3, C_6H_5, 4-$NO_2C_6H_4$, 4-$CH_3OC_6H_4$.

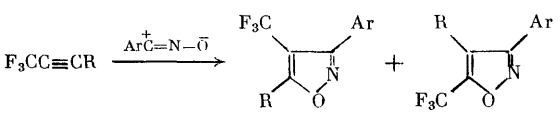
In exactly the same way, phenylperfluorohexyl-[32] and phenylpentafluorophenyl-acetylene[300] react with phenyl azide to give the corresponding 1-phenyl-4-perfluorohexyl- and 1-phenyl-4-pentafluorophenyl 1,2,3-triazoles.

Azides react similarly with non-fluorinated acetylenes.[299] Thus, in such additions, the regioselectivity is not determined by the distribution of electron-density in the substrate.

It is reported[93] that hexafluoro-2,4-hexadiyne readily reacts with two molecules of *p*-dimethylamino- and *p*-methoxy-phenyl azide to give a high yield of the corresponding *bis*(triazoles) with the trifluoromethyl groups in the 5- and 5′-positions. Here, the regioselectivity is different to that observed with the addition of azides to simple perfluoroalkylacetylene (see above), and the data requires corroboration.

Biologically active perfluoroalkyl(aryl)-substituted isoxazoles, which are normally difficult to prepare, are obtained by treatment of the corresponding perfluoroacetylenes with nitrile oxides.

In all reactions of trifluoromethylacetylenes with arylnitrile oxides, the regioselectivity is in accordance with the polarisation of the reactants and independent of the nature of the substituents either in the trifluoromethylacetylene or the benzene ring. The selectivity reaches 99% in certain cases:[50,165,303]



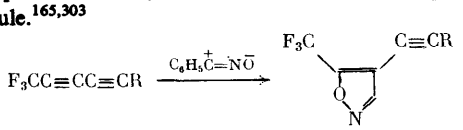
R = H, Br, CF_3, X—C_6H_4 (X = 2-Cl, 4-CH_3O, 4-NO_2, 4-NH_2); Ar = C_6H_5, 4-ClC_6H_4, 2,6-$Cl_2C_6H_3$, 3-pyridyl.

Non-fluorinated acetylenes take part in this reaction under harsher conditions, and the regioselectivity is in the opposite sense.[50] Thus, treatment of pentafluorophenylacetylene with benzonitrile oxide affords 3-phenyl-4-pentafluorophenylisoxazole,[304] while phenylacetylene gives 3,5-diphenylisoxazole.[305] If the reaction is conducted in the presence of triethylamine, there is partial replacement of the *p*-fluorine atom by the triethylammonio group.[304]

In the reaction of perfluoroacetylenecarboxylic acid ethyl esters with nitrile oxides, the regioselectivity is determined by the mesomeric effect of the carbethoxy group.[306]

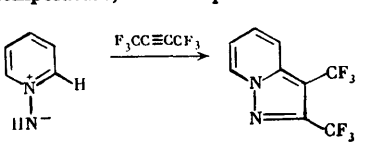
Quinoline and isoquinoline *N*-oxides react with hexafluoro-2-butyne in a more complex manner with intermediate formation of the expected ylids.[307]

Non-conjugated, methylene-bridged trifluoromethyldiacetylenes having a terminal triple bond react with nitrile oxides predominantly at the terminal bond, as is the case with non-fluorinated analogues. However, if the non-fluorinated triple bond is disubstituted, addition takes place predominantly at the acetylene group substituted by the trifluoromethyl group, as is normally the case.[165,308] This bond is also highly activated in conjugated trifluoromethyldiacetylenes. Thus, the regioselectivity of the reaction, as is the case with nucleophilic addition, is not in accord with the polarisation of the molecule.[165,303]

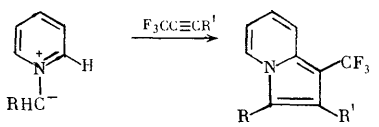


The kinetics of the reaction of 3,3,3-trifluoropropynyldiphenylphosphine with *C,N*-diphenyl- and *C*-acetyl-*N*-phenyl-nitrilimine has also been studied, although there was no product analysis.[309]

N-Nitrilimines (azomethine imides) based on pyridine, quinoline[310] and pyrazoline[311] interact smoothly with hexafluoro-2-butyne at room temperature, for example:[310]

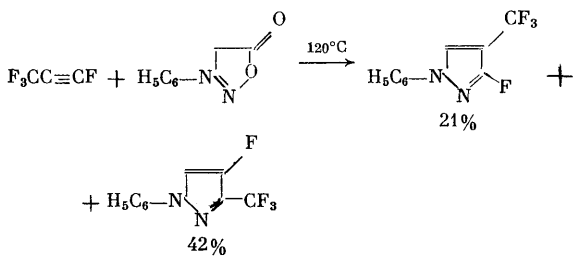


The reaction of trifluoromethylacetylenes with related ylids[312] and with *N*-(2,2,2-trifluoroethyl)pyridinium salts[313] proceeds in the same way, although by-products have also been isolated:



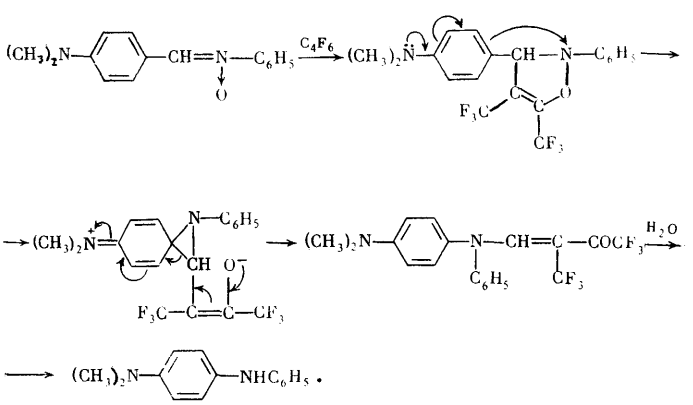
R = CF_3, COF_3; R′ = H, CF_3.

Perfluoropropyne reacts with *N*-phenylsydnone non-selectively:[302]

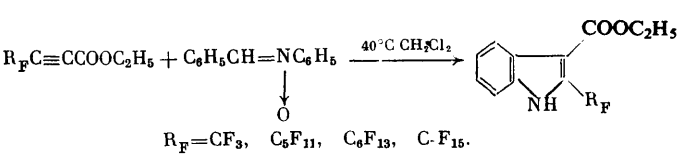


Hexafluoro-2-butyne affords 3,4-*bis*(trifluoromethyl)-1-phenylpyrazole with this same sydnone.[302]

The interaction of hexafluoro-2-butyne with phenyl-, *p*-anisyl-, *p*-nitrophenyl-, *p*-*N,N*-dimethylaminophenyl-nitrone has also been reported.[314] In all reactions, an isoxazoline is formed initially, but the ring is further transformed as reaction progresses. With the first three nitrones, re-cyclisation and hydrolysis takes place to give the corresponding 2,3-*bis*(trifluoromethyl)indole. *C*-(*p*-*N,N*-dimethylaminophenyl)-*N*-phenylnitrone condenses with hexafluoro-2-butyne as follows:[314]

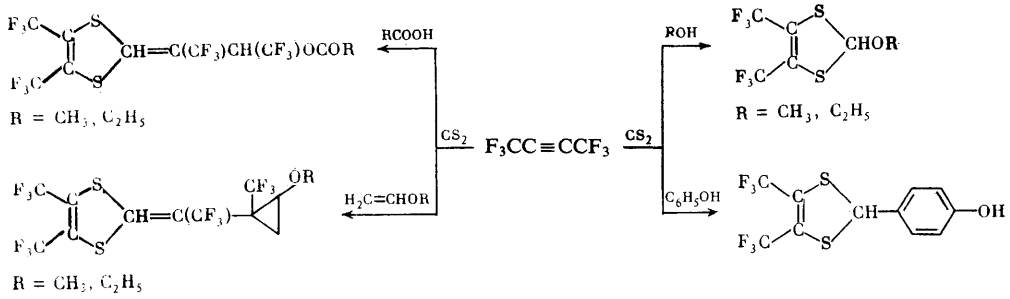


In the reaction of *C, N*-diphenylnitrone with perfluoroacetylenecarboxylic acid ethyl esters, the orientation of addition is determined largely (90%) by the carbethoxy group.[315]

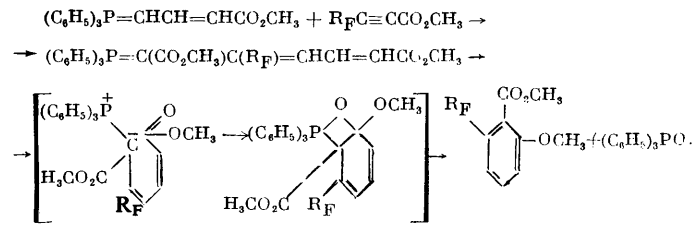


Anionic cycloaddition has only been studied with dithio-acids. Aminodithiocarbamates react with trifluoromethyl-acetylenes and -diacetylenes by nucleophilic addition (see above). 1,3-Anionic cycloaddition only takes place with 2-thienyldithiocarbamates.[221,222]

Hexafluoro-2-butyne and CS_2 participate in a variety of 1,3-anionic cycloadditions,[316–318] for example:



The reactions of perfluoroacetylenecarboxylic acid esters with phosphonium and arsonium ylids have been studied in recent years.[319–321] Thus, interaction of phosphorane (D) with methyl perfluoroalkylactylenecarboxylates takes place via intramolecular Wittig reaction to give the corresponding perfluoroalkyl-substituted *o*-methoxybenzoates:[319]



7. Diene synthesis

Alkynes and aryl-substituted acetylenes react as dienophiles with 1,3-alkadienes, but only under forcing conditions. Perfluorinated analogues, however, often react at room temperature. Under certain conditions they may even react with diene systems which are normally unreactive, such as aromatic hydrocarbons. Diene synthesis with perfluoroalkyl(aryl)acetylenes plays an important role in the preparation of mono- and poly-cyclic compounds, including heterocyclics substituted by perfluoro-alkyl and -aryl residues. Such products have potential biological activity, and the incorporation of polarising substituents is synthetically useful.

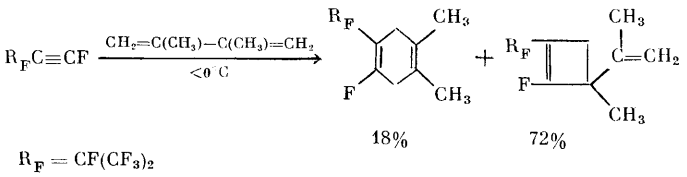
The interaction of 3,3,3-trifluoropropyne with 1,3-butadiene was first mentioned in 1956, but detailed experimental data was not presented.[5]

Recently it was shown that 3,3,3-trifluoropropyne reacts with cyclopentadiene even at room temperature, and with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene on heating at 100 °C.[76] The reactions of 3,3,3-trifluoropropyne and hexafluoro-2-butyne with hexafluoro- and perfluoro-1,3-cyclohexadienes (at 200 °C) affords the expected cycloadduct together with products formed by dimerisation of the cycloalkadienes.[322,323] Bromo-3,3,3-trifluoropropyne interacts exothermically with cyclopentadiene at room temperature, while reaction with 1,3-butadiene and 2,3-dimethylbutadiene requires heating (100 °C). These thermal cycloadditions are accompanied by tarring and dehydrogenation to give aromatic compounds.[76]

Phenylperfluorohexylacetylene readily reacts with divinyl on heating.[32]

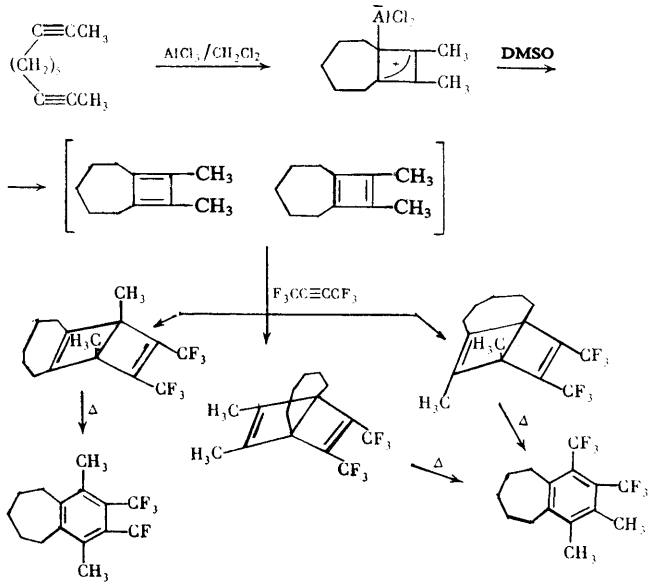
The most studied dienophile is hexafluoro-2-butyne. The latter reacts with 1,3-butadiene or 2,3-dimethyl-1,3-butadiene at room temperature or at temperatures in the region 28–100 °C.[324] The corresponding benzenoids are formed via dehydrogenation of the adducts at 700–800 °C. The major by-products are trifluoromethylbenzene and 2,3-*bis*(trifluoromethyl)-1,3-butadiene.[324]

With perfluoroacetylenes, however, [2+2]-cycloaddition prevails over [4+2]-cycloaddition,[122] as illustrated below.



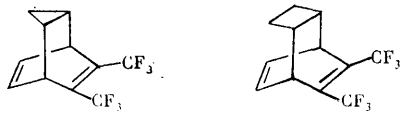
Reference has also been made to the reactions of hexafluoro-2-butyne with cyclic conjugated alkadienes having a four-, five-, six-, seven- or eight-membered ring.

Dimethylpentamethylenecyclobutadiene initially affords a 1:1 adduct which subsequently isomerises as follows:[325]



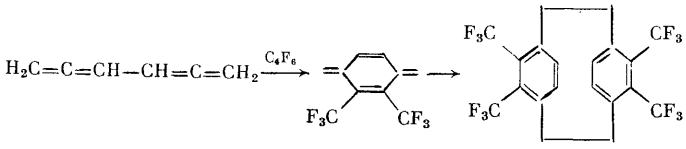
Reaction proceeds in the normal way with cyclopentadiene and variedly substituted cyclopropylfulvenes to give 2,3-*bis*(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene[326,327] and the corresponding cyclopropyl derivatives, respectively.[328,329] With cycloheptatriene,[326] its 7-cyano derivative,[330] and with cyclooctatetraene (at 150 °C),[326]

transannular ring closure of the initial cycloadducts yields the following compounds:

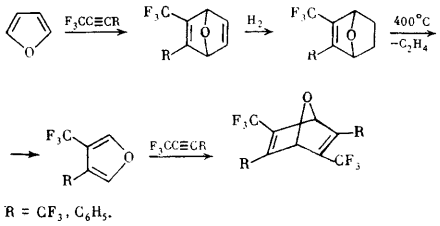


Bis(pentafluorophenyl)acetylene and pentafluorophenylacetylene react with tetraphenylcyclopentadiene to give, predominantly, hexaarylbenzenes.[112]

The adduct formed from hexafluoro-2-butyne and 1,2,3,5-hexatetradiene dimerises to give the corresponding paracyclophane:[331]

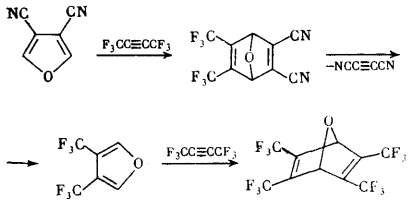


Perfluoroalkylacetylenes readily react with furan, pyrrole, triazine and substituted derivatives of these heterocyclics. At 100 °C in THF furan affords the expected [4+2]-adduct, which, after partial hydrogenation, eliminates ethylene on heating. The resulting 3,4-disubstituted furan then reacts with a second molecule of perfluoroalkylacetylene as follows:[110,332,333]



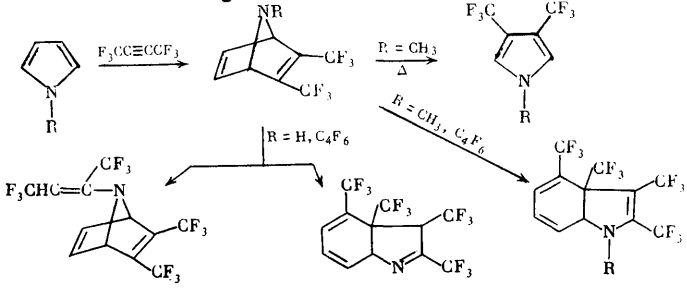
R = CF_3, C_6H_5.

In a similar way, cycloaddition of hexafluoro-2-butyne with 3,4-dicyanofuran is accompanied by elimination of dicyanoacetylene:[332]



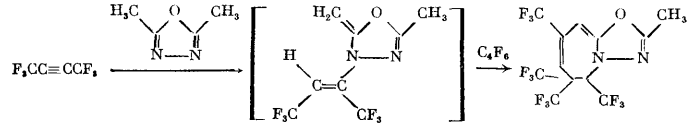
Novel and interesting cycloadducts have been obtained by reaction of furan with [α,α-*bis*(3,3,3-trifluoropropynyl)]benzyl benzoate and [1,1-*bis*(3,3,3-trifluoropropynyl)]ethyl acetate.[90]

Normally, pyrrole reacts with dienophiles by ene synthesis rather than [4+2]-cycloaddition. However, the latter prevails with hexafluoro-2-butyne, the initial cycloadduct reacting subsequently as shown in the following scheme:[334]

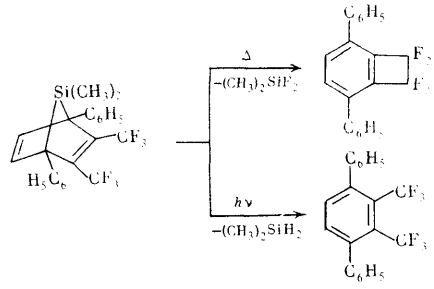


The products formed by heating hexafluoro-2-butyne with *N*-benzoyl-2,5-dialkylpyrroles at 300 °C eliminate acetylene to give the corresponding tetra-substituted *N*-benzoylpyrroles.[335]

Hexafluoro-2-butyne reacts with 2-phenyl-4,6-diaryl-1,2-dihydro-*s*-triazines to give the corresponding 4,5-*bis*-(trifluoromethyl)-2,6-diarlypyrimidines.[336] An unusual condensation of hexafluoro-2-butyne with 2,5-dimethyl-1,3,5-oxadiazole has also been reported:[337,338]

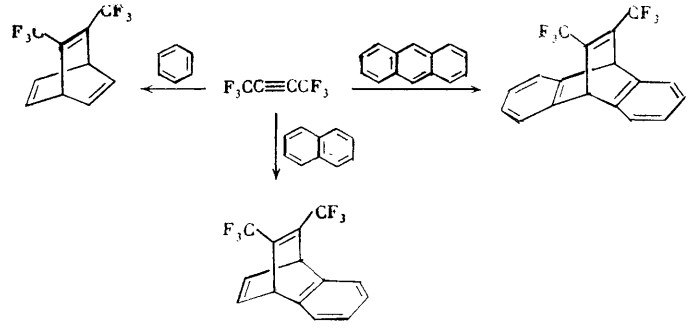


The structure of the product was established by X-ray analysis. The reaction of hexafluoro-2-butyne with five-membered and six-membered silacyclodienes proceeds in the first phase to give the expected [4+2]-adduct, which may be transformed on heating, as exemplified below:[339,340]



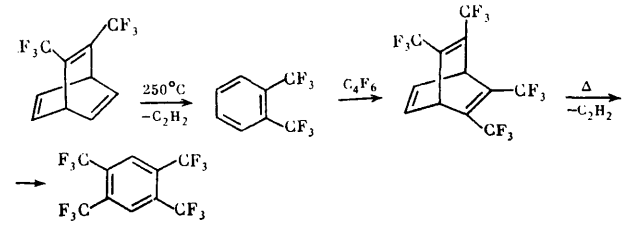
The reaction with germanium-containing analogues proceeds in the same way.[341]

Hexafluoro-2-butyne serves as an active dienophile towards aromatic hydrocarbons: benzene, toluene, xylene, 1,2,5-trimethylbenzene, durene, *p*-(polymethylene)benzenes, naphthalene and anthracene. The cycloaddition takes place at 150–200 °C.[342–344]



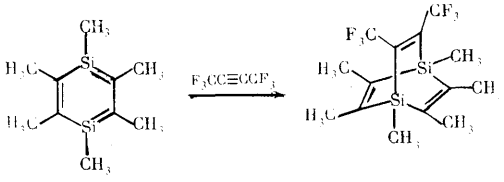
1,12-Dihydroeicosafluoro-6-dodecyne also reacts with aromatic hydrocarbons.[343]

On increasing the temperature, the adducts eliminate acetylene to give, for example, 1,2-*bis*- and 1,2,4,5-*tetrakis*-(trifluoromethyl)-benzene:[343]

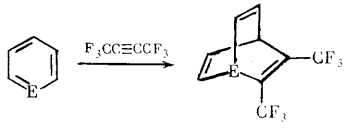


The reaction of hexafluoro-2-butyne with a number of six-membered heteroarenes has also been reported. Here, the conditions of the cycloaddition are dependent on the nature of the heteroatom.

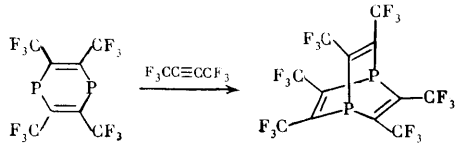
Hexamethyl-1,4-disilabenzene reacts with hexafluoro-2-butyne in the same way as benzene:[345]



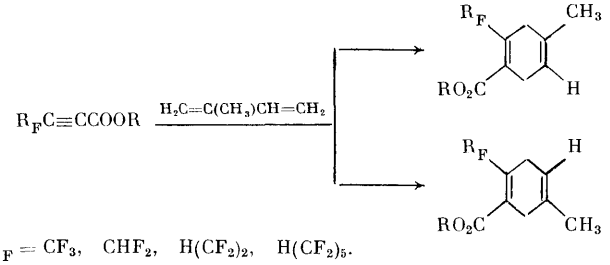
Hetero-analogues of benzene with a Group V element in the ring react under much milder conditions:[346–348]



E = P (at 100 °C); As (at room temp.); Sb, Bi (at 0 °C)



Diene syntheses with perfluoroacetylenecarboxylic acids and their esters as dienophile have been carried out with cyclopentadiene,[349] isoprene, 2,3-dimethylbutadiene and furan.[144] The carboxyl group determines the orientation of cycloaddition, as in other reactions with such acetylene derivatives. In the case of isoprene, the ratio of regioisomers is in the range 2.7 to 1.8, the ratio decreasing as the size of the substituent increases.[144] The resulting products have been used for the synthesis of substituted phthalic acids.[350]

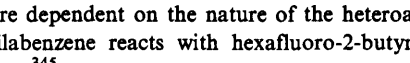


R_F = CF_3, CHF_2, $H(CF_2)_2$, $H(CF_2)_5$.

Diene synthesis with trifluoromethyl-substituted diacetylenes has been studied with two non-conjugated compounds—1,1,1-trifluoro- and 1,1,1-trifluoro-4,4-dimethyl-2,5-heptadiyne—and two conjugated compounds—1,1,1-trifluoro-6-methyl- and 1,1,1-trifluoro-6,6-dimethyl-2,4-heptadiyne.[76,151] There was no reaction between non-conjugated diynes and cyclopentadiene at room temperature. Only the triple bond substituted by the trifluoromethyl group is active at 100–150 °C. Dicyclopentadiene is formed as a by-product. Conjugated alkadiynes react with cyclopentadiene even at room temperature, again with participation of only the trifluoromethyl-substituted triple bond.[76,151]

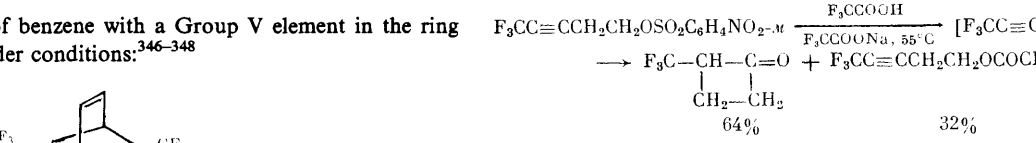
8. Molecular rearrangements

Trifluoromethyl-acetylenes,[16,202] -diacetylenes,[75] and allyltrifluoromethylacetylenes[217] undergo prototropic isomerisation in the presence of a catalytic amount of base. The triple bond is thus shifted away from the trifluoromethyl group:

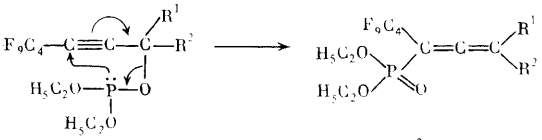


Perfluoropropyne isomerises to perfluoroallene on treatment with CsF.[17] The same isomerisation takes place during the preparation of other perfluoroacetylenes.[128]

β-Carbenium ions, formed from perfluoroalkylacetylenes, are converted to cyclobutane derivatives as a consequence of the high electron-accepting character of the perfluoroalkyl group.[86]



Acetylene-allene rearrangement takes place with certain functionalised perfluoroalkylacetylenes, for example:[351]



$R^1 = R^2 = CH_3$; $R^1 = CH_3$, $R^2 = C_2H_5$; $R^1 = R^2 = H$; $R^1 = H$, $R^2 = CH_3$.

9. Complex formation

As a result of the high electrophilicity of perfluoroalkyl(aryl)-acetylenes, the latter undergo complex formation with metals of the platinum sub-group (Pt, Pd, Ir, Ru, Rh, Os), the iron group (Fe, Co, Ni), and many other metals (Mo, W, V, Ti, Mn, Au). Group VIII complexes with hexafluoro-2-butyne have been studied most of all. The chemistry of these complexes has already been reviewed in detail,[5,6,352–354] and the volume of data in this field is too great to be incorporated in any way in this review.

Partial protection of multiple bonds by complexation with $Co_2(CO)_8$ has been widely applied in recent years as a device to increase the regioselectivity of reactions with such compounds.[355,356] However, complexes formed from trifluoromethyl- and pentafluorophenyl-substituted alkynes do not demetalate by the usual routes, and thus have a limited synthetic value.[357–361] However, such complexes may undergo certain reactions which the parent alkynes do not. For example, complexes formed with trifluoromethyl- and pentafluorophenyl-acetylenealcohols readily dehydrate to novel conjugated trifluoromethyl- and pentafluorophenyl-alkenynes, which are converted to the corresponding nitroalkenynes on treatment with $Fe(NO_3)_3.9H_2O$.[358–360] Dehydration of the trifluoromethylacetylene-alcohols is accompanied by partial dimerisation of the resulting enyne complex.[361]

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In this review, it has been noted that perfluoroalkyl(aryl)-acetylenes do not readily add halogens by an electrophilic mechanism. Such additions require radical conditions. In the addition of mixed halogens (IF, ICl) and pseudohalogens (e.g. ICN) to terminal perfluoroalkylacetylenes, the regioselectivity is not determined by the polarisation of the triple bond: attack by the cation proceeds at the terminal carbon atom. However, hydrogen halides add quite smoothly to perfluoroalkyl(aryl)acetylenes in the

presence or absence of catalysts normally used for electrophilic addition. Here, the regioselectivity of the process is in accord with polarisation factors.

Contrasting with the reactions of electrophilic reagents, nucleophiles add to perfluoroalkyl(aryl)acetylenes more readily than to alkynes, even at low temperatures. Here also, the regioselectivity is in accord with the polarisation of the triple bond.

Fluoride ion plays an important role in the reactions of perfluoroalkyl(aryl)acetylenes. The anions formed as a result of addition of fluoride ion (to reagent or substrate) participate readily in a variety of additions and cyclisations.

The addition of nucleophiles to trifluoromethyldiacetylenes does not proceed in a manner as would be anticipated with a strongly polarised conjugated system. The triple bond substituted by a trifluoromethyl group is more active than a non-perfluoroalkylated triple bond. Only by nucleophilic attack of the trifluoromethylated triple bond does a transition state develop with the participation of the entire conjugated system.

Perfluoroalkyl(aryl)acetylenes are highly active in pericyclic reactions. They participate in diene syntheses, even at room temperature, and take part in both 1,3-dipolar and anionic cycloaddition. The regioselectivity of the cycloaddition of perfluoroalkylacetylenes to unsymmetrically substituted dienophiles and dipolarophiles is in accord with polarisation factors, but with perfluoroalkyldiacetylenes mixtures of regioisomers are formed.

A special mention has been made of the usual reactions of perfluoroalkyl(aryl)acetylenes with non-metals—sulphur, selenium, phosphorus and arsenic—from which heterocyclic compounds have been isolated.

The study of addition reactions with perfluoroalkylacetylenes and perfluoroalkyldiacetylenes has made a significant contribution to the generalised theory of addition to unsaturated compounds: the regioselectivity of addition is not always in accord with polarisation factors, even where the triple bond is highly polarised, as has been seen in certain reactions with perfluoroalkylacetylenes and, especially, with diacetylenes.

Many of the properties of perfluoroalkyl(aryl)acetylenes have been widely utilised in organic synthesis, and there is much potential for even broader application. Undoubtedly, these compounds will play a more significant role in the next ten years in various fields of research as more and more is understood of the effect of perfluoroalkyl and perfluoroaryl substitution on chemical, physical and physiological properties.

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