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THE RECENT PROGRESS OF FLUOROORGANIC CHEMISTRY IN CHINA

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SUMMARY

The development of fluoroorganic chemistry in China is briefly reviewed with the emphasis on the research activity within the last few years. The following topics will be discussed, namely: (1) Fluoroolefins. (2) Fluorinated sulfonic acids, the C-O vs. S-O cleavage of sulfonate esters. (3) Sulfinatodehalogenation and other ET reactions. (4) Difluorocarbene (5) Halophilic reactions of perfluorohaloalkanes. (6) Synthesis of organofluorine compounds via organometallics.

INTRODUCTION

Organic fluorine chemistry in China started in the late 1950s when we were interested mainly in the development of fluoropolymers to meet our national needs. In the early days we started almost from scratch, then there was a period of interruption during the middle sixties to late seventies. Therefore the present review deals mainly with work carried out within the last eight to ten years with most of the work being done in the Shanghai Institute of Organic Chemistry part of the Academy of Science of our country.

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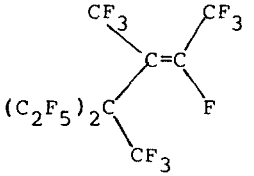
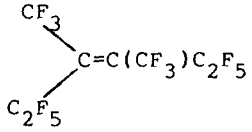
Fluoroolefins

We have studied the telomerization of tetrafluoroethylene TFE (and hexafluoropropene HFP) with various telogens including alcohols, ethers and halogenated hydrocarbons as well as simple F-alkyl iodides and have used these telomers as starting materials for further transformations. We also studied the oligomerization of TFE and studied the reaction of the pentamer and tetramer of TFE with various O, N and S nucleophiles:



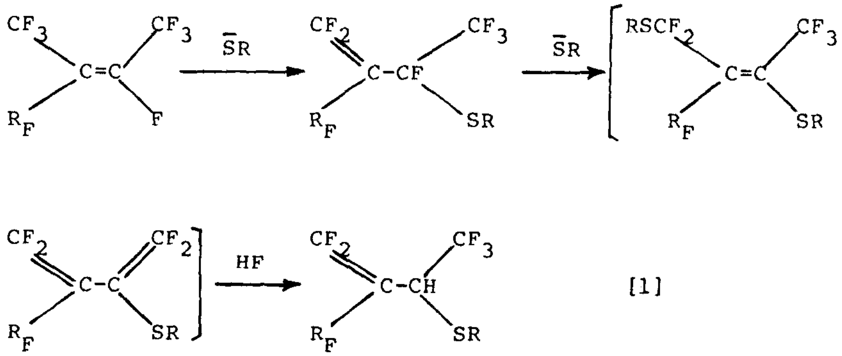
pentamer



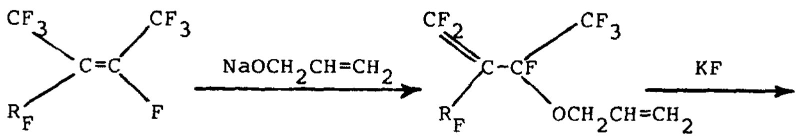
tetramer

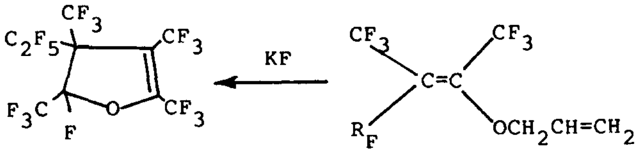
Z:E 1:1

The modes of attack were mainly of the SN2 and SN2' type, and amongst interesting products are:



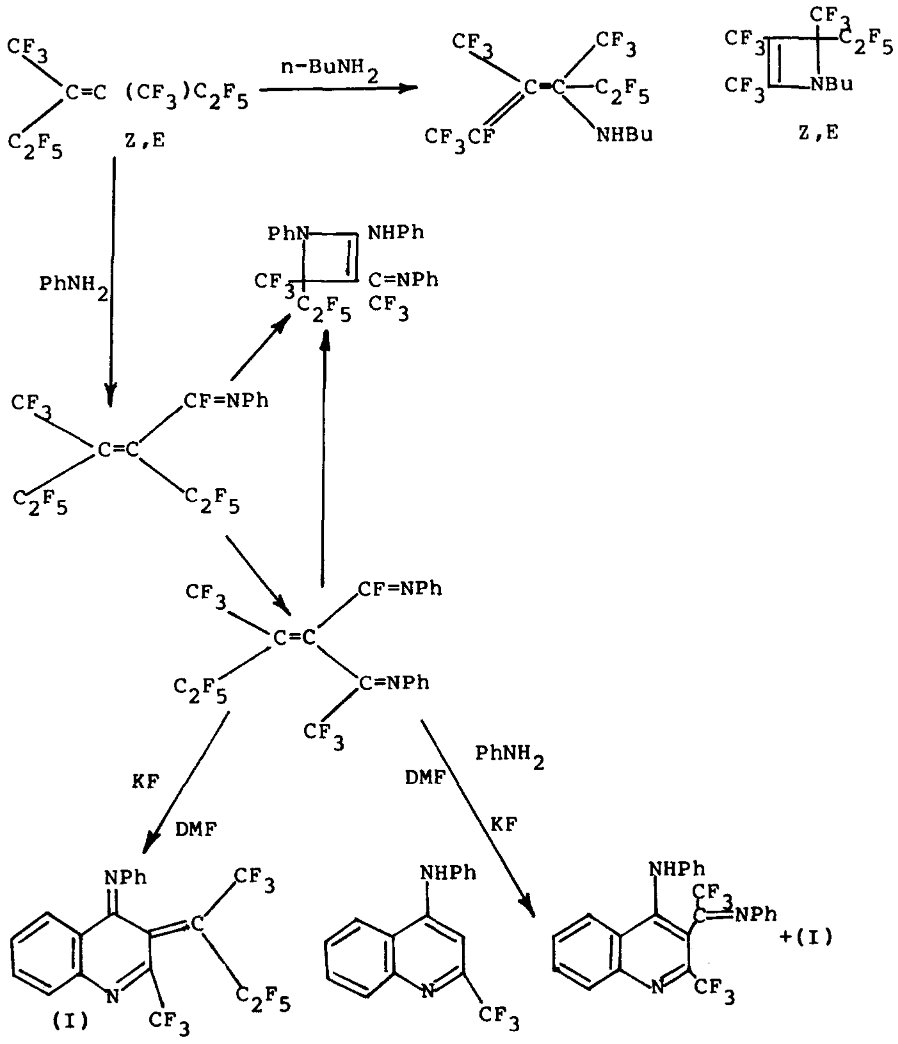
[1]





[2]

$R_F = C(C_2F_5)_2CF_3$

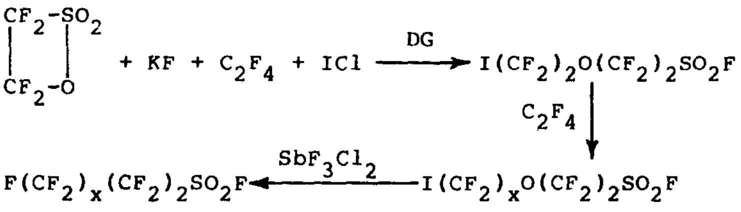


Related to fluoroolefin studies was the study of the regioselectivity of free radical addition to unsymmetrical fluoroolefins using the addition of a cyclopropyl radical to vinylidene fluoride. It was shown that a subtle solvent effect played an important role in the regioselectivity of the addition seeming to originate from the shape of the solvent molecule [4]. Furthermore, contrary to a previous report [5], the photo-initiated addition of t-BuOCl to $CF_2=CH_2$ in CCl_4 under irradiation was found to give both primary adducts $t\text{-}BuOCF_2CH_2Cl$ and $t\text{-}BuOCH_2CF_2Cl$ as well as telomers and chlorinated derivatives [6].

$$t\text{-}BuOCl + CF_2 = CH_2 \longrightarrow t\text{-}BuOCH_2CF_2Cl + t\text{-}BuOCF_2CH_2Cl$$

Fluorinated sulfonic acids, the C-O vs S-O cleavage of sulfonate esters

About 10 years ago we developed a new route for the synthesis of fluorinated sulfonic acids as shown in the following scheme [7].



x=2, 4, 6, 8........

(DG=diglyme)

This is an efficient way of making perfluorosulfonic acids through telomerization. We have studied various byproducts of the reaction and extended the reaction using other fluoroolefins and different halogens [8]. It was shown that the potassium salt of the C8 sulfonic acid is a very good surfactant. Italian Chemists at Montedison published an almost identical process at about the same time [9].

Furthermore we studied the C-O vs S-O cleavage of the various fluorinated sulfonate esters made available to us from these sulfonyl fluorides. We were able to show that the sulfonates of the type:

$R_FO(CF_2)_2SO_3CH_2R_F'$

reacted with nucleophiles to give exclusively the C-O cleavage products and S-O cleavage predominated only with phenyl sulfonates of the type $R_FO(CF_2)_2SO_3Ph$ [10].

When perfluoroalkoxides $R_FCF_2O^-$ were allowed to react with the sulfonate $R_FO(CF_2)_2SO_3CH_2R_F'$ an interesting solvent effect was observed, thus:

$$R_F^2CF_2OCH_2R_F^1 \xleftarrow[\text{HMPA}]{\text{DG,DMF}} R_FO(CF_2)_2SO_3CH_2R_F^1 + R_F^2CF_2O^- \xrightarrow{\text{DMSO}} R_F^2CO_2CH_2R_F^1$$

(DMF=N,N-dimethylformamide; HMPA=hexamethylphosphoramide; DMSO=dimethylsulfoxide)

It seems that the formation of ester may be the result of S-O cleavage:

$$R_FO(CF_2)_2SO_3CH_2R_F^1 + R_F^2CF_2O^- \longrightarrow R_FO(CF_2)_2SO_2OCF_2R_F^2 + R_F^1CH_2O^-$$

$$R_FO(CF_2)_2SO_2OCF_2R_F^2 \longrightarrow R_FO(CF_2)_2SO_2F + R_F^2CFO$$

$$R_F^2CFO + R_F^1CH_2O^- \longrightarrow R_F^2CO_2CH_2R_F^1 + F^-$$

It was further shown that the completely fluorinated sulfonate $R_FO(CF_2)_2SO_3(CF_2)_2OR_F$ previously prepared by Commeyras [11] gave exclusively S-O cleavage on reacting with nucleophiles in contrast to the behavior of the dihydro esters mentioned above This was rationalized as due to the shielding effect of the α-F atoms of the perfluoroalkoxyl group [12]. Furthermore the sulfonate $R_FO(CF_2)_2SO_3C_6F_4X$ was also S-O cleaved exclusively by various nucleophiles and the relative reactivity was shown to be

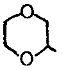
$$R_FSO_3R_F > R_FSO_3Ar_F > R_FSO_3Ar$$

Sulfinatodehalogenation and other ET reactions

During our studies on the synthesis of perfluorotriazine monomers [13], it was accidently discovered that inorganic sulfites K_2SO_3 or Na_2SO_3, in the presence of a small amount of peroxide in aqueous dioxane were able to convert a perfluoroalkyl iodide into the corresponding sulfinate [14]:

$$R_FI + K_2SO_3 \xrightarrow[\text{peroxide}]{\text{dioxane}} R_FSO_2K$$

We were able to show that the reaction involves an ET process by the fact that it was inhibited by the addition of a small amount of hydroquinone or p-dinitrobenzene and the reaction did not take place in peroxide free dioxane nor in the total absence of light. A mechanism was proposed as follows:

$SO_3^{2-} + RO\cdot \longrightarrow RO^- + SO_3^{\dot{-}}$ (R=H or )

$R_FI + SO_3^{\dot{-}} \longrightarrow [R_FI\ SO_3]^{\dot{-}} \longrightarrow R_FSO_2^- + IO\cdot$

$IO\cdot + SO_3^{2-} \longrightarrow IO^- + SO_3^{\dot{-}}$

$IO^- + SO_3^{2-} \longrightarrow I^- + SO_4^{2-}$

and $SO_3^{\dot{-}}$ generated from a different system (from the interaction of HSO_3^- with Ce(IV)) was also able to perform the same reaction i.e. sulfinatodehalogenation [15]. Later we found that another sulfur containing anion radical, $SO_2^{\dot{-}}$, generated from the spontaneous dissociation of the dithionite ion $S_2O_4^{2-}$ was an even more powerful sulfinatodehalogenation agent. It converted R_FI, R_FBr as well as R_FCCl_3 into the corresponding sulfinates [16]:

$R_FX + S_2O_4^{2-} \longrightarrow R_FSO_2^- + X^-$ (X=I, Br)

$R_FCCl_3 + S_2O_4^{2-} \longrightarrow R_FCCl_2SO_2^-$ (R_F=Cl, F, CF_3 etc.)

Here again an ET process was involved e.g.:

$S_2O_4^{2-} \rightleftharpoons 2SO_2^{\dot{-}}$

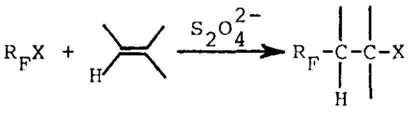
$R_FX + SO_2^{\dot{-}} \longrightarrow [R_FXSO_2]^{\dot{-}} \longrightarrow R_FSO_2^- + X\cdot$ (in cage)

$X\cdot + S_2O_4^{2-} \longrightarrow X^- + SO_2 + SO_2^{\dot{-}}$

or $[R_FXSO_2]^{\dot{-}} \longrightarrow R_F\cdot + SO_2 + X^-$

$R_F\cdot + S_2O_4^{2-} \longrightarrow R_FSO_2^- + SO_2^{\dot{-}}$ (out of cage)

Indeed we were able to trap the R_F radical with various olefins to form 1:1 adducts or telomeric products [17].

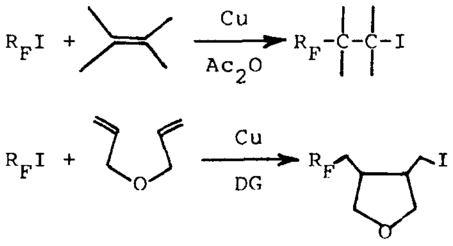


It was interesting to notice that during sulfinatodehalogenation $SO_3^{\overset{\bullet}{-}}$ reacted with R_FI with the net result of ejecting an oxygen atom whereas $SO_2^{\overset{\bullet}{-}}$ reacted without this ejection.

However up to now we have not been able to cause a secondary perfluoroalkyl iodide to undergo this reaction. Reductive deiodination occurs instead, with the formation of secondary R_FH, again by a radical mechanism, as the secondary perfluoroalkyl radical can also be trapped in the presence of olefin.

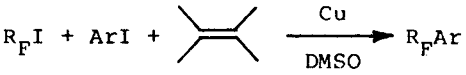
$$R_FCF(CF_3)I + S_2O_4^{2-} \longrightarrow R_FCF(CF_3)H$$

The reaction of R_FI with aryl iodides, or with other aromatic compounds or with olefins in the presence of Cu has been extensively studied by various workers [18]. We have considered the effect of solvents on the reaction and it was shown that R_FI/Cu in Ac_2O, DE or acetonitrile were also good systems for generating $R_F\bullet$ which added to olefin to yield adducts in 60-70% [19]. (DE=diethylene glycol)

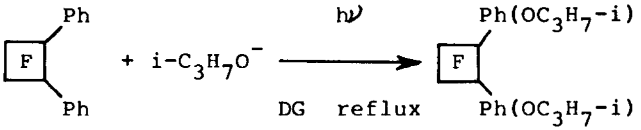


Z:E = 3:1

The addition of aryl iodide to the system did not compete with the olefin and no R_FAr was formed. The reaction was inhibited by hydroquinone or p-DNB and accelerated by UV-irradiation. The same reaction carried out in DMSO was not sensitive to radical or electron scavengers and aryl iodide competed with olefin for R_F species to give ArR_F exclusively.



Another reaction which was shown to be initiated by light and inhibited by the addition of hydroquinone or p-DNB was that shown below [20]:



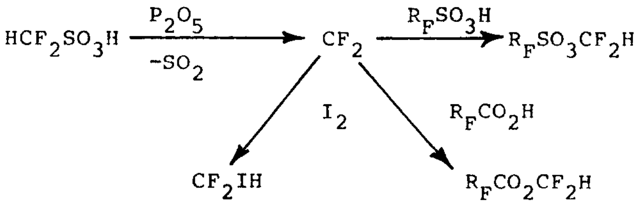
but it was peculiar that other alkoxides did not react. Furthermore, only the cis-diphenylcyclobutane reacted whereas the trans isomer did not undergo the same reaction.

Difluorocarbene

Recently we have found that difluoromethanesulfonic acid and its derivatives were very good difluorocarbene sources [21]. Thus CHF_2SO_2F reacted readily with some nucleophiles under mild conditions to generate CF_2, e.g.:

$$HCF_2SO_2F + OH^- \longrightarrow H_2O + SO_2 + F^- + CF_2 \xrightarrow{OH^-} HCO_3^-$$

and HCF_2SO_3H itself generated CF_2 on treatment with P_2O_5 or $SOCl_2$, $POCl_3$ [22], thus:



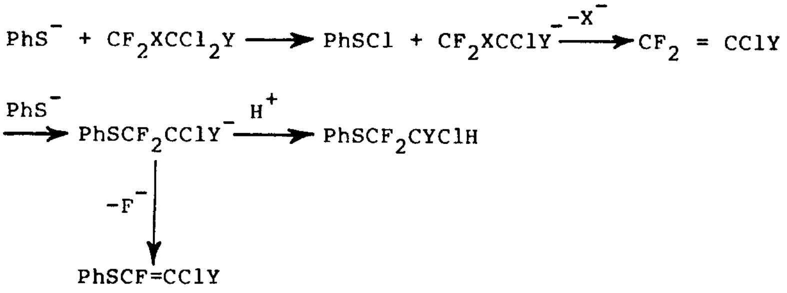
(R_F=HCF_2 or other R_F groups)

Other derivatives such as HCF_2SO_3R (R=CF_2H, Ph, C_6F_5) and HCF_2SO_2NRAr (R=H, Me) also gave CF_2 derived products on treatment with base under mild conditions [23].

The methoxycarbonyl derivative $MeO_2CCF_2SO_2F$ also generated CF_2 on treatment with nucleophiles in aprotic solvents such as LiCl/HMPA/THF, KI/dioxane or NEt_3/ dioxane. However in aqueous organic systems it produced both CF_2: and HCF_2^- in about4:1 ratios [24].

Halophilic reactions of perfluorohaloalkanes

The reaction between PhS^- and CF_2XCYCl_2 (X,Y=Cl,F; F,Cl; Cl,Cl) was shown to be a halophilic process with the initial attack of nucleophile on Cl, thus:



$$PhSCF_2CClY^- + CF_2XCCl_2Y \longrightarrow PhSCF_2CCl_2Y + CF_2XCClY^-$$

$$PhSCl + PhS^- \longrightarrow PhSSPh + Cl^-$$

PhS^- also reacted with CF_2Br_2 in a similar way, in order to get a high yield of $PhSCF_2Br$, it was necessary to use

$$CF_2Br_2 + PhS^- \xrightarrow[PTC]{} PhSCF_2Br$$

carefully purified solvent and reagents so as to decrease the H-abstraction reaction [25].

Furthermore in the presence of phase transfer catalysts, PhO^- and other alkoxides also attacked the Br atom of CF_2BrCF_2Br CF_2Br_2 and $CF_2BrCFClBr$ without initiation by PhS^- and products derived from initial bromophilic attack were formed [26]. These reactions were shown to proceed through carbanions rather than ET processes.

$$PhO^- + BrCF_2CF_2Br \xrightarrow{PTC} PhOBr + BrCF_2CF_2^-$$

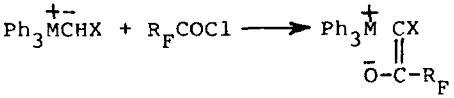
$$BrCF_2CF_2^- \longrightarrow C_2F_4 \xrightarrow{PhO^-} PhOCF_2CF_2^-$$

$$PhOCF_2CF_2^- + BrCF_2CF_2Br \longrightarrow PhOCF_2CF_2Br + BrCF_2CF_2^-$$

The presence of PhOBr was confirmed from the mass spectral detection of $BrC_6H_4OCF_2CF_2Br$ and $BrC_6H_4OCF_2CF_2H$ which might be derived from electrophilic attack of PhOBr on the phenyl ring.

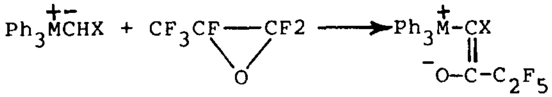
Synthesis of organofluorine compounds via organometallics

Ph_3AsCHX, the arsenic analog of a Wittig reagent when X= electron withdrawing group, was shown to be more reactive than the corresponding Wittig reagents. Therefore As ylides of this type find interesting synthetic applications e.g. both ylides react with R_FCOCl or $CF_3CF{=}CF_2$ acting as nucleophiles, thus:



$$Ph_3\overset{+-}{M}CHX + R_FCOCl \longrightarrow Ph_3\overset{+}{M}\,\underset{\overset{-}{O}-C-R_F}{\overset{CX}{\|}}$$

[27]



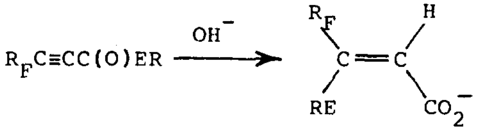
[28]

and

$$Ph_3\overset{+}{As}\overset{-}{C}HX + CF_2{=}CFR_F \longrightarrow Ph_3\overset{+}{As}\overset{-}{C}HXCF{=}CFR_F$$

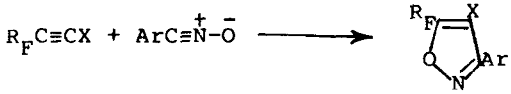
X=COR, CO_2R, CN.

Pyrolysis of the product $Ph_3PC(CO_2R){=}C(R_F)O^-$ under reduced pressure gave a good yield of $R_FC{\equiv}CCO_2R$, and the reaction was also applied to other compounds where X=C(O)SR [30], COR [31] CN [32] and $PO(OPh)_2$ [33]. When the acetylenic ester or thiol ester was hydrolysed with dilute aqueous base, an interesting rearrangement occurred, i.e. the OR or SR of the ester part migrated to add to the β-carbon of the triple bond to form a vinyl ether [34], thus:



(E =O,S)

The acetylenic derivatives $R_FC{\equiv}CX$ (X= CO_2R, $PO(OPh)_2$) reacted with aromatic nitrile oxides to give 1,3-dipolar adducts [35].

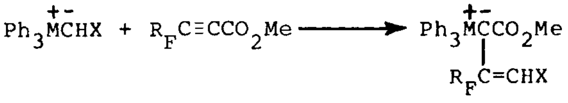


X=CO_2R, $PO(OPh)_2$

Further reaction of $R_FC{\equiv}CCO_2Me$ with $Ph_3\overset{+-}{M}CHCO_2Me$ gave the products which split to give olefins: (M=As, refluxing MeOH. M=P, 150° sealed tube)

$$Ph_3\overset{+-}{M}CXC(R_F){=}CHCO_2Me \longrightarrow CH_2XC(R_F){=}CHCO_2Me$$

and

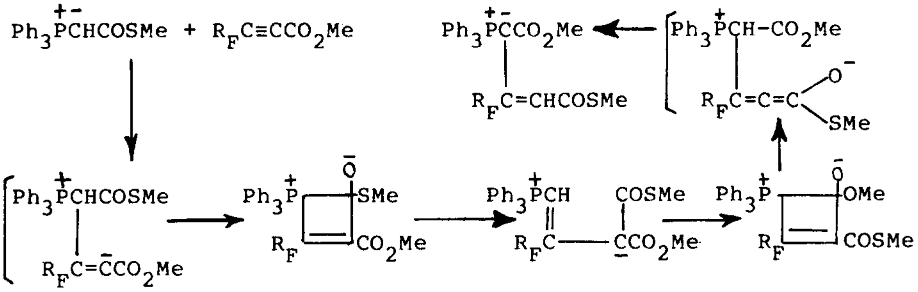


$$Ph_3\overset{+-}{M}CHX + R_FC{\equiv}CCO_2Me \longrightarrow Ph_3\overset{+-}{M}\underset{R_FC=CHX}{\underset{|}{C}}CO_2Me$$

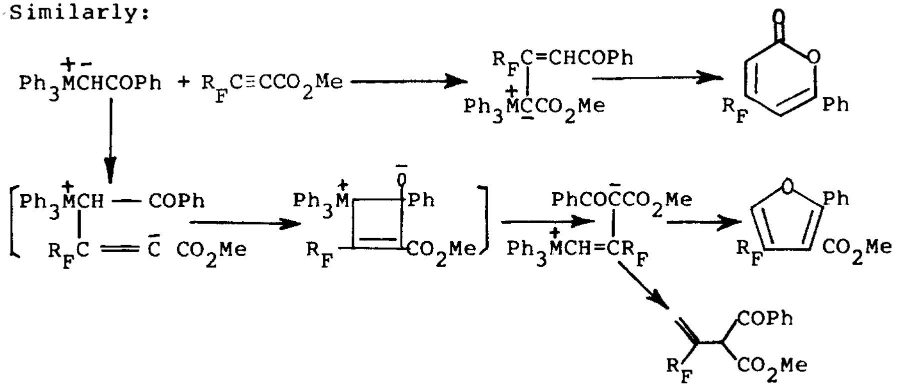
[36]

(X= COSMe, COPh.)

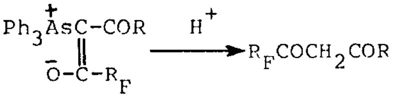
i.e:



Similarly:



Furthermore the compound $Ph_3AsC(COR){=}C(R_F)O^-$ was readily cleaved by acid to give fluorinated β-diketones in good yield:



$$\mathrm{Ph_3\overset{+}{As}\underset{\bar{O}-C-R_F}{\underset{\|}{C}}-COR \xrightarrow{H^+} R_FCOCH_2COR}$$

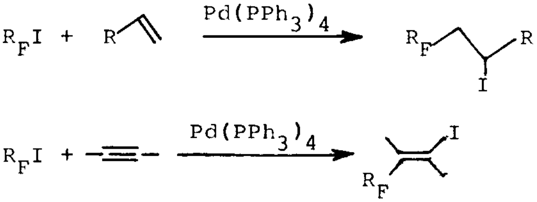
[37]

Pd(O) promoted reactions in fluoroorganic compound were also studied and two interesting reactions were observed:

$$R_FCF_2I + N(CH_2CH_2R)_3 \xrightarrow{Pd(O)} R_FCF_2CR{=}CHN(CH_2CH_2R)_2$$

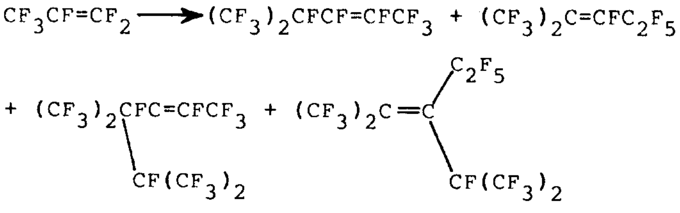
$$\longrightarrow R_FCOCR{=}CHN(CH_2CH_2R)_2 \qquad [38]$$

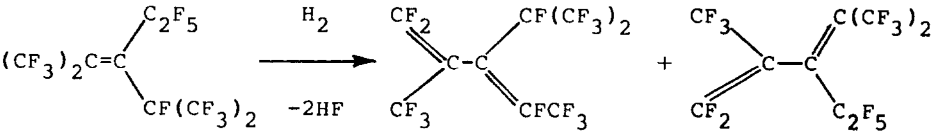
and



Other organometallics such as Pt(O), Rh(I) were also shown to catalyze the latter reactions [39].

Another interesting reaction catalysed by organometallics was the oligomerization of C_3F_6 [40] and polymerization of $CF_3C{\equiv}CCF_3$ [41] and related compounds catalysed by bis-π-arene Cr(0) in C_6H_6, thus:





It was shown that perfluorobutyne-2 and related compounds could be polymerized to give either three-dimensional infusible products or dark colored semiconducting materials under different conditions [42].

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