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REVIEW

FLUOROCARBON IODIDES - VERSATILE REAGENTS

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INTRODUCTION

It has been known for a long time that fluorocarbon iodides are useful reagents for the preparation of a variety of compounds via 1) additions across the carbon-carbon double bond of unsaturated systems or 2) reactions of organometallic reagents. Recent research on iodonium salts has widely extended the synthetic usefulness of fluorocarbon iodides.

The first fluorocarbon iodides reported [1], CF_3I and CF_3CF_2I, were prepared by the reaction of CI_4 and $CI_2{=}CI_2$ with iodine pentafluoride. Shortly thereafter a method was described [2] for preparing CF_3I from silver trifluoroacetate and iodine. This method has been widely used to prepare iodides when the starting acids were available; even diiodides have been made in good yields [3]. Excellent yields of CF_3I and n-C_3F_7I were also obtained by refluxing potassium salts of fluorocarbon acids with iodine in DMF [4], a reaction postulated to proceed via radical intermediates. The reaction of CF_3COCl with KI at 200° gave CF_3I in excellent yield [5].

Fluoroolefins have been allowed to react with 'IF' made from IF_5 and iodine to form iodides [6]. Tetrafluoroethylene gave CF_3CF_2I in 69% yield while hexafluoropropylene gave CF_3CFICF_3 in 99% yield. Longer chain iodides are made commercially by the telomerization of a fluorocarbon iodide, usually CF_3CF_2I, with tetrafluoroethylene.

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Fluorocarbon iodides react with a variety of unsaturated compounds by a radical process to give the corresponding perfluoroalkyl iodo derivative [7]:

$$R_fI + \rangle C{=}C\langle \longrightarrow R_f\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}I$$

Initiation occurs under the influence of light, heat, γ-radiation, peroxides, azo compounds or by a copper-amine mixture. The direction of addition to unsymmetrical olefins is such that the more stable intermediate radicals is usually formed,

$$\cdot CF_3 + CH_2{=}CHCH_3 \longrightarrow CF_3CH_2\dot{C}HCH_3 \longrightarrow CF_3CH_2CHICH_3$$

Higher molecular weight addition products can also be obtained by increasing the ratio of alkene to alkyl halide.

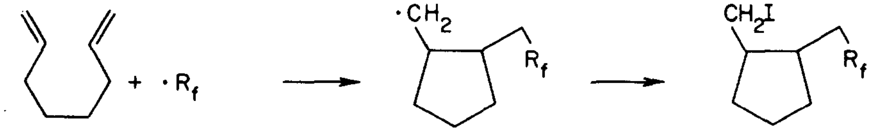
$$CF_3CF_2CF_2CF_2I + 2\ CH_2{=}CH_2 \longrightarrow CF_3CF_2CF_2CF_2(CH_2CH_2)_2I$$

Unsaturated iodides also participate in such reactions; for example,

$$CF_2{=}CFI + C{=}C \longrightarrow CF_2{=}CFC\text{-}CI.$$

Reactions between iodides and unsaturated hydrocarbon and halogenated compounds were extensively studied in the 1950's [7].

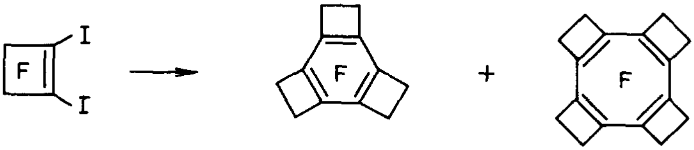
Diolefins also participate in similar reactions [8]; 1,5-hexadiene and 1,7-octadiene reaced in a normal manner to give linear adducts; however, 1,6-heptadiene reacted with only one unit of iodide to give a perfluoroalkylcyclopentyl iodide. Diallyl ether reacted in the same manner.



It should be noted that this result requires the formation of a primary radical whereas the formation of a substituted cyclohexane would occur *via* a more stable secondary radical.

Fluorocarbon iodides also add to acetylenes, allene, vinyl silanes, unsaturated alcohols, esters and acids to give functionalized derivatives [9]. Some of these materials find use in surfactants and soil repellant applications. The iodine in such compounds can be easily 1) replaced by hydrogen, 2) removed to form an alkene or even an epoxide or 3) coupled to form difunctional alcohols, esters, acids, etc.

Alkyl perfluorocarbon iodides also react via radical intermediates with aromatic compounds to give perfluoroalkyl derivatives. For example, when perfluoroheptyl iodide was heated to 250° for 10 hours with benzene, a 62% yield of perfluoroheptylbenzene was obtained [10]. The reaction generally gives good yields when used with benzene, toluene, naphthalene, halobenzene, nitriles and phthalic anhydride. In 1969 it was discovered that iodo aromatic compounds react with aryl iodides under much milder conditions in the presence of copper to give alkylated derivatives [11]; functionalized perfluoroalkyl iodides and aryl iodides also react readily. Further research [12] showed that a variety of non-iodo aromatic compounds also react with iodides under very mild conditions to give alkylated aromatic products. Unsaturated iodides also participate in reaction with aromatic compounds and also couple [13]; CFCl=CFI and iodobenzene gave $C_6H_5CF=CFCl$ and also 1,4-dichloro-tetrafluorobutadiene. Unsaturated diiodides also couple in the presence of copper and DMF under relatively mild conditions to give interesting products [14]:



Iodides can also be made to couple in the presence of zinc; for example,

$$CF_2ClCFClI \longrightarrow CF_2ClCFClCFClCF_2Cl \longrightarrow CF_2{=}CFCF{=}CF_2 \quad [15]$$

method has been used to prepare a number of α,ω-perfluorodienes [16].

Zinc, CF_3I and a wide variety of aldehydes and ketones have been found to react under ultrasonic conditions to give the corresponding alcohols in good yields [17]; even CO_2 reacts under these conditions [18]. No practical method has been developed to prepare a Grignard reagent from CF_3I and efforts to prepare longer chain reagents by the reaction of the iodide with magnesium have been largely unsuccessful. However, the magnesium derivative as well as the lithium reagent can be made by exchange methods. In 1953 the following reaction was reported [19],

$$CF_3CF_2CF_2I + C_6H_5MgBr \longrightarrow C_6H_5I(83\%) + CF_3CF_2CF_2MgBr \longrightarrow C_3F_7C(CH_3)_2OH$$

At higher temperature fluoroolefins and halofluoroolefins are obtained and an excess of the Grignard reagent causes the formation of alkylated products [20].

$$R_fCF_2CF_2I + CF_3MgBr \text{ (1:4 ratio)} \longrightarrow R_2CF{=}CFCH_3(20\%) + R_fCF{=}C(CH_3)_2 \text{ (63\%)}$$

Undoubtedly the carbon of the Grignard reagent attacks the iodine to release a fluorocarbanion which loses a fluorine atom to become $R_2CF{=}CF_2$ which reacts further.

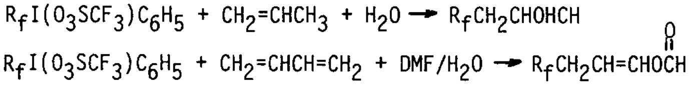
Other nucleophiles also attack the iodine rather than carbon; for example, sodium methoxide and CF_3CFICF_3 do not give $CF_3CF(OCH_3)CF_3$ but rather CF_3CHFCF_3 [6]. There was some hope that fluorocarbon iodides could be made to participate in alkylation reactions when it was reported that perfluoroalkyl ketones were obtained from enamines; however, the reaction was shown to proceed via radical intermediates [21]. The sodium salt of 2-nitropropane gave good yields but even this reaction was shown to go by a radical process [22]. However, it was reported in 1981 that when perfluoroalkyl iodides were converted to iodonium salts, the latter would undergo a displacement reaction on the carbon containing the iodine to form fluoroalkylated derivatives. Various Grignard reagents were found to give good yields of fluoroalkylalkanes.

$$RMgCl + C_8F_{17}I(O_3SCF_3)C_6H_5 \longrightarrow R\text{-}C_8F_{17}$$

Lithium reagents such as $C_6H_{13}C{=}CLi$ and the sodium salt of 2-nitropropane also reacted to give perfluoroalkyl derivatives [23]. A later paper showed that the iodonium salts would react with olefins to give good yields of alkylated alkene [24]. Furthermore, when the reaction with alkene was carried out in the presence of nucleophiles, functionalized products were obtained as shown below,

$$R_fI(O_3SCF_3)C_6H_5 + CH_2{=}CH_2 + CH_3OH \rightarrow R_fCH_2CH_2OCH$$

$$R_fI(O_3SCF_3)C_6H_5 + CH_2{=}CHCH_3 + H_2O \rightarrow R_fCH_2CHOHCH$$



$$R_fI(O_3SCF_3)C_6H_5 + CH_2{=}CHCH{=}CH_2 + DMF/H_2O \rightarrow R_fCH_2CH{=}CHO\overset{\overset{O}{\|}}{C}H$$

From the above discussion it can be seen that fluoroalkyl iodides serve as attractive starting materials for a host of organic products.

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