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Chapter 12

RECENT ADVANCES IN THE CHEMISTRY OF HALOGENOFLUOROCARBONS

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Introduction

Since the isolation of molecular fluorine by Moissan in 1886, one of the biggest advances on the industrial scene was the introduction of dichlorodifluoromethane in 1930 as an inert, non-toxic refrigerant [1, 2] (see Chapter 4). A multitude of related compounds have been made for various purposes since then [2 - 4]. Chlorofluoromethanes represent 90% of the total tonnage produced, but the much-used term *chlorofluorocarbon* does not accurately describe this group of compounds because some contain hydrogen or bromine (e.g. the tetrafluoroethylene precursor and refrigerant CHF_2Cl and the fire extinguishants CF_2ClBr and CF_2BrCF_2Br). Thus here the more suitable terms *halogenofluoroalkane* and *halogenofluorocarbon* are used, the implication being that *halogeno* means chlorine and/or bromine. Note that iodo analogues are not usually considered as representative halogenofluorocarbons because of their high costs, their different modes of preparation and uses, and the weakness of the C—I bond. The chemistry of hydrogen-containing compounds, *i.e.* halogenofluoromethanes, is dominated by their transformation into fluorinated carbenes, which can be trapped with olefins to give fluorinated cyclopropanes [5]; indeed, the reactivity of these mixed haloforms is better understood than that of their halogenofluorocarbon counterparts.

This review is focused on the chemistry of halogenofluorocarbons (*i.e.* fluorinated perhalogenoalkanes) containing chlorine or bromine atoms; iodo analogues have been reviewed recently [6, 7] and are mentioned in Chapter 11. Recent studies on the reactivities of simple bromo(chloro)fluoroalkanes were initiated with the aim of introducing fluorinated groups into organic molecules via readily-available commercial starting materials, and this is the aspect we wish to draw attention to. First, however, some comments on environmental aspects need to be made.

Chlorofluorocarbons and stratospheric ozone

A number of substances released to the atmosphere, some as a result of human activities, have the potential to affect atmospheric ozone. Some

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substances may have the potential to increase ozone concentrations, and others to decrease it. However, none acts independently since they are strongly coupled by their complex chemistry or radiative feedback processes. The extent to which ozone will be affected by human activities, if at all, remains uncertain. Among the trace gases considered to have the potential to affect stratospheric ozone in various ways are nitrogen oxides (NO_x, N_2O), chlorofluorocarbons, 'methyl chloroform' (CH_3CCl_3), carbon tetrachloride, methane and carbon dioxide.

In the hypothetical situation in which the most important chlorofluorocarbons $CFCl_3$ and CF_2Cl_2 are considered entirely in isolation, and the releases are maintained at constant rates (based on the 1977 rate), current calculations continue to estimate an eventual steady-state reduction in the total ozone column of about 3 - 5% [8, 9]. This should be compared with the 16 - 18% reported in 1979, 5 - 9% in 1982 and 3 - 5% in 1983. Such calculations concerning the effect of a single species on atmospheric ozone are useful research tools but are limited because they do not allow for known trends in other atmospheric trace-gas species which interact as indicated above.

Analysis of total column ozone, globally, gives no evidence of any statistically significant trends through the 1970s to the present day [10]. There are, however, quite large natural variations in ozone concentration and distribution which create complications; but statistical methods of ozone-trend analysis can now offer an early warning of ozone change. The magnitude and sign of the predicted change in total ozone for multiple trace-gas scenarios over the next century depends critically on the scenarios assumed. Reasonable projections suggest little change in total ozone (less than 1%) over the next few decades, unless there is sustained growth in chlorofluorocarbon usage, leading to a several-fold increase in production [10]. Overall, emissions resulting from human activities are calculated to increase ozone in the lower stratosphere and upper troposphere, and to decrease ozone by a similar amount in the middle stratosphere. A redistribution of the vertical profile of ozone may have some climatic consequences; these are as yet not understood, remain unquantified, and are the subject of current research.

Commercial production of halogenated fluoroalkanes remains considerable [11]. The prices, in 1985, for some aerosol propellants are given in French francs in Table 12.1; comparison with U.K. prices in pounds sterling in 1977 [12] shows that their costs remain moderate in view of the HF technology involved.

Reactions of halogenofluorocarbons

Radical additions

Radical-initiated addition of halogenofluorocarbons across multiple C—C linkages in olefins or acetylenes is important for synthetic purposes [13]. Similar additions of perfluoroalkyl iodides are, of course, well known

TABLE 12.1

Prices of chlorofluorocarbon propellants

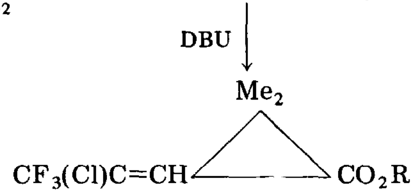
Price	Year	$CFCl_3$ (P-11)	CF_2Cl_2 (P-12)	CF_2ClCF_2Cl (P-14)
£ per tonne[a]	1977	386	430	780
fr. per tonne[b]	1985	7000	8200	16400

[a] R. J. Hodson, in R. E. Banks (ed.), *Organofluorine Chemicals and Their Industrial Applications*, Ellis Horwood, Chichester, 1979, p. 90.
[b] M. Perrier (ATOCHEM), personal communication.

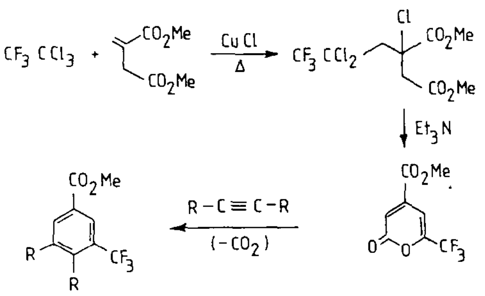
(see Chapter 11). Heat, UV light or a radical source (peroxides, azo initiators) can be used to initiate reaction via carbon–halogen homolytic cleavage, a recent example being the UV-initiated addition of $CF_2BrCFXBr$ (X = Cl, F) to ethylene. This yields intermediates which have been used for the synthesis of 1,1,2-trifluorobuta-1,3-diene and methyl trifluoroacrylate [14]. Catalysis using copper(I) chloride and ethanolamine can also be employed [15], as in the synthesis of fluorinated pyrethroids (Scheme 12.1) [16]. The condensation of CF_3CCl_3 with dimethyl itaconate gives a pyrone which is able to undergo Diels–Alder reactions with acetylenes; spontaneous decarboxylation of the cycloadducts produces benzotrifluoride derivatives (Scheme 12.2) [17].

$$CF_3CCl_3 + CH_2{=}CHCMe_2CH_2CO_2R$$

$$\xrightarrow[HOCH_2CH_2NH_2]{CuCl} CF_3CCl_2CH_2CHClCMe_2CH_2CO_2R$$



Scheme 12.1. Synthesis of fluorinated pyrethroids [16].



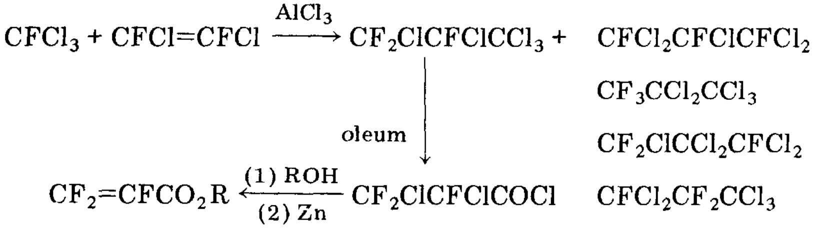
Scheme 12.2. Synthesis of trifluoromethylated benzenes [17].

Thermolysis of difluorodichloromethane in the presence of various hydrocarbons at temperatures between 150 and 250 °C yields compounds substituted by a CF_2Cl group [18].

The photochemical reduction of halogenofluorocarbons is often characterised by a high selectivity, as exemplified by the transformation $CFCl_2CF_2Cl \xrightarrow{\text{with H-donor/UV}} CHFClCF_2Cl$ [19].

Electrophilic reactions

Though not very reactive under acid conditions, halogenofluorocarbons participate in some interesting additions to fluoro-olefins in the presence of strong Lewis acids. These modified Prins reactions have been reviewed [20]. Unfortunately, such ionic addition reactions to perhalogenated olefins are not entirely product-specific. In the case of $CFCl{=}CFCl$, for example, reaction with trichlorofluoromethane/aluminium chloride gives various isomers of trifluoropentachloropropane. This mixture contains 64% of the 1,1,2-trifluoropentachloro isomer, which can be utilised for the preparation of esters of trifluoroacrylic acid [21] (Scheme 12.3). In the methane series, such ionic addition reactions are limited to $CFCl_3$: on contact with aluminium chloride, disproportionation of CF_2Cl_2 occurs, and CF_3Cl does not react under these conditions.



Scheme 12.3. Synthesis of esters of trifluoroacrylic acid [21].

Hydrolysis of the trihalogenomethyl group in fluorinated alkanes can be performed with oleum in the presence of mercury(II) salts [22], e.g. $CF_2ClCCl_3 \rightarrow ClCF_2COCl$. The reaction of CF_3CCl_3 with sulfur trioxide in the presence of a halogen catalyst leads to trifluoroacetyl chloride [23].

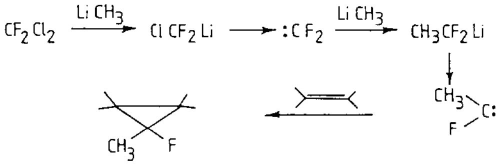
Reactions with nucleophiles

Initial observations

The first attempts to condense halogenofluorocarbons with nucleophiles (Nu) were rather disappointing: no substitution reactions at carbon were observed ($Nu^- + CX_4 \not\rightarrow NuCX_3 + X^-$) but haloforms were produced, indicative of nucleophilic displacement on a 'positive' halogen [24, 25]:

$$Nu^- + X{-}CX_3 \longrightarrow NuX + {}^-CX_3 \xrightarrow{\text{solvent}} HCX_3$$

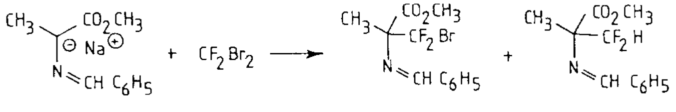
In aprotic media, decomposition of the fluorinated carbanion to a carbene which then reacts with the nucleophile can explain the successive loss of fluorine atoms as fluoride. For example, condensation of organometallic reagents with CF_2Br_2 or CF_3Br leads to non-fluorinated olefins [26]. Capture of intermediate carbenes thus generated by olefins yields fluorocyclopropanes [27] (e.g. Scheme 12.4).



Scheme 12.4. Synthesis of fluorocyclopropanes from dichlorodifluoromethane [27].

Interestingly, in 1955 the reaction of potassium phenoxide with CF_2Br_2 was reported to occur only in acetone: $C_6H_5OK + CF_2Br_2 \rightarrow C_6H_5OCHF_2$ [28], a conversion which obviously could not be interpreted as a simple substitution and is now viewed as involving a carbene process. In classical textbooks it was concluded that "these halides (halogenofluorocarbons) do not undergo the usual nucleophilic reactions of the alkyl halides" [29].

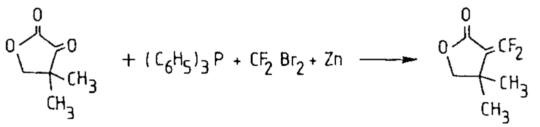
Since 1970, however, some reactions have been described which can be written like formal substitutions, e.g. the reaction of CF_2Br_2 with triphenylphosphine to yield a bromodifluoromethylphosphonium salt, *i.e.* $(C_6H_5)_3P + CF_2Br_2 \rightarrow [(C_6H_5)_3PCF_2Br]^+ Br^-$ [30], and, in cases involving perfluoroalkyl iodides, perfluoroalkylation of enamines [31, 32] and thiols [33, 34]. By contrast, condensation of CF_2Br_2 with a carbanion derived from an α-amino acid gave a mixture of two compounds, one substituted by a CF_2Br and the other by a CF_2H group [35] (Scheme 12.5). A mixture was also obtained by reaction of the ethoxide ion with 1,2-dibromotetrafluoroethane: $C_2H_5OH/KOH + BrCF_2CF_2Br \rightarrow C_2H_5OCF_2CF_2Br + C_2H_5OCF_2CF_2H$ [36]. Subsequent development of these fluoroalkylations will now be discussed according to the nucleophiles involved.



Scheme 12.5. Fluoroalkylation of alanine with dibromodifluoromethane [35].

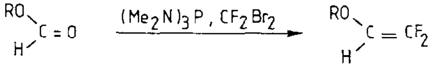
Phosphorus nucleophiles

Numerous condensations involving phosphorus-centred nucleophiles have been described, and the halogenomethylenephosphoranes prepared from the phosphonium salts have been used in Wittig reactions to obtain fluorinated olefins [37]. The phosphonium salt is usually dehalogenated by treatment with a second molar proportion of the phosphine or with a metal. The triphenylphosphine/dibromodifluoromethane/zinc reagent [38] has been used for the preparation of an α-difluoromethylene lactone [39]

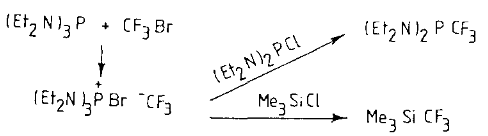


Scheme 12.6. Difluoromethylenation of an α-ketolactone with dibromodifluoromethane [39].

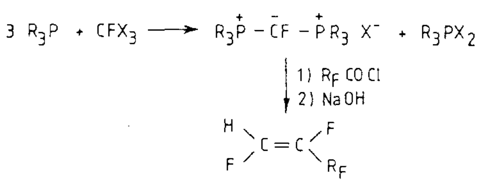
(Scheme 12.6), and difluoromethylenation of a formate ester with a mixture tris(dimethylamino)phosphine and CF_2Br_2 in triglyme has been reported [40] (Scheme 12.7). Highly nucleophilic aminophosphines like $(Me_2N)_3P$ even react with bromotrifluoromethane, and the trifluoromethyl anion generated can be captured by phosphorus or silicon chlorides [41 - 43] (Scheme 12.8). The Michaelis–Arbuzov reaction between CF_2Br_2 and trialkylphosphites has been described: $(RO)_3P + CF_2Br_2 \rightarrow (RO)_2P(O)CF_2Br$ [44]; and the first preparation of a fluorine-containing phosphoranium salt via reaction of fluorotrihalomethanes with tertiary phosphines has also been reported [45] (Scheme 12.9).



Scheme 12.7. Difluoromethylenation of a formate ester with dibromodifluoromethane [40].



Scheme 12.8. Synthesis of trifluoromethyl derivatives of phosphorus and silicon from bromotrifluoromethane [41 - 43].



Scheme 12.9. Synthesis of polyfluorinated olefins from fluorotrihalogenomethanes [45].

Sulphur and selenium nucleophiles

Various condensations with sulphur nucleophiles have been studied. Thiophenoxides react with CF_2Br_2 or CF_2BrCl to give fluorinated thioethers: $ArS^- + CF_2Br_2 \rightarrow ArSCF_2Br + ArSCF_2H$ [46 - 50]; at low temperature in DMF, disubstitution of CF_2ClBr occurs: $ArS^- + CF_2ClBr \rightarrow ArSCF_2SAr$

[48, 51]. Fluoroalkylation of thiophenoxides with $BrCF_2CF_2Br$ is possible too: $ArS^- + BrCF_2CF_2Br \rightarrow ArSCF_2CF_2Br + ArSCF_2CF_2H$ [52], and similar condensations with other polyhalogenofluoroalkanes, like 1,1,2-trichlorotrifluoroethane, are known [53 - 55].

Reactions involving CF_2Cl_2 require the use of UV irradiation or a slight pressure: $ArS^- + CF_2Cl_2 \rightarrow ArSCF_2Cl + ArSCF_2H + ArSCF_2SAr$ [51, 53, 55, 56]. Even the poorly reactive CF_3Br has been transformed to thioethers under pressure [53, 55, 56] or under UV irradiation in liquid ammonia [57, 58]: $ArS^- + CF_3Br \rightarrow ArSCF_3$.

Dehalosulphination of $CFCl_3$ and 1,1,1-trichloropolyfluoroalkanes with sodium dithionite in the presence of sodium bicarbonate in aqueous acetonitrile has been described, e.g. $CF_3CCl_3 \xrightarrow{Na_2S_2O_4/NaHCO_3} CF_3CCl_2SO_2Na$ [59].

Selenium-based nucleophiles are also reactive, e.g. $CH_3Se^- + BrCF_2CF_2Br \rightarrow CH_3SeCF_2CF_2SeCH_3$ [60]; $C_6H_5Se^- + CF_2Br_2 \rightarrow C_6H_5SeCF_2Br$ [61].

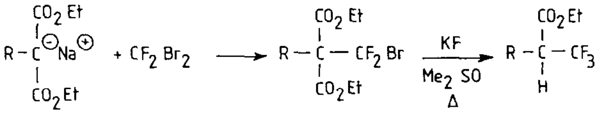
Oxygen nucleophiles

Phenoxides are less reactive than thiophenoxides. Nevertheless, fluoroalkylation has been observed with some bromofluoroalkanes. Re-examination of the behaviour of CF_2Br_2 in the presence of potassium phenoxide in acetone confirmed the formation of the difluoromethyl ether $C_6H_5OCHF_2$ [28]. However, in DMF the main product was (bromodifluoromethoxy)-benzene: $ArO^- + CF_2Br_2 \rightarrow ArOCF_2Br + ArOCF_2H$ [47, 62, 63].

Similar reactions with polyhalogenofluoroethanes were described [55, 64 - 66], but none with CF_2Cl_2 or CF_3Br. These condensations are not always spontaneous. Good nucleophiles, like thiolates, can be used for their initiation.

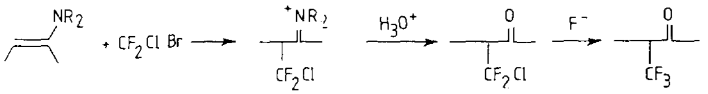
Carbon nucleophiles

The study of carbon-centred nucleophiles has shown that fluoroalkylation by means of CF_2Br_2 or CF_2ClBr occurs in the cases of lithium acetylides ($R{-}C{\equiv}C{-}Li + CF_2Br_2 \rightarrow R{-}C{\equiv}C{-}CF_2Br$) and sodium salts of substituted active-methylene compounds [67 - 69] (Scheme 12.10). Perfluorocarbanions



Scheme 12.10. Synthesis of α-trifluoromethyl esters from dibromodifluoromethane.

are also alkylated by CF_2Br_2 [70]. Enamines behave like carbon nucleophiles, and their spontaneous condensation with CF_2ClBr gave α-fluoromethylketones [71] (Scheme 12.11). On the other hand, Grignard derivatives of halogenofluoroethanes have been obtained via the exchange reaction $CF_3CYZBr + RMgX \rightarrow CF_3CYZMgX$ ($Y, Z = F, Cl, Br$) [72, 73].



Scheme 12.11. Synthesis of α-trifluoromethyl ketones from bromochlorodifluoromethane [71].

Halogen nucleophiles

The exchange of halogen for fluorine in reactions of vicinal dihalogenopolyfluoroalkanes with caesium fluoride in diglyme has been claimed [74].

Mechanisms

What exactly are the processes involved in the above reactions of halogenofluorocarbons with nucleophilic reagents? The first mechanism to be considered involves the initial formation of a carbanionic intermediate (Scheme 12.12). In the case of CF_2ClBr, decomposition of $^-CF_2Cl$ into difluorocarbene explains the formation of compounds substituted by a CF_2Br group [51] (Scheme 12.12, X = Cl). Moreover, in the condensation involving 2-allylphenoxide, the observation of double insertion of the difluoromethylene unit is in agreement with this mechanism [75]. A second process was proposed for reactions involving enamines because the observed inhibition of the condensation by nitrobenzene and formation of ketones substituted by a CF_2Cl group (from CF_2ClBr; Scheme 12.11) favour a radical-chain mechanism [71]. Reactions of thiophenoxides with CF_2Cl_2 or CF_3Br are also inhibited by nitrobenzene. Thus again an $S_{RN}1$ mechanism was considered [55, 56] (Scheme 12.13). A theoretical treatment of the thiophenoxide reaction with CF_2ClBr in DMF has shown that this condensation is a suspected case of electron-transfer oxidation of a polyhalide [76];

$$Nu^- + BrCF_2X \longrightarrow NuBr + {}^-CF_2X$$

$${}^-CF_2X \longrightarrow :CF_2 + X^-$$

$$Nu^- + :CF_2 \longrightarrow NuCF_2^-$$

$$NuCF_2^- + BrCF_2X \longrightarrow NuCF_2Br + {}^-CF_2X$$

$$NuCF_2^- + \text{“H” (solvent)} \longrightarrow NuCF_2H$$

Scheme 12.12. Carbene-mediated ionic chain mechanism.

$$Nu^- + BrCF_2X \longrightarrow Nu^{\cdot} + BrCF_2X^{\cdot-}$$

$$BrCF_2X^{\cdot-} \longrightarrow {}^{\cdot}CF_2X + Br^-$$

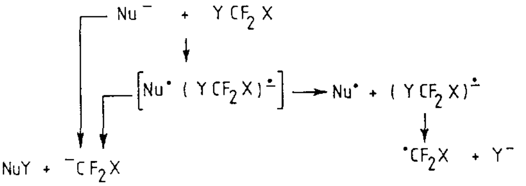
$$Nu^- + {}^{\cdot}CF_2X \longrightarrow NuCF_2X^{\cdot-}$$

$$NuCF_2X^{\cdot-} + BrCF_2X \longrightarrow NuCF_2X + BrCF_2X^{\cdot-}$$

Scheme 12.13. Radical-anion chain mechanism ($S_{RN}1$).

in fact, the coexistence of the carbene-mediated ionic chain and $S_{RN}1$ processes has been demonstrated in the case of that reaction [51].

Finally, it is possible to postulate a common first step for the two processes [51], as shown in Scheme 12.14; this is analogous to the one



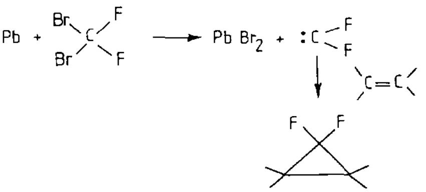
Scheme 12.14. Speculative initiation processes.

proposed by Meyers for reactions of non-fluorinated perhalogenomethanes [77]. Although questioned in the case of reactions involving phenoxides [66], the possibility that the fluoroalkylation of phosphines proceeds by a one-electron transfer process, rather than by direct displacement on halogen, has been considered [78]. Evidence has been presented in support of the occurrence of radical-chain processes in the perfluoroalkylation of 2-nitropropylanion [79, 80] and thiolates [81] with perfluoroalkyl iodides.

Reactions with metals

Halogenofluorocarbons are usually compatible with metals used in refrigeration systems. However, $CF_2ClCFCl_2$ can be transformed into chlorotrifluoroethylene, for example, by treatment with a metallic couple in aprotic solvents [82]. Reduction of the C—Cl bonds was observed with Zn in protic solvents [22]. Pyrolysis of $CFBr_3$ in a platinum tube at 630 °C yields hexafluorobenzene [83].

Reactions of metal atoms with halogenofluorocarbons has been studied [84]. The dibromide CF_2Br_2 is reduced by lead at 40 °C to 60 °C with the formation of difluorocarbene, which can be captured by olefins (Scheme 12.15) [85]. Reactions of CF_2X_2 compounds ($X_2 = Cl_2, Br_2$ or ClBr) with



Scheme 12.15. Synthesis of 1,1-difluorocyclopropanes from dibromodifluoromethane and lead [85].

zinc or cadmium in DMF leads to trifluoromethylated organometallics (Scheme 12.16) [86].

Perfluoroalkylation of aldehydes with CF_3Br and zinc in the presence of $(Ph_3P)_2NiCl_2$ yields trifluoromethylcarbinols [87]; the method can be

$$CF_2X_2 \xrightarrow{M} :CF_2 \qquad (M = Cd.\ Zn: X = Br, Cl)$$

$$:CF_2 + Me_2NCHO \longrightarrow CO + Me_2\overset{+}{N}{=}CHF\ F^-$$

$$F^- + :CF_2 \longrightarrow CF_3^- \longrightarrow CF_3MX + (CF_3)_2M$$

Scheme 12.16. Generation of trifluoromethyl derivatives of cadmium or zinc in DMF from difluorodihalogenomethanes [86].

extended to ketones by using titanocene dichloride under ultrasonic irradiation [88]. Treatment of CF_3Br with SO_2 and metals (Zn, Cd, Mn, Al) in DMF under slight pressure produces trifluoromethanesulphinate salts which can be transformed to trifluoromethanesulphonic acid: $CF_3Br + Zn + SO_2 \rightarrow CF_3SO_2ZnBr \rightarrow CF_3SO_3H$ [89].

Outlook

For many years now, the synthesis of a great variety of fluorinated compounds has hinged on the availability of halogenofluorocarbons. During the past decade the major breakthrough in this area has been the realisation that the fluoroalkylation of nucleophilic species with reagents of this class is not always impossible. The orientation between the ionic-chain mechanism and the radical-chain process is not yet well understood, hence the need for further studies. Reactions involving metals also seem very promising. We confidently expect that numerous uses for halogenofluorocarbons as starting materials for the mild introduction of fluorinated groups into organic molecules will be developed as the years roll on towards the bicentenary of Moissan's great achievement.

Acknowledgements

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BIOGRAPHIC NOTES

Claude Wakselman, who was born in 1939, received his Doctorat-es-Sciences degree in Paris in 1966. After a postdoctoral year in 1970 with Sir John Cornforth at the Shell Research Centre (Sittingbourne, England), he took up a post with the CNRS at Thiais (Centre d'Etudes et de Recherches de Chimie Organique Appliquée) in the suburbs of Paris, where he is currently Directeur de Recherche. His research interests centre on the synthesis of fluorinated steroids, acrylic derivatives and heterocycles, and involve studies on the reactivity of halogenofluorocarbons.

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