Journal of Fluorine Chemistry, *33* (1986) 377 - 396

Chapter 14

FLUORINE-CONTAINING REAGENTS IN ORGANIC SYNTHESIS

G. A. OLAH, J. G. SHIH and G. K. S. PRAKASH

The Donald P. and Katharine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, CA 90089 (U.S.A.)

Introduction

Progress in organofluorine chemistry has always depended markedly on the discovery of alternatives to fluorine as a reagent for the synthesis of C—F bonds. Indeed, Moissan himself adopted this approach (see Chapter 4), and it is a privilege for us to honour him on the centennial of his isolation of fluorine by reviewing our on-going research centered on the development of simple and easily handled fluorinating agents. Also covered briefly is the use of fluorine-containing reagents in general organic synthesis, including cationic reagents containing complex fluoroanions which we have developed in connection with our activities in the field of superacid chemistry.

Fluorinating agents

The taming of anhydrous hydrogen fluoride : pyridinium poly(hydrogen fluoride), PPHF

Anhydrous hydrogen fluoride (AHF) is one of the most widely used and inexpensive fluorinating agents. However, due to its low boiling point (19.5 °C) and corrosive nature, reactions involving its use are generally carried out in special equipment and under pressure. Efforts prior to ours were made to effect fluorinations at atmospheric pressure by complexing hydrogen fluoride with various nonbonded electron-pair donors. Thus, Hirschmann [1] first reported the use of the tetrahydrofuran/AHF system in 1956. Subsequently, stable solutions of AHF in amines [2], amides [3], carbamic acids and esters [4], trialkyl phosphines [5] and alcohols [6] were used. Basically, however, use of these complexes remained limited to fluorinations of specific organic compounds (mostly steroids), and none of them achieved wider acceptance. Our interest in the fluorination of organic compounds in general prompted us to undertake detailed examination of several amine–AHF complexes.

AHF forms remarkably stable solutions in pyridine up to a molar composition of 1 C_5H_5N:9 HF [30% C_5H_5N, 70% HF (w/w)]. Such material was first used by Bergstrom *et al.* [2c] to fluorinate steroids.

0022-1139/86/$3.50

Our studies showed it to be pyridinium poly(hydrogen fluoride) [PPHF; $C_5H_5\overset{+}{N}H\,(HF)_xF^-$], in which the complex anion exists in equilibrium with a small amount of free hydrogen fluoride. This material was found to possess a relatively low vapor pressure at temperatures up to 60 °C [7] and to be a convenient and effective replacement (at atmospheric pressure) for AHF in numerous applications. Now known as Olah's reagent, 30/70 PPHF is available commercially as a liquid which can be stored in poly(ethylene) bottles in a domestic refrigerator (or even at room temperature). Thus, AHF has been 'tamed' to allow chemists to use it under greatly simplified conditions easily adaptable to general laboratory syntheses. Note that PPHF solutions containing a lower concentration of HF can be used as well, and that other amine–poly(hydrogen fluoride) complexes, such as those derived from trimethylamine, triethylamine, substituted pyridines and triethanolamine are also useful as sources of hydrogen fluoride. Synthetic modifications achievable with 30/70 PPHF are illustrated below.

Reactions with alkenes or alkynes [*8*, *9*]

Although alkenes and alkynes are generally insoluble in pyridinium poly(hydrogen fluoride), addition of a tetrahydrofuran solution of these compounds to the reagent yields mono- and di-fluoroalkanes, respectively, in typical Markownikoff type additions ($>C{=}C< \rightarrow >CHCF<$; $-C{\equiv}C- \rightarrow -CH_2CF_2-$). When alkenes are added in a similar manner to a solution of PPHF containing *N*-halogenosuccinimides, the corresponding halogenofluoro compounds are isolated. Only vicinal fluoroiodoalkenes are formed upon addition of alkynes to a solution of PPHF containing *N*-iodosuccinimide.

Iodofluorination or bromofluorination of alkenes can also be effected using the appropriate halogen plus an equivalent amount of silver nitrate in the PPHF solution [$>C{=}C< + X_2{-}AgNO_3 + \mathrm{PPHF} \rightarrow >CXCF<$ (X = Br or I)]. The halogenofluorination method can also be modified to prepare vicinal difluorides from the corresponding alkenes without isolation of the intermediates. This is simply achieved by adding silver(I) fluoride to the solution of α-halogeno-β-fluoroalkanes to effect the halogen-exchange reaction *in situ*:

$$RCH{=}CHR' \xrightarrow[\text{or } X_2{-}AgNO_3]{\text{PPHF, } \overline{CH_2CONXCOCH_2}} \underset{(X = Br\text{ or }I)}{(RCHXCHFR')} \xrightarrow{AgF} \underset{(60-95\%)}{RCHFCHFR'}$$

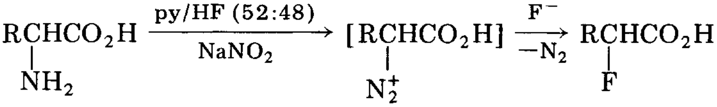
A simple variation of this procedure affords α-fluoro-β-nitroalkanes: the alkene is added to a solution of nitronium tetrafluoroborate dissolved in pyridinium poly(hydrogen fluoride), a procedure which eliminates the problem of polymerization usually found in reactions conducted in anhydrous hydrogen fluoride [10], e.g. $MeCH{=}CH_2 + [NO_2]^+[BF_4]^-$ in PPHF $\rightarrow$ $MeCHFCH_2NO_2$.

Reactions with alcohols [*9*, *11*]

Secondary and tertiary alcohols are readily converted to the corresponding fluorides by pyridinium poly(hydrogen fluoride). With tertiary alcohols, reaction proceeds conveniently even at low temperatures, e.g. t-BuOH + PPHF at 0 ℃ → t-BuF (50%)]; secondary alcohols react at room temperature. Primary alcohols are unaffected by pyridinium poly(hydrogen fluoride) itself, but their conversion to alkyl fluorides (30 - 88% yield) proceeds smoothly in the presence of added sodium fluoride. Recently, good results have also been reported in reactions of carbohydrates with pyridinium poly(hydrogen fluoride) to afford fluorides [12].

Conversions involving amino and diazo groups

Deaminative halogenations, whereby an amino group is displaced by fluoride or other halides, have been studied in the case of α-amino acids [13], carbamates [14] and aminoarenes [9]. The reaction of α-amino acids in pyridinium poly(hydrogen fluoride) solution with an excess of sodium nitrite leads, via diazotization followed by *in situ* nucleophilic dediazonization, to the formation of α-fluorocarboxylic acids. However, difficulties were experienced [15] in the case of fluorinating some α-amino acids, e.g. valine, isoleucine, phenylalanine, tyrosine and threonine, because total or partial rearrangement to β-fluorocarboxylic acids occurred owing to anchimeric assistance by alkyl, aryl or hydroxy groups during the diazotization reactions. Such rearrangements can be suppressed by carrying out the reaction in reagent media of lower HF concentration (pyridine/hydrogen fluoride, 52:48 w/w):

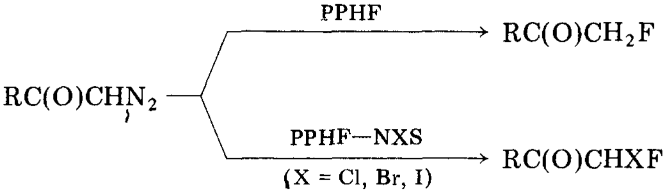


$$\underset{|\atop NH_2}{RCHCO_2H} \xrightarrow[NaNO_2]{py/HF\ (52{:}48)} [\underset{|\atop N_2^+}{RCHCO_2H}] \xrightarrow[-N_2]{F^-} \underset{|\atop F}{RCHCO_2H}$$

Treatment of alkyl carbamates dissolved in pyridinium poly(hydrogen fluoride) with an excess of sodium nitrite at room temperature gives the corresponding fluoroformates: $ROC(O)NH_2 + PPHF{-}NaNO_2 \rightarrow ROC(O)F$. The reaction is considered to proceed via diazotization followed by *in situ* dediazonization. Synthesis of alkyl fluoroformates by this procedure eliminates the necessity of using phosgene or its derivatives.

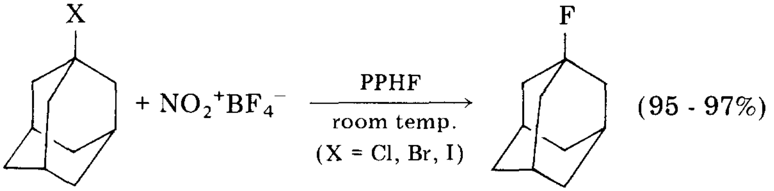
The deaminative introduction of a halogen into an aromatic nucleus is commonly accomplished via diazotization of the corresponding amine and decomposition of the resultant diazonium salts in the presence of a suitable halide donor. For the preparation of specifically fluorinated aromatic compounds, the Balz–Schiemann reaction (see Chapter 4) has been the most widely used method [16]. When aminoarenes are diazotized in pyridinium poly(hydrogen fluoride) solution with sodium nitrite, subsequent fluorinative dediazonization results in the formation of the corresponding fluoroarenes: $ArNH_2 + PPHF{-}NaNO_2 \rightarrow ArF$. The fluoroarenes formed are frequently isomerically pure compounds. The conversions proceed smoothly at room (or slightly elevated) temperatures and do not require the isolation of the diazonium salt intermediates. Mechanistic implications have been discussed elsewhere [17]. Recently, Rosenfeld and Widdowson [18] used pyridinium poly(hydrogen fluoride) to effect Wallach-type (see p. 76) conversion of aryltriazenes to aromatic fluorides, the yields often being high: $ArN{=}NNR_2$ (R_2 = $[CH_2]_5$, Me_2) + 30/70 PPHF → $[ArN_2^+]$ → ArF.

Diazo compounds can be converted to monofluorides via treatment with PPHF; in the presence of *N*-halogenosuccinimides geminal fluorohalogeno compounds result [19]:



Halogen-exchange reactions

Halogen-exchange fluorination with anhydrous hydrogen fluoride is one of the classical fluorination procedures [20]. Pyridinium poly(hydrogen fluoride) is an unsuitable reagent for the conversion of tertiary adamantanoid halides to their fluorides directly, but in the presence of nitronium tetrafluoroborate (which possesses good halide-abstraction ability [21]) the corresponding fluorides are obtained in good to excellent yields [22]:



However, reactions involving 2-halogenoadamantanes follow a different pathway, oxidation to 2-adamantanone by the reagent system occurring even at room temperature. Furthermore, when the reaction is carried out with other secondary alkyl halides such as bromocyclohexane, *exo*-2-bromonorbornane and 1-iodoheptane, complex product mixtures arise. Mercury(II)-assisted exchange of chlorine or, more readily, bromine for fluorine in α-halogenoketones ($RCOCH_2X$ + HgO—PPHF → $RCOCH_2F$) or geminal dihalogenoalkanes (RCX_2R' + HgO—PPHF → RCF_2R') can be effected with PPHF at 50 °C and atmospheric pressure. Conversion of carboxylic acid chlorides (or anhydrides) to the corresponding acid fluorides with PPHF proceeds in a manner comparable to reactions carried out with AHF itself, as described by Olah and Kuhn in 1961 [23].

Hydrofluorination of isocyanates [*9*, *24*]. When treated with PPHF at room temperature, both aliphatic and aromatic isocyanates give carbamoyl fluorides in good yields: $RN{=}C{=}O$ + PPHF → RNHCOF.

Preparation of sulfur tetrafluoride [25]

Sulfur tetrafluoride is an extremely useful reagent for the preparation of organofluorine compounds (see p. 231) [20, 26]. Although a variety of procedures for its synthesis are known [27], the most convenient laboratory procedure to date is that of Tullock *et al.* [28], in which sulfur dichloride is heated in a solvent of high dielectric constant, such as acetonitrile, with metal fluorides, such as sodium fluoride. Pyridinium poly(hydrogen fluoride), being a polar solvent as well as containing a large reservoir of fluoride ion, is also a good reagent for this conversion, which proceeds smoothly at 45 °C and at atmospheric pressure: $3SCl_2 + PPHF \rightarrow SF_4 + S_2Cl_2(S_2ClF)$.

Preparation of sulfuryl chloride fluoride [25]

Due to its low nucleophilicity [29] and wide liquid range (−124.7 °C to +7.1 °C), sulfuryl chloride fluoride, SO_2ClF, is extensively used as a solvent for the generation of stable carbocations [30]; it is also useful as a synthetic reagent. Existing syntheses of the compound involve the action of fluoride salts on sulfuryl chloride [31], treatment of potassium fluorosulfite with chlorine [32], the reaction of hydrogen fluoride, chlorine and sulfur dioxide with potassium bifluoride supported on charcoal [33], or the reaction of nitrogen trifluoride with sulfuryl chloride [34]. Also, Schack and Wilson have reported the preparation of SO_2ClF from chlorine monofluoride and sulfur dioxide at low temperature [35]. None of these methods is as convenient as the reaction of pyridinium poly(hydrogen fluoride) with sulfuryl chloride, which proceeds efficiently and smoothly under mild conditions [25].

Selenium tetrafluoride and its pyridine complex [36]

Hückel [37] predicted in 1946 that selenium tetrafluoride should exist and be capable of isolation. This was not realized until 10 years later when Clifford *et al.* [38] synthesized it by treating selenium metal with chlorine trifluoride in anhydrous hydrogen fluoride in platinum apparatus. Subsequently, other fluorination procedures such as treatment of selenium(IV) oxide with sulfur tetrafluoride [39] and of selenium metal with silver(I) fluoride [40], or cobalt(III) fluoride were developed. Procedures using elemental fluorine provide another method [41] for preparing selenium tetrafluoride, but special equipment is needed to carry out the reaction. Due to the high reactivity of fluorine and the difficulty of controlling the reaction, selenium hexafluoride is always formed as the major product. None of these preparations are thus convenient.

Olah *et al.* improved Clifford's method by using selenium tetrafluoride itself as solvent for the reaction, which can be carried out in standard glass apparatus under an atmosphere of dry nitrogen: $3\,Se + 4\,ClF_3 \xrightarrow{ca.\ 90\ ^\circ C} 3\,SeF_4\,(98\%) + 2\,Cl_2$ [36].

Selenium tetrafluoride is an efficient fluorinating agent of general use for the replacement of hydroxyl and carbonyl groups by fluorine [36]. It possesses a convenient liquid range (m.p., −10 °C; b.p., 106 °C) and is soluble in halogenated solvents, such as dichloromethane and 1,1,2-trichlorotrifluoroethane, in which fluorinations can be carried out at moderate temperatures (40 - 50 °C) under atmospheric pressure in standard glass equipment, provided that the reagent is pure and anhydrous conditions are maintained. It must be emphasized, however, that SeF_4, like selenium compounds in general, is highly toxic; hence all operations involving this reagent must be carried out with great care.

Ketones and aldehydes give geminal difluorides in 65 - 100% yield under very mild conditions. Carboxylic acids are also readily fluorinated by selenium tetrafluoride, or even more conveniently by its complex formed with pyridine.

$$R_2CO\text{ (or }RCHO) \xrightarrow{SeF_4} R_2CF_2\text{ (or }RCHF_2) + SeOF_2$$

$$RCOOH + [C_5H_5N{\rightarrow}SeF_4] \longrightarrow RCOF + SeOF_2 + C_5H_5\overset{+}{N}H\,F^-$$

Carboxylic acid anhydrides are also converted to acyl fluorides under similar conditions. *N,N*-Dimethylbenzamide smoothly and quantitatively yields the corresponding α,α-difluoroamine:

$$PhCONMe_2 \xrightarrow[20\ ^\circ C]{SeF_4} PhCF_2NMe_2$$

Alcohols react readily with SeF_4 but in some cases the more sensitive alkyl (arylalkyl, cycloalkyl) fluoride products can be lost because of extensive skeletal rearrangement or polymerization due to HF formed in the reactions. In order to avoid this unwanted side-reaction, it is advantageous to add 1 molar equivalent of pyridine, which forms a liquid 1:1 donor–acceptor complex with SeF_4. This reacts selectively with alcohols, first forming alkoxyselenium trifluorides, which decompose to the corresponding alkyl fluoride when heated. Fluorination with the selenium tetrafluoride–pyridine complex causes no rearrangement except with susceptible systems, e.g. cyclopropylcarbinyl or isobutyl alcohol.

$$ROH + [C_5H_5N{\rightarrow}SeF_4] \longrightarrow C_5H_5\overset{+}{N}H\,F^- + ROSeF_3 \xrightarrow{\text{warm}} RF + SeOF_2$$

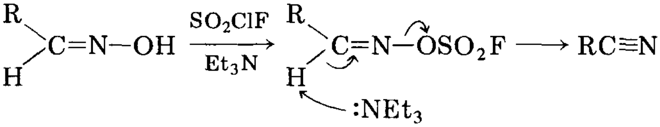
Applications of some fluorinated reagents in general organic synthesis

Sulfuryl chloride fluoride

Sulfuryl chloride fluoride [25], a compound which has found extensive use as a low-temperature solvent of poor nucleophilicity and wide liquid range (—124.7 °C to +7.1 °C) in the study of carbocations and other reactive intermediates [42] is now receiving increasing attention as a reagent in organic synthesis. Synthetic transformations involving its use usually take advantage of the relative lability of the sulfur–chlorine bond, the good leaving-group ability of the fluorosulfonyl anion and the susceptibility of sulfur to nucleophilic attack. Sulfuryl chloride fluoride offers significant advantages over alternative reagents in terms of extremely mild reaction conditions, ease of removal of any excess of reagent, and product isolation.

Dehydration of aldoximes [*43*]

Nitriles can be obtained in excellent yields via treatment of aldoximes with sulfuryl chloride fluoride in the presence of triethylamine at room temperature:



The method is applicable to both alkyl and aryl aldoximes, and constitutes one of the mildest among those available [44] for the dehydration of aldoximes to nitriles under neutral conditions. It should also be applicable to other dehydrations.

Synthesis of carboxamides [*45*] *and carboxylic acid esters* [*46*]

A number of modern methods have been developed for the synthesis of amides and esters from carboxylic acids [47 - 52], but many of these require relatively harsh reaction conditions and/or elaborate work-up procedures. By contrast, amides can be obtained in good to excellent yields under mild conditions with minimal isolation problems via a one-pot synthesis involving treatment of carboxylic acids with sulfuryl chloride fluoride in the presence of triethylamine, followed by addition of primary amines to the acyl fluorosulfonates formed. The reactions are most conveniently carried out in dichloromethane as solvent:

$$\mathrm{RCO_2H} \xrightarrow[\mathrm{Et_3N}]{\mathrm{SO_2ClF}} \mathrm{RC(O)OSO_2F} \xrightarrow[\mathrm{Et_3N}]{\mathrm{R'NH_2}} \mathrm{RC(O)NHR'}$$

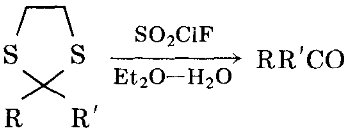
(R, R′ = alkyl, aryl, aralkyl)

With secondary amines the last stage proceeds only sluggishly.

Replacement of primary or secondary amines in the above route to amides by alcohols (1° or 2°) or phenols provides esters in high yields. Although a wide variety of methods are known for the esterification of acids, this procedure compares favorably with, and is considered in some applications preferential to, recent methods [52] in terms of product yields, and neutral and mild reaction conditions.

Dethioacetalization [*53*]

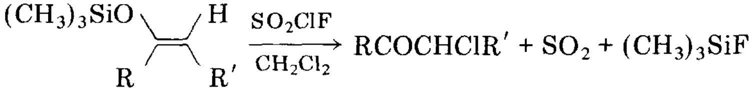
The stability exhibited by the dithioacetal moiety towards both acids and bases has led to its wide use as a protecting group in the synthesis of complex natural products. However, suitably mild procedures for the direct regeneration of carbonyl compounds from dithioacetals are limited. Sulfuryl chloride fluoride has proved to be an effective dethioacetalization reagent, addition of excess of this reagent to a solution of a 1,2-ethanediyl dithioacetal (1,3-dithiolane) in aqueous diethyl ether at room temperature causing mildly exothermic release of the parent aldehydes, ketones or ketoesters to occur in good to excellent yield:



The ring cleavage presumably involves formation of a chlorosulfonium ion, and reflects the lability of the $Cl—SO_2$ bond compared with the $F—SO_2$ link [54].

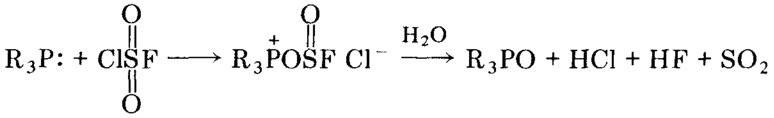
Synthesis of α-chloroketones [*55*]

α-Chloroketones are versatile synthetic intermediates. They have been prepared via treatment of ketones, epoxides or enamines with a variety of chlorinating reagents [56], or of enol silyl ethers with chlorine, *N*-chlorosuccinimide, or cupric or ferric chloride [57]. Enol silyl ethers also react with sulfuryl chloride fluoride to yield α-chloroketones under mild conditions in dichloromethane solution. The reaction works well with a variety of silyl ether substrates.



Oxidation of phosphines or arsines [*58*]

Tertiary phosphines and arsines react very readily with sulfuryl chloride fluoride at room temperature to afford the corresponding oxides. The reaction is general for alkyl- and aryl-phosphines, and NMR spectroscopic studies have indicated that attack by the phosphorus centers occurs preferentially on the oxygen atom of sulfuryl chloride fluoride to yield the corresponding intermediate phosphonium salts:



$$R_3P: + Cl\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}F \longrightarrow R_3\overset{+}{P}O\overset{\overset{O}{\|}}{S}F\ Cl^- \xrightarrow{H_2O} R_3PO + HCl + HF + SO_2$$

Miscellaneous reactions

Other synthetic applications of sulfuryl chloride fluoride include the chlorination of cyclohex-2-enones [59], and fluorination reactions with organophosphorus compounds [60].

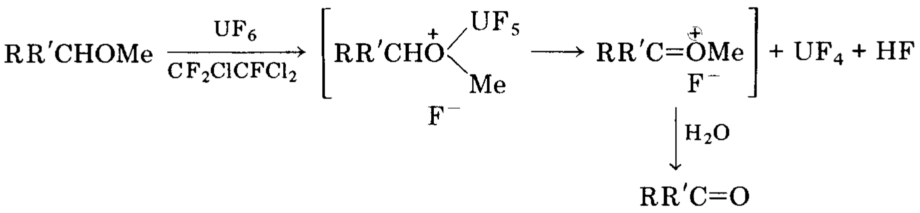
Uranium hexafluoride [61]

Uranium hexafluoride, depleted of fissionable material (<0.20% $^{235}UF_6$), is abundantly available as the by-product of enrichment plants (see p. 199) [62]. Despite its availability and remarkable properties, however, its reactions with organic compounds remained virtually unexplored until recently. It is a colorless volatile solid (sublimes at 56.5 °C), the highly covalent nature of which makes it particularly suitable for reactions in nonaqueous solvents; its stable solutions in chlorofluorocarbons or chlorohydrocarbons are convenient to use and do not attack glass.

Oxidative cleavage of ethers

The oxidative cleavage of ethers has found so far only limited preparative use. Reagents based on Hg^{II} [63] and Ag^{II} [64] will oxidize aryl methyl ethers to quinones, and trityl fluoroborate has been used effectively by Barton's group [65] to effect oxidative cleavage of ketone acetals and of ethers. Oxidative cleavage of ethers with other reagents, e.g. Frémy's radical (see footnote 27, p. 17) [66], has found little, if any, synthetic application.

Ethers undergo oxidative cleavage upon addition to a solution of uranium hexafluoride in chlorofluorocarbons or chlorohydrocarbons. The direction of cleavage of saturated ethers is predictable, which enhances the utility of ethers as protecting groups for alcohols. The regiospecific oxidation of methyl ethers, for example, is considered to hinge on the weak



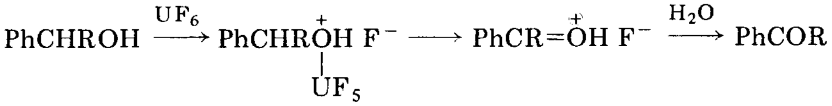
$$RR'CHOMe \xrightarrow[CF_2ClCFCl_2]{UF_6} \left[RR'CH\overset{+}{O}\begin{matrix} UF_5 \\ Me \end{matrix} \; F^- \longrightarrow RR'C{=}\overset{+}{O}Me \; F^- \right] + UF_4 + HF$$

$$RR'C{=}\overset{+}{O}Me \; F^- \xrightarrow{H_2O} RR'C{=}O$$

Lewis acid character of uranium hexafluoride [67], *in situ* treatment of the oxonium ions thus produced with a nucleophile, for example water (→ aldehydes or ketones), ethane-1,2-dithiol (→ 1,2-dithiolanes), or propane-1,3-dithiol (→ 1,3-dithianes), completes the synthetic sequence.

Oxidative fluorination of alcohols and aldehydes

Benzylic alcohols are readily oxidized by uranium hexafluoride to the corresponding carbonyl compounds. Since both alkyl and aryl aldehydes are oxidatively fluorinated to aryl fluorides by UF_6, benzyl alcohol itself, for example, yields a mixture of benzaldehyde and benzoyl fluoride:



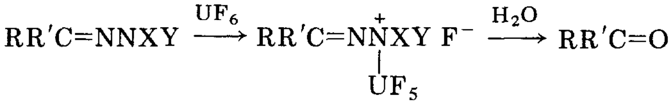
$$PhCHROH \xrightarrow{UF_6} PhCHR\underset{UF_5}{\overset{+}{O}}H \; F^- \longrightarrow PhCR{=}\overset{+}{O}H \; F^- \xrightarrow{H_2O} PhCOR$$

$$RCHO + UF_6 \xrightarrow[0\ °C]{CF_2ClCFCl_2} RCH{=}\overset{+}{O}UF_5 \; F^- \xrightarrow[\text{the solution}]{\text{evaporate}} RCOF$$

Aliphatic alcohols were observed to react in a similar manner, though the products were more complex. The preparation of acid fluorides generally involves an exchange reaction of acyl halides with HF [68] (PPHF can be used; see p. 380) or alkali fluorides [69], or by the direct reaction of the acid or anhydride with a suitable fluorinating reagent [36, 70]. The formation of acid fluorides from aldehydes without oxidation to an intermediate acid or its derivatives is therefore novel.

Oxidation of hydrazones and carboxylic acid hydrazides

Hydrazones are widely used for the characterization or protection of carbonyl compounds. Aqueous work-up of products of reactions between tosyl- or *N*,*N*-dimethyl-hydrazones and uranium hexafluoride furnishes the parent carbonyl compounds in good yield. Although the mechanism of the reaction is not certain, it may proceed as follows:



$$RR'C{=}NNXY \xrightarrow{UF_6} RR'C{=}N\underset{\substack{|\\ UF_5}}{\overset{+}{N}}XY\ F^- \xrightarrow{H_2O} RR'C{=}O$$

This method of regeneration, especially where tosylhydrazones are concerned, is as efficient as any of the other methods known.

Carboxylic acid hydrazides are oxidized to carboxylic acids by $Ce(NH_4)_2(NO_3)_6$ [71] or $Pb(OAc)_4$ [72] and to aldehydes by $K_3Fe(CN)_6$ [73]. Use of uranium hexafluoride also gives carboxylic acids, but reactions proceed slowly, largely owing to the poor solubility of the acid hydrazides in trichlorotrifluoroethane or chloroform.

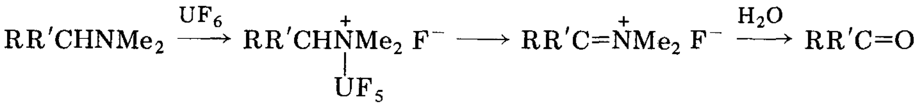
$$RCONHNH_2 \xrightarrow{UF_6} RCO_2H$$

Oxidation of oximes

Numerous methods are known for the regeneration of carbonyl compound from oximes [74]. Chloroform solutions of oximes are oxidized slowly by uranium hexafluoride to the corresponding carbonyl compounds in fair to moderate yield. The reaction is considerably slower than the corresponding one with hydrazones or ethers.

Oxidation of tertiary amines

Oxidation of tertiary amines [75] with uranium hexafluoride can be used to procure carbonyl compounds and may be viewed as the nitrogen analog of the UF_6 oxidation of ethers (see p. 385):



$$RR'CHNMe_2 \xrightarrow{UF_6} RR'CH\underset{\substack{|\\ UF_5}}{\overset{+}{N}}Me_2\ F^- \longrightarrow RR'C{=}\overset{+}{N}Me_2\ F^- \xrightarrow{H_2O} RR'C{=}O$$

Fluorination of adamantanone

Formation of C—F bonds was observed but infrequently during the course of our study of the reactivity of uranium hexafluoride with functionalized organics. Note, however, that adamantanone was fluorinated with a two-fold excess of UF_6 in 1,1,2-trichlorotrifluoroethane solution at 0 °C to form 2,2-difluoroadamantane in 41% yield. Other nonenolizable ketones such as benzophenone and fluorenone failed to react.

Molybdenum hexafluoride [*76*]

Molybdenum hexafluoride is a covalent low-boiling liquid (m.p., 17 °C; b.p., 35 °C), well known as a fluorinating agent [77, 78] and particularly useful for effecting the conversion of carbonyl groups to CF_2 [77]. We have demonstrated its usefulness as a reagent for the oxidative cleavage of *N,N*-dimethyl- or tosyl-hydrazones to regenerate the parent aldehydes or ketones. The reaction is thought to proceed in a manner analogous to that described for the reaction of UF_6 with hydrazones (see p. 386); note that yields of carbonyl products are generally higher with the Mo^{VI} reagent. Oxidation of benzylic tertiary amines can be efficiently effected with molybdenum hexafluoride also, the results being often superior to those found with UF_6.

Tungsten hexafluoride [*79*]

Compared with UF_6 or MoF_6, tungsten hexafluoride (m.p., 2.5 °C; b.p., 17 °C) is a more selective, milder oxidizing agent. Like the other hexafluorides, it is readily soluble in 1,1,2-trichlorotrifluoroethane, dichloromethane or chloroform. Tungsten hexafluoride is a relatively poor fluorinating agent, although its use as such has been reported [80].

N,N-Dimethyl- and tosyl-hydrazones can be cleaved efficiently to the parent carbonyl compounds via treatment with an ice-cold solution of tungsten hexafluoride in chloroform, followed by addition of water. The yields of carbonyl products are superior to those obtained with either uranium hexafluoride or molybdenum hexafluoride. No reaction has been observed with ethers, alcohols or halides. However, WF_6 oxidizes *N,N*-dimethylbenzylamine and *N,N*-dimethylbenzhydrylamine just as efficiently as the weaker Lewis acid MoF_6.

Cyanuric fluoride

The isolation of cyanogen fluoride (FCN, b.p., −46 °C) was first achieved conveniently [81] by pyrolysis of its trimer, cyanuric fluoride, over graphite at 1300 °C; since it polymerizes at room temperature, to give, *inter alia*, its cyclic trimer, it has little synthetic value. The trimer, however, which can be prepared by treating cyanuric chloride with cold anhydrous hydrogen fluoride [82], or in similar yield (75%) from cyanuric chloride and sodium fluoride in hot tetramethylene sulfone [28], has been used by us to fluorinate carboxylic acids and to de-oxygenate sulfoxides.

Fluorination of carboxylic acids [*82*]

Carboxylic acid fluorides are generally prepared from the corresponding acyl chlorides by halogen exchange with potassium fluoride [83], potassium hydrogen fluoride [84] or potassium fluorosulfinate [85]; sulfur tetrafluoride [86], selenium tetrafluoride (see p. 382), and thionyl fluoride [87] can be used for the direct fluorination of carboxylic acids. Halogen-exchange reactions, however, generally necessitate use of high reaction temperatures, and direct fluorination methods are not adaptable to acid derivatives containing other functional groups. By contrast, cyanuric fluoride, a very mild reagent, is suitable for the preparation of carboxylic acid fluorides (even when the substrate contains, for example, olefinic bonds or hydroxyl groups):

$$RCO_2H + (FCN)_3 \xrightarrow[C_5H_5N]{\text{MeCN, room temp.}} 3\ RCOF + (HOCN)_3$$

Deoxygenation of sulfoxides [*88*]

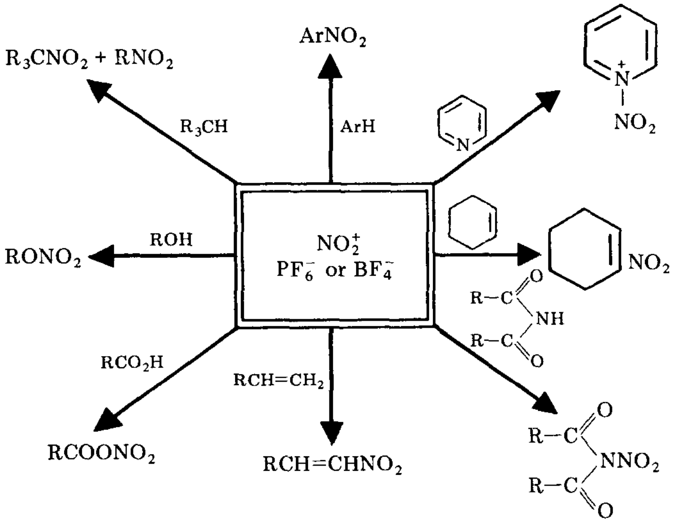
Aryl sulfoxides undergo facile deoxygenation to the corresponding sulfides when heated in 1,4-dioxan or triethyl phosphate with cyanuric chloride. By contrast, aralkyl and alkyl sulfoxides react exothermically yielding mixtures of chlorinated products even at lower temperatures. Formation of unwanted halogenated products can be avoided by using the more reactive cyanuric fluoride.

Complex fluoro nitronium and nitrosonium salts

Nitronium tetrafluoroborate and hexafluorophosphate

Nitration is one of the most studied and best understood organic reactions [89]. The reactive species responsible for electrophilic aromatic nitration is the nitronium ion, NO_2^+. Since the turn of the century extensive efforts were directed towards the identification of this ion, whose existence was first indicated by Hantzsch and later firmly established by the Ingold–Hughes School [89b] which also studied the isolated perchlorate salt. More than 15 crystalline nitronium ion salts have now been isolated and characterized, and the most important of these involve the stable counter-ions BF_4^-, PF_6^-, SbF_6^-, UO_4^-, and FSO_3^-. The most widely used salt, nitronium tetrafluoroborate ($NO_2^+BF_4^-$), easily prepared by treating a mixture of nitric acid and anhydrous hydrogen fluoride with boron trifluoride, was introduced by Olah and Kuhn as a convenient, effective, general nitrating agent [90].

Nitronium salts enable nitration of every conceivable type of aromatic substrate, and their powerful electrophilic nature is demonstrated by their ability to effect even trinitration of benzene [91]. Electrophilic nitration of alkanes, cycloalkanes and polycycloalkanes can also be achieved (e.g. adamantane to nitroadamantane) [92], and electrophilic nitrofluorination of alkenes proceeds smoothly with nitronium salts in pyridinium poly(hydrogen fluoride) solution (see p. 378). Some of the typical nitration reactions of nitronium salts are shown in Scheme 14.1.



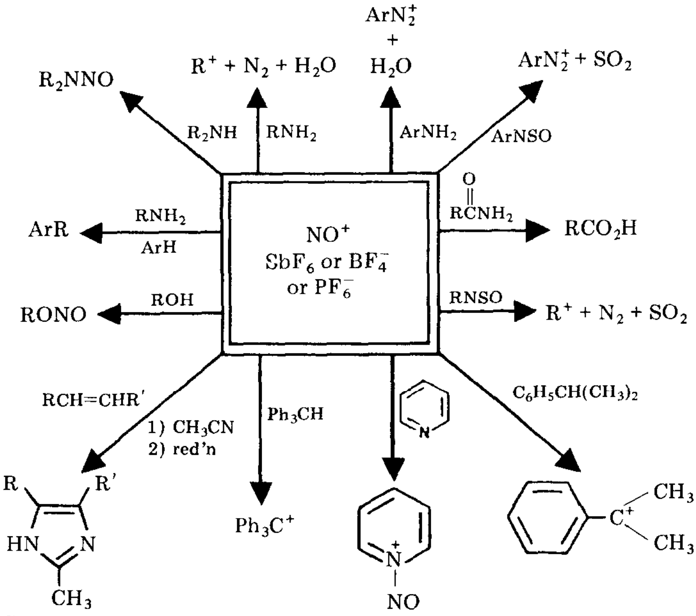
Scheme 14.1.

The nitronium ion was recognized only as a nitrating agent until recently, when it was found to possess significant ambident reactivity and so be capable of acting as an oxidizing agent [93]. Thus dialkyl-(aryl-)sulfides and -selenides as well as trialkyl-(aryl-)phosphines, triarylarsines and triarylstibines react with nitronium salts to give the corresponding oxides. Stable nitronium salts, particularly those with PF_6^- and BF_4^- counter-ions, can act as mild, selective oxidative cleavage reagents for the conversion of ethers, oximes and hydrazones, etc. to the corresponding carbonyl compounds [94]. More selective reagents such as *N*-nitropyridinium salts, which are readily prepared from the corresponding pyridine and nitronium ion salt, act as convenient transfer nitration agents.

Nitrosonium tetrafluoroborate, hexafluoroantimonate and hexafluorophosphate

The nitrosonium ion, NO^+, is the electrophilic species formed in nitrous acid media and is responsible for such reactions as the diazotization of amines. It has been isolated in the form of salts with a variety of stable counter-ions, notably BF_4^-, PF_6^- and SbF_6^-. The nitrosonium ion does not react with aromatics except in the case of highly activated systems (such as phenols); frequently, colored π-complexes are formed [95]. The nitrosonium ion is a powerful hydride-abstraction agent; e.g. cumene reacts with NO^+ to give various condensation products, and this involves initial formation of cumyl cation [96]. Similarly, the nitrosonium ion can be employed in the preparation of a variety of stabilized carbocations [97]. Some of the reactions of the nitrosonium ion are depicted in Scheme 14.2.

The hydride-abstraction ability of NO^+ has been employed in a modified Ritter-type reaction, as well as in ionic fluorination [98] of bridgehead



Scheme 14.2.

hydrocarbons. Similarly, NO^+ is also capable of halogen abstraction from alkyl halides [22a, 99]. In the presence of suitable oxygen donor such as dimethyl sulfoxide, the nitrosonium ion can act as a nitrating agent. The nitrosonium ion alone can act as a mild and selective oxidizing agent for the cleavage of oximes, hydrazones, thioketals, ethers, etc. to the corresponding carbonyl compounds.

Halonium ion and carbocation salt reagents

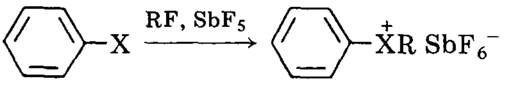
Meerwein's pioneering studies in the period 1930 - 60 established boron trifluoride as the primary Lewis-acid fluoride which featured in the development of oxonium and carboxonium ion chemistry [100]. Olah's studies in the period 1960 - 85 utilized primarily antimony pentafluoride and Brønsted superacids (see p. 389) and thereby allowed the preparation of long-elusive carbocations and other reactive ionic intermediates, such as the dialkylhalonium ions.

Dialkylhalonium salts

The well-known Meerwein trialkyloxonium tetrafluoroborate and hexachloroantimonate salts [100] are widely used as alkylating agents. However, they lack selectivity and are generally incapable of effecting *C*-alkylations. By contrast [101], dialkylhalonium salts obtainable by treatment of alkyl halides with antimony pentafluoride or hexafluoroantimonic acid and isolable in some cases [e.g. MeBr (in excess) + $HSbF_6$ ($HF{\cdot}SbF_5$) $\rightarrow$ $Me_2Br^+\ SbF_6^-$ (97%)], are very effective alkyl-transfer agents for arenes and alkenes, and for substrates containing a variety of heteroatoms. A change in the identity of the 'onium center allows the selectivities of the reagents to be varied, the order of reactivity being $R_2Cl^+ > R_2Br^+ > R_2I^+$, in keeping with the expected change in the ability of the halogen to accommodate charge as its size increases. A great variety of halonium ions have now been prepared and studied [102, 103] e.g.

$$XCH_2(CH_2)_nX \xrightarrow{SbF_5} \overline{CH_2(CH_2)_nX}^+ SbF_5X^-$$

(X = Cl, Br, I; n = 1, 3, 4)



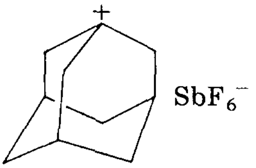
(X = Br, I; R = Me, Et)

Carbocation salts

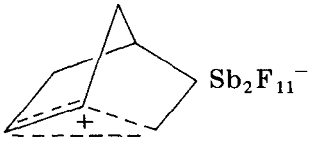
Methods developed [42] for the preparation of solutions of long-lived carbocations in fluorine-containing superacid media, such as the Brønsted acids FSO_3H and CF_3SO_3H, and the conjugate Brønsted–Lewis systems $FSO_3H \cdot SbF_5$ ('Magic Acid') and $HF \cdot SbF_5$ (fluoroantimonic acid), have been used to effect the isolation of a series of stable, crystalline carbocation salts. Isolation was generally achieved by evaporation of solvent SO_2, SO_2ClF or SO_2F_2, or by precipitation through the addition of Freon®-type solvents [103]. Typical isolated carbocation fluoroantimonate salts contain such tertiary ions as the t-butyl (1) and adamant-1-yl cation (2) [104], and stabilized secondary ions such as the norborn-2-yl cation (3) [105].

$Me_3C^+ \; Sb_2F_{11}^-$

(1)



(2)

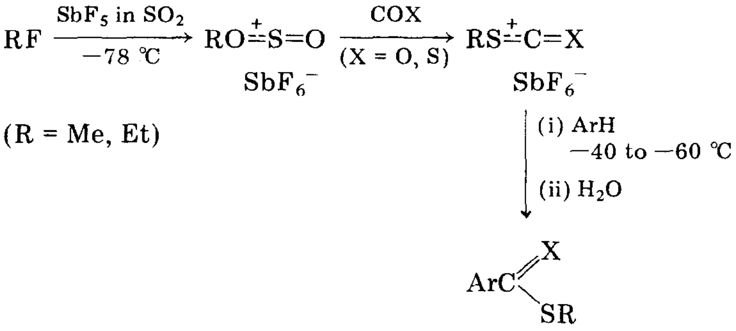


(3)

Isolable acylium salts and sulfonyl halide–antimony pentafluoride complexes are also known; these are effective acylating and sulfonylating agents, respectively [106]:

$$ArSO_2R \xleftarrow{RSO_2F \cdot SbF_5} ArH \xrightarrow{[RC{\equiv}O]^+ \, SbF_6^-} ArCOR$$

Methyl and ethyl fluoride form stable addition complexes with antimony pentafluoride which are powerful alkylating agents [107, 108] and have been used, for example, to alkylate carbonyl sulfide and carbon disulfide to provide effective thio- and dithio-carboxylation agents for aromatics [109]:



More recently, nitrous oxide has been methylated by the methyl fluoride–antimony pentafluoride complex: $N_2O + MeF{\cdot}SbF_5 \xrightarrow{\text{in } SO_2F_2 \text{ at } -100\ ^\circ\text{C}} MeON_2^+\ SbF_6^-$ [110]. The studies in the carbocation area have been reviewed [111], as have those on the chemistry of superacids [42], the availability of which represents the key to the generation of many reactive ionic intermediates.

Acknowledgements

Our study of fluorinated reagents would not have been possible without the outstanding contribution made by associates whose names appear in the references to their work. Support of the research in this field over the years by the National Science Foundation, the National Institutes of Health and the U.S. Army Office of Research is gratefully acknowledged.

References

1 R. F. Hirschmann, R. Miller, J. Wood and R. E. Jones, *J. Am. Chem. Soc.*, *78* (1956) 4956.

2 (a) G. Aranda, J. Jullien and J. A. Martin, *Bull. Soc. Chim. Fr.*, (1965) 1890; (b) *ibid.*, (1966) 2850; (c) C. G. Bergstrom, R. T. Nicholson and R. M. Dodson, *J. Org. Chem.*, *28* (1963) 2633.

3 (a) *Fr. Pat. 1 370827*(1964); [*Chem. Abs.*, *62* (1965) 2712h]; (b) T. G. Balicheva, P. M. Borodin and I. V. Pologikh, *Yad. Magn. Rezon.*, (1969) 49.

4 *Fr. Pat. 1 374591*(1964) [*Chem. Abs.*, *62* (1965) 9212a].

5 M. van der Akken and F. Jellinek, *Recl. Trav. Chim. Pays-Bas*, *86* (1967) 275.

6 (a) R. K. Thomas, *Proc. R. Soc. London, Ser. A*, *322* (1971) 137; (b) S. F. Politanskii, G. D. Ivanyk, V. N. Sarancha and V. U. Shevchuk, *Z. Org. Khim.*, *10* (1974) 693.

7 G. A. Olah and M. Nojima, *Synthesis*, (1973) 783.

8 G. A. Olah, M. Nojima and I. Kerekes, *Synthesis*, (1973) 779.

9 G. A. Olah, J. T. Welch, Y. D. Vankar, M. Nojima, I. Kerekes and J. A. Olah, *J. Org. Chem.*, *44* (1979) 3872.

10 A. I. Tikov, *Dokl. Akad. Nauk SSSR*, *149* (1963) 3301.

11 G. A. Olah, M. Nojima and I. Kerekes, *Synthesis*, (1973) 786.

12 (a) W. A. Szarek, G. Grynkiewicz, B. Doboszewski and G. W. Hay, *Chem. Lett.*, *10*

(1984) 1751; (b) M. Hayashi, S. Hashimoto and R. Noyori, *Chem. Lett.*, *10* (1984) 1747.

13 (a) G. A. Olah and J. Welch, *Synthesis*, (1974) 652; (b) G. A. Olah, G. K. S. Prakash and Y. L. Chao, *Helv. Chim. Acta*, *64* (1981) 2528; (c) G. A. Olah, J. G. Shih and G. K. S. Prakash, *Helv. Chim. Acta*, *66* (1983) 1028.

14 G. A. Olah and J. Welch, *Synthesis*, (1974) 654.

15 R. Keck and J. Retey, *Helv. Chim. Acta*, *63* (1980) 769.

16 H. Suschitzky, *Adv. Fluorine Chem.*, *4* (1965) 1.

17 G. A. Olah and J. Welch, *J. Am. Chem. Soc.*, *97* (1975) 208.

18 M. N. Rosenfeld and D. A. Widdowson, *J. Chem. Soc.*, *Chem. Commun.*, (1979) 914.

19 G. A. Olah and J. Welch, *Synthesis*, (1974) 896.

20 W. A. Sheppard and C. M. Sharts, *Organic Fluorine Chemistry*, Benjamin, New York, 1969.

21 G. A. Olah, B. G. B. Gupta and S. C. Narang, *Synthesis*, (1979) 274.

22 (a) G. A. Olah, J. G. Shih, B. P. Singh and B. G. B. Gupta, *Synthesis*, (1983) 713; (b) G. A. Olah, J. G. Shih, V. V. Krishnamurthy and B. P. Singh, *J. Am. Chem. Soc.*, *106* (1984) 4492.

23 G. A. Olah and S. J. Kuhn, *J. Org. Chem.*, *26* (1961) 237.

24 G. A. Olah, J. Nishimura and P. Kreienbuhl, *J. Am. Chem. Soc.*, *95* (1973) 7672.

25 G. A. Olah, M. R. Bruce and J. Welch, *Inorg. Chem.*, *16* (1977) 2637.

26 (a) R. D. Chambers, *Fluorine in Organic Chemistry*, Wiley, New York, 1973; (b) G. A. Boswell, Jr., W. C. Ripka, R. M. Scribner and C. W. Tullock, *Org. React.*, *21* (1974) 1; (c) C. J. Wang, *Org. React.*, *34* (1985) 319.

27 (a) D. Naumann and D. K. Padma, *Z. Anorg. Allg. Chem.*, *401* (1973) 53; (b) W. Becher and J. Massone, *Chem.-Ztg.*, *98* (1974) 117.

28 C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *J. Am. Chem. Soc.*, *82* (1960) 539.

29 P. A. W. Dean and R. J. Gillespie, *J. Am. Chem. Soc.*, *91* (1969) 7260.

30 G. A. Olah, *Carbocations and Electrophilic Reactions*, Wiley, New York, 1974.

31 (a) M. Woyski, *J. Am. Chem. Soc.*, *72* (1950) 919; (b) G. W. Tullock and D. D. Coffman, *J. Org. Chem.*, *25* (1960) 2016.

32 F. Seel, *Inorg. Synth.*, *9* (1967) 111.

33 *Br. Pat. 1 017 323*(1966) (to Allied Chemical) [*Chem. Abs.*, *64* (1966) 12 248a].

34 O. Glemser and U. Biermann, *Chem. Ber.*, *100* (1967) 2484.

35 C. J. Schack and R. D. Wilson, *Inorg. Chem.*, *9* (1970) 311.

36 G. A. Olah, M. Nojima and I. Kerekes, *J. Am. Chem. Soc.*, *96* (1974) 925.

37 W. Hückel, *Nachr. Ges. Wiss. Gottingen, Math.-Phys. Kl.*, *36* (1946).

38 A. F. Clifford, H. C. Beachell and W. M. Jack, *J. Inorg. Nucl. Chem.*, *5* (1957) 57.

39 (a) A. L. Oppegard, W. C. Smith, E. L. Muetterties and V. W. Englehardt, *J. Am. Chem. Soc.*, *82* (1960) 3835; (b) W. C. Smith, *U.S. Pat. 302 6179*(1962).

40 O. Glemser, F. Meyer and A. Haas, *Naturwissenschaften*, *52* (1965) 130.

41 P. L. Goggin, *J. Inorg. Nucl. Chem.*, *28* (1966) 661.

42 G. A. Olah, G. K. S. Prakash and J. Sommer, *Superacids*, Wiley, New York, 1985.

43 G. A. Olah, S. C. Narang and A. Garcia-Luna, *Synthesis*, (1980) 659.

44 (a) G. A. Olah, Y. D. Vankar and A. Garcia-Luna, *Synthesis*, (1979) 227; (b) G. Sosnovsky and J. A. Krogh, *Synthesis*, (1978) 703; (c) G. Sosnovsky, J. A. Krogh and S. G. Umhoefer, *Synthesis*, (1979) 7220.

45 G. A. Olah, S. C. Narang and A. Garcia-Luna, *Synthesis*, (1980) 661.

46 G. A. Olah, S. C. Narang and A. Garcia-Luna, *Synthesis*, (1981) 790.

47 M. Walter, H. Besendorf and O. Schnider, *Helv. Chim. Acta*, *44* (1961) 1546.

48 T. H. Chan and L. T. L. Wong, *J. Org. Chem.*, *34* (1969) 2766.

49 L. Caglioti, M. Poloni and G. Rosini, *J. Org. Chem.*, *33* (1968) 2979.

50 S. Yamada, Y. Kasai and T. Shioiri, *Tetrahedron Lett.*, (1973) 1595.

51 C. A. Buehber and D. E. Pearson, *Survey of Organic Synthesis*, Vols. 1 and 2, Wiley-Interscience, New York, 1970 and 1977.

52 (a) H. Lin, W. H. Chan and S. P. Lee, *Tetrahedron Lett.*, (1978) 4461; (b) A. Hassner and U. Alexanian, *Tetrahedron Lett.*, (1978) 4475.

53 G. A. Olah, S. C. Narang, A. Garcia-Luna and G. F. Salem, *Synthesis*, (1981) 146.

54 G. A. Sokolskii, *J. Gen. Chem. USSR, 36* (1966) 875.

55 G. A. Olah, L. Ohannesian, M. Arvanaghi and G. K. S. Prakash, *J. Org. Chem., 49* (1984) 2032.

56 H. House, *Modern Synthetic Reactions*, 2nd Ed., Benjamin, Menlo Park, CA, 1972.

57 (a) R. H. Reuss and A. Hassner, *J. Org. Chem., 39* (1974) 1785; (b) L. Blanco, P. Amice and J. M. Conia, *Synthesis*, (1976) 194; (c) L. A. Lazukina, V. P. Kuhar and G. V. Pesotskaza, *J. Gen. Chem. USSR, 45* (1975) 2065; (d) Y. Itoh, M. Nakatsuka and T. Saegusa, *J. Org. Chem., 45* (1980) 2022.

58 G. A. Olah, B. G. B. Gupta, A. Garcia-Luna and S. C. Narang, *J. Org. Chem., 48* (1983) 1760.

59 M. F. Grenier-Loustalot, P. Irotcabal and F. Metras, *Synthesis*, (1976) 33.

60 A. Lopusinski and J. Michalski, *J. Am. Chem. Soc., 104* (1982) 290.

61 (a) G. A. Olah, J. Welch and T. Ho, *J. Am. Chem. Soc., 98* (1976) 6717; (b) G. A. Olah and J. Welch, *J. Am. Chem. Soc., 100* (1978) 5396.

62 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 1460.

63 R. M. Barter and J. S. Littler, *J. Chem. Soc. (B)*, (1967) 205.

64 C. D. Snyder and H. Rapoport, *J. Am. Chem. Soc., 94* (1972) 227.

65 D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert and D. Zurr, *J. Chem. Soc. Perkin Trans. I*, (1972) 542.

66 R. Curci, G. Delano, F. Difuria, J. O. Edwards and A. R. Gallopo, *J. Org. Chem., 39* (1974) 3020.

67 G. A. Olah (ed.), *Friedel–Crafts and Related Reactions*, Vol. I, Wiley-Interscience, New York, 1963.

68 (a) A. Colsen, *Bull. Soc. Chim. Fr., 17* (1897) 55; (b) A. Colsen, *Ann. Chim. (Paris), 12* (1897) 255; (c) K. Fredenhagen, *Z. Phys. Chem., A164* (1933) 189; (d) D. Fredenhagen and G. Cadenbach, *ibid., A164* (1933) 201.

69 (a) G. W. Tullock and D. D. Coffman, *J. Org. Chem., 25* (1960) 2016; (b) G. A. Olah, S. Kuhn and S. Beke, *Chem. Ber., 89* (1956) 862; (c) J. Dahmlos, *Angew. Chem., 71* (1959) 274.

70 (a) W. R. Hasek, W. C. Smith and V. A. Englehardt, *J. Am. Chem. Soc., 82* (1960) 543; (b) G. A. Olah, M. Nojima and I. Kerekes, *Synthesis*, (1973) 487.

71 T. L. Ho, H. C. Ho and C. M. Wong, *Synthesis*, (1972) 562.

72 J. B. Aylward and R. O. C. Norman, *J. Chem. Soc. (C)*, (1968) 2399.

73 L. Kalb and D. Gross, *Ber., 39* (1926) 727.

74 G. A. Olah and T. L. Ho, *Synthesis*, (1976) 610.

75 (a) H. R. Snyder, S. Swaminathan and H. J. Sims, *J. Am. Chem. Soc., 74* (1952) 5110; (b) J. J. Angyal, *Org. React., 8* (1954) 197.

76 G. A. Olah, J. Welch, G. K. S. Prakash and T. L. Ho, *Synthesis*, (1976) 808.

77 (a) F. Mathey and J. Bensoam, *C. R. Acad. Sci. Ser. C, 276* (1973) 1569; (b) F. Mathey and J. Bensoam, *Tetrahedron Lett.*, (1973) 2253; (c) F. Mathey and J. Bensoam, *Tetrahedron, 31* (1975) 391.

78 (a) J. I. Darragh, A. M. Noble, D. W. A. Sharpe, D. W. Walker and J. M. Winfield, *Inorg. Nucl. Chem. Lett., 4* (1968) 517; (b) D. W. Walker and J. M. Winfield, *J. Inorg. Nucl. Chem., 34* (1972) 759.

79 G. A. Olah and J. Welch, *Synthesis*, (1976) 809.

80 (a) J. I. Darragh, A. M. Noble, W. A. David and J. M. Winfield, *J. Inorg. Nucl. Chem., 32* (1970) 1745; (b) N. Viswanathan and C. H. Van Dyke, *J. Organometal. Chem., 11* (1968) 181; (c) A. Haas and T. Maciej, *J. Fluorine Chem., 20* (1982) 581; (d) A. Haas and T. Maciej, *J. Fluorine Chem., 20* (1982) 581.

81 F. S. Fawcett and R. D. Lipscomb, *J. Am. Chem. Soc., 86* (1964) 2576.

82 G. A. Olah, M. Nojima and I. Kerekes, *Synthesis*, (1973) 487.

83 G. A. Olah, S. Kuhn and S. Beke, *Chem. Ber.*, *89* (1956) 862.

84 F. Seel and J. Langer, *Chem. Ber.*, *91* (1958) 2553.

85 W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, *82* (1960) 543.

86 N. N. Yarovenko and M. A. Radska, *J. Gen. Chem. USSR*, *29* (1959) 2175.

87 G. A. Olah and S. J. Kuhn, *Org. Synth.*, *45* (1965) 3.

88 G. A. Olah, A. P. Fung, B. G. B. Gupta and S. C. Narang, *Synthesis*, (1980) 221.

89 (a) G. A. Olah, S. C. Narang, J. A. Olah and K. Lammertsma, *Proc. Natl. Acad. Sci. USA*, *79* (1982) 4487; (b) K. Schoffield, *Aromatic Nitration*, Cambridge Univ. Press, New York, 1971.

90 G. A. Olah and S. J. Kuhn, *Org. Synth.*, *47* (1967) 56.

91 G. A. Olah and H. C. Lin, *Synthesis*, (1974) 444.

92 G. A. Olah and H. C. Lin, *J. Am. Chem. Soc.*, *93* (1971) 1259.

93 (a) G. A. Olah, B. G. B. Gupta and S. C. Narang, *J. Am. Chem. Soc.*, *101* (1979) 5317; (b) G. A. Olah, B. G. B. Gupta, A. Garcia-Luna and S. C. Narang, *J. Org. Chem.*, *45* (1983) 1760; (c) G. A. Olah and B. G. B. Gupta, *J. Org. Chem.*, *48* (1983) 3585.

94 (a) G. A. Olah and T. L. Ho, *Synthesis*, (1976) 609; (b) *ibid.*, (1976) 610; (c) G. A. Olah and T. L. Ho, *J. Org. Chem.*, *42* (1977) 3097; (d) T. L. Ho and G. A. Olah, *Synthesis*, (1977) 418; (e) G. A. Olah, S. C. Narang, G. F. Salem and B. G. B. Gupta, *Synthesis*, (1979) 273; (f) G. A. Olah, *Acc. Chem. Res.*, *13* (1980) 330.

95 C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, NY, 1953; (b) J. Allan, J. Podstata, D. Snobl and J. Jarkovsky, *Tetrahedron Lett.*, (1965) 3565.

96 G. A. Olah and N. Friedman, *J. Am. Chem. Soc.*, *88* (1966) 5330.

97 G. A. Olah, G. Salem, J. S. Staral and T. L. Ho, *J. Org. Chem.*, *43* (1978) 173.

98 G. A. Olah, J. G. Shih, B. P. Singh and B. G. B. Gupta, *J. Org. Chem.*, *48* (1983) 3356.

99 G. A. Olah, B. G. B. Gupta and S. C. Narang, *Synthesis*, (1983) 713.

100 For reviews see (a) H. Meerwein, in E. Muller (ed.), *Methoden der Organischen Chemie (Houben-Weyl)*, 4th Ed., Vol. VI/3, Thieme, Stuttgart, 1965; (b) H. Perst, *Oxonium Ions in Organic Chemistry*, Academic Press, New York, 1971; (c) H. Meerwein, *Org. Synth.*, *46* (1966) 120; (d) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. Prakt. Chem.*, *154* (1940) 83.

101 G. A. Olah and J. J. Svoboda, *Synthesis*, (1973) 203; (b) G. A. Olah and Y. K. Mo, *J. Am. Chem. Soc.*, *96* (1974) 3560, (c) G. A. Olah, *Halonium Ions*, Wiley-Interscience, New York, 1975, and references therein.

102 G. A. Olah, G. K. S. Prakash and M. R. Bruce, *J. Am. Chem. Soc.*, *101* (1979) 6463.

103 (a) G. A. Olah, *Angew. Chem.*, *85* (1973) 183; (b) *Aldrichim. Acta*, *6* (1973) 7.

104 G. A. Olah, J. J. Svoboda and A. T. Ku, *Synthesis*, (1973) 492.

105 G. A. Olah *et al.*, unpublished results.

106 (a) G. A. Olah and H. C. Lin, *Synthesis*, (1974) 342; (b) G. A. Olah, H. C. Lin and A. Germain, *ibid.*, (1974) 895.

107 G. A. Olah, J. R. DeMember and R. H. Schlosberg, *J. Am. Chem. Soc.*, *91* (1969) 2112.

108 G. A. Olah, J. R. DeMember, R. H. Schlosberg and Y. Halpern, *J. Am. Chem. Soc.*, *94* (1972) 159.

109 G. A. Olah, M. R. Bruce and F. L. Clouet, *J. Org. Chem.*, *46* (1981) 438.

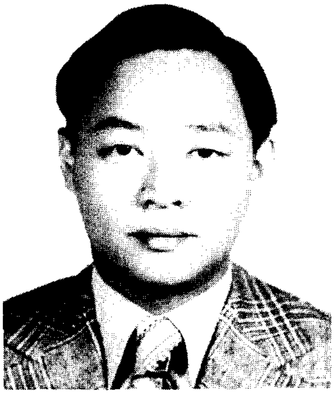
110 G. A. Olah, R. Herges, K. Laali and G. A. Segal, *J. Am. Chem. Soc.*, *108* (1986) 2054.

111 (a) G. A. Olah and P. von R. Schleyer (eds.), *Carbonium Ions*, Vols. I - V, Wiley-Interscience, New York, 1968 - 76; (b) G. A. Olah, 'From Boron Trifluoride to Antimony Pentafluoride in Search of Stable Carbocations', in *Topics in Current Chemistry*, Vol. 80, (In Memory of H. L. Meerwein), Springer, Berlin, 1979, pp. 19 - 88.

BIOGRAPHIC NOTES

George A. Olah was born in Hungary, where he received his university education. He emigrated to Canada in 1956 and subsequently moved to the USA. In 1965, he left his employment at the Dow Chemical Company to become Professor of Chemistry and Chairman of the Chemistry Department at Case Western Reserve University, Cleveland, Ohio. Since 1977 he has been the Loker Distinguished Professor of Organic Chemistry and Scientific Co-Director of the Hydrocarbon Research Institute at the University of Southern California in Los Angeles.

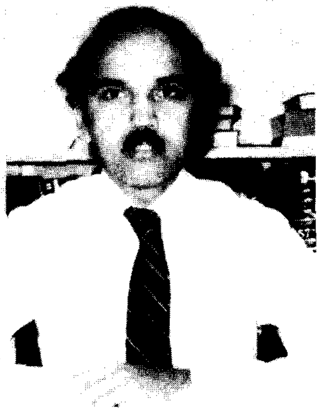
G. A. Olah



J. G. Shih

Joseph G. Shih, a native of Taiwan, obtained his Ph.D. degree in 1984 under the direction of Prof. G. A. Olah and is currently a senior research chemist at Ultrasystems Inc., Irvine, CA.

G. K. Surya Prakash, a native of India, is Research Associate Professor of Chemistry at the University of Southern California.



G. K. S. Prakash