Halofluorination of Alkenes Using Trihaloisocyanuric Acids and HF·Pyridine

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In memory of Prof. Octavio Augusto Ceva Antunes

Abstract: Halofluorination of alkenes with a new system (trihaloisocyanuric acids and HF·pyridine) results in the formation of vicinal halofluoroalkanes. The reaction is regioselective leading to Markovnikov-oriented products and the halofluorinated adducts follow *anti*-addition in the case of cyclohexene and 1-methylcyclohexene. Reaction yields range from 67–88%.

Key words: electrophilic addition, halogenation, alkenes, halides, regioselectivity

Organofluorine compounds show interesting chemical and physical properties and biological activities, raising interest in many fields.[1] The introduction of fluorine into organic compounds increases thermal and oxidative stability, alters electronic effects and lipophilicity, and also closely mimics hydrogen and oxygen in steric requirements.[2] Organofluorine compounds have been used as lubricants, coatings for cooking utensils, propellants, refrigerants, solvents, dyes, liquid crystals, surfactants, in the production of agrochemicals, and in pharmaceutical industry.[2a,3]

An important method to place fluorine into organic molecules is the halofluorination of unsaturated compounds[4] and several protocols have been developed. The 70% HF·pyridine (Olah's reagent) or Et_3N·HF are most commonly used as fluoride sources, and *N*-halosuccinimide (NXS) or *N*-halosaccharin (NXSac) as sources of electrophilic halogen.[5] Trihaloisocyanuric acids (TXCA, Figure 1) have been recently shown to be efficient halogenating agents, due to their capability of halonium ('X^+') atom transfer to unsaturated substrates.[6–8]

Trichloroisocyanuric acid (TCCA) is a stable and inexpensive solid frequently used for swimming pool disinfection and is easily available in pool supply and in some hardware stores.[6] Tribromoisocyanuric acid (TBCA) is easily and safely prepared from cyanuric acid, KBr, and oxone®,[7b] and triiodoisocyanuric acid (TICA) is synthesized from TCCA and I_2 in a sealed tube.[8a] These trihaloisocyanuric acids are very interesting from a green chemistry point of view, as they are easily handled stable solids and also present a good atom economy[9] as they can transfer most part of their mass to the substrate (Table 1). Furthermore, in these reactions, cyanuric acid precipitates as a by-product, which can be recovered by filtration and reused to prepare more trihaloisocyanuric acid.[10]

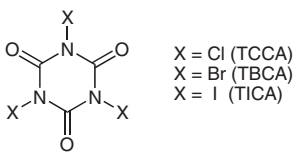


Figure 1 Trihaloisocyanuric acids

Table 1 Atom Economy of *N*-Halo Compounds[a]

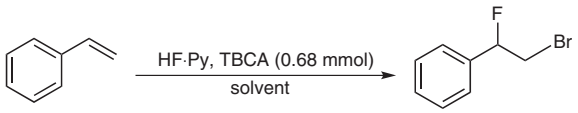
X	TXCA	NXS	NXSac
Cl	45.5	26.4	16.3
Br	65	45	30.5
I	75	56.5	41.1

[a] Active halogen content (w/w%) that can be transferred to the product.

In this work, we describe a new methodology for the regioselective halofluorination of alkenes using Olah's reagent as the source of fluorine and TXCA as the source of electrophilic halogen.

Initially, the bromofluorination of styrene using tribromoisocyanuric acid and Olah's reagent in different condi-

Table 2 Bromofluorination Reaction of Styrene with Tribromoisocyanuric Acid and Olah's Reagent



(2 mmol)

Ratio styrene–HF·Py–TBCA	Time (min)	Temp	Solvent	Conv. (%)[a]
1:10:0.34	20	r.t.	THF	41[b]
1:10:0.34	30	r.t.	MeCN	31[c]
1:10:0.34	20	r.t.	CH_2Cl_2	100
1:10:0.34	30	–10 °C	CH_2Cl_2	100
1:2:0.34	180	r.t.	CH_2Cl_2	100

[a] Determined by HRGC-MS.
[b] Formed along with two unidentified products.
[c] Formed along with incorporation of MeCN to the substrate.

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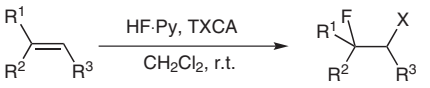
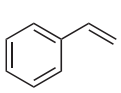
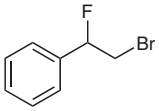
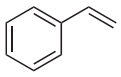
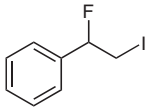
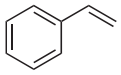
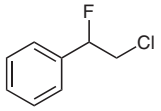
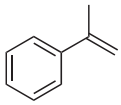
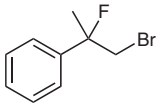
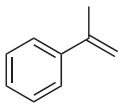
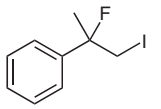
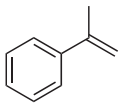
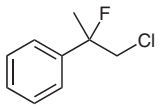
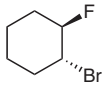
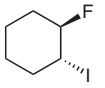
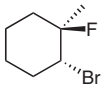
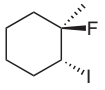
tions was evaluated (Table 2). It was observed that dichloromethane is the best solvent for halofluorination reaction in HF·Py/TBCA system. The HF·Py/TBCA molar ratio of 6 in dichloromethane is enough for the complete conversion of the substrate, leading to the corresponding bromofluorinated product. The main difference in such reactions is the reaction time, which decreases with the increase of the HF·Py/TBCA molar ratio.

Based on the above results, the halofluorination of several alkenes (styrene, α-methylstyrene, cyclohexene, and 1-methylcyclohexene) using the trihaloisocyanuric acids (0.34 mol equiv) and HF·Py (2 mol equiv) in dichloromethane was also evaluated and the results are shown in Table 3.

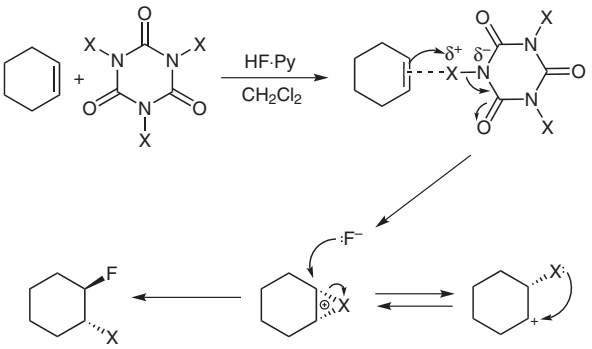
Table 3 Halofluorination of Alkenes with Trihaloisocyanuric Acids



Alkene	Time (h)	Product	Yield (%)
	3		79
	21		83
	0.5		80[a]
	3		85
	2		77
	0.5		70[b]
	19		88
	15		75
	7		67
	7		86

[a] Formed along with β-chlorostyrene (20%).
[b] Formed along with β-chloro-α-methylstyrene and α-(chloromethyl)styrene (30%).

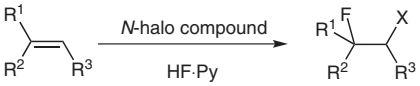
The reactions leads selectively to products according to Markovnikov's rule. Cyclohexene and 1-methylcyclohexene afford halofluorinated adducts, explained by an *anti*-addition. The *trans*-stereochemistry of the halofluorination adducts indicates the formation of a halonium ion as reaction intermediate, which is further attacked by a fluoride ion (Scheme 1).



Scheme 1 Reaction intermediates for halofluorination of alkenes with trihaloisocyanuric acids

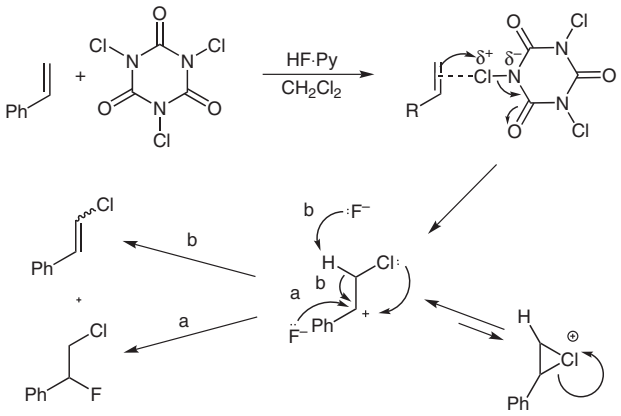
The reactions lead to pure products in most cases in good yields. The yields are comparable with the HF·Py/NXS or HF·Py/NXSac systems for cyclohexenes, but considerably higher for styrenes (Table 4). However, despite the yields, TXCA proved to be more convenient than other *N*-halo compounds in halofluorination reactions for both easy handling and, especially, their higher atom economy,[9] as shown in Table 1.

Table 4 Comparison of Yields for Halofluorination Reactions



R^1	R^2	R^3	X	TXCA	NXS	NXSac
H	$-(CH_2)_4-$		Br	88	90[5b]	–
H	$-(CH_2)_4-$		I	75	75[5b]	–
Me	$-(CH_2)_4-$		I	86	–	89[5n]
Ph	H	H	Cl	80	–	50[5j]
Ph	H	H	Br	79	53[5p]	–
Ph	Me	H	Br	85	72[5p]	–

The formation of chloroalkenes in the chlorofluorination reaction of styrene and α-methylstyrene suggest the existence of a β-chlorinated carbocation intermediate, which can be deprotonated affording the corresponding allyl or vinyl chlorides[11] (Scheme 2). The result of *cis* and *trans* products obtained by Dolenc and Sket[5j] in the reaction of indene with *N*-chlorosaccharin/HF·Py is also an evidence against the involvement of a chloronium ion as an inter-



Scheme 2 Reaction intermediates for chlorofluorination of styrene with trichloroisocyanuric acid

mediate in the chlorofluoration reactions with styryl systems.

In conclusion, the present work describes the use of trihaloisocyanuric acids as an efficient halogenating reagent for halofluorination reaction of alkenes. These reagents are inexpensive, readily prepared, easy-to-handle solids, safe, and more useful in terms of atom economy than the traditional reagents used in halofluorination reaction. Reaction yields range from 67–88%.

Alkenes (Aldrich), Olah's reagent (Alfa Aesar), and TCCA (Acros Organics) were used as received. TBCA[7b] and TICA[8a] were prepared according to published procedures. NMR spectra were recorded on a Bruker AC-200 spectrometer at 300 MHz (^{1}H) and at 75 MHz (^{13}C) in $CDCl_3$ with TMS as internal standard. ^{19}F NMR spectra were recorded in a Bruker DRX-300 spectrometer at 282 MHz in $CDCl_3$ (fluorobenzene as reference). HRGC-MS analyses were performed on a Shimadzu GCMS-QP2010S gas chromatograph with electron impact (70 eV) by using a 30 m DB-5 silica capillary column. All reactions were performed using a single-necked high density PTFE flask under argon and were monitored by HRGC. After workup, the solvent was evaporated on a rotatory evaporator at reduced pressure and controlled heating or carefully distilled. Whenever necessary, the product was purified using a 20 × 20 cm SiO_2 preparative plate.

Halofluorination of Alkenes with HF·Py/TBCA System; General Procedure

A magnetically stirred mixture of the alkene (2 mmol) and 70% HF·Py (4 mmol) in anhyd CH_2Cl_2 (10 mL) contained in a 50 mL, single-necked PTFE flask equipped with a septum and under argon, was treated with trihaloisocyanuric acid (0.68 mmol) at 0 °C. After the addition, the ice bath was removed, and the stirring continued at r.t. After completion (Table 3), the reaction was quenched with distilled H_2O (10 mL), and the product was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were subsequently washed with sat. aq $NaHCO_3$ (10 mL) and dried (Na_2SO_4). After filtration and evaporation of the solvent, the product was characterized by standard analytical techniques (Table 3).

2-Bromo-1-fluoro-1-phenylethane[5k]

Colorless liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.5–3.7 (m, 2 H), 5.5–5.8 (ddd, *J* = 46.9, 7.0, 4.6 Hz, 1 H), 7.4 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 34.4 (CH_2, d, *J* = 28.4 Hz), 92.8 (CH, d, *J* = 178.0 Hz), 125.8 (2 CH, d, *J* = 6.8 Hz), 128.8 (2 CH, s), 129.3 (CH, s), 137.2 (C, d, *J* = 20.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –174.7 (m).

MS: *m*/*z* (%) = 202 and 204 [M^+ and $(M + 2)^+$, 7], 122 (3), 109 (100), 103 (8), 77 (11), 51 (14).

1-Bromo-2-fluoro-2-phenylpropane[5l]

Yellowish liquid, after purification by preparative chromatography on SiO_2 using hexane as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.8 (d, *J* = 22.0 Hz, 3 H), 3.5–3.7 (m, 2 H), 7.4 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.6 (CH_3, d, *J* = 24.4 Hz), 40.6 (CH_2, d, *J* = 28.4 Hz), 95.0 (C, d, *J* = 178.6 Hz), 124.6 (2 CH, d, *J* = 9.1 Hz), 128.4 (CH), 128.7 (2 CH), 141.8 (C, d, *J* = 21.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –148.0 (quint d, *J* = 22.1, 16.8 Hz).

MS: *m*/*z* (%) = 216 and 218 [(M^+ and $(M + 2)^+$, 5], 196 (2), 123 (100), 103 (31), 77 (14), 51 (14).

***trans*-1-Bromo-2-fluorocyclohexane[5b]**

Yellowish liquid, after purification by preparative chromatography on SiO_2 using EtOAc–hexane (20%) as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.2–2.0 (m, 6 H), 2.0–2.4 (m, 2 H), 3.9–4.1 (m, 1 H), 4.3–4.7 (dtd, *J* = 48.3, 8.4, 4.3 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.8 (CH_2, d, *J* = 8.7 Hz), 25.0 (CH_2), 31.2 (CH_2, d, *J* = 19.1 Hz), 34.8 (CH_2, d, *J* = 3.7 Hz), 52.5 (CH, d, *J* = 19.8 Hz), 94.0 (CH, d, *J* = 179.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –168.1 (dm, *J* = 44.9 Hz).

MS: *m*/*z* = 180 and 182 [M^+ and $(M + 2)^+$, 2], 101 (31), 81 (100), 72 (8), 59 (24).

***trans*-2-Bromo-1-fluoro-1-methylcyclohexane[5k]**

Yellowish liquid, after purification by preparative chromatography on SiO_2 using EtOAc–hexane (20%) as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.5–1.6 (d, *J* = 22.5 Hz, 3 H), 1.4–2.3 (m, 8 H), 4.2 (td, *J* = 7.4, 3.9 Hz).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.1 (CH_2, d, *J* = 6.3 Hz), 22.9 (CH_2), 23.8 (CH_3, d, *J* = 24.6 Hz), 33.2 (CH_2), 34.8 (CH_2, d, *J* = 17.5 Hz), 57.2 (CH, d, *J* = 26.3 Hz), 95.6 (C, d, *J* = 172.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –137.3 (m).

MS: *m*/*z* (%) = 194 and 196 [M^+ and $(M + 2)^+$, 1], 134 (2), 132 (2), 115 (11), 99 (5), 95 (100), 73 (49).

2-Chloro-1-fluoro-1-phenylethane[5j]

Yellowish liquid, after purification by preparative chromatography on SiO_2 using hexane as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.6–3.9 (m, 2 H), 5.4–5.7 (dm, *J* = 47.1, 6.0, 4.3 Hz, 1 H), 7.4 (s, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 47.1 (CH_2, d, *J* = 28.2 Hz), 93.3 (CH, d, *J* = 178.2 Hz), 126.0 (2 CH, d, *J* = 6.8 Hz), 128.9 (2 CH), 129.5 (CH, d, *J* = 1.5 Hz), 136.8 (C, d, *J* = 20.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –179.1 (ddd, *J* = 15.9, 25.5, 46.9 Hz).

MS: *m*/*z* (%) = 158 and 160 [M^+ and $(M + 2)^+$, 10.9, 3.5], 140 (1.5), 138 (7), 109 (100), 103 (15), 77 (11), 51 (16).

1-Chloro-2-fluoro-2-phenylpropane[5m]

Yellowish liquid, after purification by preparative chromatography on SiO_2 using hexane as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.8 (d, *J* = 22.2 Hz), 3.7–3.9 (m, 2 H), 7.4 (s, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 24.5 (CH_3, d, *J* = 24.4 Hz), 51.8 (CH_2, d, *J* = 28.4 Hz), 95.8 (C, d, *J* = 178.5 Hz), 124.7 (2 CH, d, *J* = 9.1 Hz), 128.4 (2 CH), 128.7 (CH), 141.7 (C, d, *J* = 21.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –150.9 (quint d, *J* = 16.4, 22.1 Hz).

MS: *m*/*z* (%) = 172 and 174 [M^+ and $(M + 2)^+$, 5, 1.6], 154 (1), 152 (2.5), 123 (100), 103 (41), 77 (19), 51 (18).

1-Fluoro-2-iodo-1-phenylethane[5l]
Yellowish liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.4–3.6 (m, 2 H), 5.4–5.7 (dt, *J* = 46.7, 7.3 Hz, 1 H), 7.4 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.40 (CH_2, d, *J* = 28.2 Hz), 93.20 (CH, d, *J* = 177.5 Hz), 125.70 (2 CH, d, *J* = 6.5 Hz), 128.80 (2 CH), 129.20 (CH), 138.05 (C, d, *J* = 20.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –167.10 (ddd, *J* = 40.8, 24.2, 16.6 Hz).

MS: *m*/*z* (%) = 250 (M^+, 2), 230 (3), 123 (100), 109 (32), 103 (62), 77 (35), 51 (21).

2-Fluoro-1-iodo-2-phenylpropane[5l]
Yellowish liquid.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.9 (d, *J* = 21.8 Hz, 3 H), 3.6 (d, *J* = 20.3 Hz, 2 H), 7.4 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 15.7 (CH_3, d, *J* = 28.2 Hz), 27.1 (CH_2, d, *J* = 24.5 Hz), 94.6 (C, d, *J* = 178.5 Hz), 124.4 (2 CH, d, *J* = 9.1 Hz), 128.3 (2 CH), 128.7 (CH), 141.9 (C, d, *J* = 22.0 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –142.6 (sext, *J* = 21.0 Hz).

MS: *m*/*z* (%) = 264 (M^+, 2), 244 (4), 137 (100), 123 (43), 103 (30), 77 (24), 51 (32).

***trans*-2-Fluoro-1-iodocyclohexane[5b]**
Yellowish liquid, after purification by preparative chromatography on SiO_2 using EtOAc–hexane (20%) as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.3–1.6 (m, 4 H), 1.6–2.0 (m, 2 H), 2.0–2.5 (m, 2 H), 4.0–4.2 (m, 1 H), 4.4–4.7 (dtd, *J* = 47.7, 8.6, 4.1 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.0 (CH_2, d, *J* = 8.6 Hz), 26.3 (CH_2), 30.9 (CH_2, d, *J* = 18.8 Hz), 31.4 (CH, d, *J* = 19.5 Hz), 36.6 (CH_2, d, *J* = 3.7 Hz), 94.8 (CH, d, *J* = 179.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –160.0 (dm, *J* = 40.0 Hz).

MS: *m*/*z* (%) = 228 (M^+, 14), 127 (6), 101 (33), 81 (100), 59 (33).

***trans*-1-Fluoro-2-iodo-1-methylcyclohexane[5l]**
Yellowish liquid, after purification by preparative chromatography on SiO_2 using EtOAc–hexane (20%) as eluent.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.3–1.6 (d, *J* = 22.4 Hz, 3 H), 1.3–2.3 (m, 8 H), 4.4 (td, *J* = 7.8, 3.9 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 22.4 (CH_2, d, *J* = 6.7 Hz), 25.0 (CH_2), 25.9 (CH_3, d, *J* = 24.4 Hz), 34.8 (CH_2, d, *J* = 21.2 Hz), 35.6 (CH_2, d, *J* = 4.5 Hz), 38.4 (CH, d, *J* = 23.3 Hz), 95.4 (C, d, *J* = 173.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –132.6 (dm, *J* = 93.0 Hz).

MS: *m*/*z* (%) = 242 (M^+, 3), 115 (18), 95 (100), 73 (34).

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