S, 9.81. Found: C, 14.59; H, 1.07; Cl, 16.32; F, 8.64; N, 12.64; S, 9.61.

A similar experiment starting with bis(2-fluoro-2,2-dinitroethyl) thionocarbonate[2] (17.5 g, 0.05 mol), 2-fluoro-2,2-dinitroethanol (17.7 g, 0.115 mol), and trichloromethanesulfenyl chloride (12.1 g, 0.065 mol) gave 2.79 g (11%) of **3** and 26.05 g (80%) of **2**, mp 55–57 °C.

Bis[tris(2-fluoro-2,2-dinitroethoxy)methyl] Disulfide (3). A solution of 1.96 g (0.003 mol) of **2**, 1.05 g (0.003 mol) of bis-(2-fluoro-2,2-dinitroethyl)thionocarbonate,[2] and 0.6 g (0.004 mol) of 2-fluoro-2,2-dinitroethanol in 10 mL of CH_2Cl_2 was cooled in an ice bath. Tetrabutylammonium chloride (0.3 g) in 6 mL of water was added followed by the dropwise addition (0.25 h) of 0.4 g of 50% NaOH (diluted with 2 mL of H_2O) at 0–3 °C. The reaction solution was allowed to warm to dissolve a solid precipitate into the CH_2Cl_2 layer which was then separated, and the volatiles were removed to give a residue which when treated with $CHCl_3$ gave 1.44 g (48%) of a white solid, mp 130–133 °C. Recrystallization from acetone–$CHCl_3$ gave the product: mp 134–135 °C; ^1H NMR [$(CD_3)_2C{=}O$] δ 5.30 (d); mass spectrum (CI), m/e 471. Anal. Calcd for $C_{14}H_{12}F_6N_{12}O_{30}S_2$: C, 16.71; H, 1.20 F, 11.33; N, 16.70; S, 6.37. Found: C, 16.54; H, 1.15; F, 11.43; N, 16.63; S, 6.14.

Bis(2,2-dinitropropoxy)(2-fluoro-2,2-dinitroethoxy)methyl Trichloromethyl Disulfide (5). A mixture of 20.5 g (0.06 mol) of bis(2,2-dinitropropyl) thionocarbonate,[8] 14.5 g (0.078 mol) of trichloromethanesulfenyl chloride, and 21.2 g (0.138 mol) of 2-fluoro-2,2-dinitroethanol in 110 mL of CH_2Cl_2 was cooled in an ice–salt bath before 3.0 g of tetrabutylammonium chloride in 70 mL of H_2O was added. A 50% aqueous NaOH solution (10.0 g) was diluted with 30 mL of H_2O and added dropwise (0.25 h) at 0–4 °C until the reaction solution turned basic to litmus paper. The CH_2Cl_2 layer was separated and dried, and the volatiles were removed to yield an oil which was washed with 200 mL of hexane and 300 mL of H_2O before it (19.3 g) was purified by chromatography on silica gel 60 (300 g; CH_2Cl_2–hexane as the eluent). The product was then triturated with hexane to give solid: 13.4 g (35%) mp 63–66 °C; ^1H NMR [$(CD_3)_2C{=}O$] δ 5.34 (d, 2 H), 4.91 (s, 4 H), 2.39 (s, 6 H). Anal. Calcd for $C_{10}H_{12}Cl_3FN_6O_{15}S_2$: C, 18.60; H, 1.87; Cl, 16.47; F, 2.94; N, 13.01; S, 9.93. Found: C, 18.80; H, 1.89; Cl, 16.50; F, 2.93; N, 12.96; S, 9.79.

Bis(2-fluoro-2,2-dinitroethoxy)(2,2,2-trifluoroethoxy)-methyl Trichloromethyl Disulfide (6). A solution of 10.5 g (0.03 mol) of bis(2-fluoro-2,2-dinitroethyl) thionocarbonate,[2] 7.25 g (0.039 mol) of trichloromethanesulfenyl chloride, and 6.9 g (0.069 mol) of 2,2,2-trifluoroethanol in 50 mL of CH_2Cl_2 was cooled in an ice–salt bath. Tetrabutylammonium chloride (1.5 g) in 30 mL of H_2O was added followed by the dropwise addition (0.25 h) of 2.8 g of NaOH in 5 mL of H_2O at 0–3 °C. The CH_2Cl_2 layer was separated and dried, and the volatiles were removed to give 16.5 g of an oil which was extracted with boiling hexanes (3 × 50 mL). The cooled extracts were decanted from a small amount of oily precipitate, and the solvent was removed to give 6.0 g (33%) of an oil which was nearly pure by TLC analysis. An analytical sample was obtained by column chromatography on silica gel 60 (115 g) with hexane followed by CH_2Cl_2–hexane as the eluent: ^1H NMR ($CDCl_3$) δ 4.89 (d, 4 H), 4.15 (q, 2 H). Anal. Calcd for $C_8H_6Cl_3F_5N_4O_{11}S_2$: C, 16.02; H, 1.01; Cl, 17.74; F, 15.84; N, 9.34; S, 10.69. Found: C, 16.08; H, 1.02; Cl, 17.97; F, 15.63; N, 9.23; S, 10.81.

Bis(2,2,2-trifluoroethoxy)(2-fluoro-2,2-dinitroethoxy)-methyl Trichloromethyl Disulfide (7). To a well-stirred solution of 7.26 g (0.03 mol) of bis(2,2,2-trifluoroethyl)thionocarbonate,[12] 6.14 g (0.033 mol) of trichloromethanesulfenyl chloride, and 6.0 (0.039 mol) of 2-fluoro-2,2-dinitroethanol in 40 mL of CH_2Cl_2 cooled in an ice–salt bath was added 1.5 g of tetrabutylammonium chloride in 30 mL of H_2O followed by the dropwise addition (0.25 h) of 5 mL of 10 N aqueous NaOH at 0–5 °C. The reaction solution was then kept slightly basic for 15 min by the addition of a few drops of NaOH solution when required. The CH_2Cl_2 layer was separated, and the solvent was removed to give 18.0 g of oil which was purified by column chromatography on silica gel 60 (115 g; 30:70 CH_2Cl_2–hexane as the eluent). The product was an oil: 9.95 g (61%) ^1H NMR ($CDCl_3$) δ 4.90 (d, 2 H), 4.15 (q, 4 H). Anal. Calcd for $C_8H_6Cl_3F_7N_2O_7S_2$: C, 17.61; H, 1.11; Cl, 19.49; F, 24.38; N, 5.13; S, 11.75. Found: C, 17.62; H, 1.05; Cl, 19.24; F, 24.17; N, 5.19; S, 11.56.

2-Fluoro-2,2-dinitroethyl Trichloromethanesulfenate (4). Trichloromethanesulfenyl chloride (5.6 g, 0.03 mol) and 2-fluoro-2,2-dinitroethanol (5.0 g, 0.033 mol) in 30 mL of CH_2Cl_2 and 0.3 g of tetrabutylammonium chloride in 20 mL of H_2O was cooled at 0 °C during the dropwise addition (0.25 h) of 1.3 g of NaOH in 6 mL of H_2O. Separation of the CH_2Cl_2 layer and removal of solvent gave 8.2 g of oil which was extracted with hexane (2 × 40 mL). The combined extracts were passed through a silica gel 60 pad (40 g, washed with benzene), and the solvent was removed to give 5.9 g (65%) of an oil which was pure by TLC and GLC analysis: ^1H NMR ($CDCl_3$) δ 5.37 (d); mass spectrum (CI), m/e 304, 302, 267, 269. Anal. Calcd for $C_3H_2Cl_3FN_2O_5S$: C, 11.87; H, 0.66; Cl, 35.05; F, 6.26; N, 9.23; S, 10.56. Found: C, 11.85; H, 0.70; Cl, 34.90; F, 6.14; N, 9.05; S, 10.58.

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Registry No. **1**, 70096-91-2; **2**, 86803-34-1; **3**, 86803-35-2; **4**, 86803-39-6; **5**, 86803-36-3; **6**, 86803-37-4; **7**, 86803-38-5; 2-fluoro-2,2-dinitroethanol, 17003-75-7; tetrabutylammonium chloride, 1112-67-0; thiophosgene, 463-71-8; trichloromethanesulfenyl chloride, 594-42-3; 2-fluoro-2,2-dinitroethoxide, 86803-33-0; bis-(2,2-dinitropropyl) thionocarbonate, 80445-01-8; 2,2,2-trifluoroethanol, 75-89-8; bis(2,2,2-trifluoroethyl) thionocarbonate, 83486-43-5.

(12) From thiophosgene and trifluoroethanol with base.

Ionic Fluorination of Adamantane, Diamantane, and Triphenylmethane with $NO^+BF_4^-$/Pyridine Polyhydrogen Fluoride (PPHF)[1]

George A. Olah,* Joseph G. Shih, Brij P. Singh, and B. G. B. Gupta[2]

Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089

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The usual laboratory preparation of alkyl or arylalkyl fluorides involves nucleophilic exchange of the corresponding halides (iodides, bromides, chlorides) or other suitable leaving groups by fluoride ion or addition of hydrogen fluoride[3] to olefins. To overcome inconvenience of using volatile, highly corrosive, and difficult to handle anhydrous hydrogen fluoride, we have introduced pyridine polyhydrogen fluoride (PPHF) as a convenient fluorinating agent.[4] Direct fluorination of saturated hydrocarbons is difficult. Fluorination of saturated hydrocarbons using fluoroxytrifluoromethane[5] can be achieved, but the reaction necessitates well-controlled conditions, specific equipment, and precautions. No direct purely ionic fluorination of saturated hydrocarbons was so far reported.[6]

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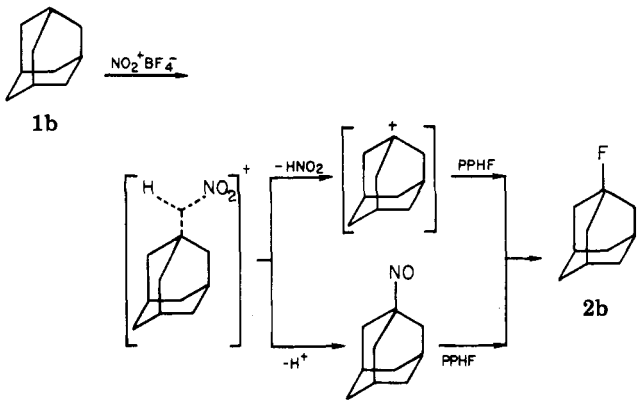
Table I. Ionic Fluorination of Tertiary Hydrocarbons with $NO^+BF_4^-$/Pyridine Polyhydrogen Fluoride (PPHF)

	substrate 1	product 2	reagent	reaction time,[a] h	yield, %	mp, °C found	mp, °C lit.	^{19}F NMR,[e] (multiplicity)
a			$NO^+BF_4^-$/PPHF	6	95	225.6	225-227[b]	−128.0 (s)
b			$NO_2^+BF_4^-$/PPHF	12	95	225	225-227[b]	−128.0 (s)
c			HF/Py, 70%	5	90	225.2	225-227[b]	−128.0 (s)
d			$NO^+BF_4^-$/PPHF	5	82[c]	245		−142.0 (s)
e	Ph_3C-H	Ph_3C-F	$NO^+BF_4^-$/PPHF	6	95	104.1	103-104[d]	−126.2 (s)

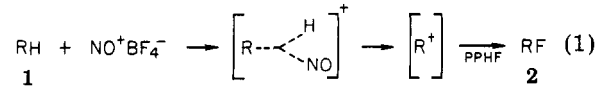
[a] Reaction time at room temperature. [b] See ref 4 and 11. [c] Product was confirmed by its ^{13}C NMR as well as by elemental analysis. ^{13}C NMR gives a set of ten peaks at 94.6 (d), 43.1 (d), 41.8 (d), 40.6 (d), 37.5 (d), 36.9 (d), 36.4 (d), 32.4 (d), 30.8 (d), and 24.8 (s) ppm. Microanalysis for 1-fluorodiamantane molecular formula $C_{14}H_{19}F$: calcd C = 81.50, H = 9.30; obtained C = 81.46, H = 8.94. [d] See ref 4. [e] Shifts in parts per million from external $CFCl_3$; negative values correspond to upfield shifts: s, singlet; d, doublet.

Scheme I



Recently, we have reported conversion of adamantane into *N*-(1-adamantyl)amides[7] using $NO^+PF_6^-$ in presence of nitriles. We have also previously described the ability of $NO^+BF_4^-$ to abstract hydrogen from tertiary hydrocarbons to give carbocations.[8] These studies prompted us to investigate the reaction of tertiary hydrocarbons with $NO^+BF_4^-$ in the presence of suitable fluoride donor such as PPHF in an attempt to obtain for the first time direct fluorination of saturated hydrocarbons.

We have found that reactive hydrocarbons such as adamantane, diamantane, and triphenylmethane (**1a–e**) react readily with $NO^+BF_4^-$ or $NO^+PF_6^-$ in pyridine polyhydrogen fluoride (PPHF) to afford a high yield of the corresponding tertiary fluorohydrocarbons **2a–e** (eq 1). In



(1)

the case of adamantane, $NO_2^+BF_4^-$ can also be used instead of $NO^+PF_6^-$ (BF_4^-) (Scheme I), albeit the reaction proceeds less readily (entry 1b, Table I). In this case the intermediate formation of 1-nitroadamantane is possible. As tertiary nitroalkanes (cycloalkanes) are, however, very sensitive to acid cleavage, it will give the 1-adamantyl cation, which in turn is quenched by fluoride ion to give 1-fluoroadamantane (Scheme I). Indeed, when 1-nitroadamantane (**1c**) is treated with PPHF, ready protolytic cleavage takes place to give a high yield of 1-fluoroadamantane. Arylmethanes such as triphenylmethane, on the other hand, are nitrated by NO_2^+ on the aromatic rings, and therefore NO^+ salts can only be used in their fluorination.

During our study we also found that needed NO^+ or NO_2^+ can be generated in situ from inexpensive $NaNO_2$ or $NaNO_3$, respectively, in pyridine polyhydrogen fluoride which can replace the less readily available $NO^+BF_4^-$ or $NO_2^+BF_4^-$ salt.

We have also studied the reaction of $NO^+BF_4^-$/PPHF with other tertiary hydrocarbons such as isobutane, isopentane, methylcyclopentane, isopropylbenzene, and cyclohexylbenzene, but in these cases we could not isolate the tertiary fluorides in satisfactory yields. This is due to facile elimination of hydrogen fluoride and subsequent polymerization of the formed reactive olefins under the reaction conditions. The present method thus is limited to such tertiary hydrocarbons where the intermediate tertiary carbocation cannot undergo proton elimination to olefin.

Experimental Section

All the melting points are uncorrected. Fluorine-19 and carbon-13 nmr spectra were recorded on a Varian XL-200 spectrometer. Adamantane and triphenylmethane were obtained from the Aldrich Chemical Co. Diamantane[9] and 1-nitroadamantane[10] were prepared by literature procedures.

General Procedure for the Conversion of Tertiary Hydrocarbons to Fluorohydrocarbons with $NO^+BF_4^-$/PPHF. To a solution of $NO^+BF_4^-$ (25 mmol) in 70% pyridine polyhydrogen fluoride[4,12] (30 mL) in a 100-mL Teflon bottle at 0 °C

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was added slowly a solution of the hydrocarbon (20 mmol) in 10 mL of CH_2Cl_2 with continuous stirring. After the addition the reaction was stirred at room temperature. On completion of the reaction it was poured into ice–water and extracted with ether (2 × 100 mL). The organic layer was washed successively with water, with $NaHCO_3$ solution, and finally with brine solution and dried over anhydrous $MgSO_4$. Removal of solvent gave excellent yields of fluorohydrocarbons which were crystallized with petroleum ether–chloroform solvent and characterized by their physical and spectral data (Table I).

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Registry No. **1a**, 281-23-2; **1c**, 7575-82-8; **1d**, 2292-79-7; **1e**, 519-73-3; **2a**, 768-92-3; **2d**, 77052-09-6; **2e**, 427-36-1; $NO^+BF_4^-$, 14635-75-7; PPHF, 62778-11-4; isobutane, 75-28-5; isopentane, 78-78-4; methylcyclopentane, 96-37-7; isopropylbenzene, 98-82-8; cyclohexylbenzene, 827-52-1.

(12) **Caution**: Proper precautions must be taken when handling anhydrous hydrogen fluoride and PPHF. Hydrogen fluoride is extremely corrosive to human tissue, contact resulting in painful, slow-healing burns. Laboratory work with HF should be conducted only in an efficient hood, with the operator wearing a full-face shield and protective clothing. Hydrogen fluoride burns should be immediately treated first with prolonged rinsing with cold water followed by soft, bulky dressings liberally soaked with iced benzalkonium chloride (Zephiran or Hyamine) that may be applied up to 1–4 h.

Zinc Iodide Catalyzed Preparation of Aroyl Azides from Aroyl Chlorides and Trimethylsilyl Azide[1]

G. K. Surya Prakash, Pradeep S. Iyer, Massoud Arvanaghi, and George A. Olah*

Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089

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Acid azides are important intermediates as they undergo Curtius rearrangement leading to isocyanates.[2] Isocyanates are generally prepared[2] in a one-pot procedure by treating the acid chloride with ammonium or metal azide without isolating the intermediate acid azide. Although alkanoyl azides are generally unstable and explode on heating, the corresponding aroyl azides are thermally stable and can be isolated.[3] However, the preparation of aroyl azides involves a three-step sequence starting from an aryl ester.[4]

Trimethylsilyl azide reacts with azide chlorides under reflux to give the corresponding isocyanates directly.[5] No attempt has been made thus far to isolate the intermediate acid azides. We report now that aroyl chlorides react with trimethylsilyl azide under zinc iodide catalysis at room

Table I. Zinc Iodide Catalyzed Preparation of Aroyl Azides from Aroyl Chloride and Trimethylsilyl Azide

aroyl azide	rxn time, h	yield,[a] %	mp,[b] (bp/mmHg), °C	lit.[c] mp (bp/mmHg), °C	^{13}C NMR[c] C=O	C_1	C_2	C_3	C_4	C_5	C_6	others
4-$(OCH_3)C_6H_4CON_3$	3	96	70–71	70–71	171.6	123.2	131.7	114.0	164.7	114.0	131.7	55.6 (OCH_3)
4-$(CH_3)C_6H_4CON_3$	3	84	32–33	35	172.6	127.6	129.0	128.9	144.9	128.9	129.0	21.1 (CH_3)
3-$(CH_3)C_6H_4CON_3$	3	93	*d*		172.0	130.4	134.8	138.3	129.7	126.4	128.3	20.8 (CH_3)
$C_6H_5CON_3$	3	95	25–27	27	172.3	130.6	129.4	128.6	134.3	128.6	129.4	
4-$BrC_6H_4CON_3$	5	86	48	47	171.5	129.3	131.9	130.7	129.6	130.7	131.9	
4-$ClC_6H_4CON_3$	3	95	39–42	43	171.5	132.7	130.7	129.0	140.9	129.0	130.7	
4-$FC_6H_4CON_3$	30	85	(72/1.0)		171.0	126.8	132.0 ($^3J_{C-F}$ = 9.8 Hz)	115.6 ($^2J_{C-F}$ = 22.0 Hz)	166.5 ($^1J_{C-F}$ = 255.6 Hz)	115.6 ($^2J_{C-F}$ = 22.0 Hz)	132.0 ($^3J_{C-F}$ = 9.8 Hz)	
3-$FC_6H_4CON_3$	34	94	(74–77/1.0)		171.2 ($^4J_{C-F}$ = 3.2 Hz)	132.6 ($^3J_{C-F}$ = 7.3 Hz)	121.3 ($^2J_{C-F}$ = 22.0 Hz)	162.5 ($^1J_{C-F}$ = 247.9 Hz)	116.1 ($^2J_{C-F}$ = 23.2 Hz)	130.3 ($^3J_{C-F}$ = 7.3 Hz)	125.1 ($^4J_{C-F}$ = 3.3 Hz)	
4-$(NO_2)C_6H_4CON_3$	72	83	64–66	65	170.7	123.9	130.4	123.7	151.4	123.7	130.4	

[a] Purity confirmed by ^{1}H, ^{13}C NMR, and IR analysis. [b] Melting point and boiling points are uncorrected. [c] In $CDCl_3$ solution at 24 or 37 °C. Chemical shifts are in parts per million from tetramethylsilane. [d] Decomposes upon distillation (to an isocyanate via Curtius rearrangement).

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