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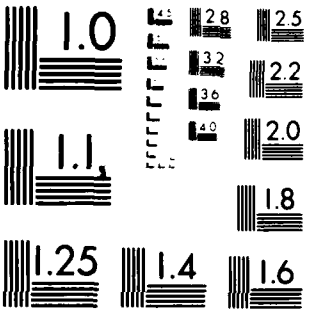

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AEROSOL DIRECT FLUORINATION SYNTHESES: ALKYL HALIDES I, NEOPENTYL CHLORIDE AND BROMIDE, FREE RADICALS VERSUS CARBOCATIONS

by

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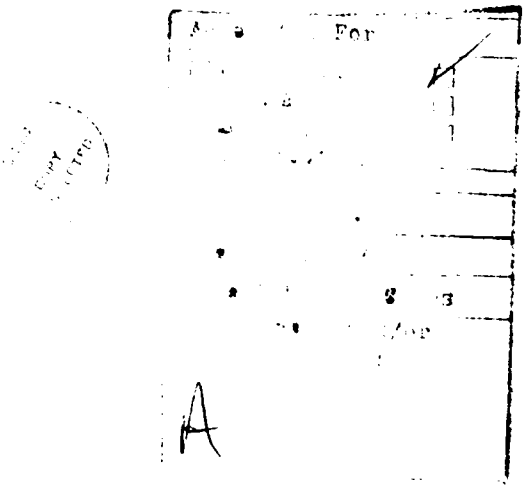


Aerosol Direct Fluorination Syntheses: Alkyl Halides I, Neopentyl Chloride and Bromide-Free Radicals versus Carbocations

by

J. L. Adcock, W. D. Evans and L. H. Grossman

The direct fluorination of alkyl halides to perfluoroalkyl halides would provide a method of obtaining specific fluorocarbons in which the site for further reaction has been preselected prior to fluorination. The fluorination of chloroalkanes by metathesis using HF, F^- or SbF_3 does not provide for prior selection of residual halogens although specific fluorocarbon halides may be obtained as products.[1] Several investigators have shown the feasibility of maintaining carbon-chlorine bonds during cobalt trifluoride fluorinations,[2] and during electrochemical fluorinations.[3] There has to our knowledge however, been only one published report of an elemental direct fluorination of an alkyl halide to a perfluoroalkyl halide.[4] In this paper we would like to demonstrate the facility of maintaining a primary chlorine substituent during aerosol direct fluorinations. The stability of this chlorine substituent to both elemental and photochemically generated atomic fluorine at 20°C is exceptional. The stability of bromine substituents is, however, very low and they tend to be oxidized by elemental fluorine at temperatures as low as -60°C. Generation of carbocations is indicated in the fluorinations of alkyl bromides but not in the fluorinations of alkyl chlorides.

Results and Discussions

The aerosol direct fluorination process has been described in detail elsewhere.[5] Two major elements of the process involve contact of elemental fluorine with a finely-divided-particulate reactant aerosol over a gradual temperature and fluorine concentration gradient followed by "photochemical finishing" of the highly fluorinated product by ultraviolet irradiation of the effluent under ambient fluorine concentration conditions at ca. 20°C. The two steps may be separated for analytical purposes simply by making control runs with the mercury lamp off. The reactant aerosol is formed by adsorption/condensation of hydrocarbon onto a sodium fluoride preaerosol.

Initially two prototype molecules for probing the feasibility of the alkyl halide reactions were chosen because of their sensitivity to mechanistic reaction paths and their expected, near-ideal, reactor-process behavior. The first candidate, neopentyl chloride, was prepared by the method of Wiley, et. al. from neopentyl alcohol.[6] It was shown to be uncontaminated with isopentyl chloride by gas chromatography and by proton nuclear magnetic resonance. The aerosol fluorination of this molecule was uneventful and produced product in 79.6% purity (glc assay) direct from the reactor trap. Isolated yields of pure perfluoroneopentyl chloride were 74% of theoretical. The remaining 20% of the material in the product trap was composed of approximately 20% F-isobutane, 20% F-isobutyl chloride, 40% F-pivaloyl fluoride and the remainder numerous very small peaks with retention times greater than F-neopentyl chloride.

The second candidate, neopentyl bromide, was produced also by the method of Wiley, et. al.,[6] and was shown to be free of isopentyl bromide by gas chromatography and proton nmr. The aerosol fluorination of neopentyl bromide was carried out under conditions similar to those for the chloride. The

product consisted of 80% F-isopentane, 10% F-isobutane, elemental bromine and lesser products.

The most significant result of the neopentyl bromide fluorinations is the near total rearrangement of the neopentyl moiety to the isopentyl. Such rearrangements must certainly occur early in the fluorination because low fluorine, control runs without photochemical finishing [Rxns (2) → (5), Table 1] produce exclusively rearranged products or unreacted starting material. Reactions 2 through 5 represent stepwise reductions in neopentyl bromide to fluorine mole ratios from approximately 1:12 to 1:1. Product distributions for neopentyl bromide reactions (1) through (5) are also given in Table 1.

The major product isolated at 1:1 stoichiometry (Rxn 5) is 2-methyl-2-butene (9). As the fluorine to neopentyl bromide ratio is increased (Rxn 4) 2-methyl-2-butene (9) disappears and 2,3-difluoro-2-methylbutane (10) becomes the prevalent product. However "abnormal" products having the geminal difluoromethylene group are collectively of near equal prevalence. These abnormal products increase as the relative amount of fluorine increases (Rxns 3 and 2) and the amount of 2,3-difluoro-2-methylbutane actually decreases in reaction 2. Compounds having this geminal difluorosubstitution (Cmpds 3, 4, 5, 6 and 7 Table 1) are classified "abnormal" because none are the statistically probable products expected from fluorine attack on the products (9 and 10) prevalent at the lowest stoichiometries.

The facility with which neopentyl cations rearrange to isopentyl cations is a well known phenomenon.[7] It is also known that neopentyl radicals do not show a pronounced tendency to rearrange.[8] This leads to the inescapable conclusion that the fluorination of neopentyl bromide must produce intermediate carbocations, although highly polar species or carbene type

TABLE 1

RESULTS OF AEROSOL FLUORINATIONS OF NEOPENTYL BROMIDE

	Reaction Number	(1)[a]	(2)	(3)	(4)	(5)
	Fluorine:Hydrocarbon mole ratio	105	12	4	2.5	1
Prod No.	Product Name	Product Distribution[b]				
1	Neopentyl Bromide[c]	-	-	15	28	50
3	3,3-Difluoro-2-methylbutane	-	18	14	6	-
4	2,3,3-Trifluoro-2-methylbutane	-	10	2	4	-
5	1,3,3-Trifluoro-2-methylbutane	-	18	6	2	-
6	3,3,4-Trifluoro-2-methylbutane	-				
7	1,3,3,-Trifluoro-2-fluoromethylbutane	-	}[e] 16	5	5	-
8	F-Isopentane	80	-	-	-	-
9	2-Methyl-2-butene	-	-	-	-	30
10	2,3-Difluoro-2-methylbutane	-	11	20	20	-
	F-Isobutane	10	-	-	-	-
	Residual Peaks[d]	10	27	38	35	20

(a) Photochemical stage operative here only.

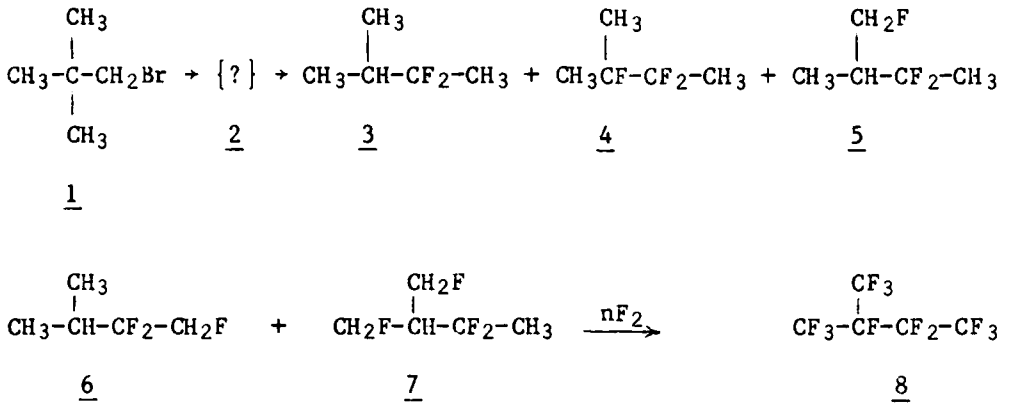
(b) Area Percent of total injection by peak integration of the thermal conductivity gas chromatogram.

(c) Unreacted starting material.

(d) Small peaks in gas chromatogram.

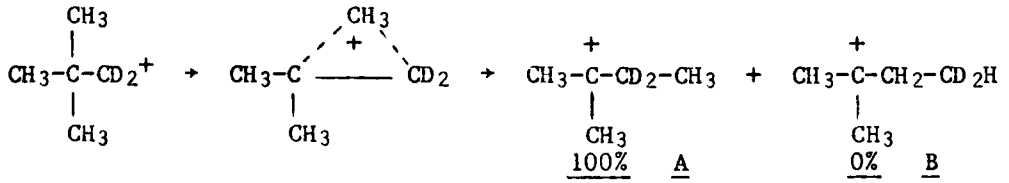
(e) Inseparable mixture, tentative identification by ^{19}F and ^{1}H NMR.

intermediates cannot be totally eliminated. Furthermore these carbocations and their precursor intermediate(s), {?} (2) Scheme I, must account for the "abnormal" fluorine products (3-7) containing the difluoromethylene group [Scheme I].



Scheme I

The nature of these intermediates are not known but their behavior bears a striking resemblence to the rearrangements of the neopentyl cation observed by Skell, et al. [Scheme II].[7] Skell, et. al. observed that all derived products of the rearrangement were consistent with the deuterium label in the 3-position, i.e. exclusively derived from A.



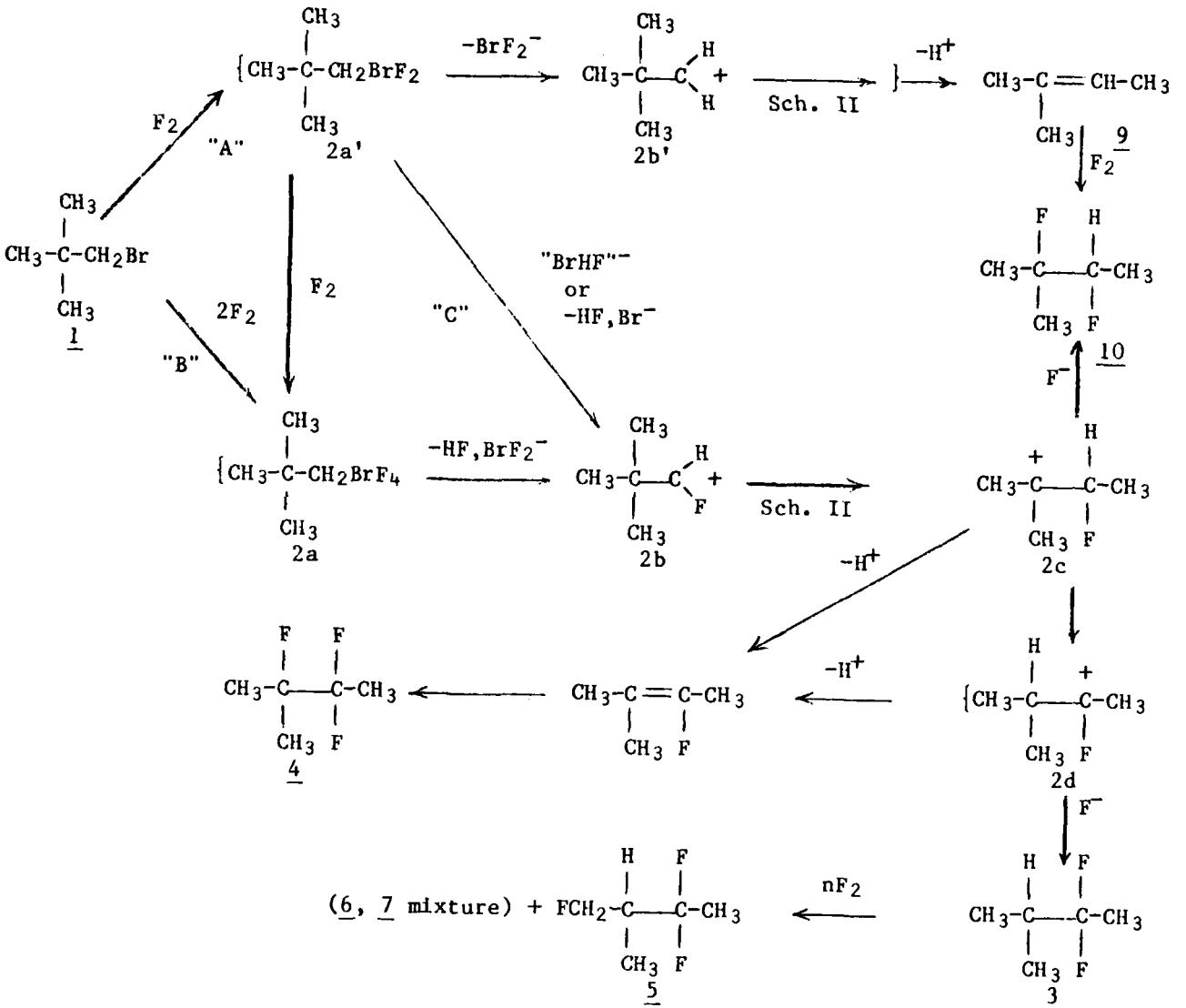
Scheme II

A protonated cyclopropane derivative was thus discounted because it could cleave either of two ways producing t-amyl derivatives consistent with the deuterium label in the 4-position (derived from B) also, which was not

observed. Karabatsos, et. al. observed this rearrangement of neopentyl cations using a 13-C label and obtained the same result.[10]

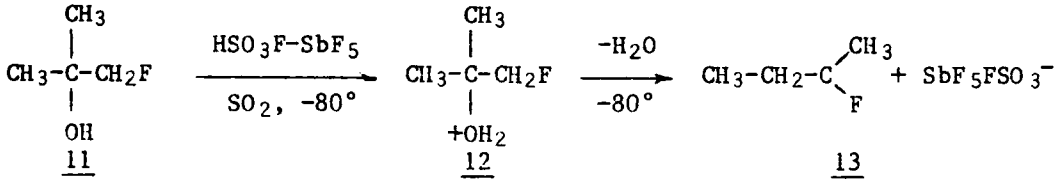
One hypothetical scheme (Scheme III) which not only provides a reasoned approach to all of the products produced, but also addresses the product shift as the fluorine stoichiometry is increased, is in effect two schemes. The basic postulate supported by reaction 5 (Table 1) is that fluorine attacks only the bromine and that depending on the stoichiometry either (or both) an alkylbromine difluoride (2a') or an alkylbromine tetrafluoride (2a) is formed. Conceivably 2a' may disproportionate giving the known interhalogen anion, BrF_2^- and the carbocation 2b' which through Scheme II produces the t-amyl cation "A" and by loss of a proton 2-methyl-2-butene (9) the largest single product in reaction 5. As the fluorine to alkylbromide ratio is increased significant amounts of the alkylbromine tetrafluoride (2a) are produced leading to formation of the fluorinated carbocation (2b) which through Scheme II produces the fluorinated t-amyl cation (2c). The major product in reaction 4, 2,3-difluoro-2-methylbutane, may be produced by fluorine addition to 9 or by fluoride ion trapping of 2c. Both routes "A" and "B" are probably operating. As the fluorine:alkylbromide ratio is increased further (reactions 3 and 2) the proportion of route "A" is diminished over route "B" since the other products produced by route "B" alone (3,4 and 5) are increasing while that product (10) produced by route(s) "A" (and "B") is diminishing. It is also likely that the beta fluorinated t-amyl cation (2c) contributes less to product 10 than expected because of its ready rearrangement (1,2-hydride shift) to the alpha fluorinated secondary butyl cation (2d). The sigma inductive destabilization of (2c) by the beta fluorine coupled to the resonance (π-donor) stabilization of (2d) by

Scheme III


$CH_3-C(CH_3)-CH_2Br$
1
F_2
"A"
$CH_3-C(CH_3)(CH_2BrF_2)-CH_3$
2a'
$-BrF_2^-$
$CH_3-C(CH_3)(H)-C(H)(CH_3)^+$
2b'
Sch. II
$-H^+$
$CH_3-C(CH_3)=CH-CH_3$
F_2 9
$CH_3-C(F)(CH_3)-C(H)(F)-CH_3$
F^- 10
$2F_2$
"B"
F_2
"C"
"BrHF"⁻ or $-HF,Br^-$
$CH_3-C(CH_3)(CH_2BrF_4)-CH_3$
2a
$-HF,BrF_2^-$
$CH_3-C(CH_3)(H)-C(F)(CH_3)^+$
2b
Sch. II
$CH_3-C(CH_3)(H)-C(F)(CH_3)-CH_3^+$
2c
$-H^+$
$CH_3-C(F)(CH_3)-C(F)(CH_3)-CH_3$
4
$CH_3-C(CH_3)=C(F)-CH_3$
$-H^+$
$CH_3-C(H)(CH_3)-C(F)(CH_3)-CH_3^+$
2d
F^-
(6, 7 mixture) + $FCH_2-C(CH_3)(F)-C(H)(F)-CH_3$
5
nF_2
$CH_3-C(H)(CH_3)-C(F)(CH_3)-CH_3$
3

the alpha fluorine inverts the usual 1° < 2° < 3° carbocation stabilization.[11] Fluoride ion trapping of (2d) leads to 3,3-difluoro-2-methylbutane (3), which by statistically-directed, radical-chain, direct fluorination leads to product (5), 1,3,3-trifluoro-2-methylbutane and to the tentatively identified 3,3,4-trifluoro-2-methylbutane (6) and 1,3,3-trifluoro-2-fluoromethylbutane (7) and, ultimately, to F-isopentane (8). Together products 3, 5 and the 6, 7 mixture make up 52% of the total products in reaction 2 with product 4, 2,3,3-trifluoro-2-methylbutane produced by proton abstraction f 2c and/or 2d followed by fluorine addition to the olefin produced, makes an additional 10% of the total.

Support for this hypothesis is provided by Olah and Bollinger in whic the protonation studies of 1-fluoro-2-methyl-2-propanol in "magic acid," HSO_3F-SbF_5/SO_2, at -80°C produced the results shown in Scheme IV.[11]



Scheme IV

The only carbocation detected in this system was 13 although the chloro analog produced the chloro-t-butyl cation. Carbocation 13 requires, in effect, two hydride shifts and one methide shift to occur for it to be produced from a transient fluoro-t-butyl cation which was not detected by Olah and Bollinger.[11] The only unsubstantiated or unsupported parts of our hypothesis (Scheme III) is the formation of 2a and 2a' and their "disproportionation" to 2b and 2b' respectively. The formation of perfluoroalkyl bromine tetrafluorides is however documented.[12] Although a potential route

"C" from 2a' to 2b is shown in Scheme III our evidence does not support or require it, although it cannot be eliminated a priori. It is also problematical whether 2a' will have sufficient lifetime to interact with a second mole of fluorine to form 2a, or whether two moles of fluorine must act in concert as implied by route "B" Scheme III. Whatever the mechanism insufficient data exist to more than simply pose the question. The solution of this problem might be obtained through matrix isolation studies. It is however clear that fundamental differences in the mode of fluorine attack on alkyl chlorides and bromides exist and that the consequences will likely involve "carbocation" type rearrangements of the organic substituent.

Acknowledgement. This work was supported in part by the Office of Naval Research whose support is gratefully acknowledged. Supplementary Material Available. Detailed reaction parameters, full characterization of compounds 3-8 (7 pages). Ordering information is given on any current masthead page.

EXPERIMENTAL

The basic aerosol fluorinator design and a basic description of the process is presented elsewhere.[5] Workup of products following removal of hydrogen fluoride and possibly fractional collection at ambient pressures using in-line cold traps, consisted of vacuum line fractionation; infrared assay of fractions; gas chromatographic separation of components using either a 7 meter x 3/8" 13% Fluorosilicone QF-1 (Analabs) stationary phase on 60-80 mesh, acid washed, Chromosorb p conditioned at 225°C (12 hrs) or a 4 meter x 3/8" 10% SE-52 phenyl-methyl silicone rubber on acid washed 60-80 mesh Chromosorb p, conditioned at 250°C (12 hrs). Following gas chromatographic separation (Bendix Model 2300, subambient multi-controller) all products of significance were collected, transferred to the vacuum line, assayed and characterized by vapor phase infrared spectrophotometry, PE1330; electron impact (70eV) and chemical ionization (CH_4 plasma) mass spectrometry (Hewlett-Packard GC/MS, 5710A GC, 5980 A MS, 5934A Computer); and ^{1}H and ^{19}F nuclear magnetic resonance (JEOL FX900, omniprobe) in $CDCl_3$ with 1% $CFCl_3$ internal standard. Elemental Analyses where necessary are performed by Schwartzkopf Microanalytical Laboratories, Woodside, N.Y. Detailed reaction parameters and compound characterizations (7 pages) are available as Supplementary Material, ordering information is given on any current masthead page.

Aerosol Fluorination of Neopentyl Chloride: 1-Chloro-2,2-dimethylpropane was prepared by the method of Wiley, et. al. from neopentyl alcohol.[6] Its vapor pressure at -10°C is such that a flow of 85 mL/m helium through ~50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.38 g/hr (3.6 mmol/h). Details of the aerosol fluorination parameters are available as supplementary materials. For a 3h photochemically finished run, 2.659g of crude product was collected which when vacuum

line fractionated [-131°C (2.56g), -196°C (0.09g discarded)] and gas chromatographically purified on the SE-52 column (15°C/5 m; 10°C/m to 75°C; 50°C/m to 150°C/7 m) produced 2.03g of F-neopentyl chloride 79.6% of the crude material collected, 74% yield based on calculated throughput. Characterization by ^{19}F NMR gave ϕ_{CF_3} = -64.18 ppm (t) [9], ϕ_{CF_2Cl} = -52.29 ppm (dectet) [2], J = 10.7 hz. Elemental Analyses: Calculated for $C_5F_{11}Cl$: %C 19.72, %F 68.63; Found %C 19.67, %F 68.60. Detailed IR, Mass Spec (CI, EI) are available as supplementary material.

Aerosol Fluorination of Neopentyl Bromide: 1-Bromo-2,2-dimethylpropane was prepared by the method of Wiley, et. al. from neopentyl alcohol.[6] Its vapor pressure at -10°C is such that a flow of 25 mL/m helium through ~20 mL of the material contained in a sparge tube evaporator produces a throughput of 1.4 mmol/h. Details of the aerosol fluorination parameters are available as Supplementary Material. Five fluorination runs were carried out differing mainly in the photochemical finishing (i.e. run #2-#5 uv lamp off), and the fluorine to hydrocarbon stoichiometry (Table 1). All products were vacuum line fractionated (-131°C, -196°C discarded) and the -131°C trap separated gas chromatographically on the SE-52 column (10°C/4 m; 2°/m up to 55°C/1 m; 50°C/m to 125°C/10 m).

The photochemically finished, two-hour run (Rxn. 1) produced 0.629g of crude product after removal of elemental bromine with the following product distribution: 80% F-isopentane (62.5% yield), 10% F-isobutane and 10% other unidentified lesser products. F-Isopentane collected displayed spectra identical to the infrared and ^{19}F NMR spectra published.[13,14] Detailed Mass Spectra, Infrared and ^{19}F NMR are available from Supplementary Materials.

The runs without the ultraviolet lamp (Rxns. 2-5, Table 1) produced

similar quantities of crude product containing elemental bromine with the product distributions listed. Characterizations of intermediate products are available from supplementary materials; 3,3-Difluoro-2-methylbutane (3),[15] 2,3-Difluoro-2-methylbutane (10)[16] are known compounds. 2,3,3-Trifluoro-2-methylbutane (4) and 1,3,3-Trifluoro-2-methylbutane (5) have not been previously characterized.

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APPENDIX I

Supplementary Material

Characterization of Intermediate Products

SUPPLEMENTARY MATERIAL

TABLE A

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS

Starting Compound	Fluorine Flow ml./m				Helium Diluent ml./m				Reaction Temp. °C			Main Helium Carrier ml./m	Hydrocarbon Throughput millimoles/hr (H.C.carrier)	Overall[a] Stoichiometry hc:F_2	Percent I_2 Conc. Final Stage	Reactor Volume ml. (a length)	Reaction Time Sec.
	Reactor	Mod. 1	Mod. 2		Reactor	Mod. 1	Mod. 2		Reactor	Mod. 1	Mod. 2						
Neopentyl Chloride	20	20	20	-	80	80	80	-	-45°	-30°	10°	1000	3.60 (85)	1:41	4.3%	1355	59
Neopentyl Bromide(1)	20	20	20	-	60	60	60	-	-40°	-30°	10°	1000	1.4 (25)	1:105	4.7%	1355	53
Neopentyl Bromide(2)	20	20	10	-	120	100	100	-	-40°	-30°	10°	1000	~10 (160)	1:12	3.2%	1355	
Neopentyl Bromide(3)	1.7	-	-	-	100	-	-	-	-48	-30°	10°	1000	1.2 (20)	1:4	0.15%	1355	
Neopentyl Bromide(4)	1.4	-	-	-	100	-	-	-	-40°	-30°	10°	1000	1.4 (25)	1:2.5	0.12%	1355	
Neopentyl Bromide(5)	0.6	-	-	-	100	-	-	-	-40°	-30°	10°	1000	1.4 (25)	1:1	0.57%	1355	

[a] 1 ml./min F_2 delivers 2.44 millimoles/hr. F_2

[b] Neopentyl Bromide (2)-(5) run with photochemical stage lamp off.

Supplementary Material

TABLE B

CHARACTERIZATION OF AEROSOL FLUORINATION PRODUCTS

F-Neopentyl Chloride:

Infrared (cm^{-1}): 1320(sh), 1302(vs), 1294(vs), 1239(m), 1008(s), 880(m), 773(w), 750(dblt. m).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 287 (10) $C_5F_{10}{}^{37}Cl$; 285 (44) $C_5F_{10}{}^{35}Cl$; 269 (39.7) C_5F_{11}; 247 (95.5) C_5F_9O or $C_5F_8{}^{35}Cl$ (?^{37}Cl); 181 (100) C_4F_7; 87 (21) $CF_2{}^{37}Cl$; 85 (70) $CF_2{}^{35}Cl$; 69 (38) CF_3.

EI (70eV): 285 (.3) $C_5F_{10}{}^{35}Cl$; 269 (20) C_5F_{11}; 181 (31) C_4F_7; 87 (19) $CF_2{}^{37}Cl$; 85 (60) $CF_2{}^{35}Cl$; 69 (100) CF_3.

^{19}F NMR ($\phi_{CFCl_3} \equiv 0$ ppm) [Integ]

ϕ_{CF_3} = -64.18 ppm (t) [9]

J = 10.7 hz.

ϕ_{CF_2Cl} = -52.29 ppm (dectet) [2]

Elemental Analyses:	$C_5F_{11}Cl$	
Calc.	%C 19.72	%F 68.63
Observed	%C 19.67	%F 68.60

TABLE B (CONTINUED) (2)

F-Isopentane:

Infrared (cm^{-1}):[a] 1260(sh), 1255(vs), 1225(vs), 1147(mw), 1090(w), 1060(vw), 980(m), 930(w), 888(m), 720(m), 635(vw), 610(vw), 525(w)

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 182 (100.0) C_4F_7H; 136 (36.5) C_5F_4; 132 (51.6) C_3F_5H; 69 (50.3) CF_3.

EI (70eV): 269 (5.5) C_5F_{11}, M-F; 219 (1.6) C_4F_9; 200 (2.5) C_4F_8; 181 (11.8) C_4F_7; 150 (4.5) C_3F_6; 131 (21.6) C_3F_5; 119 (34.7) C_2F_5; 100 (616) C_2F_4; 69 (100) CF_3.

^{19}F NMR ($\Phi CFCl_3 \equiv 0$ ppm), $CDCl_3$)[b]

CF_3-CF_2-$CF(CF_3)_2$
a b c d

ϕ_a = -81.2 ppm (undecet) [3] J_{ac} = 1.47 J_{ab} = ?[c]

ϕ_d = -72.92 ppm (nonet•d) [6] J_{ad} = 5.86 Hz J_{cd} = 1.47 hz

ϕ_b = -119.9 ppm (heptet•d) [2] J_{bd} = 10.99 hz

ϕ_c = -187.4 ppm (mult) [1] J_{bc} = 2.93 hz

(a) Sadtler, Infrared # 41640P(1967).
(b) R. D. Dresdner, F. N. Thimoe and J. A. Young, J. Amer. Chem. Soc., 1960, 82, 5831.
(c) Some uncertainties exist in coupling constants because 1.47 x 2 = 2.94, 2.93 x 2 = 5.86.

TABLE B (CONTINUED)(3)

3,3-Difluoro-2-methylbutane:

Infrared (cm^{-1}): 2980(s), 2900(m), 1480(m), 1390(s), 1360(w), 1260(s) 1200(sh,s), 1160(vw), 1110(s), 1050(m), 920(s), 880(w), 730(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 125 (0.6) $C_5H_{10}F_2 + CH_5^+$, 107 (0.7) $C_5H_9F_2$, 89 (100) $C_5H_{10}F$, 69 (2.1) C_5H_9.

EI (70eV): 93 (13.5) $C_4H_7F_2$; 78 (2.0) $C_3H_4F_2$; 77 (7.6) $C_3H_3F_2$; 69 (18.4) C_5H_9; 65 (69.7) $C_2F_2H_3$; 47 (8.2) C_2H_4F; 43 (100) C_3H_7.

$^{19}F + {}^{1}H$ NMR[d,e] $CH_3-CF_2-CH(CH_3)_2$ (a b c d)

δ_a = 1.51 ppm (t) J_{ab} = 18.8 hz

δ_c = 1.5-2.15 ppm (mult)

δ_d = 1.0 ppm (d) J_{cd} = 6.83 hz

ϕ_b = -97.96 ppm (q.d) J_{ab} = 18.9hz, J_{bc} = 12.81hz

d. $\phi CFCl_3 \equiv 0.0$ppm; 1.0% $CFCl_3$/99% $CDCl_3$; $\delta CHCl_3 \equiv 7.25$ppm.

e. V. I. Golikov, A. M. Aleksandrov, L. A. Alekseeva, and L. M. Yagupol'skii, Zhurnal Organicheksoi Khimii, 1974, 10, 297-99 (In Translation UDC 7.412.22 + 463.4).

TABLE B (CONTINUED)(4)

2,3-Difluoro-2-methylbutane:

Infrared (cm^{-1}): 3000(s), 2950(m), 1465(m), 1385(s), 1170(s), 1120(s), 1085(s), 960(m), 865(m), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 107 (2.1) $C_5H_9F_2$; 89 (100) $C_5H_{10}F$; 69 (9.6) C_5H_9, 61 (1.7) C_3H_6F.

EI (70eV): 93 (13.0) $C_4H_7F_2$; 79 (25.6) $C_3H_5F_2$; 61 (100) C_3H_6F; 60 (17.7) C_3H_5F; 47 (14.4) C_2H_4F.

$^{19}F + {}^{1}H$ NMR[d,e]

CH_3-C H F C $F(CH_3)_2$
a b c d e

δ_a = 1.32 (d•d•d)
δ_b = 4.47 (d•q•d)
δ_e = 1.34 (d•d)
ϕ_c = -151.60 (d•d•hept.)
ϕ_d = -184.32 (m•d•q•d)

J_{ab} = 6.6 hz
J_{ac} = 23.2 hz
J_{ad} = 1.0 hz
J_{bc} = 47.6 hz
J_{bd} = 12.7 hz
J_{cd} = 9.8 hz
J_{ce} = 2.0 hz
J_{de} = 21.5 hz

d. $\phi CFCl_3 \equiv 0.0$ppm; 1.0% $CFCl_3$/99% $CDCl_3$; $\delta CHCl_3 \equiv 7.25$ppm.

e. W. J. Middleton, J. Org. Chem., 1975, 40, 574-8. ϕ-152.0 & -185.5 ppm.

TABLE B (CONTINUED)(5)

2,3,3-Trifluoro-2-methylbutane:

IR (cm^{-1}): 3000(m), 2980(w), 1880(vw), 1485(w), 1390(m), 1260(m), 1170(vs), 1100(w), 1030(w), 940(m), 850(w), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 143 (10.5) $C_5H_9F_3 + CH_5^+$; 125 (17.0) $C_5H_9F_3$; <u>107 (100) $C_5H_9F_2$</u>; 89 (24.6) $C_5H_{10}F$; 87 (13.7) C_5H_8F.

EI (70eV): 111 (3.6) $C_4H_6F_3$, M-CH_3; 95 (8.3) $C_4H_9F_2$; 93 (16.2) $C_4H_7F_2$; 69 (15.3) C_5H_9, CF_3; 65 (51.9) $C_2H_3F_2$; <u>61 (100) C_3H_6F</u>; 47 (15.6) C_2H_4F; 43 (17.5) C_3H_7, C_2F; 41 (19.2) C_3H_5.

^{19}F and ^{1}H NMR[d] CH_3-CF_2-$CF(CH_3)_2$
a b c d

δ_a = 1.65 (t•d) J_{ab} = 18.05 hz (^1H), J_{ac} = 1.95 hz

δ_d = 1.737 (d•t) J_{cd} = 21.73 hz (^1H), J_{bc} = 1.22 hz

ϕ_b = -105.70 ppm (q) J_{ab} = 18.3 hz (^{19}F)

ϕ_c = -154.21 ppm (heptet) J_{cd} = 21.36 hz (^{19}F)

d. $\phi CFCl_3 \equiv 0.0$ppm; 1.0% $CFCl_3$, 99% $CDCl_3$; $\delta CHCl_3$ = 7.25 ppm.

TABLE B (CONTINUED)(6)

1,3,3-Trifluoro-2-methylbutane:

IR (cm^{-1}): 2990(m), 2940(sh), 1750(w), 1470(m), 1400(s), 1300(sh,m), 1250(s), 1215(s), 1170(s), 1110(vs), 1040(s), 990(m), 930(s), 870(sh,m), 740(w).

Mass Spectra [m/e (int.) Formula]:

CI (CH_4): 143 (12.9) $C_5H_9F_3 + CH_5^+$; 125 (60.4) $C_5H_8F_3$; 123 (19.3) $C_5H_6F_3$; 107 (100) $C_5H_9F_2$, 89 (54.6) $C_5H_{10}F$; 87 (63.1) C_5H_8F.

EI (70eV): 93 (10.4) $C_4H_7F_2$; 78 (25.6) $C_3H_4F_2$; 77 (23.2) $C_3H_3F_2$; 69 (86.4) C_5H_9; 65 (100) $C_2H_3F_2$; 61 (18.4) C_3H_6F.

^{19}F and ^1H NMR[d] $CH_3-CF_2-CH(CH_3)(CH_2F)$
a b c d e f

δ_a = 1.60 ppm (t) J_{ab} = 19.05 hz
δ_c = 1.5-2.0 ppm (broad multiplet)
δ_d = 1.10 ppm (d) J_{de} = 6.83 hz
δ_e = 4.5 ppm (d•m) J_{ef} = 47.37 hz (^1H)
ϕ_b = -95.5 ppm (m)
ϕ_f = -226.77 ppm (t•d) J_{ef} = 47.3 hz (^{19}F), J_{cf} = 21.37 hz

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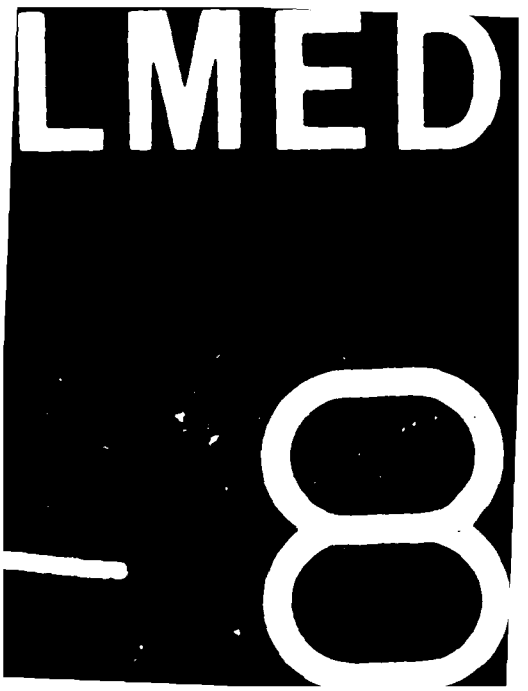
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