

AD-A139 214

AEROSOL DIRECT FLUORINATION: ALKYL HALIDES II CHLORINE
SHIFTS AND THE STA. (U) TENNESSEE UNIV KNOXVILLE DEPT
OF CHEMISTRY J L ADCOCK ET AL. 15 MAR 84 TR-11

1/1

UNCLASSIFIED

N00014-77-C-0685

F/G 7/2

NL



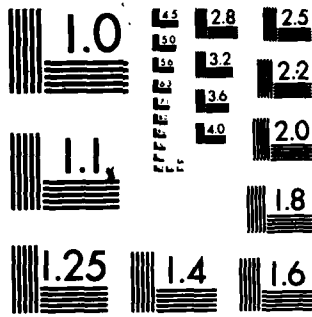
END

DATE

FILMED

DTIC

DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(12)

OFFICE OF NAVAL RESEARCH

Contract No. N00014-77-C-0685

Task No. NR 053-669

AD A139214

TECHNICAL Report No. 11

AEROSOL DIRECT FLUORINATION: ALKYL HALIDES II, CHLORINE SHIFTS
AND THE STABILITY OF RADICALS

by

James L. Adcock and
William D. Evans

Department of Chemistry
University of Tennessee
Knoxville, Tennessee 37996-1600

March 15, 1984

Prepared for Publication in the
Journal of Organic Chemistry
MS #3-322C Revised

DTIC
ELECTE
MAR 21 1984
A

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited

DTIC FILE COPY

84 03 20 005

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 11	2. GOVT ACCESSION NO. ADA 09 214	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Low Temperature Fluorination of Aerosol Suspensions of Hydrocarbons Utilizing Elemental Fluorine-"Aerosol Direct Fluorination: Alkyl Halides II, Chlorine Shifts and the Stability of Radicals".		5. TYPE OF REPORT & PERIOD COVERED Interim
7. AUTHOR(s) James L. Adcock and William D. Evans		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry University of Tennessee-Knoxville Knoxville, Tennessee 37996-1600		8. CONTRACT OR GRANT NUMBER(s) N00014-77-C-0685
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-669
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE March 15, 1984
		13. NUMBER OF PAGES 22
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; it distribution is unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Aerosol, Direct Fluorination, Elemental Fluorine, Alkyl Chlorides, Perfluoroalkyl Chlorides, Free Radicals, 1,2-Chloride shifts Beta Chloroalkyl Radicals		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Unlike alkyl bromides and iodides, alkyl chlorides are shown to be stable to direct fluorination, even under ultraviolet irradiation, at temperatures of 30°C and below. Although less reactive than the bromides and iodides, F-alkyl chlorides may be derivatized presenting another example of direct fluorination-survivable functionality. High (63%) to moderate (32%) isolated yields of the analogous perfluoroalkyl chlorides can be synthesized by aerosol direct fluorination of 1-chloropropane, 1-chlorobutane, 1-chloro-2-methylpropane, 1-chloro-3-methylbutane, 1-chloro-2-methylbutane and chloro-cyclopentane		

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Abstract (continued)

with generally less than 20 percent C-Cl bond cleavage.

Tertiary alkyl chlorides generally undergo intramolecular 1,2-chloride shifts in the earliest stages of reaction in a manner characteristic of beta chloro radicals forming principally primary F-alkyl chlorides. Thus 2-chloro-2-methylpropane produces 1-chloro-F-2-methylpropane (47%), and 2-chloro-2-methylbutane produces a 16:6.3:1 ratio of 1-chloro-F-2-methylbutane, 1-chloro-F-3-methylbutane and 2-chloro-F-3-methylbutane respectively in 32% combined yield.

Secondary alkyl chlorides undergo a similar but incomplete rearrangement producing mixtures of primary and secondary F-alkyl chlorides. Thus 2-chloropropane produces a 2:1 mixture of 2-chloro-F-propane and 1-chloro-F-propane in 50% combined yield; 2-chlorobutane produces a 1:1.5 mixture of 2-chloro-F-butane and 1-chloro-F-butane in 34% combined yield, and 3-chloropentane produces a 2:3:1 mixture of 3-chloro-F-pentane, 2-chloro-F-pentane and 1-chloro-F-pentane respectively in a combined yield of 30%. Because secondary alkyl chlorides partially rearrange but primary alkyl chlorides do not rearrange at all on fluorination, doubt is cast on the postulate that the intermediate radicals are equilibrating.



Preparation For	
IS GRA&I	<input checked="" type="checkbox"/>
ERIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

S/N 0102-LF-014-6601

Aerosol Direct Fluorination: Alkyl Halides II, Chlorine Shifts
and the Stability of Radicals

by

James L. Adcock* and
William D. Evans

Department of Chemistry
The University of Tennessee
Knoxville, Tennessee 37996-1600

Submitted to the
Journal of Organic Chemistry

ABSTRACT

Unlike alkyl bromides and iodides, alkyl chlorides are shown to be stable to direct fluorination, even under ultraviolet irradiation, at temperatures of 30°C and below. Although less reactive than the bromides and iodides, F-alkyl chlorides may be derivatized presenting another example of direct fluorination-survivable functionality. High (63%) to moderate (32%) isolated yields of the analogous perfluoroalkyl chlorides can be synthesized by aerosol direct fluorination of 1-chloropropane, 1-chlorobutane, 1-chloro-2-methylpropane, 1-chloro-3-methylbutane, 1-chloro-2-methylbutane and chloro-cyclopentane with generally less than 20 percent C-Cl bond cleavage.

Tertiary alkyl chlorides generally undergo intramolecular 1,2-chloride shifts in the earliest stages of reaction in a manner characteristic of beta chloro radicals forming principally primary F-alkyl chlorides. Thus 2-chloro-2-methylpropane produces 1-chloro-F-2-methylpropane (47%), and 2-chloro-2-methylbutane produces a 16:6.3:1 ratio of 1-chloro-F-2-methylbutane, 1-chloro-F-3-methylbutane and 2-chloro-F-3-methylbutane respectively in 32% combined yield.

Secondary alkyl chlorides undergo a similar but incomplete rearrangement producing mixtures of primary and secondary F-alkyl chlorides. Thus 2-chloropropane produces a 2:1 mixture of 2-chloro-F-propane and 1-chloro-F-propane in 50% combined yield; 2-chlorobutane produces a 1:1.5 mixture of 2-chloro-F-butane and 1-chloro-F-butane in 34% combined yield, and 3-chloropentane produces a 2:3:1 mixture of 3-chloro-F-pentane, 2-chloro-F-pentane and 1-chloro-F-pentane respectively in a combined yield of 30%. Because secondary alkyl chlorides partially rearrange but primary alkyl chlorides do not rearrange at all on fluorination, doubt is cast on the postulate that the intermediate radicals are equilibrating.

Aerosol Direct Fluorination: Alkyl Halides II, Chlorine Shifts
and the Stability of Radicals

by James L. Adcock* and William D. Evans

The fluorination of compounds with survivable functionality permits the preparation of fluorinated compounds with preselected sites for further reaction. The survivability of acyl fluorides,^{1,2} ethers,^{3,4} ketals,⁴ and to a lesser extent, esters¹ and amines^{5,6} to elemental fluorine attack are well documented in the literature. More recently reliable ketone direct fluorinations have been documented⁷ although isolated cases of direct fluorination syntheses of ketones, albeit in poor yields, have been noted previously.⁸ The stability of perfluoroketones to photochemically finished aerosol direct fluorination is remarkable given their known photolability.⁹

Perhaps the most useful monovalent substituent groups on perfluorocarbons are the iodides.¹⁰ Perfluoroalkyl bromides are less reactive and are rarely used if the iodides are available. However neither of these substituents will survive attack by elemental fluorine. Until the recent aerosol direct fluorination of neopentyl chloride the useful survivability of a chloro group was in doubt.¹¹ Many previous attempts to direct fluorinate alkyl chlorides resulted in extensive fragmentation, chlorine loss and significant free radical chlorination competing with fluorination.¹²⁻¹⁹ For example, the reaction of elemental fluorine with 1,2-dichloropropane at 100°-200°C gave large amounts of CF₄, C₂F₆ and C₃F₈ as well as small amounts of 1,2-dichloro-F-propane, 1,3-dichloro-F-propane and materials containing three or more chlorines.²⁰ The ease with which the C-Cl bond was cleaved

and the degree of free radical chlorination giving rise to polychlorinated products were in retrospect obviously a result of the high temperatures involved. In contrast to the above works this work demonstrates the exceptional stability of a number of chloroalkanes toward fission of the C-Cl bond by photochemically finished aerosol direct fluorination. The predictable occurrence of 1,2-chloride shifts giving rearranged products in some instances has been studied systematically as well.

RESULTS & DISCUSSION

A previous contribution in the area of aerosol direct fluorination of alkyl halides, showed that alkyl chlorides underwent exclusively free radical attack by elemental fluorine.¹¹ This is in contrast to the carbocation generation which occurred, at least initially, when alkyl bromides were subjected to aerosol direct fluorination.¹¹ The extremely low degree of C-Cl bond fission occurring in the aerosol fluorination of neopentyl chloride prompted us to look more extensively into the aerosol direct fluorination of other alkyl chlorides as a means by which preselected, survivable sites for subsequent reaction could be incorporated into organic molecules prior to their fluorination.

The aerosol direct fluorination process has been described in detail elsewhere.^{4,7} The process is a steady state flow process in which a hydrocarbon vapor is condensed onto a sodium fluoride preaerosol and then subjected to attack by a 50% to 100% excess over the stoichiometric amount of elemental fluorine at low (2-5%) concentration in helium at low (-70° to 0°C) temperatures in the dark. The partially (50% to 70%) fluorinated hydrocarbons are then subjected to ultraviolet irradiation at ambient fluorine concentrations to remove residual hydrogen atoms. Partial fluorination runs are conducted under precise stoichiometric control usually without photochemical finishing.

Primary alkyl chlorides such as n-propyl chloride, n-butyl chloride and isobutyl chloride show exceptional stability to both elemental and photochemically generated atomic fluorine (Table I). In contrast, the aerosol direct fluorination of tertiary alkyl chlorides results in a 1,2-chloride shift giving primary perfluoroalkyl chlorides (Table I). For example in the aerosol fluorination of tert-butyl chloride, complete conversion to F-isobutyl chloride is observed. No fluorinated tertiary chlorine products were observed. A second reaction with only 6 mmol/h of fluorine with 3 mmol/h. tert-butyl chloride and without photofinishing gave unreacted tert-butyl chloride (30%), 1-chloro-2-fluoro-2-methylpropane (30%), 1-chloro-2,3-difluoro-2-methylpropane (20%), 1-chloro-1,2-difluoro-2-methylpropane (2%) plus more highly fluorinated material (15%). The only tertiary chloride that was observed, occurred on unreacted starting material. No free chlorine was observed, nor were any products found to contain more than one chlorine. This reaction shows that the chloride shift occurs on radical formation early in the fluorination. Chlorine fission due to photolysis or fluorine displacement apparently does not occur with observable significance.

In the aerosol fluorination of tert-amyl chloride (2-chloro-2-methylbutane, Table I) three rearranged perfluoroalkyl chlorides were collected. The relative, near statistical, proportions of 1-chloro-F-2-methylbutane (43.1%) and 1-chloro-F-3-methylbutane (17.0%), while only a trace of 2-chloro-F-3-methylbutane (2.7%) was collected, shows that multiple 1,2-chloride shifts occur readily during perfluorination. Perfluoro-tert-amyl chloride was not produced.

Secondary alkyl chlorides show intermediate stability when fluorinated giving both primary and secondary perfluoroalkyl chlorides (Table I).

Table 1

AEROSOL DIRECT PERFLUORINATIONS OF CHLOROALKANES

Starting Compound	Product 1	Effluent concn. %	Yield % ^a	Product 2	Effluent concn. %	Yield %	Product 3	Effluent concn. %	Yield %
1-Chloropropane	1-Chloro-F-propane	85	63						
1-Chlorobutane	1-Chloro-F-butane	60.2	42.4	F-butane		b	Hydriyl-1-Chloro-F-butanes		b
1-Chloro-2-methylpropane	1-Chloro-F-2-methylpropane	76.4	41	F-2-methylpropane	15.6				
1-Chloro-3-methylbutane	1-Chloro-F-3-methylbutane	67	32	F-2-methylbutane	19				
1-Chloro-2-methylbutane	1-Chloro-F-2-methylbutane	66	39	F-2-methylbutane	19				
2-Chloro-2-methylpropane	1-Chloro-F-2-methylpropane	80.4	47						
2-Chloro-2-methylbutane	1-Chloro-F-2-methylbutane	43.1	c	1-Chloro-F-3-methylbutane	17.0	c	2-Chloro-F-3-methylbutane	2.7	c
2-Chloropropane	2-Chloro-F-propane	52	d	1-Chloro-F-propane	28	d			
2-Chlorobutane	2-Chloro-F-butane	30	e	1-Chloro-F-butane	43	e			
3-Chloropentane	3-Chloro-F-pentane	30	f	2-Chloro-F-pentane	45	f	1-Chloro-F-pentane	15	f
Chlorocyclopentane	Chloro-F-cyclopentane	49.5	40.2	F-cyclopentane	12.5		F-pentane ^g	12.5	

(a) Yields are based on total starting compound injected which are not corrected for recovered unreacted starting material collected at the close of the reaction; (b) combined yield 6.9%; (c) combined yield 31.8%; (d) combined yield 50%; (e) combined yield 34%; (f) combined yield 30%; (g) three isomeric chloro-F-pentanes make up 15.5% of effluent.

Evidence for multiple 1,2-chloride shifts are seen again in the perfluorination of 3-chloropentane.

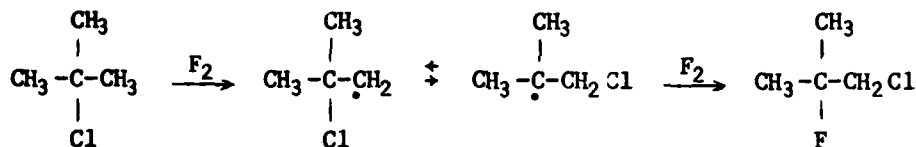
These results are for the most part supported by literature accounts of rearrangements associated with free radical reactions. For example, Skell, Allen and Gilmour observed that chlorination of 2-bromopropane and 2-bromo-2-methylpropane produced 1-bromo-2-chloropropane and 1-bromo-2-chloro-2-methylpropane respectively.²¹ These findings indicated complete rearrangement. An initial hydrogen abstraction from one of the methyl groups leading to a primary radical was immediately followed by a 1,2-bromide migration to form a more stable tertiary radical which then added chlorine to form the rearranged products. Juneja and Hodnett observed the same 1,2-bromide shift in the chlorination of 2-bromo-2-methylpropane as did Skell, et. al.²² They also observed that no rearrangement occurred in the chlorination of 1-bromo-2-methylpropane. The latter rearrangement would not be expected to occur as it would involve forming a primary radical from a tertiary radical. Formation of a tertiary radical is also statistically unfavorable.

Wiley, et. al., noted the isomerization of 1-chloropropane to 2-chloropropane during radiolysis but not the reverse reaction.²³ This seeming contradiction was re-investigated by Benson and Willard who observed that this reaction was catalyzed by hydrogen chloride and that the hydrogen atom exchanges, not the chlorine atom.²⁴ Mayo postulated that an equilibrium between secondary and primary radicals could explain this rearrangement.²⁵ If the reactions of these radicals require little or no activation energy, the products will conform to the more stable radical. However if the reactions of these radicals require a large activation energy and are therefore relatively difficult, then the products will conform to those

derived from the minor proportions of the less stable, but more reactive radical. In this way the seeming contradiction is resolved; i.e. only the more reactive radicals formed by radiolysis, C-H bond fission, will react with HCl to produce the observed product because of the relatively high activation energy required.

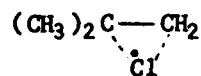
The above postulate would also explain why products derived from the interactions of intermediate free radicals with fluorine molecules, a low activation energy process, should predominately correspond to those derived from the more stable radicals. Other free radical rearrangements involving 1,2-chloride shifts have been reviewed by Freidina.²⁶

When a 1:2 molar ratio of tert-butyl chloride to fluorine aerosol fluorination was carried out 1-chloro-2-fluoro-2-methylpropane was the major product observed. This suggests a mechanism (Scheme I) similar to that



Scheme I

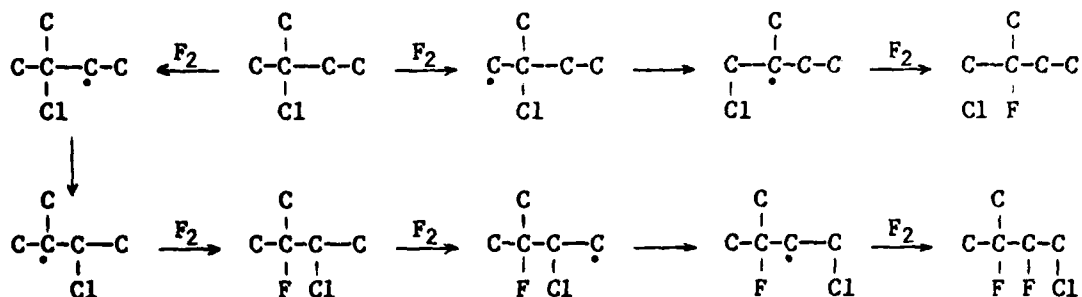
observed by Skell, et. al. in which initial H abstraction from a methyl group results in a rapid 1,2-chloride shift to produce a more stable tertiary radical.²¹ This could occur by the formation of a bridged radical intermediate (below) which would open preferentially to the more



stable tertiary radical.²⁷ If Mayo's postulate is general, the concentration of the tertiary radical would far exceed that of the primary radical giving the observed primary F-alkyl chloride. This postulate also explains

the lack of rearrangements encountered during the fluorination of primary alkyl chlorides having alpha tertiary hydrogens.

In the analogous fluorination of tert-amyl chloride, the tertiary-chlorine can rearrange from a 1° to 3° radical by a 1,2-chloride shift giving the primary F-alkyl chloride. However, the tertiary chloride can also rearrange by a 1,2-chloride shift giving a secondary chloride if the initial radical is formed by H abstraction at the methylene group. The secondary chloride can subsequently rearrange by a second 1,2-chloride shift giving the other possible primary alkyl chloride, 1-chloro-F-3-methylbutane, if a subsequent hydrogen abstraction by fluorine occurs on the 3-methyl group adjacent to the methylene group (Scheme II). This final shift would occur, however, only if the 3-methyl group has not been previously fluorinated.



Scheme II

The partial rearrangement of secondary alkyl chlorides during fluorination can also be rationalized by Mayo's postulate.²⁵ However in the case of equilibrium between primary and secondary alkyl radicals, the concentration of secondary radical would not be so predominant nor would their reactivity differ as much. The more similar concentrations would therefore result in a mixture of products representing both rearranged and unrearranged products. The problem with Mayo's rationalization is that it should

work in reverse, i.e. when primary alkyl chlorides are fluorinated some secondary alkyl chloride should be isolated. Since this does not occur, there must be kinetic and/or other effects operating. This observation certainly casts some doubt on Mayo's postulation and a more careful look at the problem is indicated.

EXPERIMENTAL

The basic aerosol fluorinator design and a basic description of the process are presented elsewhere.^{4,7} Detailed parameters for reactor variables are given in Table 2. Workup of products following removal of the hydrogen fluoride formed during the fluorination 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-h) 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-h). 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 ^1H and ^{19}F nuclear magnetic resonance (JEOL FX90Q, omniprobe) in CDCl_3 with 1% CFCl_3 internal standard.

Aerosol Fluorination of n-Propyl Chloride 1-Chloropropane (Matheson) has a vapor pressure at -45°C such that a helium flow of 75 mL/min produces a throughput of 0.24g/h (3.0 mmol/h). A 2 hour run produced 0.909g of crude material after fractionation. Separation isothermally at -20°C on the SE-52 column gives 1-chloro-F-propane (85%) at retention time of 6 m (rt = 6m).

TABLE 2

TYPICAL AEROSOL FLUORINATION REACTION PARAMETERS^a

Starting Compound	Fluorine Flow ml/m		Helium Diluent ml/m		Reaction Temp. °C		Helium Carrier ml/m	Hydrocarbon Throughput millimoles/hr (H.C. carrier)	Overall ^b Stoichiometry hc:F ₂	Percent F ₂ Conc. Final Stage	Reaction Time Sec.	Product Effluent Conc. % Collected	Product Yield % Theoretical
	Reactor Mod. 1	Reactor Mod. 2	Reactor Mod. 1	Reactor Mod. 2	Reactor Mod. 1	Reactor Mod. 2							
n-Propyl Chloride	15	15	80	80	-40°	-30°	1000	3.0 (75)	1:25	2.4	65	85%	63%
iso-Propyl Chloride	20	20	80	80	-40°	-30°	800	4.0 (75)	1:25	3.9	75	80%	50%
n-Butyl Chloride	20	20	80	80	-45°	-30°	1000	3.1 (48)	1:42	4.4	60	60.2%	42.2%
iso-Butyl Chloride	20	20	80	80	-45°	-30°	1000	1.4 (20)	1:54	3.2	66	76.4%	41.2%
sec-Butyl Chloride	19	19	75	75	-45°	-30°	1000	2.8 (33)	1:46	4.5%	61	72.8%	32.8%
tert-Butyl Chloride	20	20	70	70	-40°	-30°	1000	3.0 (13)	1:45	4.7%	63	80.4%	46.5%
tert-Butyl Chloride	2.5	-	70	-	-45°	-30°	800	3.0 (13)	1:2	0.3	91	-	--- h
1-Chloro-3-methylbutane	20	20	80	80	-40°	-35°	1000	3.0 (12)	1:40	4.5	62	67%	32%
1-Chloro-2-methylbutane	20	20	80	80	-40°	-35°	1000	3.0 (12)	1:40	4.5	62	66%	39%
3-Chloropentane	20	20	80	80	-45°	-30°	1000	1.2 (20)	1:122	4.5	62	90%	31%
tert-Amyl Chloride	20	30	80	120	-40°	-30°	800	2.5 (53)	1:44	4.5%	74	62.8%	31.8%
Cyclopentyl Chloride	20	20	80	80	-40°	-30°	1000	2.0 (135)	1:73	4	57	49.5%	40.2%

(a) See references 4 and 7 for significance, meaning of parameters (Mod = Module). (b) 1.0 ml/m F₂ delivers 2.44 mmol/h F₂. (c) Reactor volume 1.355 L. (d) All isomers (e) 17% F-n-Propyl Chloride plus 31% F-iso-Propyl Chloride. (f) 13% F-n-Butyl chloride plus 19.8% F-sec-Butyl Chloride. (g) F-iso-Butyl Chloride. (h) Mixture, non photochemically finished, UV lamp off, non perfluorinated products. (i) 10.3% 3-Chloro-Pentane, 15.5% 2-Chloro-Pentane and 5.2% 1-Chloro-Pentane.

This corresponds to a 63% yield based on theoretical throughput. The IR spectrum matches that published.²⁸

Aerosol Fluorination of iso-Propyl Chloride: 2-Chloropropane (Eastman) has a vapor pressure at -45°C such that a helium flow of 75 mL/m produces a throughput of 0.31g/h (4.0 mmol/h). A 2.5 h run produced 1.2393g of crude product after fractionation. Separation isothermally at -20°C on the SE-52 column gives an unresolved peak (80%) (rt = 6 m). A second separation on the QF-1 column a broad peak (80%) (rt = 18 m). This mixture corresponds to 48.5% of the calculated yield. The IR spectrum shows a 1:2 mixture of 1-chloro-F-propane and 2-chloro-F-propane matching those published.^{28,29}

Aerosol Fluorination of n-Butyl Chloride: 1-Chlorobutane (Fisher Scientific) was used as received. Its vapor pressure at -10°C is such that a flow of 58 mL/m helium through -50 mL of the material contained in a sparge tube evaporator produces a throughput of 0.29g/h (3.15 mmol/h). For a 2 h photochemically finished run, 1.1676g of crude product was collected after vacuum line fractionation. Purification of the products on the GC SE-52 column ($0^{\circ}\text{C}/5\text{ m}$; $10^{\circ}\text{C}/\text{m}$ to 30°C ; $25^{\circ}\text{C}/\text{m}$ to $180^{\circ}\text{C}/10\text{ m}$) produced 6.9% F-n-butane (rt = 3 m) and 60.2% 1-chloro-F-butane (Cmpd 1) (rt = 6 m). The yield of Cmpd 1 based on the calculated throughput was 43.8%. IR of Cmpd 1 (cm^{-1}): 1351(m), 1285(sh), 1240(vs), 1213(vs), 1160(w), 1148(s), 1110(s), 1020(sh), 997(m), 866(m), 848(sh), 802(s), 745(sh), 732(s), 694(m). ¹⁹F NMR (1% $\text{CFCl}_3/\text{CDCl}_3$): (multiplicity, relative area) $\text{CF}_3^{\text{A}}\text{CF}_2^{\text{B}}\text{CF}_2^{\text{C}}\text{CF}_2^{\text{D}}\text{Cl}$, $\phi_{\text{A}} = -81.7\text{ ppm}$ (t·t, 3); B -126.1 (t·m,2); C -121.6 (q·m,2); D -68.9 (t·q,2); $J_{\text{AB}} = J_{\text{AD}} = 1.1\text{ Hz}$, $J_{\text{AC}} = 9.89\text{ Hz}$, $J_{\text{BD}} = 12.64\text{ Hz}$, $J_{\text{CD}} = 1.46\text{ Hz}$. Major mass cations were [m/e(int)Formula]: [EI] 237(25.4) $\text{C}_4\text{F}_8^{37}\text{Cl}$, 235(77.6) $\text{C}_4\text{F}_8^{35}\text{Cl}$, 219(100) C_4F_9 , 149(5.2) $\text{C}_3\text{F}_4^{37}\text{Cl}$, 147(17.5) $\text{C}_3\text{F}_4^{35}\text{Cl}$, 131(9.6) C_3F_5 , 119(12.2) C_2F_5 , 87(4.4) $\text{CF}_2^{37}\text{Cl}$, 85(15.2) $\text{CF}_2^{35}\text{Cl}$, 69(2.7) CF_3 .

Aerosol Fluorination of iso-Butyl Chloride 1-Chloro-2-methylpropane (Eastman) has a vapor pressure at -10°C such that a helium flow of 25 mL/m produces a throughput of 0.13g/h (1.4 mmol/h). A 2 h run produced 0.3881g of crude material after fractionation. Separation on the SE-52 column ($0^{\circ}\text{C}/5\text{ m}$; $15^{\circ}\text{C}/\text{m}$; $25^{\circ}\text{C}/\text{m}$ to $200^{\circ}\text{C}/10\text{ m}$) gave 15.6% F-iso-butane (rt = 3 m), and 76.4% F-isobutyl chloride (Cmpd 2) (rt = 6 m). This corresponds to a 41.6% yield for Cmpd 2. IR of Cmpd 2 (cm^{-1}): 1300(sh), 1280(vs), 1195(s), 1162(s), 1070(w), 1042(m), 988(s), 916(m), 863(s), 751(m), 722(ms). ^{19}F NMR (1% $\text{CFCl}_3/\text{CDCl}_3$): $(\text{CF}_3^{\text{A}})_2\text{CF}^{\text{B}}\text{CF}_2^{\text{C}}\text{Cl}$ $\phi_{\text{A}} = -73.0$ ppm (t·d,6); B -178.5 (hept·d,1); C -62.0 (t·hept,2); $J_{\text{AB}} = 10.74$ Hz, $J_{\text{AC}} = J_{\text{BC}} = 5.88$ Hz. Major mass cations were [m/e(int) Formula]: 237(24.2) $\text{C}_4\text{F}_8^{37}\text{Cl}$, 235(77.1) $\text{C}_4\text{F}_8^{35}\text{Cl}$, 219(100) C_4F_9 , 197(23.8) $\text{C}_4\text{F}_6^{35}\text{Cl}$, 131(5.1) C_3F_5 , 87(3.7) $\text{CF}_3^{37}\text{Cl}$, 85(11.8) $\text{CF}_2^{35}\text{Cl}$.

Aerosol Fluorination of sec-Butyl Chloride 2-Chlorobutane (Eastman) has a vapor pressure at -10°C such that a helium flow of 33 mL/m produces a throughput of 0.26g/h (2.8 mmol/h). A 3 h run produces 0.9708g of crude product after fractionation. Separation on the SE-52 column with the same program as for F-n-butyl chloride gives two overlapping peaks (rt = 5.5 to 6 m) consisting of (30%) 2-chloro-F-butane (Cmpd 3) and (43%) 1-chloro-F-butane (Cmpd 1). The calculated yield of Cmpd 1 was 19.5%. The yield of Cmpd 3 was 13.69%. ^{19}F NMR of Cmpd 3 (1% $\text{CFCl}_3/\text{CDCl}_3$): $\text{CF}_3^{\text{A}}\text{CF}^{\text{B}}\text{ClCF}_2^{\text{C}}\text{CF}_3^{\text{D}}$ $\phi_{\text{A}} = -78.1$ ppm (q·t,3); B -139.2 (t·q,1); C -121.1 (q·q,2); D -79.6 ppm (q·d,3); $J_{\text{AC}} = 10.99$ Hz, $J_{\text{BD}} = 9.77$ Hz, $J_{\text{AD}} = 3.66$ Hz. Major mass cations were [m/e(int)Formula]: 237(23.1) $\text{C}_4\text{F}_8^{37}\text{Cl}$, 235(75.3) $\text{C}_4\text{F}_8^{35}\text{Cl}$, 219(100) C_4F_9 , 185(1.6) $\text{C}_3\text{F}_6^{35}\text{Cl}$; 169(8.4) C_3F_2 , 131(6.1) C_3F_5 , 119(7.9) C_2F_5 , 69(41.8) CF_3 .

Aerosol Fluorination of tert-Butyl Chloride: 2-Chloro-2-methylpropane (Eastman) has a vapor pressure at -10°C such that a helium flow of 13 mL/m

produces a throughput of 0.28g/h (3.0 mmol/h). A 2 h run produced 0.8884g of crude material after fractionation. Separation of the fraction on the SE-52 column with the isobutyl chloride program gave 79.49% F-iso-butyl chloride (Cmpd 2) (rt = 6 m) a 46.8% yield of the calculated throughput. No products were found which matched published IR & ^{19}F NMR spectra of F-tert-butyl chloride.³⁰ A second 2 h run with the same throughput and only 3.0 mmol/h fluorine flow and no photochemical finishing gave 0.513g of partially fluorinated materials. Identifiable compounds produced were: 30% unreacted starting material, 30% 1-chloro-2-fluoro-2-methylpropane,³¹ 20% 3-chloro-1,2-difluoro-2-methylpropane (Cmpd 4), and 2% 1-chloro-1,2-difluoro-2-methylpropane (Cmpd 5). The yield of Cmpd 4 is 13%. ^{19}F NMR of Cmpd 4 (1% $\text{CFCl}_3/\text{CDCl}_3$): $(\text{F}^{\text{A}}\text{CH}_2^{\text{C}})\text{CF}^{\text{B}}(\text{CH}_2^{\text{D}}\text{Cl})(\text{CH}_3^{\text{E}})$ $\phi_{\text{A}} = -244$ ppm (m,t,1), B -185 (m,1); $J_{\text{AB}} = 9$ Hz; ^1H NMR (0.2% $\text{CHCl}_3/\text{CDCl}_3$) $\delta_{\text{C}} = 4.45$ ppm (d,d,2), D 3.65 (d,m,2), E 1.45 (d,d,3); $J_{\text{AC}} = 47$ Hz, $J_{\text{BC}} = J_{\text{BD}} = J_{\text{BE}} = 19$ Hz, $J_{\text{AD}} = J_{\text{AE}} = 2$ Hz. The yield of Cmpd 5 is 1.3%: ^{19}F NMR of Cmpd 5 (1% $\text{CFCl}_3/\text{CDCl}_3$): $\text{CF}^{\text{A}}\text{H}^{\text{C}}\text{ClCF}^{\text{B}}(\text{CH}_3^{\text{D}})_2$ $\phi_{\text{A}} = -144$ ppm (m,d,1), B -187 (m,1); $J_{\text{AB}} = 9$ Hz; ^1H NMR (0.2% $\text{CHCl}_3/\text{CDCl}_3$), $\delta_{\text{C}} = 5.95$ ppm (d,d,1), D 1.45 (m,d,6); $J_{\text{AC}} = 56$ Hz, $J_{\text{BD}} = 19$ Hz, $J_{\text{BC}} = 9$ Hz, $J_{\text{AD}} = 2$ Hz.

Aerosol Fluorination of 1-Chloro-3-methylbutane: 1-Chloro-3-methylbutane has a vapor pressure at 220°C such that a helium flow of 12 mL/m produces a throughput of 0.42g/h (3.0 mmol/h). A 3 h run produced 1.323g of crude product. Separation on the SE-52 column (15°C/5 m; 10°C/m to 75°C/0 m; 70°C/m to 160°C/10 m) gave 19% F-isopentane and 67% 1-chloro-F-3-methylbutane (Cmpd 6) (rt = 7 m). The yield of Cmpd 6 is 32%. IR of Cmpd 6 (neat): 3000(sh), 1260(vs), 1250(vs), 1225(vs), 1180(s), 1145(m), 1100(s), 975(s), 740(m), 710(m). ^{19}F NMR (1% $\text{CFCl}_3/\text{CDCl}_3$): $(\text{CF}_3^{\text{A}})_2\text{CF}^{\text{B}}\text{CF}_2^{\text{C}}\text{CF}_2^{\text{D}}\text{Cl}$ $\phi_{\text{A}} = -72.8$ ppm (m,6), B -185.7 (m,1), C -113.2 (m,2), D -68.3 (m,2). Major mass cations were [m/e(int)Formula]: 287(10.3) $\text{C}_5\text{F}_{10}^{37}\text{Cl}$, 285(32.1) $\text{C}_5\text{F}_{10}^{35}\text{Cl}$.

269(63.4)C₅F₁₁, 137(5.8)C₂F₄³⁷Cl; 135(18.7)C₂F₄³⁵Cl, 131(19.2)C₃F₅,
119(20.9)C₂F₅, 100(11.4)C₂F₄, 87(18.5)CF₂³⁷Cl, 85(56.7)CF₂³⁵Cl, 69(100)CF₃.

Aerosol Fluorination of 1-Chloro-2-methylbutane: 1-Chloro-2-methyl-

butane was reacted under the same conditions as for 1-chloro-3-methylbutane and produced 1.629g of crude product after fractionation. GC separation gave 19% F-isopentane and 66% 1-chloro-F-2-methylbutane (Cmpd 7). The yield of Cmpd 7 is 39%. IR of Cmpd 7 (cm⁻¹): 1330(m), 1270(sh), 1240(vs), 1200(s), 1170(m), 1140(m), 1090(m), 1020(m), 950(m), 925(m), 900(m), 870(m), 835(m), 795(m), 740(m), 720(m). ¹⁹F NMR (1% CFCl₃/CDCl₃):

(CF₂^ACl)(CF₃^B)CF^CCF₂^DCF₃^E φ_A = -60.6 ppm (m,2); B -71.4 (m,3); C -177.0 (m,1); D - 117.5 (m,2); E - 80.8 (m,3). Major mass cations were [m/e(int)Formula] 287(15.6)C₅F₁₀³⁷Cl, 285(49.1)C₅F₁₀³⁵Cl, 269(52.0)C₅F₁₁, 181(14.5)C₄F₇, 137(2.7)C₂F₄³⁷Cl, 135(8.5)C₂F₄³⁵Cl, 131(22.1)C₃F₅, 119(42.0)C₂F₅, 87(20.7)CF₂³⁷Cl, 85(61.2)CF₂³⁵Cl, 69(100)CF₃.

Aerosol Fluorination of 3-Chloropentane: 3-Chloropentane was prepared

by the method of Darzens from 3-pentanol by reaction with SOCl₂/pyridine.³² 3-Chloropentane has a vapor pressure at 28°C such that a helium flow of 20 mL/m produces a throughput of 0.13g/h (1.2 mmol/h). A 1.5 h run produced 0.1913g of crude material after fractionation. Separation on the SE-52 column (15°C/5 m; 10°C/m to 75°C/0 m; 25°C/m to 180°C/10 m) gave a mixture of 3-chloro-F-pentane (Cmpd 8) (30%), 2-chloro-F-pentane (Cmpd 9) (45% rt = 6 m) and 1-chloro-F-pentane (Cmpd 10) (15%, rt = 7 m). The combined calculated yield is 31%. The IR spectrum of Cmpd 10 matched that published.³³ The ¹⁹F NMR spectra (1% CFCl₃/CDCl₃): Cmpd 8

CF₃^ACF₂^BCF^CCl-CF₂-CF₃ φ_A = -79.0 ppm (d,3), B -120.1 (s,2), C -137.0 (m,1); J_{AC} = 9.2 Hz; Cmpd 9 CF₃^ACF^BClCF₂^CCF₂^DCF₃^E φ_A = -77.8 ppm (d+t,3), B -138.7 (m,1), C -117.6 (m,2), D -124.3 (m,2), E -81.3 (t,3); J_{AC} = 9.2 Hz,

$J_{AB} = 12.2$ Hz, $J_{CE} = 4.5$ Hz; Cmpd 10 $CF_2^A CClCF_2^B CF_2^C CF_2^D CF_3^E$ $\phi_A = -68.6$ ppm (t,2), B -120.8 (m,2); C -122.6 (m,2); D -126.7 (m,2); E -81.2 (t,3); $J_{AC} = 12.2$ Hz, $J_{CE} = 12.2$ Hz.

Aerosol Fluorination of tert-Amyl Chloride: 2-Chloro-2-methylbutane (Eastman) has a vapor pressure at $0^\circ C$ such that a helium flow of 53 mL/m produces a throughput of 0.27g/h (2.5 mmol/h). A 2.5 h run produced 0.9626g of crude material after fractionation. Separation on the SE-52 column ($15^\circ C/5$ m; $10^\circ C/m$ to $75^\circ C$; $50^\circ C/m$ to $180^\circ C/10$ m) gives 6.2% F-isobutane, (rt = 3 m), 22.1% F-isopentane (rt = 3.5 m), and 62.8% of an unresolved mixture (16:6.5:1) (rt = 7 m), of 1-chloro-F-2-methylbutane (Cmpd 7), 1-chloro-F-3-methylbutane, (Cmpd 6), and 2-chloro-F-3-methylbutane (Cmpd 11). No 2-chloro-F-2-methylbutane was observed. The ^{19}F NMR spectrum of Cmpd 11 is (1% $CFCl_3/CDCl_3$): $(CF_3^A)_2 CF^B CF^C ClCF_3^D$ $\phi_A = -70.7$ ppm (m,6), B -176.0 (m,1), C -135.3 (m,1), D -77.8 (m,3).

Aerosol Fluorination of Chlorocyclopentane: Chlorocyclopentane (Aldrich) has a vapor pressure at $-10^\circ C$ such that a helium flow of 135 mL/m produces a throughput of 0.21g/h (2.0 mmol/h). A 3 h run produces 1.30g of crude product after fractionation. Separation on the QF-1 column ($10^\circ C/13$ m; $10^\circ C/m$ to $60^\circ C/5$ m; $50^\circ C/m$ to $180^\circ C/5$ m) gives 2.6% F-butane (rt = 5 m), 12.5% F-cyclopentane (rt = 12 m), 5% $C_4 F_{11} Cl$ (Cmpds 1&3) (rt = 15 m), 12.5% F-pentane (rt = 18 m), 49.5% 1-chloro-F-cyclopentane (Cmpd 12) (rt = 22 m), and 15.5% unresolved $C_5 F_{11} Cl$ isomers (Cmpds. 8,9,10) (rt = 25-26 m). The yield of Cmpd 12 is 40.2%. IR of Cmpd 12 (cm^{-1}) 1310(s), 1275(m), 1240(s), 1220(vs), 1120(m), 1065(vw), 1020(m), 970(s), 920(w), 870(s), 740(w); ^{19}F NMR (1% $CFCl_3/CDCl_3$): $\phi_{CFCl} = -139.8$ ppm (m,1) $\phi_{CF_2} = -118.0$ and -136.5 ppm (A B pattern, 2,5- and 2',5'-, $J_{22'} = J_{55'} = 262.5$ Hz, 4) $\phi_{CF_2} = -126.5$ and -129.0 ppm (A B pattern, 3,4- and 3',4'-, $J_{33'} = J_{44'} = 253.3$

H₂, 4). Major mass cations were [m/e(int)Formula] 199(31)C₄F₆³⁷Cl, 197(100)C₄F₆³⁵Cl, 149(40)C₃F₄³⁵Cl, 131(56)C₃F₅, 100(22)C₂F₄.

Acknowledgement

This work was supported in part by the Office of Naval Research whose support is gratefully acknowledged. Earlier support by the Research Corporation, Cottrell Research Fund is also acknowledged.

References

- (1) Adcock, J. L.; Lagow, R. J. J. Am. Chem. Soc., 1974, 96, 7588.
- (2) Adcock, J. L.; Beh, R. A.; Lagow, R. J. J. Org. Chem., 1975, 40, 3271.
- (3) Adcock, J. L.; Lagow, R. J. J. Org. Chem., 1974, 38, 3617.
- (4) Adcock, J. L.; Horita, K.; Renk, E. B. J. Am. Chem. Soc., 1981, 103, 6937.
- (5) Adcock, J. L.; Catsikis, B. D.; Thompson, J. W., Lagow, R. J. J. Fluorine Chem., 1976, 7, 197.
- (6) Bishop, B. C.; Hynes, J. B., Bigelow, L. A., J. Am. Chem. Soc., 1964, 86, 1827.
- (7) Adcock, J. L.; Robin, M. L. J. Org. Chem., 1983, 48, 2437.
- (8) Holub, F. F.; Bigelow, L. A. J. Am. Chem. Soc., 1950, 72, 4879.
- (9) Giacometti, G.; Okabe, H.; Price, S. J., Steacie, E. W. R. Can. J. Chem., 1960, 38, 104.
- (10) Banks, R. E., "Fluorocarbons and Their Derivatives"; Oldbourne Press: London; p 56.
- (11) Adcock, J. L.; Evans, W. D.; Heller-Grossman, L. J. Org. Chem., 1983, 48, 4953-4957.
- (12) Miller, W. T.; Koch, S. D. J. Am. Chem. Soc., 1957, 79, 3084.
- (13) Ruff, O.; Keim, R. Z. Anorg. Allgem. Chem., 1931, 201, 245.
- (14) Bockmuller, W. Ann., 1933, 506, 20.
- (15) Miller, W. T.; Calfee, J. D.; Bigelow, L. A. J. Am. Chem. Soc., 1937, 59, 198.
- (16) a) Calfee, J. D.; Bigelow, L. A. J. Am. Chem. Soc., 1937, 59, 2072. b) Young, D. S.; Fukuhara, N.; Bigelow, L. A. J. Am. Chem. Soc., 1940, 62, 1171.
- (17) Calfee, J. D.; Fukuhara, N.; Young, D. S.; Bigelow, L. A. J. Am. Chem. Soc., 1940, 62, 267.

- (18) Hadley, E. H.; Bigelow, L. A. J. Am. Chem. Soc., 1940, 62, 3302.
- (19) Miller, W. T. J. Am. Chem. Soc., 1940, 62, 341.
- (20) Schmeisser, M.; Ehlers, K. P.; Sartori, P. Angew. Chem. Internat. Edit., 1967, 6, 627.
- (21) Skell, P. S.; Allen, R. G.; Gilmour, N. D. J. Am. Chem. Soc., 1961, 83, 504-5.
- (22) Juneja, P. S.; Hodnett, E. M. J. Am. Chem. Soc., 1967, 89, 5685-7.
- (23) Wiley, R. H.; Miller, W.; Jarboe, C. H., Harell, J. R.; Parish, D. J. Radiation Research, 1960, 13, 479-88.
- (24) Benson, H. L., Jr.; Willard, J. E. J. Am. Chem. Soc., 1961, 83, 4672-3.
- (25) Mayo, F. R. J. Am. Chem. Soc., 1962, 84, 3964-5.
- (26) Freidlina, R. KH. Advan. Free Radical Chem., 1965, 1, 211-278.
- (27) Kochi, J. K. ed., Free Radicals, Vol. 2, Wiley, N.Y. (1973); Skell, P. S.; Shea, K. J. "Bridged Free Radicals, pp 829-832.
- (28) Hauptschein, M; Nodiff, E. A.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 1347.
- (29) Hauptschein, M.; Braid, M. J. Am. Chem. Soc., 1961, 83, 2383.
- (30) Burger, H.; Pawelke, G. Spectrochim. Acta, 1979, 35A, 559.
- (31) Olah, G. A.; Bolinger, J. M. J. Am. Chem. Soc. 1968, 90, 947.
- (32) Darzens, G.; C. R. Hebd. Séances Acad. Sci., 1911, 152, 1314.
- (33) Hauptschein, M.; Kinsman, R. L.; Grosse, A. V. J. Am. Chem. Soc., 1952, 74, 849.

APPENDIX I

Distribution List

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No.</u> <u>Copies</u>		<u>No.</u> <u>Copies</u>
Office of Naval Research Attn: Code 472 800 North Quincy Street Arlington, Virginia 22217	2	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 1211 Research Triangle Park, N.C. 27709	1
ONR Western Regional Office Attn: Dr. R. J. Marcus 1030 East Green Street Pasadena, California 91106	1	Naval Ocean Systems Center Attn: Mr. Joe McCartney San Diego, California 92152	1
ONR Eastern Regional Office Attn: Dr. L. H. Peebles Building 114, Section D 666 Summer Street Boston, Massachusetts 02210	1	Naval Weapons Center Attn: Dr. A. B. Anster, Chemistry Division China Lake, California 93555	1
Director, Naval Research Laboratory Attn: Code 6100 Washington, D.C. 20390	1	Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko Port Hueneme, California 93401	1
The Assistant Secretary of the Navy (RE&S) Department of the Navy Room 4E736, Pentagon Washington, D.C. 20350	1	Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Commander, Naval Air Systems Command Attn: Code 310C (H. Rosenwasser) Department of the Navy Washington, D.C. 20360	1	Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12	Naval Ship Research and Development Center Attn: Dr. G. Bosmajian, Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. Fred Saalfeld Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto, Marine Sciences Division San Diego, California 91232	1
		Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
		Mr. A. M. Anzalone Administrative Librarian PLASTE/ARRADCOM Bldg 3401 Dover, New Jersey 07801	1

**DA
FILM**